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AN EFFICIENT METHOD FOR THE SYNTHESIS OF NEW SUBSTITUTED CHROMENS

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ABSTRACT

The chromen derivatives can be obtained in excellent yields, in three steps, using first the phase transfer catalysis for the synthesis of phenol ether followed by cyclisation and the Perkin reaction.

KEYWORDS: Lipoxygenase inhibitors, Phase Transfer Catalysis (PTC), Chromens

RESUMO:

Derivados do cromeno foram obtidos com rendimentos excelentes a partir de benzaldeídos em tres etapas usando primeiro catálise por transferência de fase por ciclização e a reação de Perkin.

INTRODUCTION

Inhibitors of the lipoxygenase enzymes and antagonists of leukotrines are now being developed and it remains to be seen if these componds will have the predicted therapeutic value in the treatment of human asthma and inflamation. A general strategy and design for such inhibitors has been under development in our laboratories.

The synthesis of new molecules containing both cinnamic acid and chromene groups is reported in this paper. Such molecules have wide therapeutic possibilities, being able to inhibit the lipoxygenase pathway of arachidonic acid metabolism.

Conversion of arachidonic acid by the 5 - lipoxygenase enzyme results in the formation of 5 - hydroperoxy - 6, 8, 11, 14 - eicosatetraenoic acid which is subsequently metabolized to a series of highly potent leukotrienes. These oxygenated eicosanoids are implicated in inflammatory and allergic reactions. Little is known at present about the way in which 5 - lipoxygenase acts and any type of information about this mechanism may contribute to the treatment of vascular diseases[1,2].

It has been recentely proved that the caffeic acid[3,4] and a series of chromene derivatives[5] are good inhibitors of 5 - lipoxygenase. In an attempt to understand the physicochemical background of the structural effects of the side chains as well as the ring systems on the inhibition, we synthesized two new compounds that contain a chromene moiety and a cinnamic acid side chain. At the present, only the 2,2 dimethyl - 6 - carboxyethenyl - 2H - 1 - benzopyran is known and it was isolated and identified from Brazilian propolis[6] but it was never synthesized *in situ*.

Conventionaly[7] the chromens are synthesized in two steps. The first is the reaction of the 3 - chloro - 3 methylbutyne with a convenient phenolic substrate, in the presence of potassium iodide and potassium carbonate. This step requires aproximately 65 hours and the O - dimethylprop - 2 - ynyl ether is obtained in a rather poor yield (24%). In the second step the O - dimethyl prop - 2 - ynyl ether, heated at 218°C for 2 hours in diethylaniline to give chromen (56%) by means of the acetylene version of the Claisen rearrengement. Besides the poor yield, this method has a number of disadvantages like the long time required for the synthesis of the ether and the laborious chromatographic procedure required for its purification.

This paper reports an efficient procedure to obtain the chromen derivative (figure 1). This synthesis is based on the observations of McKillop[8] who used the phase - transfer catalysis (P.T.C.) for the preparation of the phenol ether. Compared with the classical methods, the new route proposed for the synthesis of the O - dimethylprop - 2 - ynyl ether gave a very good yield (85%), was carried out in a relatively short time (8 - 10 h) and no further purification by chromatographic method was necessary.

EXPERIMENTAL PROCEDURE

A mixture of 50 mL of dichloromethane, 50 mL of water, 10 mmoles of the hydroxy benzaldehyde **1** (Figure1), 20 mmoles of sodium hydroxide, 20 - 30 mmole of 3 - chloro - 3 methylbutyne and 1 - 1.5 mmole of quaternary ammonium bromide was stirred at room temperature for 8 - 10 h. After this time a volume of 25 ml solution of NaOH (1 M) was added and stiring was continued for 15 minutes. The organic layer was separated and the aqueous layer was extracted with methylene chloride. Removal of the solvent yielded the pure ether **2**. This ether was disolved in diethylaniline and the procedure described by

Crombie was applied to obtain the chromene derivative **3**. The product with the cinnamic side chain **4** was obtained (90% yield) using the general procedure of the Perkin reaction[9].

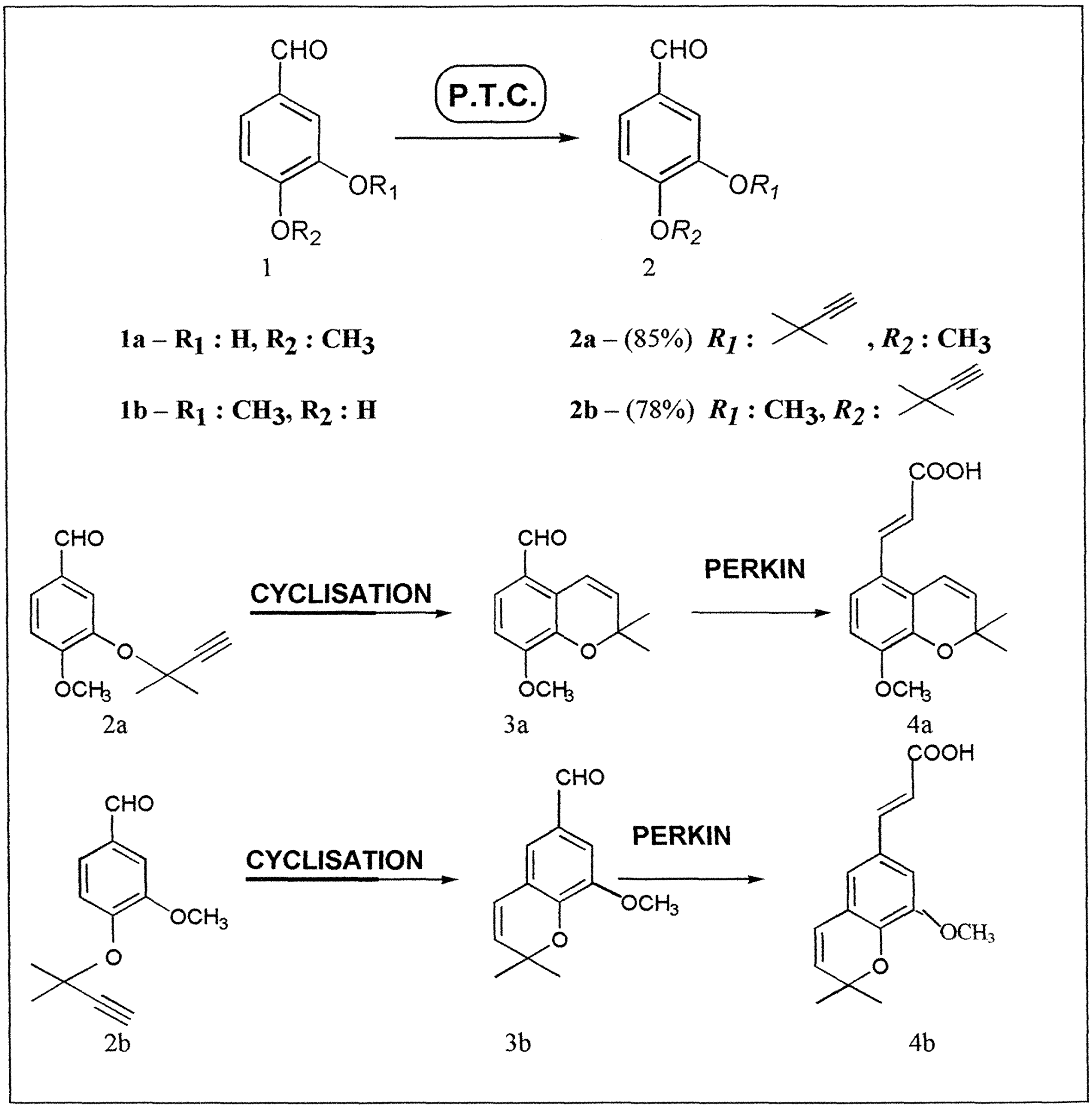

Figure 1. Synhtesis of substituted chromens using the new route proposed

Analytical characterization of the products gave the following results:

3 a : ***5 - formyl - 8 - methoxy - 2,2 dimethyl chromen*** (92%) **^{1}H NMR** ($CDCl_3$) 1,47 ppm (s, 6 H -2x CH_3); 3,90 ppm (s, 3 H - OCH_3); 5,80 ppm (d, 1H, ^3J = 10,13 Hz); 6,87 ppm (d, 1H_{arom} ^3J = 8,49 Hz); 7,30 ppm (d, 1H_{arom} ^3J= 8,49 Hz); 7,44 ppm (d, 1H ^3J= 10,14 Hz); 9,96 ppm (s, 1H - CHO); **MS m/e** (percent, relative abundance) 218 (M^+, 13,77); 203 (M^+-CH_3, 100); **IR (ν cm^{-1})** 3100 - 2700 (ν_{C-H}); 1690 ($\nu_{C=O}$); 1495 ($\nu_{C-Carom}$).

3b : ***6 - formyl - 8 - methoxy - 2,2 dimethyl chromen*** (88%) **^{1}H NMR** ($CDCl_3$) 1,44 ppm (s, 6 H -2x CH_3); 3,85 ppm (s, 3 H - OCH_3); 5,62 ppm (d, 1H, ^3J = 9,90 Hz); 6,28 ppm (d, 1H, ^3J = 9,90 Hz); 7,09 ppm (d, 1H_{arom} ^3J = 1,72 Hz); 7,24 ppm (d, 1H_{arom} ^3J = 1,69 Hz); 9,78 ppm (s, 1H, CHO); **MS m/e** (percent, relative abundance) 218 (M^+, 16,27); 203 (M^+-CH_3, 100); **IR (ν cm^{-1})** 3000 - 2800 (ν_{C-H}); 1695 ($\nu_{C=O}$); 1460 ($\nu_{C-Carom}$).

4a : ***5 - carboxyethenyl - 8 - methoxy - 2,2 dimethyl chromen*** (90%) **^{1}H NMR** ($CDCl_3$) 1,50 ppm (s, 6 H -2x CH_3); 3,88 ppm (s, 3 H - OCH_3); 5,78 ppm (d, 1H, ^3J = 10,04 Hz); 6,28 ppm (d, 1H, ^3J = 15,72 Hz); 6,70 ppm (d, 1H, ^3J= 10,09 Hz); 6,80 ppm (d, 1H_{arom} ^3J = 8,68 Hz); 7,17 ppm (d, 1H_{arom} ^3J = 8,64 Hz); 8,01 ppm (d, 1H, ^3J = 15,72 Hz); **MS m/e** (percent, relative abundance) 260 (M^+, 18,19); 245 (M^+-CH_3, 100); **IR (ν cm^{-1})** 3600 - 2890 (ν_{O-H} et ν_{C-H}); 1690 ($\nu_{C=O}$); 1490 ($\nu_{C-Carom}$).

4b : ***6 - carboxyethenyl - 8 - methoxy - 2,2 dimethyl chromen*** (85%) **^{1}H NMR** ($CDCl_3$) 2,10 ppm (s, 6 H -2x CH_3); 3,90 ppm (s, 3 H - OCH_3); 5,60 ppm (d, 1H, ^3J = 9,86 Hz); 6,22 ppm (d, 1H, ^3J = 9,62 Hz); 6,25 ppm (d, 1H, ^3J= 15,72 Hz); 6,83 ppm (s, 1 H_{arom}); 6,94 ppm (s, 1 H_{arom}); 7,66 ppm (d, 1H, ^3J = 15,83 Hz); 11,58 ppm (s, 1 H, COOH); **^{13}C NMR** ($CDCl_3$) 15,1 ppm (q, CH_3); 25,6 ppm (q, CH_3); 28,1 ppm (q, CH_3); 30,2 ppm (d, CH); 56,2 ppm (d, CH); 65,9 ppm (d, CH); 111,2 ppm (d, CH); 114,4 ppm (d, CH); 120,2 ppm (d, CH); 121,7 ppm (s, C); 123,5 ppm (s, C); 131,4 ppm (s, C); 147,2 ppm (s, C); 149,2 ppm (s, C); 175,0 ppm (s, C); **MS m/e** (percent, relative abundance) 260 (M^+, 18,07); 245 (M^+-CH_3, 100); **IR (ν cm^{-1})** 3600 - 2500 (ν_{O-H} et ν C-H); 1690 ($\nu_{C=O}$); 1420 ($\nu_{C-Carom}$).

Summarising, a simple, rapid and highly eficient procedure for the synthesis of chromen derivatives is now available.

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A VERSATILE PROCEDURE FOR THE SYNTHESIS OF NEW PRENYLATED CINNAMIC ACIDS

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ABSTRACT

The prenylated cinnamic acids can be obtained in excellent yields, in two steps, using first a one - step conversion of corresponding bromobenzaldehydes to corresponding prenylated benzaldehydes.

KEYWORDS: lipoxygenase inhibitors, metallation, n butyl lithium, prenylated cinnamic acid

RESUMO:

Os ácidos cinâmicos prenilados podem ser obtidos com rendimentos excelentes em duas etapas, a primeira sendo a conversão correspondente dos bromobenzaldeídos aos benzaldeídos prenilados. A segunda etapa envolve a reação de Perkin.

INTRODUCTION

Leukotrienes (LTs) are a family of important inflamatory mediators produced by an enzymic cascade which is initiated by the action of 5 - lipoxygenase (5 - LO) on arachidonic acid. Leukotrienes are significantly involved in immunoregulation and in a variety of diseases, including asthma, inflammation and various allergic conditions.

Our research group is interesed in the design, synthesis, isolation, conformations, dynamics and structure - biological activity relationships of this new class of inhibitors of arachidonate lipoxygenases. This paper reports our findings on the synthesis of new prenylated cinnamic acids. The inhibitory effect and the bio - analytical behaviour of 3 - [3,4 dimethoxy - 5 - (3-methylbut-2-enyl) phenyl] 2 propenoic acid have been tested in our laboratories.

Although a few selective inhibitors have been reported, most of them are difficult to be obtained[1,2]. Caffeic acid[3,4], which is one of the most common reagents, is a selective inhibitor for 5-LO and therefore of leukotriene biosynthesis. The phenolic natural products bearing isoprenoid substituents have been reported by many authors[5] to posses anti-inflamatory, antiallergic, antiviral and antitumor properties. This observation is important for us in future design strategy. The search for new synthetic approaches for the prenylated compounds is a continously growing area of investigation. Prenylated benzaldehydes are very rarely synthesized by the direct introduction of a prenyl group, the reason being that the methods used often give low yields, involve a multistep sequence and overoxidation problems[6,7,8].

An original and efficient procedure to obtain the prenylated benzaldehydes which are precursors in the synthesis of cinnamic acids is reported in this paper. To accomplish direct metallation of 3,4 dimethoxy benzaldehyde it was decided to look at the bromobenzaldehyde derivative, as an easily available substrate.

The 3,4 dimethoxy-(3-methylbut-2-enyl) benzaldehydes were synthesised using a modified procedure applied for the one-step convertion of bromobenzaldehyde to the corresponding hydroxybenzaldehydes[9]. Figure 1 shows the importance of achieving metallation in a direct manner.

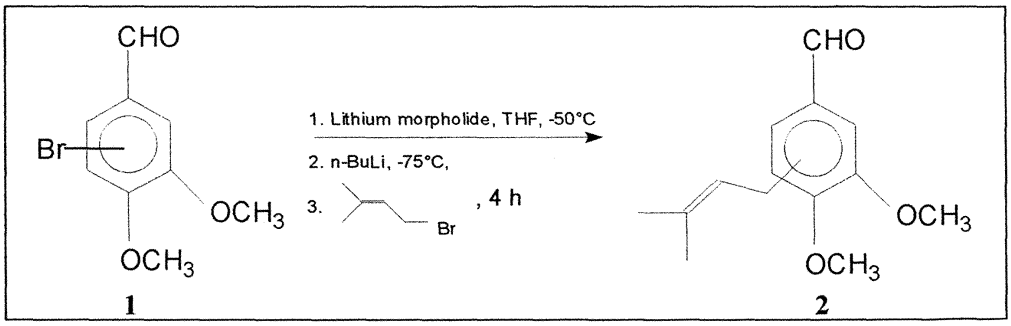


Figure 1. Conversion of bromobenzaldehyde to corresponding prenylated benzaldehyde

The method involves the in situ protection of the aldehyde function of the bromobenzaldehyde as its lithium morpholinoalkoxide, followed by lithium - bromide exchange and reaction with 1-bromo-3- methyl-but-2-enyl at -78°C. The usual procedure provided a crude mixture of 3,4 dimethoxy - (3-methylbut-2-enyl) benzaldehyde and 3,4 dimethoxybenzaldehyde which was purified by chromatography on silica gel with ethyl acetate : petroleum ether (3 : 2, v/v) as eluent, thus furnishing pure 3,4 dimethoxy-5-(3-methylbut-2-enyl) benzaldehyde in a 50 - 55% yield.

EXPERIMENTAL PROCEDURE

All chemicals used were analytical reagent grade. Packing material for column chromatography was Merck, silica gel 60 (70 - 230 mesh). Solvent used for metallation was thoroughly dried prior to use. Morpholine was stored over NaOH pellets under argon in a septum - capped bottle.

An oven - dried three - necked, round bottom flask equipped with a stirring bar, septum cap, thermometer and argon inlet was charged with morpholine (1 mL) and THF (20 - 30 mL). The mixture was cooled to - 50°C and a solution of n – butyl lithium in hexane was added all at once. After 10 minutes a solution of the bromobenzaldehyde (10 mmol) in 20 mL of THF was injected over a period of 5 min. and the mixture was allowed to cool to -70°C over 20 min. A solution of n – butyl lithium in hexane was then added dropwise, keeping the temperature at ~ -75°C. After 35 min a solution of 1-bromo-3-methylbut-2-enyl was added dropwise. Stirring was continued for an additional 4 h and the temperature was slowly increased to 0°C. The mixture was quenched with cold water, the solvent was removed in vacuo and the remaining aqueous phase was extracted twice with hexane. The basic aqueous solution was acidified with cold HCl and extracted with methylene chloride or ether. The extracts were washed successively with brine and water and dried over anhydrous sodium sulfate. Removal of the solvent yielded a crude material which was chromatographed.

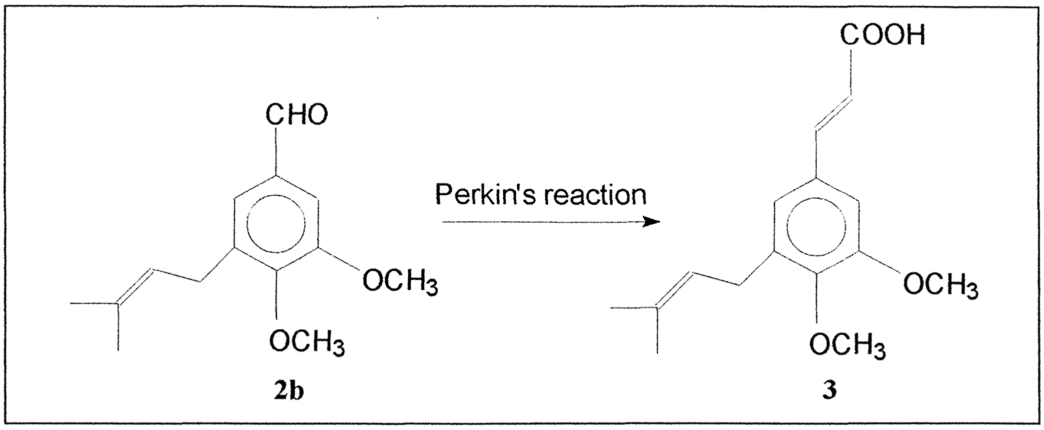
Analytical characterization of the products gave the following results:

2a* : ***3,4 dimethoxy-2-(3-methylbut-2-enyl) benzaldehyde*** (12% from the NMR spectrum); **NMR ^{1}H** ($CDCl_3$) δ 1,68 (s, 3H, CH_3), 1,75 (s, 3H, CH_3), 3,70 (d, 2H Ph-CH_2=CH, J=7,20 Hz), 3,95 (s, 6H, 2xOCH_3), 5,16 (bt, 1H), 6,80 (d, 1H_{arom}, J=9 Hz), 7,40 (d, 1H_{arom}, J=9 Hz) 10,00 (s, 1H-CHO).*This compound can be obtained with a better yield using the procedure described by Crombie[7].

2b : ***3,4 dimethoxy-5-(3-methylbut-2-enyl) benzaldehyde*** (57%): pale yellow oil; **^{1}H NMR** ($CDCl_3$) δ 1,65 (s, 6H-2xCH_3), 3,30 (d, 2H Ph-CH_2=CH, J=7,34 Hz), 3,95 (s, 6H, 2xOCH_3), 5,16 (bt, 1H), 7,20 (s, 2H_{arom}), 9,74 (s, 1H-CHO); **^{13}C NMR** ($CDCl_3$) 17,6 ppm (q, CH_3); 25,6 ppm (q, CH_3); 28,4 ppm (t, CH_2); 55,6 ppm (q, CH_3); 60,3 ppm (q, CH_3); 108,3 ppm (d, CH_{arom}); 121,9 ppm (d, CH); 125,9 ppm (d, CH_{arom}); 132,1 ppm (s, C); 133,0 ppm (s, C); 135,9 ppm (s, C); 152,6 ppm (s, C); 153,2 ppm (s, C); 191,3 ppm (d, CH); **IR** ($CHCl_3$) cm^{-1} 2900 - 2790, 1695, 1590, 1460;. **MS m/e** (percent, relative abundance) 234 (M^+, 40), 219 (M^+-CH_3, 27), 150 (100); Anal. Calcd for $C_{14}H_{18}O_3$ C, 71.76; H, 7.75 found C, 71.85; H,7.80.

2c : ***3,4 dimethoxy-6-(3-methylbut-2-enyl) benzaldehyde*** (48%) **^{1}H NMR** ($CDCl_3$) δ 1,70 (s, 6H-2xCH_3), 3,70 (d, 2H Ph-CH_2=CH, J=7,34 Hz), 3,95 (s, 6H, 2xOCH_3), 5,21 (bt, 1H), 6,70 (s, 1H_{arom}), 7,35 (s, 1H_{arom}), 10,17 (s, 1H-CHO); **^{13}C NMR** ($CDCl_3$) 18,0 ppm (q, CH_3); 25,6 ppm (q, CH_3); 30,4 ppm (t, CH_2); 55,9 ppm (q, OCH_3); 56,0 ppm (q, OCH_3); 110,6 ppm (d, CH); 112,4 ppm (d, CH); 123,1 ppm (d, CH); 126,6 ppm (s, C); 132,7 ppm (s, C) ; 140,0 ppm (s, C); 147,6 ppm (s, C); 153,8 ppm (s, C); 190,1 ppm (d, CHO); **IR** ($CHCl_3$) cm^{-1} 3000 - 2800, 1680, 1510, 1485;. **MS m/e** (percent, relative abundance) 234 (M^+, 40), 205 (M^+-CHO, 62); Anal. Calcd for $C_{14}H_{18}O_3$ C, 71.76; H, 7.75 found C, 71.70; H,7.60.

As the research was focused only on the synthesis of the 3 - [3,4 dimethoxy - 5 – (3-methylbut-2-enyl) phenyl] 2 propenoic acid (Figure 2), this compound was prepared using the general procedure of the Perkin reaction[10] changing only the time of reaction.



2b **3**

Figure 2. Synthesis of 3 - [3,4 dimethoxy - 5 - (3-methylbut-2-enyl) phenyl] 2 propenoic acid

3 - [3,4 dimethoxy - 5 - (3-methylbut-2-enyl) phenyl] 2 propenoic acid ^{1}**H NMR** ($CDCl_3$) δ 1,75 (s, 6H-2xCH_3), 3,45 (d, 2H Ph-CH_2=CH, ^{3}J=7,34 Hz), 3,85 (s, 6H, 2xOCH_3), 5,25 (bt, 1H), 6,30 (dd 1H, ^{3}J=15,90 Hz), 6,90 (dd, $2H_{arom}$, ^{4}J=1,93 Hz), 7,70 (dd, 1H, ^{3}J=15,90 Hz); ^{13}**C NMR** ($CDCl_3$) 17,7 ppm (q, CH_3); 25,7 ppm (q, CH_3); 28,3ppm (t, CH_2); 55,6 ppm (q, OCH_3); 60,4 ppm (q, OCH_3); 109,1 ppm (d, CH_{arom}); 115,8 ppm (d, CH); 122,2 ppm (d, CH); 123,2 ppm (d, CH_{arom}); 129,6 ppm (s, C); 133,1 ppm (s, C); 136,1 ppm (s, C); 147,4 ppm (d, CH); 148,9 ppm (s, C); 152,9 ppm (s, C); 172,6 ppm (s, CH); **IR** ($CHCl_3$) cm^{-1} 3600 - 2400, 1700, 1630, 1410;. **MS m/e** (percent, relative abundance) 276 (M^{+}, 100), 206 (M^{+}-CH=CH-COO, 27), ; Anal. Calcd for $C_{16}H_{20}0_4$ C, 69.55; H, 7.30 found C, 69.55; H,7.36.

In a preliminary test the potency of these compouns as inhibitors of lipoxygenases was determined[11].

Summarising, a new and highly effective procedure for the synthesis of prenylated cinnamic acid is now available. Further work is in progress.

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RESPONSE OF THE COMMON CABBAGE (*Brassica oleracea* L. var. capitata L.) TO BORON FERTILIZATION

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ABSTRACT: *The response of the common cabbage (Brassica oleracea L. var. capitata L.) to boron fertilization in soils of the state of Paraná, Brazil, is provided. Six types of soils, LRd; LRe, Ca_1; Ca_2, TRd and LEd were selected, treated with macronutrient fertilizer, their pH was corrected, according to routine. Experiment was conducted in 2.5-L capacity pots, with 2 kg of each soil, in a greenhouse. Each type of soil, in triplicate samples, received boron treatment with boric acid: 0.0 g; 0.1 g; 0.2 g. Pots were kept at 70% water capacity retention during 7 days, after which they received 6 cabbage shoots. Two shoots were maintained and later only one was kept in each pot. Duration of experiment was 8 weeks, after which harvest was undertaken. Plants were dried in stoves, weighted, ground and conditioned for further analysis. Extractor HCl 0.05 mol L^{-1} was used to determine boron in soils. Although soils Ca_1, LRd and LEd gave significant responses to treatments, concentrations of available boron over 4 $\mu g\ g^{-1}$ were toxic to cabbages.*

Key words: boron; micronutrients, cabbage, fertilization.

RESUMO: *O presente trabalho teve como objetivo avaliar a resposta do repolho (Brassica oleracea L., var. capitata L.) à adubação boratada em solos do Estado do Paraná. Para isto, foram selecionados 6 tipos de solos: LRd; LRe; Ca_1; Ca_2; TRd; LEd; nos quais realizaram-se a adubação com o micronutriente boro e a correção do pH, seguindo-se a análise de rotina. Em casa de vegetação foi montado o experimento em vasos de 2,5-L. Em triplicata, cada solo recebeu tratamento com B (boro): 0,0 g; 0,1 g; 0,2 g na forma de ácido bórico. Os vasos foram mantidos a 70% da capacidade de retenção água durante 7 dias, quando receberam 6 mudas de repolho, conservando-se posteriormente duas, e em seguida apenas uma planta em cada vaso. O experimento foi conduzido por 8 semanas, quando foram feitas as coletas das plantas, as quais, foram secadas em estufa, pesadas, moídas e acondicionadas em frascos plásticos para posterior análise. O extrator utilizado para determinar o boro no solo foi a solução de HCl 0,05 mol L^{-1}. Os solos Ca_1, LRd e LEd mostraram respostas significativas aos tratamentos realizados e as concentrações superiores a 4 $\mu g\ g^{-1}$ mostraram serem tóxicas para o repolho.*

INTRODUCTION

Soil nutrients are divided into two important classes: macronutrients found in large quantities in the plant dry matter (%) and micronutrients found in smaller quantities (ppm). Micronutrients are essential chemical elements, such as Fe, Cu, Mn, Zn, Mo, Cl and B required by plants in small quantities[1]. Maze and later on Warigton stressed that boron is essential[2].

The researchers Wear and Berger and Truog, *apud* Ribeiro and Sarabia[3], showed that only a tiny fraction of total boron in soil is available to plants. Deficiencies are shown in clay soils with low activity clay, poor in organic matter and low CTC[4].

The soil low fertility, great upheavals during the harvest of some cultivated plants and the increasing use of lime and phosphate manure cause lower availability of this specific micronutrient[5]. Boron fertilization is necessary to avoid decrease of produce in places where heavy K fertilization and intense cultures are practiced[6].

Coffee and citric plants, sunflowers, tomatoes and other vegetable species are especially sensitive to boron deficiencies in soil[7] with consequent losses in productivity[8]. Boron deficiency in plants may be detected when its concentrations in soil range between 0.1 and 0.7 $\mu g\ g^{-1}$, Buzetto and Muroka[9].

In plants its functions amount to carbohydrate metabolism, sugar transportation, synthesis of nucleic acids, phytohormones, formation of cell walls and cell division[10, 11]. Boron deficiency symptoms are generally found in the plant younger sections. In the alfalfa and clover boron deficiency is marked by color variation (yellow-red). Toxicity is confirmed by the appearance of burns or tanning in the leaves edges. One of the chief effects of boron deficiency in plants is the excessive decrease of nitrate in leaves[12]. The concentration of boron between 20 and 50 $\mu g\ g^{-1}$ is considered basic for the development of plants[13] (Gupta, 1991). More than the cabbage, the genus *Brassica*, represented by the cauliflower and broccoli, is more sensitive to boron deficiencies[14].

The general objective of the present research work is the collection of data for the monitoring of deficiency and toxicity of micronutrients in arable soil. Its specific aim is the analysis of the response of boron fertilization in six different types of soil. The plant used is the cabbage since it is conspicuous in Brazilian food, it is consumed both uncooked and otherwise, it is a cheap nutrient source, albeit rich in mineral salts and vitamins.

MATERIALS AND METHODS

Sampling

Six types of soils of five different classes from the state of Paraná, Brazil, were used: dystrophic Red Latosol (LRd); eutrophic Red Latosol (LRe); allic Cambisol (Ca_1); allic Cambisol (Ca_2); structured Dark Red Latosol (TRd); dystrophic Dark Red Latosol (LEd). The above-mentioned soils were also used by Favero[15] in another experiment to evaluate response of the cotton plant to boron application.

Physical analysis of soils

Folk's granulometric classification[16] and Suguio's methodology[17] were employed in the Pedology, Sedimentology and Palinology Laboratory of the Department of Geography of the State University of Maringá, Maringá PR Brazil.

Experiment

Pots of 2.5-L capacity, internally lined with plastic bags, were filled with 2 kg of six types of soil, respectively. Pots were organized as follows: LRd was placed in pots from 1 to 9, corresponding to the three soil boron treatments in triplicate; LRe in pots from 10 to 18; Ca_1 in pots from 19 to 27; CA_2 in pots from 28 to 36; TRd in pots from 37 to 45; LEd in pots from 46 to 54. Soils were fertilized with 3.72 g of $NH_4H_2PO_4$, 4.5 g of K_2SO_4 and lime according to routine analysis. Boron treatments consisted of 0.0; 0.1 and 0.2 g of boric acid (H_3BO_3) corresponding to: 0,0; 0,010 and 0,10 g kg^{-1}, with three replications, respectively. After the soils were placed in the pots and fertilized, distilled and de-ionized water was added until humidity of 70% of water retention capacity was reached. Irrigation continued for 7 days in the greenhouse. Six cabbage plants were then planted in each pot. Plants with low development were discarded and only one was finally left. Plants were maintained at 70% field capacity during 8 weeks, after which they were harvested.

Yield of vegetal material and samples of soil in the pots

After eight weeks the plants were harvested close to the ground, washed with distilled and de-ionized water, dried in porcelain capsules in a stove at 60 °C to constant weight. Evaluation of the total mass of plants after treatment was accomplished by weighing of the samples.

After harvest, soils were removed from the pots, air-dried, triturated, and passed though 2mm-mesh sieves, homogenized and placed in plastic bags for further analysis.

Extraction and determination of boron in soils

Volumes of 20 mL of HCl 0.05 mol L^{-1} were added to each 10 g of sample of air-dried fine soil, shaken for 5 minutes and then filtered with a n^0. 42 Whatman filter paper. Analyses of boron concentration in soils were undertaken from extracts by UV-Vis spectrophotometry with Azomethina-H[18].

Statistics

Variance analysis was applied to the results. When significant difference ranged between 5 and 1%, Tukey test was employed for differentiation at the same levels of significance.

RESULTS AND DISCUSSION

Table 1 shows the characteristics of soils *in natura* used in the experiment. pH values varied from 5.7 to 7.2, with highest value in LEd. Low rate of organic matter and the high percentage of sand in LEd showed that the added and solved limestone in samples of this soil practically remained in the solution. Consequently, it had the highest pH value. Soils TRd and LRd contained the highest percentage of clay.

Table 1. Chemical and Physical Properties of Pre-Treatment Soils.

Parameters	Ca_1	Ca_2	TRd	LRd	LRe	LEd
pH (H_2O)	5.7	5.7	6.6	6.2	6.3	7.2
C (%)	3.49	3.99	2.01	2.21	1.37	0.74
O.M.(%)	6.00	6.86	3.46	3.80	2.36	1.27
Clay (%)	39.57	52.62	65.40	65.47	38.77	9.65
Silt (%)	55.43	45.38	33.60	31.53	34.55	3.35
Sand (%)	5.0	2.0	1.0	3.0	6.0	87.0

$Ca_{(1 \text{ and } 2)}$ - allic Cambisol; LEa - allic Dark Red Latosol; TRd - Structured Dark Red Soil; LRd - Dystrophic Red Latosol; LRe - eutrophic Red Latosol; LEd - dystrophic Dark Red Latosol.

Treatments caused a 5% significant increase in boron level in soil, as may be seen in Table 2.

Table 2. Tukey's Test at 5% Level in Boron Concentration Means in Soil Solution, in μg g^{-1}, per Treatment after Harvest.

Soil	Ca_2	Ca_1	TRd	LRd	LRe	LEd
Reference	0.910 *b*	0.36 *b*	0.09 *c*	0.19 *c*	0.57 *b*	0.41 *c*
Treatment 1	1.48 *b*	2.19 *a*	1.55 *b*	1.75 *b*	1.25 *ab*	3.86 *b*
Treatment 2	2.91 *a*	3.40 *a*	3.20 *a*	4.09 *a*	2.31 *a*	8.36 *a*

$Ca_{(1 \text{ and } 2)}$ - allic Cambisol; TRd - structured dystrophic Red Soil; LRd - dystrophic Red Latosol; LRe - eutrophic Red Latosol; LEd - dystrophic Dark Red Latosol; Reference – soil reference with no boric acid; Treatment 1 – treatment with 0.1 g boric acid; Treatment 2 – treatment with 0.2 g boric acid; (*a*, *b*, ...) -Values followed by the same letter are not significantly different at 5% level, using the Tukey's test (SANEST software).

Many boron concentrations in reference treatments without boron fertilization were within micronutrient deficiency levels, or rather, 0.7 μg g^{-1}, according to Buzetto and Muroka[9]. Soils Ca_2 and LEa are exceptions.

Soils TRd, LRd and LEd had highest increase in available boron levels, as Table 2 shows. In treatments 1 and 2 LEd had highest concentration of extractable boron, 3.86 and 8.36 μg g^{-1} respectively. This may be due to the fact that LEd is a sandy soil with low concentration of clay and organic matter. Practically almost all added boron is available (or present) in the soil solution.

Figure 1 shows values in grams of dry mass of cabbage plants cultivated in three treatments in six types of soil.

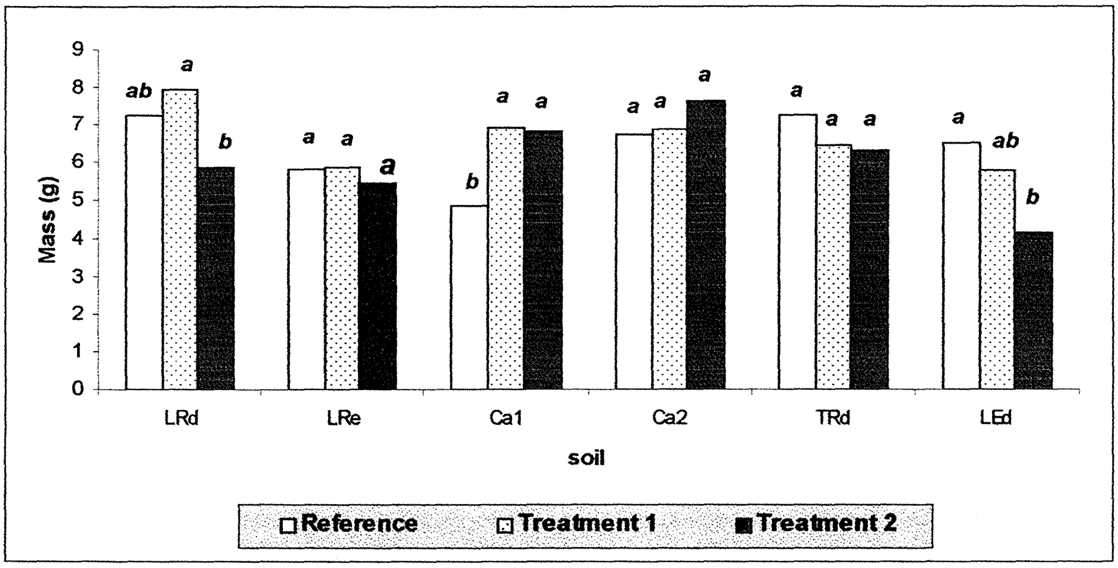

Figure 1. Mass of Plants (in grams) with Respective Treatments.

According to variance analysis there was a significant difference between masses of plants cultivated in treatments with Ca_1, LRd and LEd. It may be remarked that in the case of Ca_1 the plant response to boron fertilization was positive. On the other hand, growth of plants in treatments of LEd was impaired. Negative effect to fertilization is shown by decrease of dry matter of plants to Treatment 1 and more pronounced to Treatment 2. Although in the case of LRd plants response was positive to Treatment 1, fertilization for this type of soil in Treatment 2 was toxic to plants and impaired their growth. The same fact has been noted by Luchese *et al.*[19] with the cotton plant.

Treatments in LEd, LRd and Ca_2 had the most significant response with regard to mass of cabbage plants and boron concentration in soils. Figure 2 shows this correlation in detail. Curve *a* and *b* of the figure show that boron concentrations up to 2 μg g^{-1} in these soils did not impair the development of cabbage plants. Treatments with 0.2 g of boric acid caused an increase of over 4 μg g^{-1} in available boron concentrations for LEd and LRd. Plants cultivated in these soils presented toxicity levels when concentrations were higher than 4 μg g^{-1}. This proves that levels between deficiency and toxicity in this micronutrient for the plant under analysis are relatively low[20].

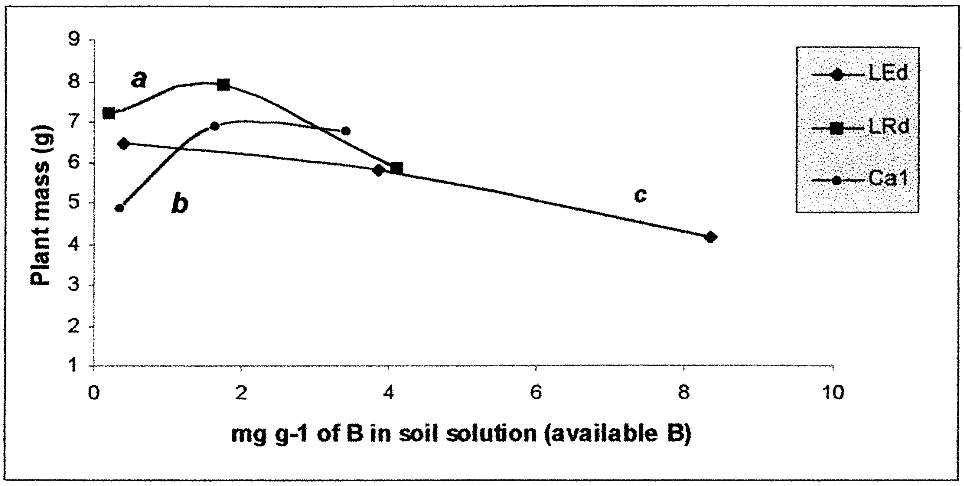

Figure 2. Relation between Boron Concentrations in Soil Solution (available B) and Dry Masses of Plants for Treatments in LRd, LEd and Ca_1.

Soil LRd has low sand concentration, high concentration of clay and organic matter. These factors caused a greater development of the plants in response to fertilization with 0.1 g of boric acid. However, fertilization with 0.2 g surpassed the 4 μg g^{-1} of boron available concentration in the soil solution and a lower development of plants occurred. In the case of LEd high presence of sand and low presence of clay and organic matter gave the soil a greater tendency of ion concentration in the solution and more boron was available to the plants. Consequently their growth was impaired, as may be seen in curve *c* of Figure 2.

CONCLUSION

Boron concentration extractable by HCl 0.05 mol L^{-1} in soil samples showed that with treatments (0,00 g kg; 0,010 g kg and 0,10 g kg) there was a significant increase in the level of available boron in the soil.

The cabbage presented a diagnosis of deficiency and toxicity of the boron micronutrient in the six types of soil. Tukey's test showed significant differences in the dry masses of plants in LEd, LRd and Ca_1. In Ca_1 there was a positive response of the plant to boron fertilization. In LEd the response was negative, and in soil LRd only Treatment 2 impaired the plant development.

Treated soils with available boron concentrations over 4 μg g^{-1} may be toxic to the cabbage plant.

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STUDIES ON N-[2-THIENYLMETHYLIDENE]-2-AMINOPYRIDINE COMPLEXES OF Fe(II), Co(II), Ni(II), Cu(II), Zn(II) AND Cd(II)

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ABSTRACT

Metal complexes ML_2Cl_2, where M is Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II} and L is Schiff base formed by condensation of 2-thiophenecarboxaldehyde and 2-aminopyridine, N-[2-thienylmethylidene]-2-aminopyridine (TNAPY), have been prepared and characterized by elemental analysis, magnetic and spectroscopic measurements. IR and NMR spectra show that the nitrogen of the azomethyne group and the sulphur of the thiophene ring take part in coordination. Magnetic, ESR and electronic spectral studies show a distorted octahedral structure for the Fe(II), Co(II), Ni(II) and Cu(II) complexes and a tetrahedral geometry for the Zn(II) and Cd(II) complexes. Conductance measurements suggest the nonelectrolytic nature of the complexes, with the exception of the $Zn(TNAPY)_2Cl_2$ and $Cd(TNAPY)_2Cl_2$ compounds which are 1:2 electrolytes.

KEYWORDS: Schiff base, N-[2-thienylmethylidene]-2-aminopyridine, NMR, ESR, Transition Metal Complexes

RESUMO

Complexos metálicos do tipo ML_2Cl_2 [M = Fe(II), Co(II), Ni(II), Cu(II), Cd(II) e L é o ligante N- [2-tienilmetilideno] -2-aminopiridina (TNAPY)] foram preparados e caracterizados usando análise elementar e métodos espectroscópicos e magnéticos. Espectros de ressonância magnética nuclear (RMN) e infravermelho (IV) demonstraram que o nitrogênio do grupo azometina e o enxofre do tiofeno participam da coordenação. Estudos de espectros eletrônicos, magnéticos e ressonância de spin do elétron (RSE) idicam uma estrutura octaédrica distorcida para os complexos de Fe(II), Co(II), Ni(II) e Cu(II) e geometria tetraédrica para os complexos de Zn(II) e Cd(II). Medidas de condutância sugerem que a maioria dos complexos não são eletrólitos, com exceção de $Zn(TNAPY)_2Cl_2$ e $Cd(TNAPY)_2Cl_2$ que são eletrolitos 2:1 .

INTRODUCTION

The pyridine ring occurs in molecules of many natural and synthetic biologically active compounds. Pyridine derivatives have also found application in hydrometallurgy and metal complexes with pyridine bases have been used as catalysts in a number of technological processes[1-4].

In continuation of our work on a metal complexes of Schiff bases[5,6] we report here the results of our studies on the complexes of a Schiff base derived from 2-thiophenecarboxaldehyde (2-TFCA) and 2-aminopyridine (2-APy), N-[thienylmethylidene]-2-aminopyridine (TNAPY), with Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

Tentative structures have been proposed on the basis of analytical, spectral, magnetic and conductance data.

EXPERIMENTAL

Reagents: $FeCl_2 \cdot 4H_2O$ (Merck, 99%), $CoCl_2 \cdot 6H_2O$ (Merck, 99.99%), $NiCl_2 \cdot 6H_2O$ (Merck, 99.99%), $CuCl_2 \cdot 2H_2O$ (Merck, 99.99%), 2-thiophenecarboxaldehyde (Merck, 98%), 2-aminopyridine (Merck, 98%).

Synthesis of bidentate Schiff base. An ethanolic solution of 2-TFCA (0.002 mol, 25 ml) was added to an ethanolic solution of 2-APy (0.002 mol, 25 ml) and refluxed for 6h on a water-bath. After the concentration of the solution, the precipitate was filtered, washed with ethanol and dried over $CaCl_2$ in vacuum. *Anal.* Calcd. for TNAPY : C, 63.83; H, 4.25; N, 14.89; S, 17.02. Found: C, 63.79; N, 14.96; S, 17.43. ^1H NMR: δ_1 8.7; δ_2 7.4; ^{13}C NMR: $\delta_1$162.7; δ_2 132.5; δ_3 111.2.

Synthesis of the ML_2Cl_2 complexes. A mixture of 2-TFCA (0.004 mol, 50 ml) and 2-APy (0.004 mol, 50 ml) in ethanol was added to an ethanolic solution of metal chlorides (0.002 mol, 50ml), at pH=8-8.5. The mixture of reactants was refluxed on a water-bath for 6-8 h. The excess of solvent was then distilled. The compounds separated were filtered, washed with ethanol and dried over $CaCl_2$ in vacuum. *Anal.* Calcd. for $Co(TNAPY)_2Cl_2$: Co, 11.63; C, 47.35; N, 11.05; S, 12.63; Cl, 14.18. Found: Co, 11.71; C, 47.29; N, 11.28; S, 12.60; Cl, 14.67. Calcd. for $Ni(TNAPY)_2Cl_2$: Ni, 11.59; C, 47.37; N, 11.05; S, 12.63; Cl, 14.19. Found: Ni, 11.31; C, 47.05; N, 10.86; S, 12.76; Cl, 14.38. Calcd. for $Cu(TNAPY)_2Cl_2$: Cu, 12.42; C, 41.92; N, 10.95; S, 12.51; Cl, 14.06. Found: Cu, 12.11; C, 41.72; N, 11.15; S, 12.52; Cl, 14.11. Calcd. for $Zn(TNAPY)_2Cl_2$: Zn, 12.47; C, 46.76, N, 10.91; S, 12.47; Cl, 14.00. Found: Zn, 12.44; C, 46.58, N, 10.66; S, 12.45; Cl, 13.56. ^1H NMR: δ_1 9.1; δ_2 7.5; ^{13}C NMR: $\delta_1$165.7; δ_2 137.2; δ_3 116.7. Calcd. for $Cd(TNAPY)_2Cl_2$: Cd, 20.06; C, 42.83, N, 9.99; S, 11.42; Cl, 12.83. Found: Cd, 20.41; C, 42.56, N, 9.40; S, 11.73; Cl, 13.03. ^1H NMR: δ_1 9.1; δ_2 7.6; ^{13}C NMR: $\delta_1$166.6; δ_2 138.7; δ_3 114.8. Calcd. for $Fe(TNAPY)_2Cl_2$: Fe, 11.08; C, 47.64, N, 11.11; S, 12.70; Cl, 14.27. Found: Fe, 11.64; C, 47.98, N, 11.03; S, 12.92; Cl, 14.11.

Instruments. The ligand and the complexes were analysed for M, S and Cl by conventional methods[7,8] , while C and N by microanalytical methods. The IR spectra were obtained with KBr pellets using a BIO-RAD FTS 135 spectrophotometer. The UV-VIS spectra were recorded on an UNICAM UV-VIS UV-4 spectrophotometer in DMF solution. The reflectance spectra were recorded on a VSU-2P spectrometer at room temperature.

The ^{1}H-NMR spectra (in $CDCl_3$) were recorded on a Varian T60, and the ^{13}C-NMR spectra were obtained using a Bruker WH 270 spectrometer. The ESR spectrum was recorded on an ART 5 spectrometer at room temperature.

The magnetic moments have been determined by the Faraday method. A digital conductivity meter K 612 was used to measure the molar conductivities in DMF solution.

RESULTS AND DISCUSSION

The complexes of Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with N-[2-thienylmethylidene]-2-aminopyridine (TNAPY) (Fig. 1) appear as powders. They are not soluble in methanol, ethanol and ethyl ether but soluble in DMF.

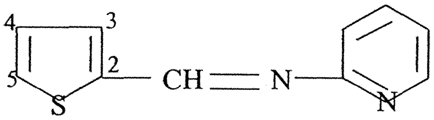


Figure 1. The structure of N-[2-thienylmethylidene]-2-aminopyridine

Based on the elemental analysis, the formula ML_2Cl_2 (Table I) has been suggested for all compounds.

Table I. Analytical and Physical Data of the Complexes*

Compounds	Melting point (°C)	Colour	μ_{eff} (BM)	Λ_M** ($\Omega^{-1}cm^2mol^{-1}$)
$Fe(TNAPY)_2Cl_2$	160	red	5.20	9.5
$Co(TNAPY)_2Cl_2$	180	pink	4.88	5.2
$Ni(TNAPY)_2Cl_2$	175	greenish	3.10	19.8
$Cu(TNAPY)_2Cl_2$	220	blue	1.88	13.5
$Zn(TNAPY)_2Cl_2$	240	white	-	126.9
$Cd(TNAPY)_2Cl_2$	210	yellowish	-	133.2

**All the complexes give satisfactory metal, C, S, N and Cl analyses*
*** in DMF solution*

IR and NMR spectra. Some important IR bands of TNAPY and its complexes along with their assignments are presented in Table II.

Table II. Characteristic Infrared Absorption Frequencies (in cm^{-1}) of Ligand and Complexes

Compound	$\nu_{C=N\ azomethyne}$	$\nu_{C=N\ pyridine}$	ν_{C-S-C}	ν_{C-S}	ν_{M-N}
TNAPY	1675	1456	920	673	-
$Fe(TNAPY)_2Cl_2$	1635	1449	843	640	423
$Co(TNAPY)_2Cl_2$	1621	1455	841	654	419
$Ni(TNAPY)_2Cl_2$	1626	1456	859	650	430
$Cu(TNAPY)_2Cl_2$	1625	1450	851	645	420
$Zn(TNAPY)_2Cl_2$	1640	1451	860	635	418
$Cd(TNAPY)_2Cl_2$	1630	1453	835	630	415

The IR spectrum of the ligand shows a band at 1675 cm^{-1} which is assigned to the $\nu_{C=N}$ of the azomethyne group and an intense band at 1456 cm^{-1} corresponding to the C=N stretching of the pyridine ring. The comparison of the positions of these bands with those observed in the IR spectra of the complexes indicates that the band at 1675 cm^{-1} shifts towards lower frequencies ($\Delta\nu$=35-55 cm^{-1}) , while that at 1456 cm^{-1} does not show a marked shift. This behaviour suggests that TNAPY is coordinated to the central metal ion through the azomethyne nitrogen. The proof of the coordination to the N atom is provided by the occurrence of the bands in the 415-430 cm^{-1} region in the IR spectra of the compounds.

The band observed in the free ligand spectrum at 920 cm^{-1} can be ascribed to ν_{C-S-C} stretching vibration[9]. This band shifted to lower values with 60-85 cm^{-1}, for all compounds, suggesting the involvement of the sulphur atom in bonding with the metal ions. The band observed at 673 cm^{-1} in the ligand spectrum, assigned to the ν_{C-S} stretching vibration, is similarly shifted. This also confirms that the thiophene ring sulphur is a donor atom[10].

In the ^{1}H-NMR spectrum of the ligand, the thiophene ring proton 5-H appears at δ 7.4 ppm and the azomethyne proton (-CH=N-) at 8.7 ppm. These signals register downfield shifts (1-2 ppm) in the Zn(II) and Cd(II) complexes. These observations support the bonding of TNAPY through nitrogen and sulphur atoms.

The ^{13}C-NMR spectra provide further support for the mode of coordination of TNAPY. In the complexes spectra, the signals due to azomethyne carbon, 2-C and 5-C (thiophene ring) show a distinct downfield shift by nearly 3-6 ppm clearly demonstrating the coordination of the ligand via the nitrogen and sulphur atoms.

Electronic and ESR spectra. Within the UV spectrum of the ligand, the existence of two absorption bands assigned to the transition $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ at 41 518 and 37 340 cm^{-1}, respectively, has been observed.

These transitions are to be found also in the spectra of the complexes, but they are shifted to lower frequencies ($\Delta\nu$=2000-2500 cm^{-1}), confirming the coordination of the ligand to the metal ions. The relevant electronic spectral data are reported in the Table III.

Table III. Electronic Spectra of the Complexes

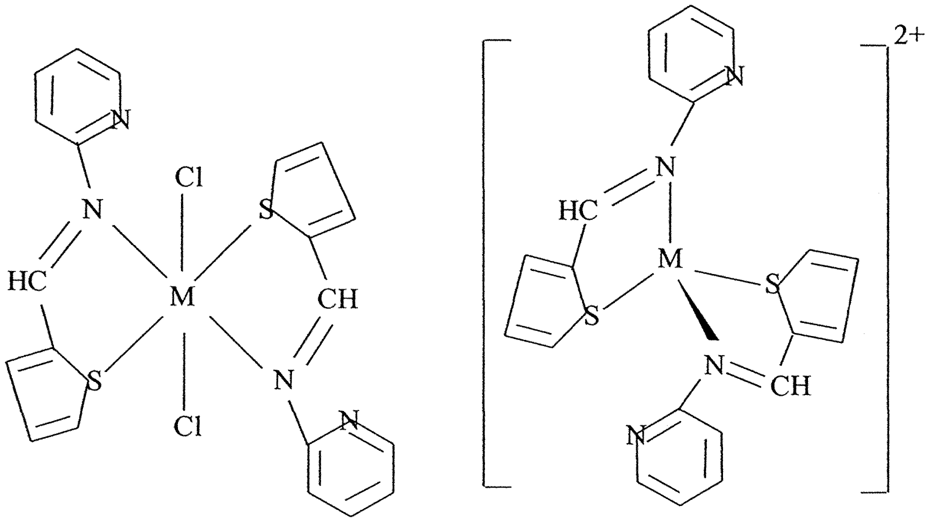
Compound	Absorption maxima (cm^{-1})				
[Fe(TNAPY)$_2$Cl$_2$]		12 800	11 200		
[Co(TNAPY)$_2$Cl$_2$]	21 270	19 040	15 600	9 210	8 330
[Ni(TNAPY)$_2$Cl$_2$]		22 320	17 000	9 200	
[Cu(TNAPY)$_2$Cl$_2$]			16 500		

The electronic spectrum of the iron(II) complex consists of a pair of low intensity bands at 12800 and 11200 cm^{-1} arising from $^5T_{2g} \rightarrow {}^5E_g$ transitions, similar to those found for distorted octahedral complexes. The doublet is attributed to Jahn-Teller distortion in the excited state[11]. The room temperature magnetic moment (5.2 BM) corresponds with the octahedral symmetry.

The reflectance spectrum of the Co(TNAPY)$_2$Cl$_2$ complex exhibits five bands. The bands at 21270 and 19040 cm^{-1} arise from the $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition which is split in complexes of D_{4h} symmetry. That at 15600 cm^{-1} arise from the $^4T_{1g} \rightarrow {}^4A_{2g}$ transition and those at 9210 and 8549 cm^{-1} from the $^4T_{1g} \rightarrow {}^4T_{2g}(F)$ transition.

The ligand field spectrum of the Ni(II) compound could be assigned assuming that the stereochemistry is pseudo-octahedral. The bands may be assigned to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ (ν_1), $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3), respectively. The low energy band is broad indicating (tetragonal) distortion and the room temperature. A magnetic moment (3.1 BM) in the region is expected for the octahedral complexes of the Ni(II) ion.

The proposed structural formulas of Fe(II), Co(II), Ni(II) and Cu(II) complexes is given in figure 2a and those of the Zn(II) and Cd(II) complexes is show in figure 2b.



a. b.

Figure 2. The proposed formulas of the complexes:
a.[M(TNAPY)$_2$Cl$_2$] (M = Fe^{II}, Co^{II}, Ni^{II} and Cu^{II});
b.[M(TNAPY)$_2$]Cl$_2$ (M = Zn^{II} and Cd^{II}).

The electronic spectrum of $Cu(TNAPY)_2Cl_2$ complex shows only one broad absorption band at 16500 cm^{-1} indicating probably a distorted octahedral configuration. The magnetic moment value is 1.88 BM. The ESR spectrum for this compound, measured in a polycrystalline sample at room temperature, gives the following values: $g_{II}=2.067$ and $g_{\perp}=2.146$. The value $g_{II} < g_{\perp}$ is well consistent with a primarily d_{z2} ground state and the spectrum is characteristic of axial (compressed octahedral) symmetry. The parameter G, determined as $G =(g_{II}-2)/(g_{\perp}-2)$, is found to be much less than 4 suggesting a considerable interaction in the solid state[12].

Zinc(II) and cadmium(II) complexes do not show d-d transitions hence their stereochemistry can not be determined from UV and visible reflectance spectra. From stoichiometry and other physicochemical evidence, a four-coordinated tetrahedral geometry is suggested for Zn(II) and Cd(II) complexes (see figure 2b).

The molar conductance of the complexes, in DMF (10^{-3} M) solution, is in the range 5.2-19.8 $\Omega^{-1}cm^2mol^{-1}$ indicating their nonelectrolytic nature, with the exception of the Zn(II) and Cd(II) compounds which are 1:2 electrolytes.

CONCLUSIONS

In this paper we report the preparation, isolation and characterisation of a new bidentate Schiff base ligand derived from 2-thiophenecarboxaldehyde and 2-aminopyridine, and its complexes with Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

The products were characterised by elemental analysis, magnetic and spectroscopic measurements.

From the infrared and NMR spactral studies of the ligand and complexes it is obvious that the ligand act as bidentate coordinating through the azomethine nitrogen and the thiophene sulphur.

Correlating the experimental data, one can predict the stereochemistry of the prepared complexes: distorted octahedral for the $[M(TNATZ)_2Cl_2]$ ($M = Fe^{II}, Co^{II}, Ni^{II}$ and Cu^{II}) and tetrahedral for the $[M(TNATZ)_2]Cl_2$ ($M= Zn^{II}$ and Cd^{II}) compounds.

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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
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A QUEUEING MODEL FOR SOME CATALYTIC REACTIONS

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ABSTRACT

The waiting model associated to the catalytical process given by the chemical equation $C + S \underset{k_2}{\overset{k_1}{\leftrightarrows}} CS \xrightarrow{k_3} C + P$ (1), *is described by the Markov process:* $\{X_i(t); t \geq 0\}$, $(i = 1, 2, 3, 4)$, *where the random variables are the concentrations of the species* C *(the catalyst),* S *(the substrate),* CS *(the intermediate complex formed by the substrate* S *and the catalyst) and* P *(the reaction product) at time* t. *The equations, that describe the evolution of the process, have been obtained.*

KEYWORDS: waiting model, catalytic processes , Markov process.

RESUMO

O modelo de "fila de espera" associado com o processo catalítico descrito pela equação

$$C + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CS \xrightarrow{k_3} C + P \quad (1)$$

é descrito pelo processo de Markov $\left[X_i(t);\ t \geq o\right]$, $\left[i=1,2,3,4\right]$, onde as variáveis casuísticas são as concentrações das espécies C (catalizador), S (substrato), CS (o complexo intermediário formado entre o substrato e o catalizador) e P (o produto da reação) no tempo t. Foram obtidas as equações que descrevem o processo (1) .

1 Introduction

A catalytic reaction may be represented as follows

$$C + S \underset{k_2}{\overset{k_1}{\leftrightarrows}} CS \xrightarrow{k_3} C + P \tag{1}$$

or, more explicitly,

$$\begin{cases} (T_1): \ C + S \xrightarrow{k_1} CS \\ (T_2): \ CS \xrightarrow{k_2} C + S \\ (T_3): \ CS \xrightarrow{k_3} C + P \end{cases} \tag{2}$$

We have denoted by C -the catalyst, S -the substrate, CS -the intermediate complex formed by the substrate S and the catalyst, P -the reaction product, k_i $(i = 1, 2, 3)$ -the rate constants of reaction associated with each step of the process.

1. It is probable that the catalyst's reaction with the substrate S is reversible, forming the intermediate complex CS (the bimolecular process T_1) which may dissociate then into the initial reactants (the unimolecular transformation T_2) or may decompose into the reaction product and the catalyst in the initial form (the unimolecular decomposition T_3).

We suppose that the balance between the initial reactants and the complex CS involves very fast reactions with respect to the decomposition step (T_3), *i.e.* $k_3 \ll k_1$ and $k_3 \ll k_2$, so that the balance is not interrupted by an ordinary decomposition.

Many deterministic models for the kinetics of the catalytic processes were suggested and studied. The deterministic approach still has some deficiencies. Thus, the catalytic processes are developed for the individual molecular species and for the complexes. Actually, the transformations take place only for groups and it is interesting to find a mathematical model for which the number of moles per second is considered, from the mathematical point of view, a continuous variable.

In all the formulations used for a catalytic process involving one or more intermediates probabilistic laws are employed and these should be included in the mathematical model. This is not the case for the deterministic models. The deterministic approach of the catalytic processes does not take into account all the random fluctuations which frequently appear in practice.

In the mathematical model considered, some of these deficiencies typical to the deterministic models are removed by describing more accurately the catalytic process.

We shall consider the catalytic process as a waiting phenomenon. If we take into consideration the action of a catalyst molecule we see that after an "effective" collision with a molecule of the substrate S, it will be free to collide with another molecule of the substrate S.

This leads us to the idea of considering the catalyst molecules as "serving stations" and the molecules of the substrate S as "clients". The transformation of a molecule of the S substrate into the complex means serving one client.

The mechanism of the catalytic processes being generally complicated, its description by a waiting model which takes into consideration all the intervening factors is difficult, and therefore we shall consider a simpler case. We suppose that we introduce in a container x_{10} catalyst molecules (the stations). We suppose that each catalyst molecule is capable at a certain moment of time to transform into intermediary complex CS only a molecule of the S substrate. From (2) we notice that the transformations (T_2) and (T_3) impose to the catalytic process a distinct feature from the point of view of the waiting theory namely the fact that the "serving" mechanism of the client by the station may be terminated either through the "unsatisfied" request (the complex CS may dissociate into the substances C and S which formed it), or through the "satisfied" request, namely the effective serving of the client (the complex CS may decompose in the reaction product P with the catalyst C). In both cases, the station remains free so that the next client may be served.

Another feature of this model is that the catalyst molecules (the stations) and the molecules of substrate S (the clients) have random motions, of Brownian type, changing permanently their positions. If we take into consideration that the number of inefficient collisions between a C and an S molecule is randomized, we deduce that serving is made on the principle "the first arrived is the first served". The whole arriving mechanism is hence random, because there might be more random collisions which did not lead to the formation of the complex before an effective collision.

2 Waiting Model

The waiting model associated with the catalytic process given by the chemical equations (1) or (2) is described by the Markov process:

$$\{X_i(t)\,; t \geq 0\} \;\; (i = 1, 2, 3, 4)$$

where the random variables $X_i(t)$ $(i = 1, 2, 3, 4)$ are the concentrations of the species C, S, CS and P at time t.

The state space X is the space of all the possible values x_i $(i = 1, 2, 3, 4)$ which might be taken by the random variable $X_i(t)$ $(i = 1, 2, 3, 4)$.

We suppose that during the infinitesimal interval of time $(t, t + \Delta t)$ either one of the three processes can take place: the formation of the complex CS (T_1), or its dissociation (T_2), or its decomposition to form the product (T_3).

We denote by μ_1, μ_2, μ_3 the stochastic parameters corresponding to the reaction rate constants k_1, k_2, k_3. The chemical process described by the equations (2) could be defined by using the following probabilities:

1^0. $\mu_1 x_1 x_2 \Delta t + 0(\Delta t)$, the probability that in the interval of time $(t, t + \Delta t)$ the complex CS is formed through the transformation (T_1), knowing that at the initial time $t = 0$ there were x_{10} and x_{20} of the type C and S respectively and that at time t $(t > 0)$ there were x_1 and x_2 molecules of C and S, respectively.

2^0. $\mu_2 x_3 \Delta t + 0(\Delta t)$, the probability that in the interval of time $(t, t + \Delta t)$ the complex CS dissociates by transformation (T_2), knowing that at the time t $(t > 0)$ there were x_3 molecules of the type CS.

3^0. $\mu_3 x_3 \Delta t + 0(\Delta t)$, the probability that in the interval of time $(t, t + \Delta t)$ the complex CS dissociates by means of transformation (T_3), knowing that at the moment t $(t > 0)$ there were x_3 molecules of type CS.

4^0. $0(\Delta t)$, the probability that in the interval of time $(t, t + \Delta t)$ more than one molecule of the type CS is formed or that more than one molecule of the type CS reacts to form C and S or C and P.

5^0. $1 - (\mu_1 x_1 x_2 + \mu_2 x_3 + \mu_3 x_3)\Delta t + 0(\Delta t)$, the probability that in the time interval $(t, t + \Delta t)$ there is no change in the concentrations of the species C, S, CS and P, knowing that at the moment t $(t > 0)$ there were x_i $(i = 1, 2, 3)$ molecules of type C, S and CS.

The process defined above, not being linear with respect to the concentrations x_i of the reacting species, is not a simple process of birth and death. The concentrations of the species C, S, CS and P are statistically independent. Let

$$P(x_1, x_2, x_3, x_4; t) = P\{X_i(t) = x_i, i = 1, 2, 3, 4\}$$

be the probability that at the moment t $(t > 0)$ there are in the system x_1 molecules of the catalyst species C, x_2 molecules of the substance S, x_3 CS complex molecules and x_4 molecules for the reaction product P.

Using the probabilities $1^0 - 5^0$ we may write the equation:

$$P(x_1, x_2, x_3, x_4; t + \Delta t) = [1 - (\mu_1 x_1 x_2 + \mu_2 x_3 + \mu_3 x_3)\Delta t] P(x_1, x_2, x_3, x_4; t) +$$

$$+\mu_1 (x_1 + 1)(x_2 + 1) \Delta t P(x_1 + 1, x_2 + 1, x_3 - 1, x_4; t) +$$

$$+\mu_2 (x_3 + 1) \Delta t P(x_1 - 1, x_2 - 1, x_3 + 1, x_4; t) +$$

$$+\mu_3 (x_3 + 1) \Delta t P(x_1, x_2, x_3 + 1, x_4 - 1; t) \Delta t$$

Taking into consideration also that

$$x_1 = x_{10} - x_3, \; x_4 = x_{20} - (x_2 + x_3)$$

it follows that:

$$P(x_2, x_3; t + \Delta t) = \{1 - [\mu_1 x_2 (x_{10} - x_3) + \mu_2 x_3 + \mu_3 x_3] \Delta t\} P(x_2, x_3; \Delta t) +$$

$$+\mu_1 (x_{10} - x_3 + 1)(x_2 + 1) \Delta t P(x_2 + 1, x_3 - 1; t) +$$

$$+\mu_2 (x_3 + 1) \Delta t P(x_2 - 1, x_3 + 1; t) +$$

$$+\mu_3 (x_3 + 1) \Delta t P(x_2, x_3 + 1; t) + 0(\Delta t)$$

Substituting in the first term $P(x_2, x_3; t)$, dividing by Δt and taking the limit $\Delta t \to 0$, we get the partial derivative equation:

$$\frac{\partial P(x_2, x_3; t)}{\partial t} = -[\mu_1 x_2 (x_{10} - x_3) + \mu_2 x_3 + \mu_3 x_3] P(x_2, x_3; t) +$$

$$+\mu_1 (x_{10} - x_3 + 1)(x_2 + 1) P(x_2 + 1, x_3 - 1; t) + \tag{3}$$

$$+\mu_2 (x_3 + 1) P(x_2 - 1, x_3 + 1; t) + \mu_3 (x_3 + 1) P(x_2, x_3 + 1; t)$$

We introduce the generating function:

$$G(s_2, s_3; t) = \sum_{x_2=0}^{x_{20}} \sum_{x_3=0}^{x_{30}} P(x_2, x_3; t)\, s_2^{x_2} s_3^{x_3}, \ |s_2| \leq 1, |s_3| \leq 1$$

Multiplying in the equation (3) by $s_2^{x_2} s_3^{x_3}$ and suming over x_2 and x_3, we obtain the partial derivative equation:

$$\frac{\partial\, G(s_2, s_3; t)}{\partial\, t} = \mu_1 x_{10} \left(s_3^2 - s_2\right) \frac{\partial\, G(s_2, s_3; t)}{\partial\, s_2} + (\mu_3 + \mu_2 s_2 - \mu_2 s_3 - \mu_3 s_3) \cdot \tag{4}$$

$$\cdot \frac{\partial\, G(s_2, s_3; t)}{\partial\, s_3} + \mu_1 s_3 (s_2 - s_3) \frac{\partial^2\, G(s_2, s_3; t)}{\partial\, s_2\, \partial\, s_3}$$

Aplying the cumulative generating function:

$$K(u, v; t) = \log G(s_2, s_3; t)$$

to equation (4) we get:

$$\frac{\partial\, K(u, v; t)}{\partial\, t} = \mu_1 x_{10} \left(e^{2v-u} - 1\right) \frac{\partial\, K(u, v; t)}{\partial\, u} +$$

$$+ \left(\mu_2 e^{u-v} + \mu_3 e^{-v} + \mu_2 - \mu_3\right) \frac{\partial\, K(u, v; t)}{\partial\, v} + \tag{5}$$

$$+ \mu_1 \left(1 - e^{v-u}\right) \frac{\partial^2\, K(u, v; t)}{\partial\, u\, \partial\, v} + \mu_1 \left(1 - e^{v-u}\right) \frac{\partial\, K(u, v; t)}{\partial\, u} \frac{\partial\, K(u, v; t)}{\partial\, v}$$

On the other hand, using the relation between the differential cumulant generating function and the moments of the random variables $X_2(t)$ and $X_3(t)$ and the usual notations, we obtain:

$$K(u, v; t) = uM(X_2(t)) + vM(X_3(t)) + \frac{1}{2} u^2 D^2 (X_2(t)) + \frac{1}{2} v^2 D^2 (X_3(t)) +$$

$$+ uvCov(X_2(t), X_3(t)) + \cdots$$

Calculating the partial derivatives:

$$\frac{\partial\, K(u, v; t)}{\partial\, t}, \frac{\partial\, K(u, v; t)}{\partial\, u}, \frac{\partial\, K(u, v; t)}{\partial\, v}, \frac{\partial^2\, K(u, v; t)}{\partial\, u\, \partial\, v}$$

and substituting them into (5) we get:

$$\frac{d\,M\left(X_2\left(t\right)\right)}{d\,t} = -\mu_1 x_{10} M\left(X_2\left(t\right)\right) + \mu_2 M\left(X_3\left(t\right)\right) +$$

$$+\mu_1 Cov\left(X_2\left(t\right), X_3\left(t\right)\right) + \mu_1 M\left(X_2\left(t\right)\right) M\left(X_3\left(t\right)\right)$$

$$\frac{d\,M\left(X_3\left(t\right)\right)}{d\,t} = 2\mu_1 x_{10} M\left(X_2\left(t\right)\right) - \left(\mu_2 - \mu_3\right) M\left(X_3\left(t\right)\right) -$$

$$-\mu_1 Cov\left(X_2\left(t\right), X_3\left(t\right)\right) - \mu_1 M\left(X_2\left(t\right)\right) M\left(X_3\left(t\right)\right) + 2\mu_2 D^2\left(X_3\left(t\right)\right)$$

$$\frac{d\,D^2\left(X_2\left(t\right)\right)}{d\,t} = 2\mu_1\left[M\left(X_3\left(t\right)\right) - x_{10}\right] D^2\left(X_2\left(t\right)\right) + \mu_1 x_{10} M\left(X_3\left(t\right)\right) -$$

$$-\mu_1 M\left(X_2\left(t\right)\right) M\left(X_3\left(t\right)\right) + \left[2\mu_2 - \mu_1 + 2M\left(X_2\left(t\right)\right)\right] Cov\left(X_2\left(t\right), X_3\left(t\right)\right)$$

$$\begin{aligned}\frac{d\,D^2\left(X_3\left(t\right)\right)}{d\,t} &= -2\left[\mu_2 + \mu_3 + \mu_1 M\left(X_2\left(t\right)\right)\right] D^2\left(X_3\left(t\right)\right) + 4\mu_1 x_{10} M\left(X_2\left(t\right)\right) + \\ &\quad + \left(\mu_2 + \mu_3\right) M\left(X_3\left(t\right)\right) - \mu_1 M\left(X_2\left(t\right)\right) M\left(X_3\left(t\right)\right) + \\ &\quad + \mu_1\left[4x_{10} - 1 - 2M\left(X_2\left(t\right)\right)\right] Cov\left(X_2\left(t\right), X_3\left(t\right)\right)\end{aligned}$$

$$\frac{d\,Cov\left(X_2\left(t\right), X_3\left(t\right)\right)}{d\,t} = \left\{\mu_1\left[1 - x_{10} - M\left(X_2\left(t\right)\right) + M\left(X_3\left(t\right)\right)\right] - \mu_2 - \mu_3\right\} \cdot$$

$$\cdot Cov\left(X_2\left(t\right), X_3\left(t\right)\right) + \mu_1\left[2x_{10} - M\left(X_3\left(t\right)\right)\right] D^2\left(X_2\left(t\right)\right) +$$

$$+\left[\mu_1 + x_{10} M\left(X_2\left(t\right)\right) + \mu_2 + \mu_1 M\left(X_2\left(t\right)\right)\right] D^2\left(X_3\left(t\right)\right) -$$

$$-2\mu_1 x_{10} M\left(X_2\left(t\right)\right) - \mu_2 M\left(X_3\left(t\right)\right)$$

which are exactly the equations describing the evolution of the catalytic process with time.

The stochastic model presented may be considered an extension of the deterministic model known in chemical kinetics.

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CHROMIUM (III) COMPLEX ANIONS IN THE CHEMICAL ANALYSIS. THIORIDAZINE DETERMINATION

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ABSTRACT

Complex anions of Cr(III) analogues of Reinecke's salt, $[Cr(NCS)_4(amine)_2]^-$ are good analytical reagents with high sensibility and selectivity for N-organic bases of pharmaceutical importance. We have observed that the phenothiazinic type drug, thioridazine, prescribed for the treatment of maniac-depressing psychosis precipitates with Cr(III) complex anions. Some new oxidative methods for the determination of thioridazine (10-[2-(1-methyl-2-piperidinyl)ethyl]-2-(methylthio)-10H-phenothiazine) are described. The results were evaluated statistically.

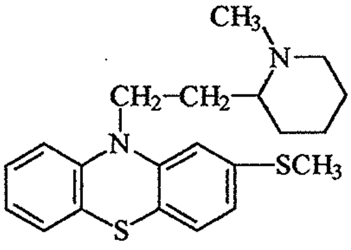
KEYWORDS : chromium (III), thioridazine, drugs, oxidimetric and spectrometric methods

RESUMO

Complexox aniônicos de Cr(III), análogos do sal de Reinecke, são reagentes analíticos excelentes e possuem sensibilidade e seletividade alta para para bases orgânicas de N que tem importância farmacêutica. O presente estudo demonstrou que a tioridazina, um medicamento do tipo fenotiazínico, receitado para tratamento de psicóse maniaco-depressiva, forma precipitados com ânions complexos de Cr(III). Vários métodos oxidativos para a determinação de tioridazina (10- 2-(1-metil-2-piperdinil)etil -2-(metiltio)-10H-fenotiazina) sao descritos. Os resultados experimentais foram avaliados estatisticamente.

INTRODUCTION

Thioridazine is a piperidine phenothiazine with the structural formula:



that contains the methyl mercapto radical (-S-CH_3) at position 3 of the phenothiazine skeleton. Thioridazine, like the other three major groups of phenothiazine tranquilizers, is a drug that has principally a nonpsychotic sedative effect and is indicated for the treatment of acute or chronic schizophrenia, psychosis, maniac depressive psychosis, tension, anxiety, epileptic psychosis and old age psychosis.

Thioridazine is very useful drug in therapeutics and it less toxic than chlorpromazine. It is well absorbed by the alimentary tract and is eliminated both by the kidney and the intestine in 24 hours [1].

The common qualitative analysis methods used for the identification of thioridazine are, in general, those used for the phenothiazine derivatives. Because of the piperidine function ($K_0=1.6x10^{-3}$), thioridazine forms salts that are characterised by reduced solubility and high melting points with $HClO_4$, silicotungstic acid, sodium tetraphenyl borate etc. Oxidizing agents form compounds of different colours with thioridazine. Some common oxidizing agents are $FeCl_3$ [2,3], persulfates, HNO_3, MnO_2, PbO_2, etc.

EXPERIMENTAL PROCEDDURE

Combinations analogous to Reineck's salts have been obtained by Gănescu's method[8] using substitution reactions with $K_3[Cr(NCS)_6]$ without water and the respective amines in the absence of any solvent. Some combinations used involved aniline, morpholine, diethylphosphine, etc.

Complex salts of the type ThioridazineH$[Cr(NCS)_4(amine)_2]$ were studied with respect to their thermal stability in combustion process, having in view the gravimetric determination of this drug. The study showed a remarkable stability up to 150°C.

For the synthesis of these complexes, samples of 10 mmole of thioridazine·HCl in 100 mL of water were treated with a small excess of $K_3[Cr(NCS)_6]$ in 2% alcohol solution. The red – violet precipitates were filtered under vacuum and dried in air until the filtrate was colorless. Some of the new thioridazine salts prepared are summarized in Table 1.

Table I. New complex salts of the type ThioridazineH$[Cr(NCS)_4(aniline)_2]$

No	Formula	Molecular Weight calcd.	Yield [%]	Analysis [%]	
				Calcd.	Found
1	$A_3H_3[Cr(NCS)_6]$	1515.16	97	Cr** 3.43 S** 16.93 N** 11.12	3.40 16.86 11.12
2	$AH[Cr(NCS)_4(NH_3)_2]$	689.98	96	Cr 7.53 S 18.58 N 16.24	7.50 18.52 16.20
3	$AH[Cr(NCS)_4$(aniline)$_2]$	842.04	98	Cr 6.17 S 15.23 N 13.31	6.09 15.20 13.26
4	$AH[Cr(NCS)_4$(benzilamine)$_2]$	870.08	95	Cr 5.97 S 14.74 N 12.88	5.92 14.70 12.76
5	$AH[Cr(NCS)_4$(morfoline)$_2]$	830.16	93	Cr 6.26 S 15.45 N 13.50	6.15 15.41 13.44
6	$AH[Cr(NCS)_4$(imidazole)$_2]$	792.08	89	Cr 6.56 S 16.19 N 17.68	6.50 16.05 17.60
7	$AH[Cr(NCS)_4$(benzimidazole)$_2]$	892.16	92	Cr 5.82 S 14.37 N 15.70	5.76 14.24 15.61
8	$AH[Cr(NCS)_4$(benztriazole)$_2]$	894.12	94	Cr 5.81 S 14.34 N 18.80	5.76 14.24 18.72

* The obtained combinations have a microcrystalline aspect and have red-violet colour.
**Chromium was determined as Cr_2O_3, sulphur as $BaSO_4$ and nitrogen by volumetric method.
A= Thioridazine

Indirect Oxidative Determination of Thioridazine after Precipitation in the Form of ThioridazineH$[Cr(NCS)_4(aniline)_2]$

A sample of 1.82 – 14.56mg of thioridazine·HCl was precipitated from an aqueous alcohol solution (2%) in the form of Reinecke's salt. The precipitate was filtered under vacuum using a Büchner funnel with a 5 cm diameter and washed 3-4 times with 10 mL of water, until the filtrate was colorless. After washing, the precipitate was transferred to a Berzelius cup and the funnel was washed with 10 mL of 5% NaOH and 10 mL of water. This represent the initial volume ($V_{initial}$) in the relation below giving V_{HCl}. The cup was heated until the appearance of the green color of $Cr(OH)_3$. It was then cooled with tap water and concentrated HCl was added, the quantity being calculated according to the relation:

$$V_{HCl} = \frac{1.7(V_{initial} + V_{oxidizer})}{10.4}$$

In each test the normality of HCl was constant (1.7N). The normality of concentrated HCl with a density of 1.19 g/cm^3 was 12.1N. After the addition of the calculated quantity of HCl, 5 mL of CCl_4 and 10 drops of ICl [17] indicator were added to the solution and NCS^- was titrated with 0.1N $KMnO_4$ under continuos stirring until the nonaqueous violet layer became colorless. The reaction that took place was the following:

$$5NCS^- + 6MnO_4^- + 13H^+ \rightarrow 6Mn^{2+} + 5SO_4^{2-} + 5HCN + 4H_2O$$

respectively:

$$2NCS^- + 3BrO_3^- + 4H^+ \rightarrow 2SO_4^{2-} + 3Br^+ + 2HCN + H_2O$$
$$2NCS^- + 3IO_3^- + 4H^+ \rightarrow 2SO_4^{2-} + 3I^+ + H_2O$$

A volume of 1mL $KMnO_4$ (KIO_3, $KBrO_3$) is equivalent with 1.54 mg thioridazine.

The experimental results are given in the Tables 2 and 3.

Table 2. Permangante Oxidative Determination of Thioridazine after Precipitation in the form ThioridazineH[$Cr(NCS)_4(aniline)_2$] (A) and ThioridazineH[$Cr(NCS)_4(Et_2PhP)_2$] (B), respectively.

No	The form of determination						
	A				B		
	Thioridazine mg taken	Thioridazine mg found	Error		Thioridazine mg found	Error	
			mg	%		mg	%
1	1.82	1.83	+0.01	0.54	1.81	-0.01	0.54
2	3.64	3.65	+0.01	0.27	3.62	-0.02	0.54
3	5.46	5.43	-0.03	0.54	5.48	+0.02	0.36
4	7.28	7.25	-0.03	0.41	7.30	+0.02	0.27
5	10.92	10.96	+0.04	0.36	10.93	+0.01	0.09
6	14.56	14.54	-0.02	0.14	14.60	+0.04	0.27

1 mL $KMnO_4$ 0.1N is equivalent to 1.544 mg thioridazine

A
$\overline{x}=14.57$
$s=2 \cdot 10^{-2}$
$s^2=4 \cdot 10^{-4}$
t=0.5
$t_{n-1,\alpha}=2,26$; $\alpha=95\%$
$\overline{x} - ts < A < \overline{x} + ts$
14.55 < 14.56 <14.57

B
$\overline{x}=10.93$
$s=2.58 \cdot 10^{-2}$
$s^2=6.65 \cdot 10^{-4}$
t=0.39
$t_{n-1,\alpha}=2,26$; $\alpha=95\%$
$\overline{x} - ts < A < \overline{x} + ts$
10.91 < 10.92 < 10.94

Table 3. Bromate Oxidative Determination of Thioridazine after Precipitation in the form ThioridazineH[$Cr(NCS)_4(NH_3)_2$] (A) and ThioridazineH[$Cr(NCS)_4(morfoline)_2$] (B), respectively.

No	The form of determination						
	A				B		
	Thioridazine mg taken	Thioridazine mg found	Error		Thioridazine mg found	Error	
			mg	%		mg	%
1	1.82	1.83	+0.01	0.54	1.84	+0.02	1.09
2	3.64	3.63	-0.01	0.27	3.66	+0.02	0.54
3	5.46	5.44	-0.02	0.37	5.44	-0.02	0.36
4	7.28	7.26	-0.02	0.27	7.25	-0.03	0.41
5	10.92	10.95	+0.03	0.27	10.94	+0.02	0.18
6	14.56	14.58	+0.02	0.13	14.60	+0.04	0.27

1 mL $KBrO_3$ 0.1N is equivalent to 1.544mg thioridazine

A
$\overline{x}=14.57$
$s=2.66 \cdot 10^{-2}$
$s^2=7.07 \cdot 10^{-4}$
t=0.38
$t_{n-1,\alpha}=2,26$; $\alpha=95\%$
$\overline{x} - ts < A < \overline{x} + ts$
14.55 < 14.56 < 14.58

B
$\overline{x}=10.93$
$s=1.82 \cdot 10^{-2}$
$s^2=3.33 \cdot 10^{-4}$
t=0.77
$t_{n-1,\alpha}=2,26$; $\alpha=95\%$
$\overline{x} - ts < A < \overline{x} + ts$
10.91 < 10.92 < 10.94

From statistic interpretation of the experimental data[15,16] we conclude that oxidative methods are reproducible, rapid, sufficiently accurate, in comparison with other dosing methods of phenothiazine found in the literature. Titration is made without extra consumption of reagent. For these reasons we believe that this method may be of use and interest for laboratories concerned with drug analysis and control.

Spectrometric Determination of Thioridazine after Precipitation in the Form of Thioridazine·H[$Cr(NCS)_4(aniline)_2$]

A stock solution of a thioridazine hydrochloride of known titre was first prepared. Samples containing 2.2-30.8 mg of thioridazine were precipitated with a small excess of the reagent in the form ThioridazineH[Cr(NCS)$_4$(aniline)$_2$]. After 10 – 15 minutes, the precipitate was filtered using a G$_4$ filter crucible and washed 2-3 times with 10 mL of water until the filtrate flowed colourless. The precipitate was then dissolved in acetone, the red-violet solution was transferred to a 50 mL volumetric flask and diluted with acetone to the mark. The absorbance of the respective solutions was then measured at 535-540 nm using a Spekol Zeiss Jena spectrophotometer.

The experimental absorbance values follow the Beer- Lambert law in the 0.088 to 1.232 mg of thioridazine/mL concentration range. The experimental results are illustrated in Figure 1 and Table 4. The molar absorptivity coefficient, ε, determined was at 218.44 L cm^{-1} mol^{-1}.

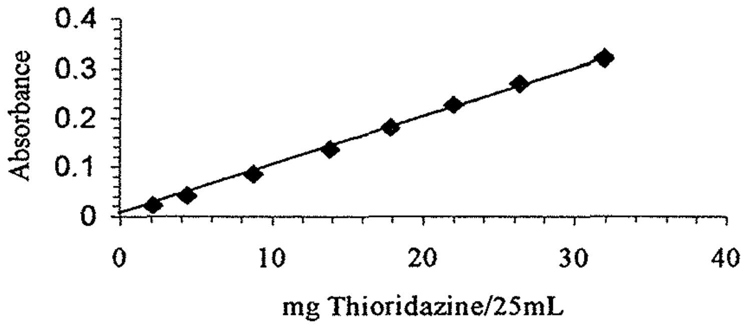


Figure 1. Calibration curve for the Spectrometric Determination of Thioridazine as ThioridazineH[Cr(NCS)$_4$(aniline)$_2$]

Table 4. Spectrometric Determination of Thioridazin after Precipitation in the Form of ThioridazineH[Cr(NCS)$_4$(aniline)$_2$]

No	x mg	x^2	y	y^2	xy	x+y	(x+y)^2
1	2.20	4.84	0.022	0.000484	0.0484	2.222	4.9373
2	4.40	19.36	0.045	0.002025	0.1980	4.445	19.7580
3	8.80	77.44	0.091	0.008281	0.8008	8.891	79.0499
4	13.20	174.24	0.136	0.018496	1.7952	13.366	177.8489
5	17.60	309.76	0.181	0.032761	3.1852	17.781	316.1639
6	22.00	484.00	0.227	0.051529	4.9940	22.227	494.0395
7	26.40	696.96	0.272	0.073984	7.1808	26.672	711.3956
8	30.80	948.64	0.320	0.102400	9.8560	31.120	968.4544
Total	125.40	2715.24	1.294	0.28996	28.0588	126.694	2771.6475

The statistical analysis presented in Table 4 was done using the following equations:

$$\Sigma (x+y)^2 = \Sigma (x^2 + 2xy + y^2) = \Sigma x^2 + \Sigma y^2 + 2\Sigma xy$$

So $\Sigma (x+y)^2 = 2771.647$

$$\Sigma x^2 + \Sigma y^2 + 2\Sigma xy = 2715.24 + 0.28996 + 2x28.0588 = 2771.647$$

The comparison of the experimental results from Table 2 and Table 4 shows that the spectrometric method proposed in the present study for dosing thioridazine is reproducible and exact and can be applied in the laboratory for the analysis and control of this drug.

The equation that gave the best agreement between the absorbance and the concentration of the active product (Thioridazine) in the test samples expressed in mg or μg obtained by linear regression analysis [15-16] was the following:

$y-\bar{y}=r\frac{\sigma_y}{\sigma_x}(x-\bar{x})$ where $\bar{y}=0.16175$; σ_x and σ_y are standard calculated with the help of the relations:

$\sigma_x=\sqrt{\frac{\sum x^2}{n}-\bar{x}^2}$ in our case:

σ_x being equal with 9.6798 and $\bar{x}=15.675$

$\sigma_y=\sqrt{\frac{\Sigma y^2}{n}-\bar{y}^2}$ in our case:

$\sigma_y=0.10004$

$y=0.01037x-0.00083$ respectively

$x=96.4123y+0.08030$ $\qquad x-\bar{x}=r\frac{\sigma_x}{\sigma_y}(y-\bar{y})$

The calculation of the correlation (regression) coefficient is done according to the relation:

$$r=\frac{[\frac{1}{n}\ \Sigma xy]-xy}{\sigma_x\sigma_y}$$

The angle between the two straight lines was very small, the dependence between the absorbance and the concentration of thioridazine was linear and the correlation coefficient r was 1.000.

Using the same method we determined the thioridazine concentrations shown in Tables 2 and 3. (One tablet contains 0.05g thioridazide hydrochloride). Twenty samples were weighed on an analytical balance and pulverized in a mortar. A sample of this powder, about one gram in weight (representing the average weight of a tablet) was placed in a porcelain capsule, 10 mL of water were added, followed, by stirring for 15-20 minutes. The contents of the capsule was filtered, and the capsule was washed several times with water. The filtrate and all the washings were collected in a 100 mL volume flask and diluted to the mark.

A 10 mL aliquot was transferred to a Berzelius cup and the active principle was precipitated according to the reaction mentioned above. The precipitate was filtered, washed with water and dissolved in acetone or absolute methanol. The red-violet solution was transferred to 50 mL volumetric flask and diluted to the mark with acetone. The absorbance was measured at λ=540nm and the amount of thioridazine was determined using the calibration curve shown in Figure 1. The tablets contained between 0.048 g and 0.050 g of thioridazine.

RESULTS AND DISCUSSIONS

Researching the analytical characteristics of thioridazine, the specialized literature mentions some methods of determination of this drug, a lot of them being the same as for the other phenothiazine derivatives. R. Semionovici and his collaborators[4] as well as Karkhuff and his collaborators [5], dose Melleril (Thioridazine·HCl) by means of the surfactant, sodium laurylsulfonate and Morait and his collaborators dose this pharmaceutical product using sodium tetraphenylborate [6].

Because of its basic function, thioridazine is also determined in nonaqueous solvents such as acetonitrile, chloroform, dioxane, acetone, etc., using $HClO_4$ in dioxane as a reagent and methyl and blue methylene, as an indicator (1:1). Since the drug under consideration is a hydrochloride, mercury acetate is added to the titration medium in order to bind the halogen ion [7] in the form of undissociated $HgCl_2$.

Gănescu and his collaborators noticed that all the drugs with phenothiazine skeleton precipitate in acid medium with Cr(III) anions complex like $[Cr(NCS)_6]^{3-}$, Reinecke salt and its analogous of the type $[Cr(NCS)_4(amine)_2]^-$, where amine = Py, aniline, toluidine, imidazole and even urotropine, resulting in heavy soluble violet crystalline complexes [8-14]. This led to the possibility of establishing new gravimetric, volumetric and spectroscopic methods for the determination of these drugs [8-14].

Like other phenothiazine drugs studied by us thioridazine forms stable crystalline salts soluble in water with $K_3[Cr(NCS)_6]$, $NH_4[Cr(NCS)_4(NH_3)_2]$, and respectively $NH_4[Cr(NCS)_4(amine)_2]$. These salts can be easily filtered washed with water and dried at 110°C and directly weighed. The great SCN^- content of the reagents used has allowed the elaboration of new oxidative methods (permanganometric, bromatometric and iodometric) that are very sensible and have a clear and point in CCl_4, using ICl as an indicator [10]. Thioridazine complex salts with the reagents already mentioned are slightly soluble in acetone forming red–violet solution. This allowed the elaboration of spectrophotometric methods for the dosing of this drug.

CONCLUSIONS

Eight new complexes, salts of the ionic type association have been obtained. New oxidative and spectrophotometric methods, for the determination of thioridazine were developed.

Statistical analysis of our results showed that the new methods are very reliable compared to others described in the Romanian Farmacopea and specialized literature.

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FLUORIDES EVALUATION IN SPENT POT LINER: TOXICITY CHARACTERISTIC LEACHING PROCEDURE LIMITATIONS

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ABSTRACT

The spent potliner (SPL) is a solid waste generated in the process of aluminum production and is considered hazardous because of its fluoride and cyanide content. The purpose of this study was to analyze the SPL fraction with low cyanide coming from Aluminio Brasileiro S.A. (ALBRAS). For all the pots studied the pH of the spent potliner (SPL) was very high and ranged from 10 to 11.80. The total fluoride content determined at high pH varied from 5.13 to 11.41 %, while the total fluoride determined in leached fluid at pH 5.0 had low values that ranged from 0.26 to 3.46 %, indicating the low solubility of waste fluorides at low pH values. With leaching fluid above pH 12, the total fluoride content varied from 6.45 to 9.39 %. The experimental results indicate that the Brazilian Standard NBR 10.004, based on leaching at pH 5.0 is not adequate for classification of hazardous waste, since it underestimates fluoride content.

Keywords: Fluoride, Spent potliner, Solid Waste, Ion Selective Electrode, Leaching Test.

RESUMO:

O resíduo gasto de cuba (RGC) é um resíduo sólido gerado no processo de produção de alumínio e é considerado perigoso devido ao seu teor de fluoreto e cianeto. O objetivo deste estudo foi analisar a fração do RGC com baixo teor de cianeto proveniente da empresa Alumínio Brasileiro S. A. (ALBRAS). Para todas as cubas estudadas o pH do RGC foi muito elevado e variou entre 10 e 11,80. O teor de fluoretos totais determinado em pH alto variou de 5,13 a 11,41 %, enquanto que o teor de fluoretos totais determinado em fluido de lixiviação com pH 5,0 teve valores baixos que variaram de 0,26 a 3,46 %, indicando a baixa solubilidade dos fluoretos do resíduo em baixos valores de pH. Com fluido de lixiviação em pH acima de 12, o teor de fluoretos totais variou de 6,45 a 9,39 %. Os resultados experimentais indicam que a Norma Brasileira NBR 10.004, com base na lixiviação em pH 5,0, não é adequada para a classificação de resíduos perigosos, pois subestima o teor de fluoretos.

INTRODUCTION

In the process of aluminum production, alumina is dissolved in cryolite in electrolytic cells, called pots, which consist of a steel shells lined with carbon. A number of pots, more than 100, are arranged in series to form a potline. In a typical aluminum production plant there are several potlines. The pots contain a molten electrolyte consisting primarily of cryolite (Na_3AlF_6) and operate at approximately 930 to 1000 °C. Other materials are added to the electrolyte to improve the efficiency of the operation or to reduce power consumption, such as alumina, aluminum fluoride, sodium fluoride, soda ash, calcium fluoride, lithium carbonate and magnesium oxide.

The hearth or lining of the cell is composed of carbon, which is backed by insulation and contained within a steel container called a potshell. The carbon portion of the lining serves as the cathode and contains the molten electrolyte. The carbon lining is composed of prefabricated carbon blocks joined together by a carbon paste, which is hydraulically rammed in the seams between the carbon blocks. The sidewalls of the lining are typically formed with carbon paste, but may contain prefabricated carbon blocks. The carbon material within the lining, both blocks and paste, is predominantly anthracite-based material. It may contain some graphite to improve its electrical and thermal properties. Insulation packages for a cell are mostly of insulating and refractory bricks.

During the life of the cathode and its cell lining, the carbon and insulating materials become impregnated with fluoride-containing salts. As the addition of salts continues, the integrity of the lining is adversely affected. Sodium, in particular, can actually intercalate within the crystalline lattice of the carbon materials, causing distortion and stresses within the lining. The insulating materials become more thermally conductive as they are impregnated by these fluoride salts. Failure can occur by cracking or excessive heaving of the lining. When these failures occur, the cell is taken off the line and the cathode lining material is removed from the potshell by mechanized digging equipment. This spent cathodic material is referred to as spent potliner (SPL). The life cycle of a cathode varies about three to about ten years. Since there are numerous pots located at a single aluminum reduction plant, the decommissioning and relining of cathodes is a continuous process.
In addition to containing fluoride salts, SPL contains cyanides that are formed by the entrance of air through openings in the potshell and subsequent reaction of nitrogen with the carbon lining. Due to the fluorides and cyanides content, spent potliner was listed by the Environmental Protection Agency (EPA) on Sep. 13, 1988 (53 Fed. Reg. 35412) as a hazardous waste (K088) and it is not allowed to be deposited on normal deposits. There has been proposed a number of methods for treatment this waste of such way it can be safely deposited [1,2] . Alumínio Brasileiro S. A. (ALBRAS) industry, located at Barcarena, Pará state, produces about 350.000 tons per year of aluminum and generates several tons of spent potliner which has been maintained in controlled deposits. Seeking for a more viable destination for this waste, the SPL was separated in two fractions, one of which composed of material without the cathode, with low cyanide content. The purpose of this work was to determine the fluoride content of this SPL fraction following the Brazilian Standards and discuss critically the results considering the limitations of the toxicity characteristic leaching procedure.

MATERIALS AND METHODS

a) Sampling and Sample Preparation

The waste to be studied was arranged in piles and the material was collected by simple random sampling [3-5]. The waste mass collected was fragmented and homogenized, random sampling again was used. This material was taken to laboratory and was prepared for analysis according to extraction procedure requirements.

b) pH Measurement

Waste sample pH was measured by electrometric procedure according to the EPA Method 9.045C [6], where 20 g of solid sample was placed in a 50 ml beaker, added 20 ml of reagent water, and at 25 ± 1 °C stirred the suspension for 5 minutes. The waste suspension was let stand for about 15 minutes, filtered off aqueous phase, and measured the pH.

c) Leaching and Solubilization Tests

The leaching and solubilization tests were carried out according to the procedures established by Brazilian Standards NBR 10.005 [7] and NBR 10.006 [8], respectively. In the leaching test procedure 100 g of the waste were mixed with a leaching fluid at pH = 5,0 ±0,2. The solubilization test was done by mixing 250 g of the solid waste with 1.000 ml of distilled water and leaving it rest for 7 days. Considering the waste pH and the low solubility of the waste fluorides in acidic solutions, the leaching tests were also carried out under a more aggressive conditions, where the pH of the leaching fluid was maintained above 12 during the experiments.

d) Total Fluoride Extraction

Total fluoride extraction was done by alkaline fusion, where a sample of 0.5 g of the solid waste was mixed with 15 ml of 10 % (w/w) $Ca(OH)_2$ solution and heated until completely dry. To this mixture was added 3 g of solid NaOH and heated to 800 °C for 30 minutes. After cooling, 40 ml of distilled water were added, heated gently until complete dissolution. Then 40 ml more of distilled water were added and distilled [9, 10].

e) Fluoride Determination

The extracts obtained from the steps c) and d) were distilled following the procedure as established by the Standard Methods [11] and the distilled fluorides evaluation carried using the ion selective electrode method, instrument Orion Model 96-09 [12].

RESULTS AND DISCUSSION

The pH of the solid wastes generated by pots with different operation times is presented in the Figure 1.

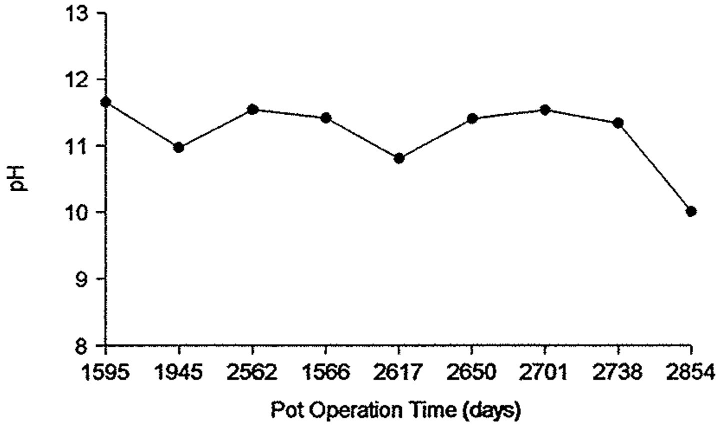

Fig. 1 - Behavior of the inorganic fraction of SPL pH as a function of the pot operation time (days)

The SPL total fluorides, fluoride concentrations of the extracts obtained by using a leaching fluid with pH = 5,0 and pH > 12 and fluoride concentrations of the extract obtained from the waste solubilization as a function of the pot operation time are presented in the Figure 2.

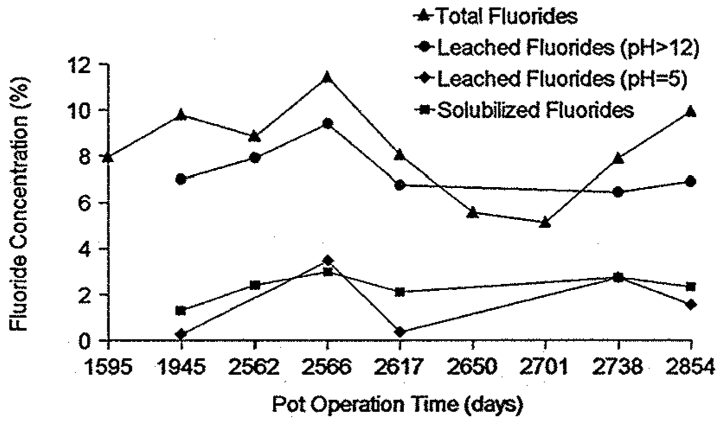

Fig. 2 – Changes of total fluoride, leached fluorides (pH > 12), leached fluorides (pH = 5) and solubilized fluorides concentrations (% w/w) as a function of the pot operation time (days).

From the results shown in the Figure 1 it can be observed that the SPL pH is very high, changing from 10 to 11.80, with an average value of 11.18 and very little oscillation with operation time of the pots. These very high pH values influenced the results of the leaching and solubilization tests.

In Figure 2 it is observed that the total fluoride concentration of the waste changed from 5.13 to 11.41 %, with an average value equal to 8.29%, but from the results obtained for the leaching test carried out according to Brazilian Standard NBR 10.005, where the extraction fluid was maintained at pH = 5.0, the leached fluoride concentration changed from 0.26 to 3.46 %, with an average value equal to 1.67 %, much lower than the actual fluoride content of the waste. These values are very close to those ones obtained from the solubilization tests, where the average value was 2.33%. This indicates that at low pH values the fluorides of this waste have low solubility.

Under a more aggressive conditions, where the leaching fluid pH was maintained above 12, it can be observed the leached fluoride concentration varying from 6.45 to 9.39 %, with an average value of 7.41 %. These values are close to those obtained for total fluoride, indicating the high solubility of the waste fluorides under alkaline conditions.

According to the Brazilian Standard "Solid Waste Classification - NBR 10.004" a fluoride content above 150 ppm or 0.015 % (w/w) of an extract obtained following the procedure established by NBR 10.005 would classify the waste as hazardous. From the results presented in the Figure 2 it can be seen that some pots could have their waste classified as non hazardous, but based on the average value, all of them would be hazardous. If the waste is non- hazardous, it is necessary to check if it is inert or not. The extract obtained from the solubilization tests (NBR 1.006) must have a fluoride concentration below 1.5 ppm. From the results it can be seen that none of the pots studied generated an inert waste.

From the leaching test results it can be concluded that the spent potliner studied as a whole is a hazardous waste, but this is not a safe classification for some pots due to the proximity between the concentration values obtained for the waste and the limit established by Brazilian Standards. These doubts only appeared because the leaching test underestimated the waste fluoride content, as it was shown by comparing the total and leached fluorides. Moreover, considering the pH of the waste, the leaching under natural environment conditions would be different from that done with a leaching fluid at pH equal to 5. The leaching procedure as established by Brazilian Standard (NBR 10.005) is not an adequate test for the evaluation of spent potliner fluoride contents.

Acknowledgements

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CHEMICAL ELEMENTS, ALLOYS AND MINERALS OCCURRING NATURALLY IN METEORITES

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ABSTRACT

The present article deals with some interesting aspects of meteorites, their origin, formation, impact on Earth and their possible role in the origin of life. In particular, chemical elements, alloys and minerals present in meteorites are considered.

KEY WORDS: *meteorites; minerals of meteorites; natural alloys; mineralogy; origin of life.*

RESUMO

O presente trabalho trata de alguns aspectos importantes sobre meteoritos, incluindo sua origem, formação, impactos com a Terra e o possível papel na origem da vida. Em particular, são considerados os elementos químicos, ligas e minerais presentes em meteoritos.

This article deals with chemical elements, alloys and compounds occurring naturally, present in meteorites. There are eighty nine known mineralogic species that have been confirmed as making part of meteorites. Of these, forty seven minerals are exclusively present in meteorites and are not found in the Earth's crust[1-6].

Meteorites are stony or metallic bodies that ocasionally are seen to fall on Earth from outer space or from the sky. It is generally believed that they formed from solar matter and for this reason meteorites have undergone less chemical change than any type of material on the surface of the Earth[7-13].

The word meteorite comes from the Greek terms *μέτα* (meta) meaning within or between and *ἔορα* or *ἄιωρα* meaning suspension air or mist. It is not to be confused with meteors which are the luminous shooting stars seen in the night sky, especially during the months of August and November.

The spectacular light flashes across the night sky are seen when swarms of small particles called meteoroids enter the Earth's upper atmosphere at high speed (up to 45 miles per second) and upon collision dissipate their kinetic energy in the form of light, heat and ionized gases. Most meteoroids are extremely small, the average size being that of a grain of sand and their origin are the swarms of particles formed during the last phase of a comet's life. Sometimes the orbit of a planet comes moderately close to the path of the Earth and in such cases the small particles (meteoroids) strike the terrestrial atmosphere producing the spectacular streaks of light. The coincidence between various comets (Tempel, Biela, Halley, Encke and Giacobini-Zinner) and the showers of meteors (Tears of St. Laurence-Perseids, Bielids, Orionids, Aquarids, Lyrids and Draconids) is well known[10,14-16].

The comets are generally believed to be material left over from the primaeval process in which the Sun and the planets were formed. According to Fred Hoyle[10], "when we see the momentary flash of a meteor in the sky, we might remember that the particle responsible for it was an old particle, a survivor from the episode in which the Earth itself was born".

Meteorites, on the other hand, are lumps of solid matter that reach the surface of the Earth and generally weigh from a few grains to several tons and occasionally their impact causes violent explosions and leads to the formation of meteorite craters. Meteorites are formed from solar matter. Radioactive age determinations show that no significant changes have taken place in most meteorites since the Solar System was formed 4.6×10^9 years ago[17-19].

Meteorites are impressive objects, being of celestial origin and coming from the heights, the sky or Heaven[20,21]. Long before the smelting of iron, man valued meteoritic iron and knew of its celestial origin. The use of meteoritic iron marks the beginning of metallurgy on Earth, long before metals like gold, copper and silver[22]. In many languages the name of iron contains references to the sky and the meteorites, coming from the gods, became objects of cult and were venerated in temples[20-21]. The oldest word used to designate iron is "An Bar" and comes from the Sumerian sky and fire and may be interpreted as "celestial metal", "metal star" or "celestial lightning". When Ferdinand Cortez asked the Aztecs from where they obtained their knives, they pointed to the sky.

In other cultures, like the aborigenes from Australia the sky was made up of rock crystals and the throne of the God of the heavens was made of quartz. Among the best known cases of worship of meteorites are the Palladion of Troy, the statue of Artemis (Diana) in Ephesus that fell from the sky; the meteorite of Pessinontes in Phrigia venerated as an image of Cybele; the holy stone in Delphi along with Apollo, the "iron shield" that fell in Rome during the reign of Numa Pompilius and the "black stone" of Ka'aba in Meca (Saudi Arabia), the holiest of holies of the Muslims. There are cases of meteorites guarded in churches and stones in India that are worshipped, decked with flowers and anointed daily.

In a more mythological sense, meteorites are "lighting stones", "teeth of lighting" or "God's axes"[20,21], that cleaved or opened the Earth and represented the union between Earth and Heaven. Earth is generally associated with fertility, the feminine principle, and the Sky represents masculinity. Delphus, the most famous abyss in Greece owes its name to a mythical image. Delphus (δελφύσ) in fact, means uterus.

The collision of cometary material (meteors) with the Earth is different and and should not be confused with the collision of meteorites. Meteorites are pieces of solid material that weigh from a few grams to tens of tons and usually vary in size from a few centimeters to meters in diameter. The originate in the region between Mars and Jupiter, the region of the asteroids belt[10-14]. Generally, they do not follow orbits that cross the path of the Earth, but occasionally they are disturbed by Mars, Jupiter and each other into new trajectories that have a chance of intersecting the Earth[7-12]. Rare collisions, when they occur, usually have a speed of 15 km per second and the impact velocity has sufficient kinetic energy to volatilize the meteorite. If the energy is released in a very short time it causes violent explosions and results in the formation of meteorite craters.

The passage of a meteorite through the atmosphere is often marked by a very bright trail and audible bangs. Often they explode before reaching the ground and scatter fragments over a large area.

One unusual meteorite reported recently is the Portales Valley that exploded and scattered materials near the city of Portales, home Eastern New Mexico University, on June 13, 1998 (Figure 1).

It was preliminarly classified as an ordinary "H-type chondrite"[23]. Chondrites consist of chondrules, small millimiter-sized spheres of rocks that once were molten drops of solar nebula dust. The letter "H" refers to the high iron content. This meteorite is believed to have originated in the asteroid belt between Mars and Jupiter. The belt, between the orbits of the two planets originated 4,6 billion years ago when small just-forming planets collided with each other and pulverized.

The most unusual feature of this meteorite are the very large number of veins of an iron-nickel alloy. Meteorites usually contain small veins that form upon impact or collisions that heat the rocks and separate the metals from the silicate base. The very large metal streaks present in the Portales Valley meteorite are something new and different[23].

Another interesting meteorite is the Allende that fell in February, 1969 near the town of Allende, Chihuahua, Mexico and showered more than 2 tons of carbonaceous chondrites over a region of more than 150 km^2 of Northern Mexico (Figure 2).

Its age determined with K and Ar isotopes was estimated to be 4,5 billion years ago, approximately the age of the Solar System. It was probably in the interior part of an asteroid and became subject to cosmic radiation 4 or 5 million years ago as indicated by He^3 dating. It composition is intermediary between C_3 and C_4 chondrites and it contained short lived isotopes of Na^{24} and Mn^{52}. Formaldehyde was among the organic compounds found in the Allende meteorite.

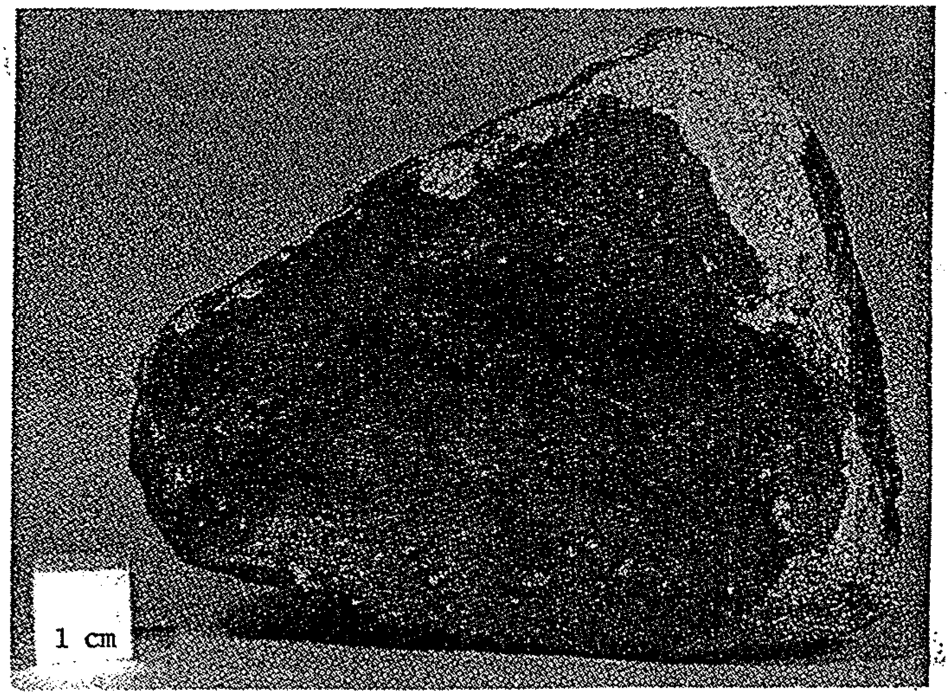

Figure 1. Fragment of the Portales Valley meteorite (1998) that contains large veins of nickel-iron alloy. (Courtesy of Sarmisegetusa Research Group, Las Cruces and Santa Fe, New Mexico, USA).

Among the meteorites that have fallen on Brazilian soil the most common ones are: Putinga fallen in State of Rio Grande do Sul in 1937, in Encantado County (a stony-iron exposed in the Science Museum of Passo Fundo University), Bendegó fallen in State of Bahia (1784) in the region of Vaza-Barris River in Monte Santo County (an iron meteorite that contains Fe, Ni and traces of Co, P, C, Ga, Ge, Ir, Zn, Cr and troilite exposed in the National Museum in Rio de Janeiro – the biggest meteorite found in Brazil with 5.3 tons.) and Nova Petrópolis that fell in Nova Petrópolis County in the State of Rio Grande do Sul (a stony-iron meteorite chemically similar to Putinga meteorite, containing troilite, kamacite, taenite and Ga, Ge and Ir as traces elements). Others of minor importance are: Itatinga that fell in Itatinga County in the State of Minas Gerais (a stony-iron-nickel meteorite with traces of Ga, Ge and Ir); Avanhanduva a stony-iron meteorite that fell in Avanhanduva County, São Paulo in 1952, containing silicates and oxides of magnesium, iron, aluminium, titanium, chromium, manganese, calcium, sodium and potassium; Ipitinga (a chondrite that fell in the State of Pará in 1989 composed of silicates and oxides); Santa Luzia (an iron meteorite that fell in Santa Luzia de Goiás in 1921 similar to Bendengó meteorite); Soledade I and II (iron-nickel meteorites); Cratheus (an iron-nickel meteorite that fell in the State of Ceará); Paranaíba (a stony-iron meteorite that fell in Sant'Ana in the State of Mato Grosso composed of silicates and oxides of iron, aluminium, sodium and very fine crystals of olivine).

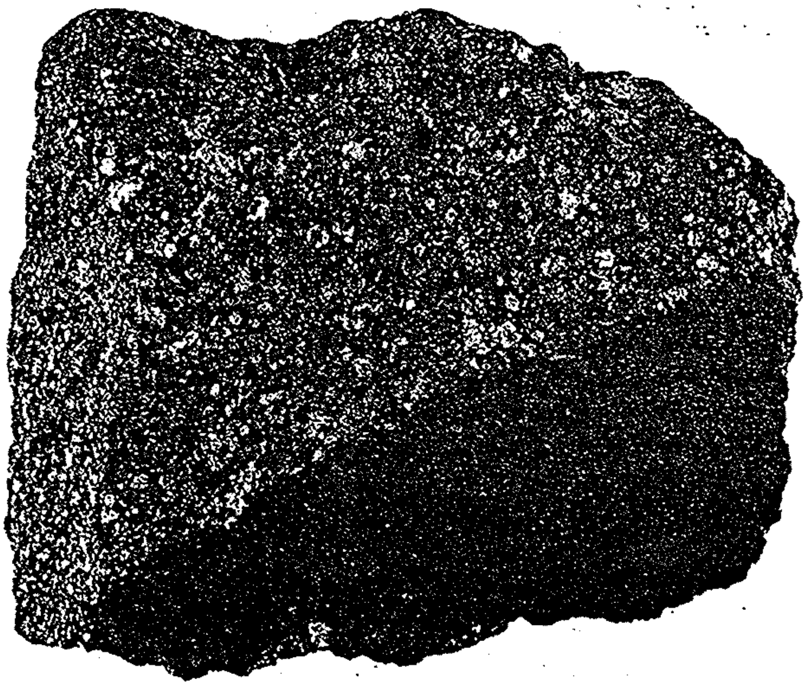

Figure 2. Fragment of the Allende meteorite that fell in the State of Chihuahua, Mexico in 1969. This carbonaceous chondrite contained much organic matter, including formaldehyde (Courtesy of Sarmisegetusa Research Group, Las Cruces and Santa Fe, New Mexico, USA).

Small fragments of the Nova Petrópolis and Bendegó meteorites are exposed in the Mineralogy Museum of the Lutheran University of Brazil in Canoas, in the State of Rio Grande do Sul. Also exposed in that Museum are small fragments of the Nandan meteorite a siderite (octahedrite), that fell in Nandan, Lihu Province, Popular Republic of China, containing akaganéite, feroxhyte, goethite, lepidocrocite, cohenite, iron, nickel, kamacite, lawrencite, maghemite, schreibersite and taenite; Vaca Muerta meteorite, a mesosiderite, that fell in Taltal, Atacama Desert, Chile, composed of troilite, osbornite, schereibersite, cohenite and olivine; Cape York meteorite (a siderite), that fell in Agpalik, Greenland, composed by plessite an intergrowth of kamacite and taenite; Moldavite meteorite, a vitreous meteorite that fell in the Czech Republic; Thailandite meteorite, a tektite composed of silica and Al_2O_3, that fell in Konkai Province, Thailand.

An interesting crater formed by the impact of a meteorite on Brazilian soil is found in Colonia (about 35 km south of the city of São Paulo). Its consists of a ring feature, with 3.64 km in diameter and is filled by at least 263 m of sediments within Precambrian crystaline basement. Probably the meteorite fell in Colonia during the Tertiary Period in the Oligocene Epoch[24].

As mentioned above, meteorites are relatively rare and since there is much more sea than land on Earth, most of them fall into the oceans. Some large ones, however, such as the Huba West meteorite of South Africa that weighs 60 tons and the Ahnighitu meteorite of Greenland, weighing 36 tons have been found[10-11].

When a meteorite fell in the valley of the Stony Tunguska River, Siberia in 1908 the impact blew trees flat for 60 miles around; the explosions were heard up to 600 miles away and the shock waves were very strong more than 100 miles away. Some think it was the nucleus of a small comet.

Meteor Crater near Winslow, Arizona is three-quarters of a mile in diameter, 600 feet deep and its rim of uptilted and broken strata rises 120-150 feet above the surrounding plain. Masses of meteoritic iron strewed the whole area outside the crater for several miles but no iron was found in it. Meteor Crater in Arizona is the result of a prehistoric meteorite that must have weighed about 50,000 tons (Figure 3).

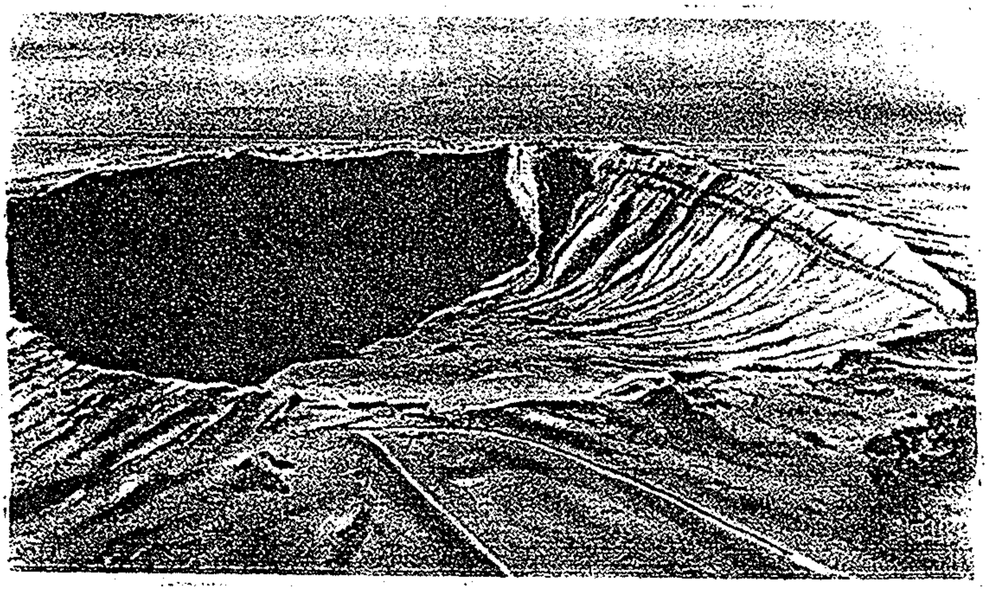

Figure 3. Meteor Crater near Winslow, Arizona (Courtesy of Sarmisegetusa Research Group, Las Cruces and Santa Fe, New Mexico, USA).

Other examples of meteorite craters are found in Henbury, Central Australia; Boe Hole, Dulgavanga and Wolf Creek, Australia; Wabar, Saudi Arabia; öesel, Estonia;

Haviland, Kansas and Odessa, Texas (USA). A similar origin was proposed for the Panonian on Hungarian Plain, and the Caribbean Sea.

A cataclysmic collision that triggered widespread extinction of life on Earth 65 million years ago is believed to have been caused by an asteroid. A huge circular structure about 180 km in diameter is centered beneath the town of Chicxulub near Merida in the northern Yucatán Peninsula. Among the most compelling evidence are crystals of quartz found at the Cretaceous-Tertiary (K-T) boundary[25]. Chicxulub means "horns of the devil" in the Mayan languages and the discovery of the meteoritic material was found during the drilling of an exploratory well by Petroleos Mexicanos (Pemex) [25].

Meteorites are generally classified into four classes: stony meteorites, composed principally of rock called aerolites or chondrites, nickel-iron meteorites known as siderites (Figure 4), stony-iron meteorites known as siderolites and tektites.

Tektites are generally regarded as glass meteorites and there are many theories concerning their origin. They are small round pieces of a glass-like substance and vary in color from botlle green glass to deep brown. They are found in Moldavia, ex-Czechoslowakia, Australia, Island of Tasmania, Indonesia, Thailand, Philippines, Malay Peninsula, Ivory Coast, Mauritania and Texas, USA (Figure 5).

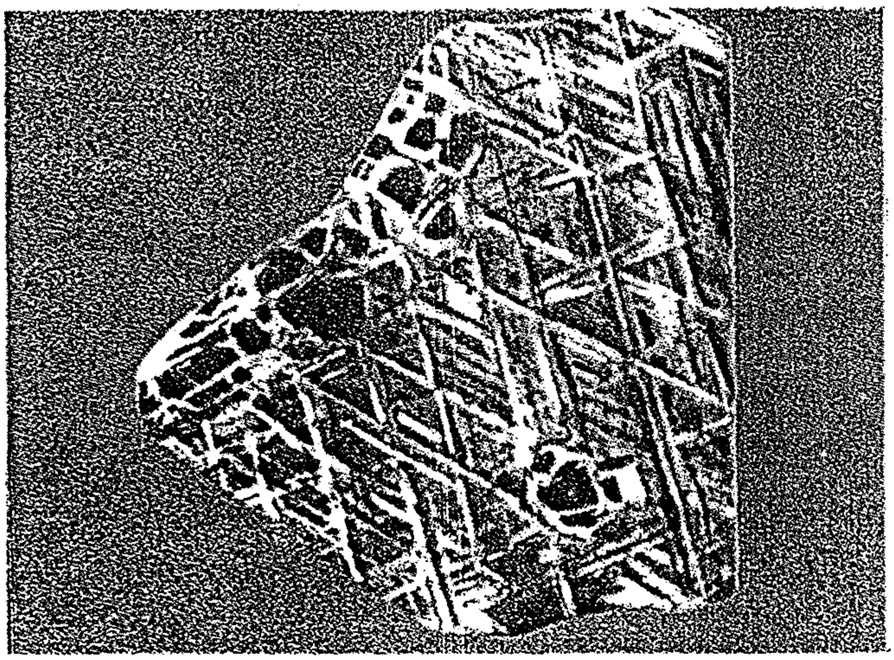

Figure 4. Fragment of an iron meteorite showing the characteristic Widmanstätten pattern (Courtesy of Sarmisegetusa Research Group, Las Cruces and Santa Fe, New Mexico, USA).

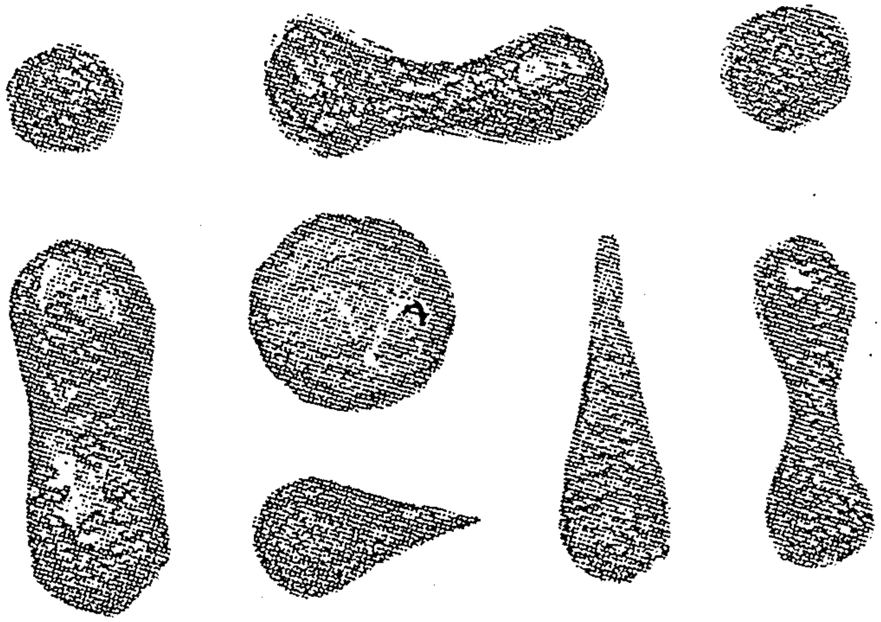

Figure 5 - Some examples of tektites (Photograph courtesy of Griffith Observatory - Astronomical Society of Las Cruces, New Mexico, USA).

They usually contain 70-80% SiO_2, 10-13% Al_2O_3, 2-5% Fe_2O_3 and 1-3% K_2O. The most generally accepted view is that tektites are glass meteorites, but they differ considerably in appearance and composition from ordinary stony meteorites. They are found at various geological horizons on Earth and most tektite fields are found near known or probable meteorite craters of comparable age. Detailed studies of australites indicate that they are remains of larger glassy lumps that have undergone ablation during the passage at high velocity through the atmosphere.

A lunar origin has also been proposed for tektites. Supposedly they were formed from lunar material after collisions of the surface of the Moon with asteroids. Subsequently the fragments were attracted by the gravity of the Earth.

On the other hand, the large masses of silica glass present in the Libyan Desert are believed to be of terrestrial origin and more similar to the first man made "mineral" trinitite, formed by the explosion of the first atomic bomb in 1945 and found around the crater at Trinity Site near Alamogordo and Socorro, New Mexico, USA.

Meteorites contain the same elements that are present in terrestrial matter. The isotopic composition of many elements is constant in terrestrial and meteoritic materials. In a few cases there are exceptions; the bombardment of cosmic rays produces a variety of stable and unstable isotopes. This difference may yield valuable information about the history of meteorites [8,17]. The elements present in iron meteorites are Fe, Ni, Co, P, S, C, Cu, Cr, Ga, Ge and Ir; in stoney meteorites are O, Fe, Si, Mg, Al, Ni, Ca, Na, Cr, P, Mn, Co, K and Ti.

A more comprehensive classification of meteorites, excluding tektites and the newly discovered meteorites in Antarctic ice is given in Table I[7,8,26].

Table I. General Classification of Meteorites

I. Irons-Main phases:
  kamacite (Fe,Ni), α-nickel (4-7.5%)-iron, body-centered Cubic System
  taenite (Ni,Fe), γ-nickel-iron, face-centered Cubic System
  troilite FeS - Hexagonal System
  graphite C - Hexagonal/Trigonal Systems
  Classification:
  a) Nickel-rich ataxites (42 known): generally nickel greater than 12%. Fine crystals.
  b) Octahedrites (442 known): nickel 6-12% (mostly 7-10%). Extended interleaved crystals of kamacite and taenite (Widmanstätten figures).
  c) Hexahedrites (69 known): nickel less than 6%. Mainly kamacite.

II. Stony-irons – Main phases: as above. Also:
  olivine $A^{2+}{}_2SiO_4$, A^{2+} = Fe, Mg, Mn, Ni;
  pyroxene ABZ_2 - A = Ca, Fe^{2+}, Li, Mg, Mn^{2+}, Na, Zn; B = Al, Fe^{2+}, Fe^{3+}, Mg, Mn^{2+}, Sc, Ti, V^{3+}; Z = Al, Si.
  feldspars (complex Na, Ca and K aluminosilicates).
  Classification:
  a) Pallasites (43 known): mostly metal (exterior phase) like octahedrites. Olivine.
  b) Mesosiderites (25 know): metal, pyroxene, feldspar.

III. Stones-Main phases as above, with silicates predominant.
  Classification:
  a) Chondrites (1004 known): contain chondrules, millimeter-scale spheroidal bodies of uncertain origin. All but carbonaceous have olivine, pyroxene, feldspar, metal phases and troilite.
  a_1) Clinoenstatite $Mg_2Si_2O_6$ – Monoclinic System – chondrites (17 known): highly reduced, all iron in metal and troilite.
  a $_2$) Ordinary chondrites: H-group (459 known). Less reduced, some iron in olivine and pyroxene also. Total iron about 28%;
  L-group (459 known): less iron and less metal than H-group. Total iron about 21%;
  LL-group (67 known): little free metal; total iron about 19%.
  a_3) Carbonaceous chondrites (33 known): contain organic matter, H_2O, hydrated minerals, little or no free metal; magnetite ($Fe^{2+}Fe^{3+}{}_2O_4$), sulfate. Subdivided further into types I, II, and III; type I having organic and H_2O content. Total iron about the same as in the H-group.
  b) Achondrites (69 known): many classes, some with only one member.
  The more abundant classes are:
  b_1. Aubrites-diogenites (calcium-poor; 16 known): mainly pyroxene.
  b_2. Eucrites-howardites (calcium-rich; 44 known): feldspar and pyroxene.

The type of chemical fractionation that apparently occured during the formation of most of the meteorites in the separation into three mineralogical phases: a metal pahse, a sulfide phase and a silicate phase.

Goldschmidt[27,28] divided the chemical elements of the Periodical Table into three groups present in meteorites: siderophile, chalcophile and lithophile. A fourth group, not present in meteorites he called atmophiles. Such a classification, however, is not vigorous, as many elements are distributed among two or three phases in varying proportions, depending on oxygen fugacity.

One difficulty that arises in calculating the composition of primordial solar matter from elemental composition of meteorites comes from our ignorance about the relative amounts of the three phase in present bodies of meteorites. Iron meteorites are better preserved during their fall and on the surface of the Earth than are stony meteorites and pallasites.

Therefore, meteorites that reach the surface of the Earth cannot readily serve as a basis of estimation of the relative amounts of mineralogical phases.

The high abundance of Fe in meteorites led von Tamman[29] to propose the "blast furnace model" for the Earth in 1923. Table II summarizes the metal content estimated for Planet Earth. Information about the Earth's composition at moderate depths near the surface (10 km) has been obtained the Hot Dry Rock Geothermal Power Project[34] of the Los Alamos Laboratory, Los Alamos, New Mexico, USA and by similar classified studies in Siberia, Russia. The radius of the Earth is 6,370 km.

Table II. Metal Content of Planet Earth*

	Metal	Sulfide
Noddack[30]	68	9.8
Fersman[31]	20	4
Goldschmidt[27]	20	10
H. Brown[32]	67	0
Urey[33]	10.6	7

* Parts by weight relative to silicates = 100

There is a logical combination between the three main classes of meteorites and the more common model for Planet Earth. The chondrite, silicate meteorites or assiderites are mineralogically similar to the Earth's crust[35,36]. The stony-iron meteorites or lithosiderites have a chemical composition similar to that of volcanic lava that comes from the mantle and eventually forms basaltic rocks and the third group, the iron meteorites that consist mainly of Fe and about 8% Ni are associated with the nucleus or the interior of the Earth, or the "blast furnace model".

There are about 2,000 individual meteorites described in the literature, excluding the several thousands. newly recovered meteorites from Antarctic ice. The chemical elements present in them are mostly combined in the form of well-defined chemical compounds and a few are present as free elements or alloys.

Many of these minerals are formed in terrestrial rocks and others are only present in meteorites.

Table III presents a list of 89 mineralogic species related to meteorites. Those marked by an asterisk are present only in meteorites. The crystal systems and chemical compositions follow the classification of Mandarino[3].

The minerals listed include silicates, sulfides, chlorides, carbonates, oxides, hydroxides, phosphates, sulphates, chromates, native elements and metallic alloys, phosphites, silicides, nitrides and carbides.

Table III. Mineralogic Species Related to Meteorites

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a. SILICATES

1. Aegirine $NaFe^{3+}SiO_6$ – Monoclinic System – Pyroxene Group.
2. Albite $NaAlSi_3O_8$ – Triclinic System – Feldspar Group.
3. Anorthite $CaAl_2Si_2O_8$ – Triclinic System – Feldspar Group.
4. Augite $(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$ – Monoclinic System – Pyroxene Group.
5. *Calderite $(Mn^{2+},Ca)_3(Fe^{3+},Al)_2(SiO_4)_3$ – Cubic System – Garnet Group.
6. *Clinoenstatite $Mg_2Si_2O_6$ – Monoclinic System – Pyroxene Group.
7. *Clinoferrosilite $(Fe^{2+},Mg)_2Si_2O_6$ – Monoclinic System – Pyroxene Group.
8. Coesite SiO_2 – Monoclinic System.
9. Cristobalite SiO_2 – Tetragonal System.
10. Diopside $CaMgSi_2O_6$ – Monoclinic System – Pyroxene Group.
11. Enstatite $Mg_2Si_2O_6$ - Orthorhombic System - Pyroxene Group.
12. Forsterite Mg_2SiO_4 – Orthorombic System – Olivine Group.
13. *Knorringite $Mg_3Cr_2(SiO_4)_3$ – Cubic System – Garnet Group.
14. *Krinovite $Na_2Mg_4Cr_2Si_6O_{20}$ - Triclinic System – Aenigmatite Group.
15. *Kosmochlor (*Ureyite variety) $NaCr^{3+}Si_2O_6$ – Monoclinic System – Pyroxene Group.
16. *Majorite $Mg_3(Fe,Al,Si)_2(SiO_4)_3$ – Cubic System – Garnet Group.
17. Orthoclase $KAlSi_3O_8$ – Monoclinic System – Feldspar Group.
18. *Perrierite $(Ca,Ce,Th)_4(Mg,Fe^{2+})_2(Ti,Fe^{3+})_3Si_4O_{22}$ – Monoclinic System.
19. Stishovite SiO_2 – Tetragonal System – Rutile Group.
20. Tridymite SiO_2 – Monoclinic System.
21. Yagiite $(Na,K)_{1.5}Mg_2(Al,Mg)_3(Si,Al)_{12}O_{30}$ – Hexagonal System – Osumilite Group.
22. Zircon $ZrSiO_4$ - Tetragonal System.

b. SULFIDES

23. Alabandite $Mn^{2+}S$ – Cubic System.
24. *Brezinaite Cr_3S_4 – Monoclinic System.
25. Chalcopyrite $CuFeS_2$ - Tetragonal System.

---

26. *Daubréelite $Fe^{2+}Cr_2S_4$ – Cubic System – Linnaeite Group.
27. *Djerfisheerrite $K_6(Fe,Cu,Ni)_{25}S_{26}Cl$ - Cubic System.
28. Marcasite FeS_2 – Orthorombic System – Marcasite Group.
29. Millerite NiS – Trigonal System.
30. *Niningerite $(Mg,Fe^{2+},Mn)S$ – Cubic System.
31. *Oldhamite (Ca,Mg,Fe,Mn)S – Cubic System.
32. Pentlandite $(Fe,Ni)_9S_8$ - Cubic System.
33. Pyrite FeS_2 – Cubic System – Pyrite Group.
34. Pyrrhotite $Fe_{1-x}S$ – Monoclinic and Hexagonal Systems.
35. *Troilite FeS – Hexagonal System.

c. CHLORIDES

36. *Lawrencite $(Fe^{2+},Ni)Cl_2$ – Trigonal System.

d. CARBONATES

37. Dolomite $CaMg(CO_3)_2$ - Trigonal System.

e. OXIDES

38. *Ferrihydrite $5Fe_2O_3.9H_2O$ – Trigonal System.
39. Ilmenite $Fe^{2+}TiO_3$ – Trigonal System – Hematite Group.
40. *Maghemite γ-Fe_2O_3 - Trigonal System.
41. Magnetite $Fe^{2+}Fe^{3+}{}_2O_4$ – Cubic System - Spinel Group.
42. Perovskite $CaTiO_3$ - Orthorombic System – Perovskite Group.
43. Rutile TiO_2 – Tetragonal System – Rutile Group.
44. Spinel $MgAl_2O_4$ – Cubic System – Spinel Group.

f. HYDROXIDES

45. *Akaganéite β-$Fe^{3+}(O,OH,Cl)$ – Monoclinic System.
46. *Feroxyhyte $\delta Fe^{3+}O(OH)$ – Hexagonal System.
47. *Lepidocrocite γ-$Fe^{3+}O(OH)$ - Orthorhombic System.

g. PHOSPHATES

48. *Arupite $Ni_3(PO_4)_2.8H_2O$ – Monoclinic System – Vivianite Group.
49. *Brianite $Na_2CaMg(PO_4)_2$ - Monoclinic System.
50. *Chladnnite $Na_2CaMg_7(PO_4)_6$ - Trigonal System.
51. Chlorapatite $Ca_5Mg(PO_4)_3Cl$ - Monoclinic Syystem - Apatite Group.
52. *Farringtonite $Mg_3(PO_4)_2$ – Monoclinic System.
53. *Galileiite $NaFe^{2+}{}_4(PO_4)_3$ – Trigonal System.
54. *Johnsonmervilleite $Na_2Ca(Mg,Fe^{2+},Mn)_7(PO_4)_6$ - Trigonal System.
55. *Mundrabillaite $(NH_4)_2Ca(HPO_4)_2.H_2O$ - Monoclinic System.
56. *Stanfieldite $Ca_4(Mg,Fe^{2+},Mn^{2+})_5(PO_4)_2$
57. Vivianite $Fe^{2+}{}_3(PO_4)_2.8H_2O$ - Monoclinic System - Vivianite Group.
58. Whitlockite (*Merrilite variety) $Ca_9(Mg,Fe^{2+})(PO_4)_6(PO_3OH)$ - Trigonal System.

h. SULPHATES

59. Epsomite $MgSO_4.7H_2O$ - Orthorombic System.
60. Gypsum $CaSO_4.nH_2O$ - Monoclinic System.

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61. Jarosite $K_2Fe^{3+}_6(SO_4)_4(OH)_{12}$ - Trigonal System - Alunite Group

i. CHROMATES

62. Chromite $Fe^{2+}Cr_2O_4$ - Cubic System - Spinel Group.

j. NATIVE ELEMENTS AND NATURAL METALLIC ALLOYS

63. Awaruite Ni_2Fe to Ni_3Fe - Cubic System.
64. *Chaoite C - Hexagonal System.
65. Copper Cu - Cubic System.
66. Diamond C - Cubic System.
67. Gold Au - Cubic System.
68. Graphite C - Hexagonal and Trigonal Systems.
69. Iron α-Fe - Cubic System.
70. *Kamacite (Fe,Ni) - Cubic System.
71. Londslaeite C - Hexagonal System.
72. Nickel Ni - Cubic System.
73. Sulfur S - Orthorrhombic System.
74. *Taenite (Ni,Fe) - Cubic System.
75. *Tetrataenite FeNi - Cubic System.
76. *Zhanghengite CuZn - Cubic System.

k. PHOSPHIDES

77. *Barringerite $(Fe,Ni)_2P$ - Hexagonal System.
78. *Perryite $(Ni,Fe)_8(Si,P)_3$ - Trigonal System.
79. *Schereibersite $(Fe,Ni)_3P$ - Tetragonal System.

l. SILICIDES

80. *Suessite $(Fe,Ni)_3Si$ - Cubic System.

m. NITRITES

81. *Carlsbergite CrN - Cubic System.
82. *Osbornite TiN - Cubic System.
83. *Roaldite Fe_4N - Cubic System.

n. CARBIDES

84. *Cohenite $(Fe,Ni,Co)_3C$ - Orthorombic System.
85. *Haxonite $(Fe,Ni)_{23}C_6$ - Cubic System.
86. *Moissanite SiC - (?) Unknown System.
87. *Niocarbide (Nb,Ta)C - Cubic System.
88. *Tantalcarbide (Ta,Nb)C - Cubic System.
89. *Tongbaite Cr_3C_2 - Orthorombic System

The existence of approximatelly 200 different molecules in interstellar space comets and asteroids has been confirmed. They range from simple commom diatomic and triatomic molecules such as H_2, OH, CO, CN, H_2O, CO_2, NH_3 to polyatomic ones including amino acids, aromatics and a wide variety of chemical compounds including most functional organic groups and inorganic compounds such as silicates and carbonates. Among the more complex ones are fullerene and porphyrin, discovered by Fred M. Johnson and Charles E. Castro of the University of California, Riverside[37,38].

Simple sugars such as glucose and many polyols have been found in the Murchison meteorite which fell in Australia in 1969 and the Murray meteorite that fell in Kentucky, USA in 1950[39,40].

The idea that simple compounds may be converted to move complex ones related to the origin of life was originally proposed by the Moldavian scientist A. I. Oparin, and many primordial conditions have been simulated in the laboratory[41,42].

As far as the terrestrial origin of life is concerned[37,38,41-48] there are three hypotheses, the first one, "the primordial soup", being the more accepted one. According to this theory life originated in the oceans after the cooling of the Planet Earth. The second one involves "the primordial clay" and the third one suggests that life may have originated near "hydrothermal vents", in the bottom of the oceans near regions of volcanic activity.

The extraterrestrial origin of life may not be excluded[37,38,43,44]. The most common theory is Whipple's ball of "dirty ice" according to which life originated in comets. Other hypothesesinclude the Nebulosity of Orion, near the cradle or birthplace of stars or even meteorites[47,48].

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NEW Cr(III) COMPOUNDS IN ANALYTICAL CHEMISTRY. BI(III) CONDUCTOMETRIC DETERMINATION

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ABSTRACT

This study presents the synthesis and characterization of the complex $[Bi(Rhodanine)_3][Cr(NCS)_4(Aniline)_2]_3$. The new complex was analyzed by thermogravimetric, oxidation, infra red and other spectrometric techniques and was used for the determination of bismuth in drugs. The dosage of Bi(III) in Ulcerotrat was done by conductometric titration with rhodanine and complex anions of Cr(III), respectively.

RESUMO:

Este estudo trata da síntese e caracterização do complexo $[Bi(Rhodanine)_3][Cr(NCS)_4(Aniline)_2]_3$. O novo complexo foi analisado através de vários métodos, incluindo termogravimetria, oxidação, infravermelho e outros e foi usado para quantificar Bi(III) em medicamentos. A dosagem de Bi(III) no Ulcerotrat foi obtida attravés de titulação conductimétrica com rodanina e ânions complexos de Cr(III), respectivamente.

KEYWORDS: Cr(III) Complexes, Rhodanine, Bismuth Determination, Conductometric Titrations

INTRODUCTION

Bismuth based drugs are used as dressings in the treatment of gastro-duodenal affections.

The determination of bismuth in drugs by classic laborious methods implies a previous destruction of the organic compound. A direct approach to avoid these operations is based on complexometric titration with EDTA. For bismuth dosage in Dermatol and Airol drugs pirocathehine violet it is used as indicator[1], and its dosage from Gastrosedol and Ulcerotrat is made in the presence of taron[2].

Because at the equivalence point the color change is not very clear and cannot be easily observed, we propose the determination of Bi(III) from Ulcerotrat by conductometric titration with Rhodanine and with complex anions of Cr(III) with which bismuth forms stable complex combinations. Rhodanine is (2-thio-4-keto-thiazolidine),  $SCH_2C(O)NHCS$.

EXPERIMENTAL

The synthesis and characterization of $[Bi(Rhodanine)_3][Cr(NCS)_4(Aniline)_2]_3$ complex. A sample of 100 mL Bi(III) (pH=1.8) solution was treated with 1 % Rhodanine alcoholic solution in excess. A yellow complex compound $[Bi(Rhodanine)_3]^{3+}$ which remained stable with time and also at high temperatures was formed. We studied the structure of this complex and also the influence of various factors on its stability.[3]

The sample was brought to a constant volume of 25 mL with distilled water followed by the precipitation with complex anions of Cr(III), 3% aqueou-alcoholic solution.

A red-orange precipitate was obtained which was filtered with a filtering crucible G_4, it was washed tow or three times with distilled water, subsequently it was dried for 1 hour at 105 °C.

The complex salt obtained, $[Bi(Rhodanine)_3][Cr(NCS)_4(Aniline)_2]_3$, was analyzed termogravimetrically, oxidimetrically and by spectrometric methods.[4]

The I.R. analysis of the complex was performed with a Perkin-Elmer 1600 spectrometer and the results are presented in Table 1.

RESULTS AND DISCUSSION

The I.R. spectral studies of the complex anions of $[Cr(NCS)_4(Aniline)_2]_3$ type[5-8] show that the vibration frequencies $\nu_{C=N}$ of the NSC group appears at 2110-2140 cm^{-1}, and the vibration frequencies ν_{C-S} at 760-810 cm^{-1}, respectively, which proves the covalent nature of the Cr(III)-NCS bond. The bond between Cr(III) and SCN is through the N atom and not the S atom[9].

The very intense absorption maximum at the vibration frequency of 2079 cm^{-1} is assigned to the SCN group.

The data mentioned in the literature[10-12] confirm that the coordination effect has an insignificant influence on the line of the complexes of $NH_4[Cr(NCS)_4(Aniline)_2]$ type. The $\nu_{C=N}$ and ν_{C-S} bands do not shift if there are aliphatic or aromatic amines in the internal sphere of coordination.

In the case of combinations with aniline in the internal sphere of coordination the vibration frequencies of the N-H bond are around 3100-3200 cm^{-1} (the shift being insignificant (120-200 cm^{-1}) in comparison with free uncoordinated amines). This confirms that the Cr-N bond (with amines) had a strong covalent character.

Table 1. The I.R. absorbtion maximum for [Bi(Rhodanine)$_3$][Cr(NCS)$_4$(Aniline)$_2$]$_3$.

Vibration attribution	Frequency (cm^{-1})
$\nu_{C\text{-}H}$	3396 v.w.
$\nu_{NH_2} + \nu_{C=S\text{-}NH_2}$	3190 m.
$\nu^{as}_{CH_2\text{-}S}$	3114 m.
ν_{CH_2OR}	2920 v.w.
ν_{SCN}	2079 v.i.
$\nu_{C=O}$	1601 w.
δ_{NH}	1576 m.
$\delta_{NH} + \delta_{CN}$	1526 m.
δ_{CH_2}	1492 m.
$\delta_{CN} + \nu_{NH}$	1283 m.
$\nu_{C=S}$	1130 i.
	1026 w.
$\nu_{C=N}$	693 w. and 481 m.

w. - weak; m - medium; i - intense; v.w. - very weak; v.i. - very intense; as - antisymmetric; s - symmetric; ν - valence vibration; δ - deformation vibration

The Bi(III) dosage from Ulcerotrat by conductometric titration with Rhodanine. Ulcerotrat is a drug used as a dressing in gastric injuries. It appears in the form of tablets (1.1022 g/tablet).

To 1 g Ulcerotrat 20 mL of concentrated HNO_3 is added and then the solution is diluted with distilled water is up to 1L. A sample of 100 mL of the solution obtained is titrated under magnetic stirring with 1% Rhodanine alcoholic solution. The results obtained are presented in Figure 1. From the graphic representation the volume at the equivalence point, V_e = 3.2 mL was determined in perfect concordance with the calculated value (V_e = 3.215 mL).

The experiments was repeated 5 times using sample with the same content of Bi(III) and the experimental data were statistically interpreted. The results are presented in Table 2.

Table 2. Statistic interpretation of the experimental data for Bi(III) dosage from Ulcerotrat by conductometric titration with Rhodanine.

No.	V Rhodanine (mL)	X Bi(III) found (mg)	X-X$_i$	(X-X$_i$)^2	
1	3.15	16.4819	0.2093	0.0438	$S^2 = 0.0222$
2	3.20	16.7435	-0.0523	0.0027	$S = 0.1490$
3	3.175	16.6127	0.0785	0.0062	$S_x = 0.06$
4	3.20	16.7435	-0.0523	0.0027	$t = 4.616$
5	3.225	16.8743	-0.1831	0.0335	
		$\bar{x} = 16.691$			

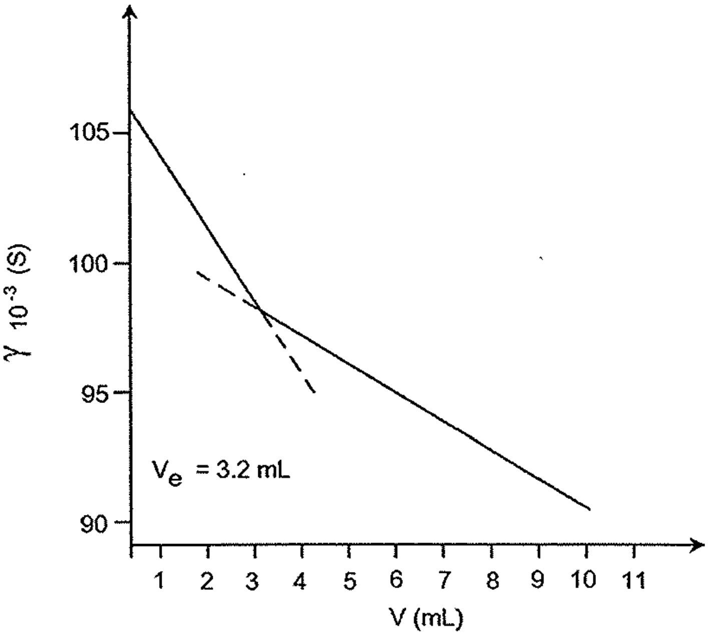

Fig. 1. The Bi(III) conductometric titration from Ulcerotrat using Rhodanine.

The Bi(III) dosage from Ulcerotrat after complexation with Rhodanine by conductometric titration with $[Cr(NCS)_4(Aniline)_2]^-$.

To 100 mL Ulcerotrat solution, prepared as above, 10 mL Rhodanine (in excess) is added and it is titrated under magnetic stirring with 3% alcoholic solution $NH_4[Cr(NCS)_4(Aniline)_2]\ H_2O$. The experimental results are presented in Figure 2.

In this case, too, the V_e = 5.6 mL obtained by experimental methods is in agreement with the one determined by calculations (V_e = 5.65 mL).

The data obtained by repeating the titration five times using samples with the same content of Bi(III) were statistically interpreted. The results are presented in Table 3.

Table 3. Statistic interpretation of the experimental data for Bi(III) dosage from Ulcerotrat after complexation with Rhodanine by conductometric titration with $[Cr(NCS)_4(Aniline)_2]^-$.

No.	V Rhodanilate (mL)	X Bi(III) found (mg)	$X\text{-}X_i$	$(X\text{-}X_i)^2$	
1	5.650	16.7487	0.03854	0.001485	$S^2 = 1.27582 \times 10^{-3}$
2	5.670	16.8080	-0.0208	0.000433	$S = 0.03572$
3	5.650	16.7487	-0.03854	0.001485	$S_x = 0.01597$
4	5.670	16.7487	-0.0208	0.00433	$t = 4.616$
5	5.675	16.8228	-0.0356	0.001267	
		$\bar{x} = 16.787$			

Comparing the experimental data from both cases presented one can observe that the better result was with the titration with Rhodanine. This may be explained by a more reduced mobility of the complex salt obtained following the titration, in the second case.

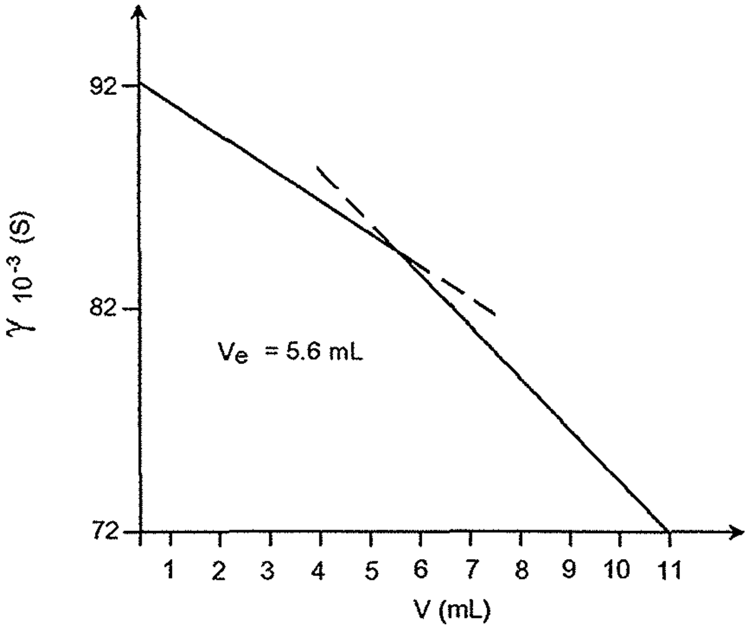

Fig. 2. . The Bi(III) conductometric titration from Ulcerotrat as $[Bi(Rhodanine)_3]^{3+}$ using $NH_4[Cr(NCS)_4(Aniline)_2]H_2O$.

The suggested method for the determination of Bi(III) in drugs (Ulcerotrat) is, rapid, particularly, sensitive and accurate.

The method used for determination the Bi(III) could be used also in the presence of other ions[4].

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PROMINENT PHYSICAL CHEMIST AND EDUCATOR
(1902 - 1991)

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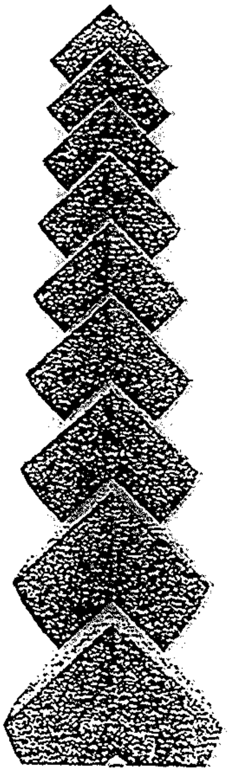

Endless Column; 1937; cast iron
CONSTANTIN BRÂNCUSI

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DACIAN SANCTUARY IN SARMISEGETUSA, ROMANIA

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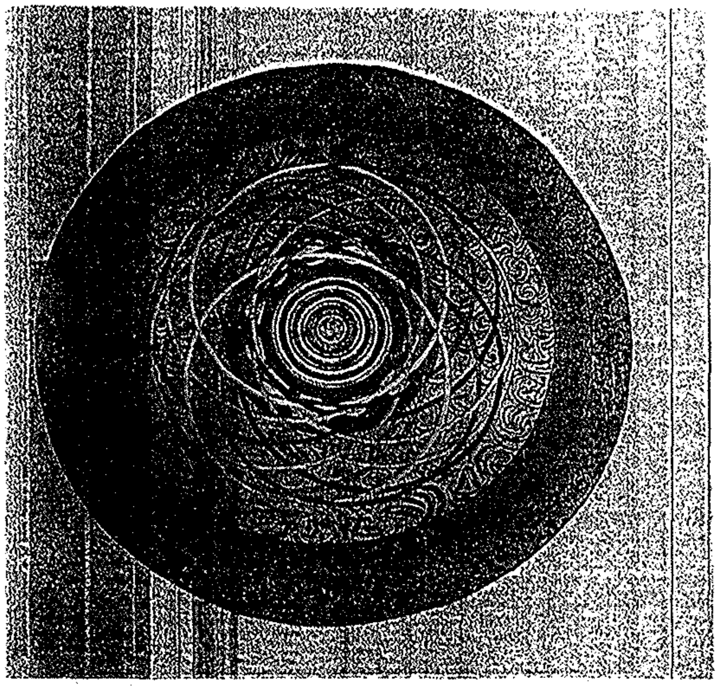

MANDALA CÓSMICA DO TEMPLO PARO DZONG,
BUTÃO OCCIDENTAL

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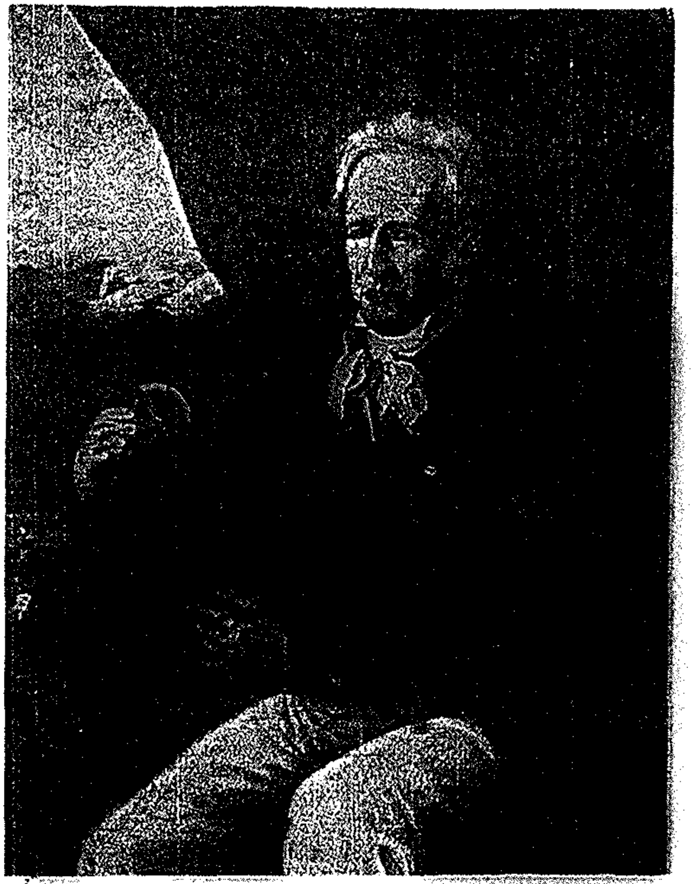
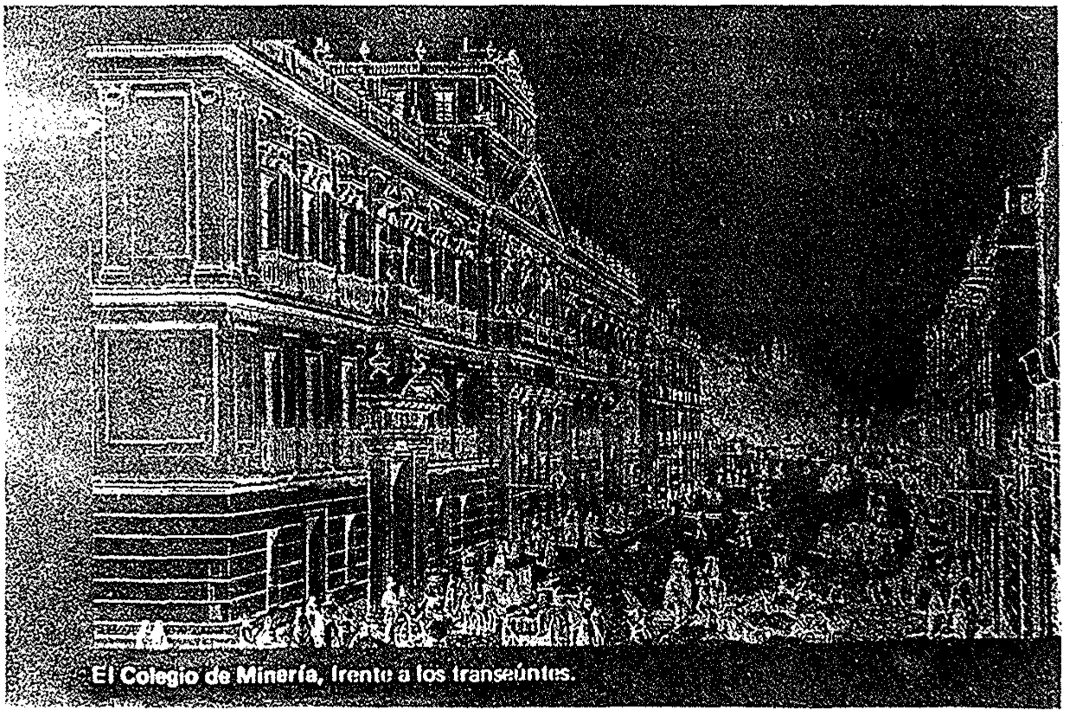


ANDRÉS MANUEL DEL RIO (1764-1849), DISCOVERER OF VANADIUM.



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White Sands Missile Range
NEW MEXICO
U.S. ARMY
U.S. ARMY


USAF
Missile Display at White Sands
Photo by Lou Candelaria

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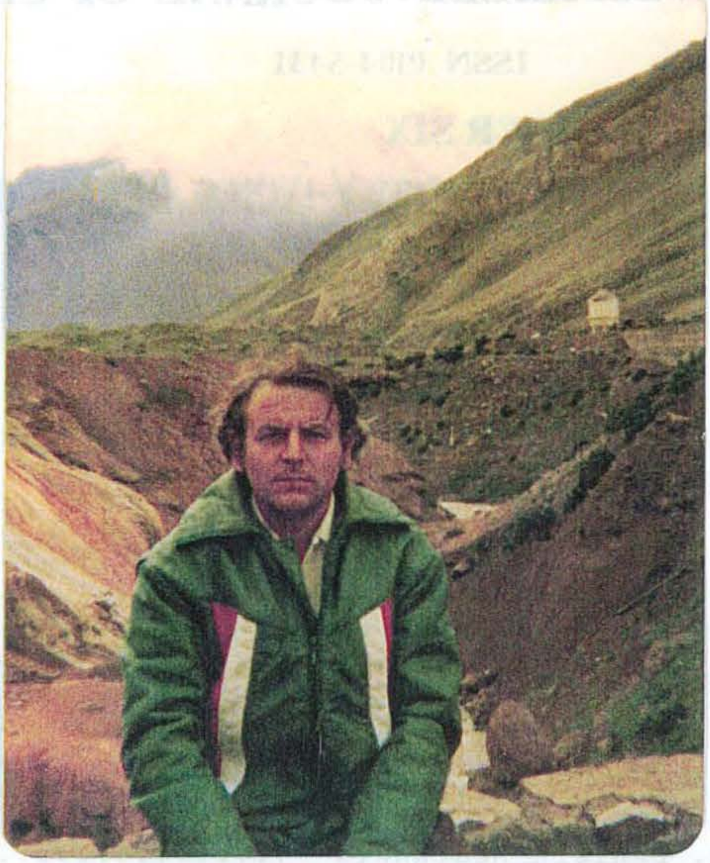

AT THE FEET OF ACONCAGUA, PUENTE DEL INCA, PROVINCIA DE MENDOZA, REPUBLICA ARGENTINA.

ACONCAGUA, SOUTH AMERICA'S HIGHEST PEAK IN THE CORDILLERA OF THE ANDES (6958 or 7035m).

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"En el Partido del Chocó, habiendo muchas minas de *Lavadero*, como las que se acaban de explicar, se encuentran también algunas, en donde por estar disfrazado, y envuelto el *Oro*, con otros cuerpos metálicos, Jugos y Piedras, necesita para su beneficio el auxilio del *Azogue*; y tal vez se hallan minerales, donde la *Platina* (Piedra de tanta resistencia, que no es fácil romperla, ni desmenuzarla con la fuerza del golpe sobre *Yunque de Acero*), es causa de que se abandonen; porque ni la calcinación la vence, ni hay arbitrio para extraer el *Metal* que encierra, sino a expensas de mucho trabajo y costo" **.

** *Relación Histórica del Viaje a la América Meridional hecho de orden de S. Mag. para medir algunos grados del meridiano terrestre y venir por ellos en conocimiento de la verdadera figura y magnitud de la Tierra, con otras observaciones astronómicas y físicas:* Por Don Jorge Juan, Comendador de Aliaga en el Orden de San Juan, socio correspondiente de la Real Academia de Ciencias de París y Don Juan Antonio de Ulloa, de la Real Sociedad de Londres: Ambos capitanes de Fragata de la Armada. Impresa de orden del Rey Nuestro Señor en Madrid por Antonio Marín. Año de MDCCXLVIII - Primera Parte Tomo II. p. 606.

ANTONIO DE ULLOA (1716-1796)

SPANISH PHYSICIST, MATHEMATICIAN, NAVAL COMMANDER, DISCOVERER OF PLATINUM, GOVERNOR OF LOUISIANA AND FLORIDA, EXPLORER OF THE AMERICAS.

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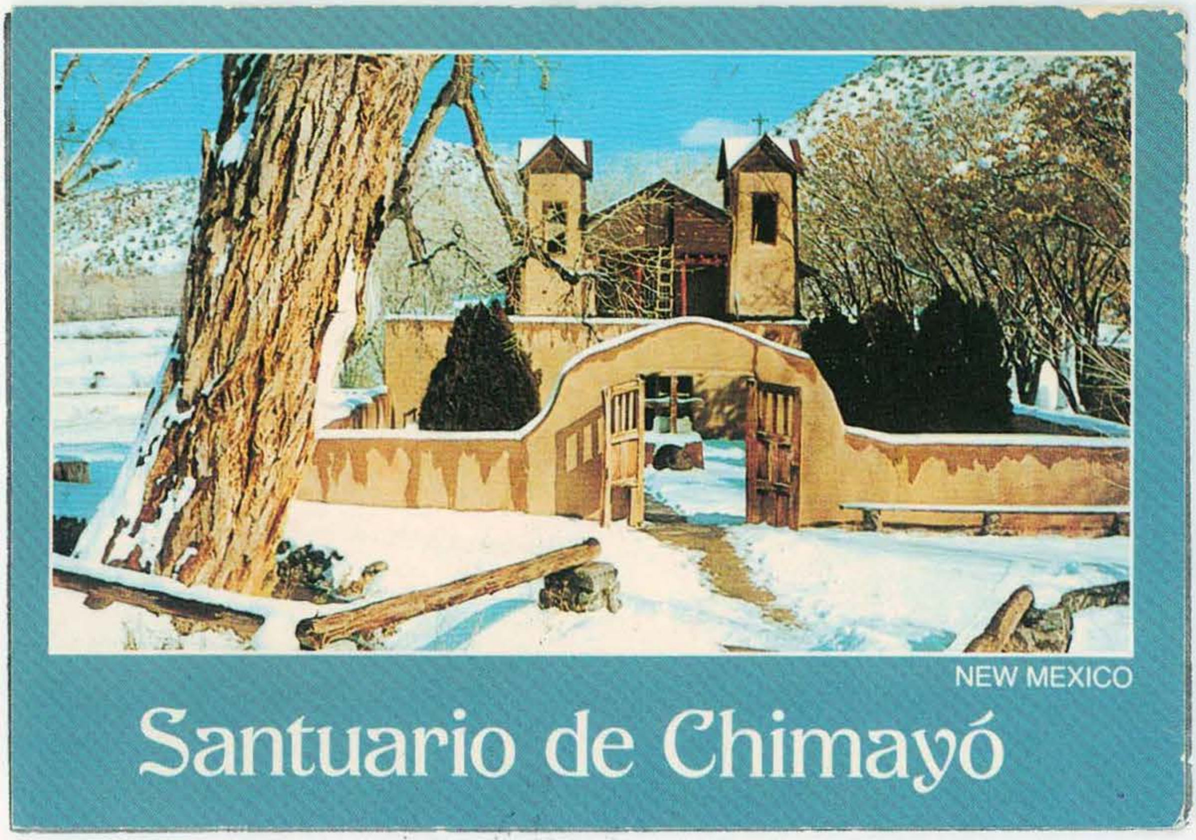

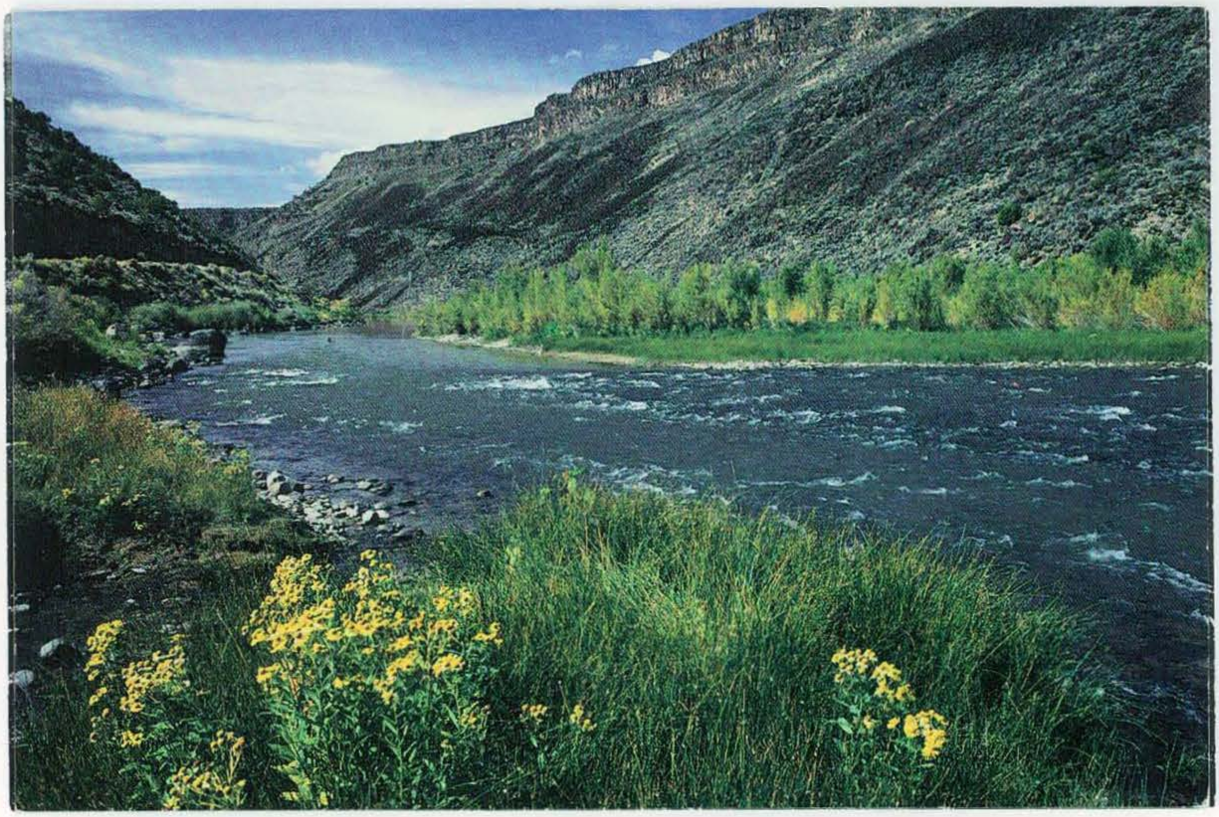

RIO GRANDE RIVER NEAR ESPAÑOLA, NEW MEXICO, USA.

RIO GRANDE DEL NORTE (RIO BRAVO) PERTO DE ESPAÑOLA, NOVO MÉXICO, ESTADOS UNIDOS.

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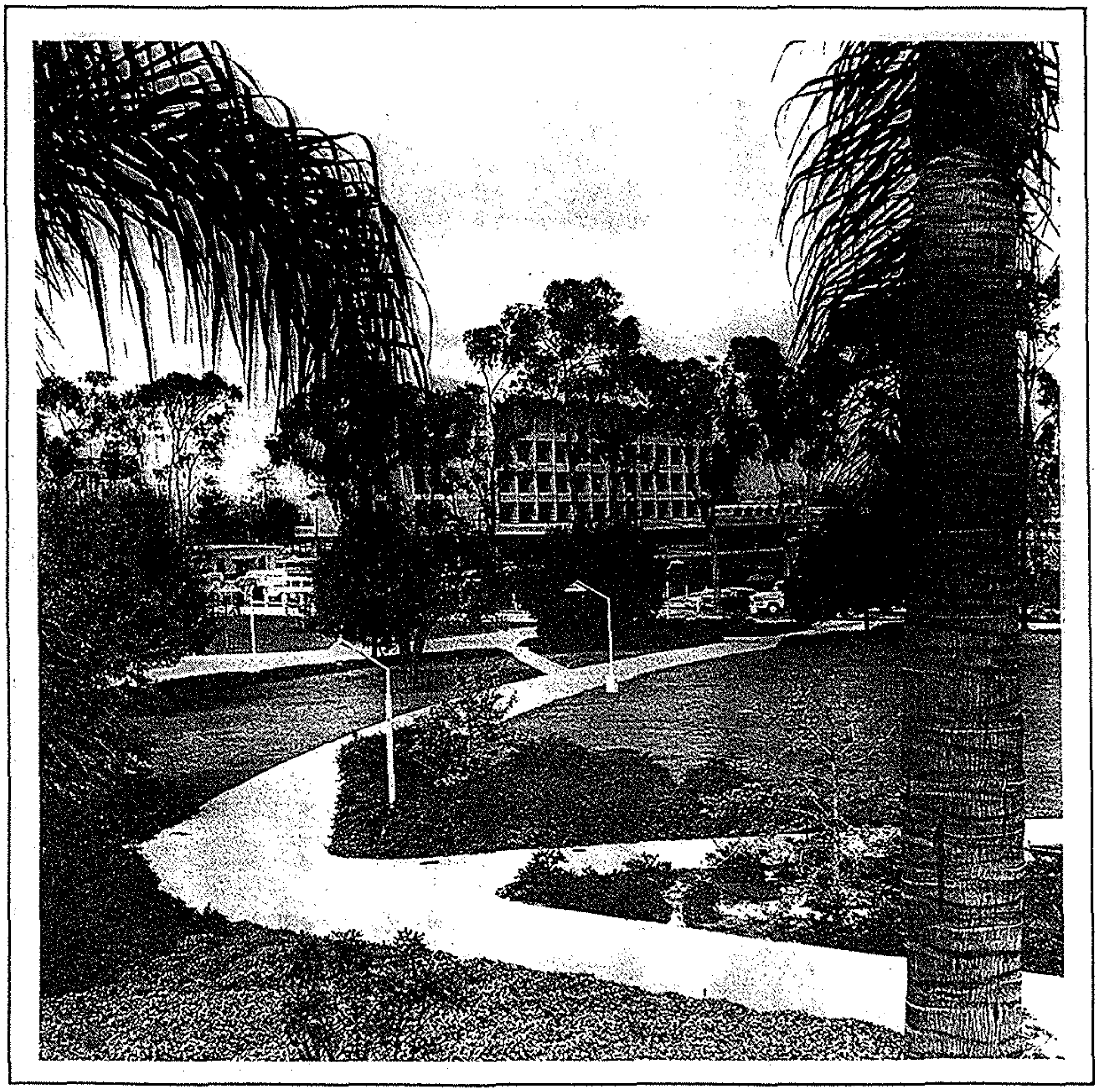

CHEMISTRY BUILDING, UNIVERSITY OF CALIFORNIA,
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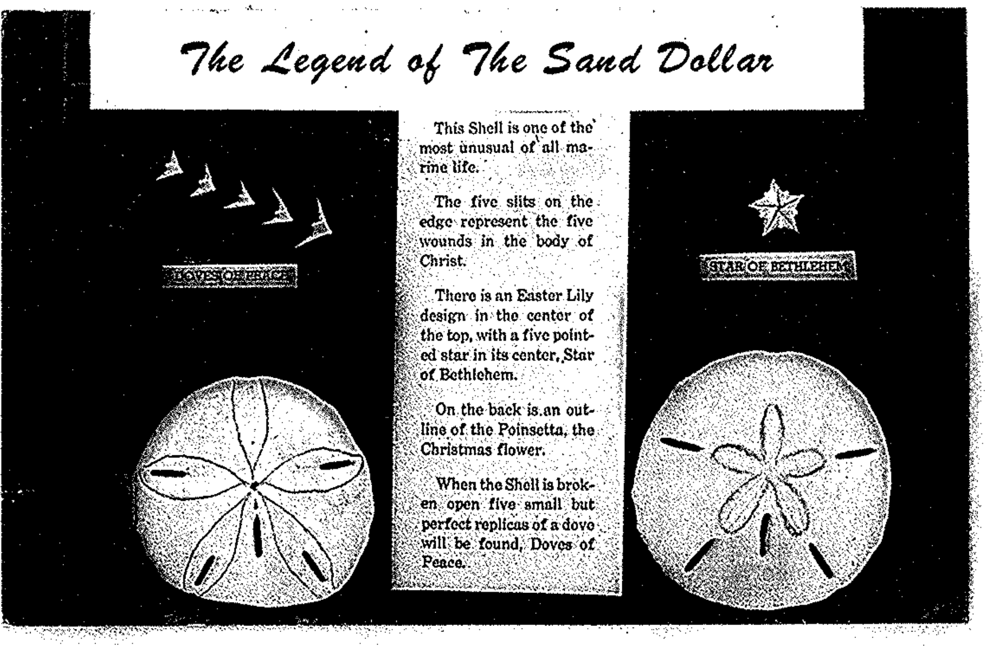


The Legend of The Sand Dollar

This Shell is one of the most unusual of all marine life.

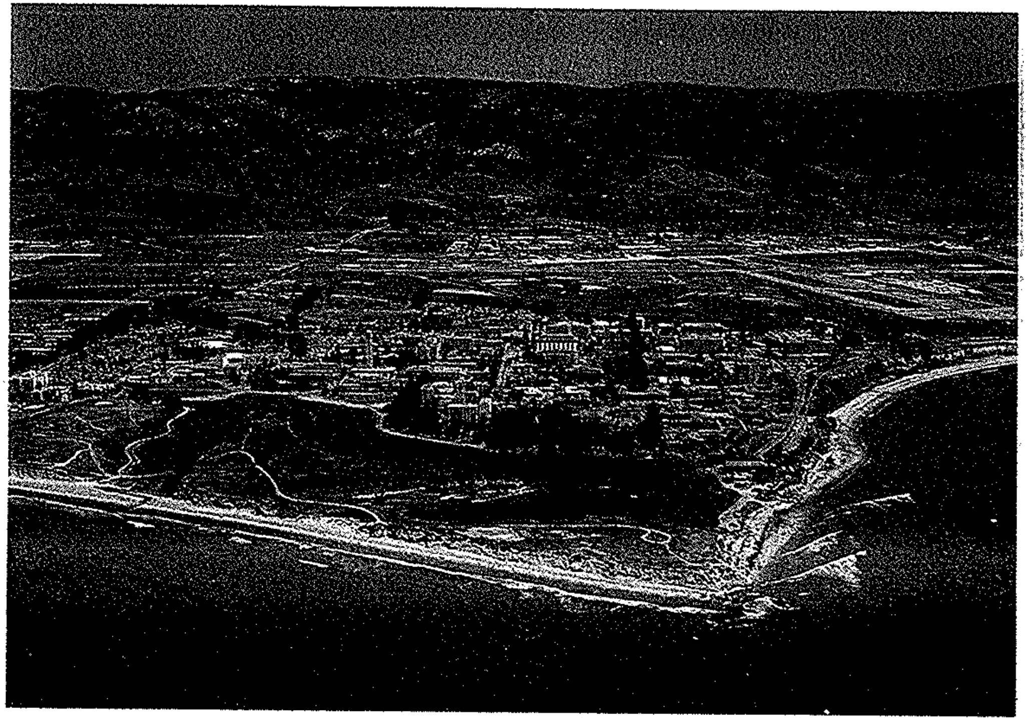
The five slits on the edge represent the five wounds in the body of Christ.

There is an Easter Lily design in the center of the top, with a five pointed star in its center, Star of Bethlehem.

On the back is an outline of the Poinsetta, the Christmas flower.

When the Shell is broken open five small but perfect replicas of a dove will be found, Doves of Peace.

A LENDA DA BOLACHA DE AREIA



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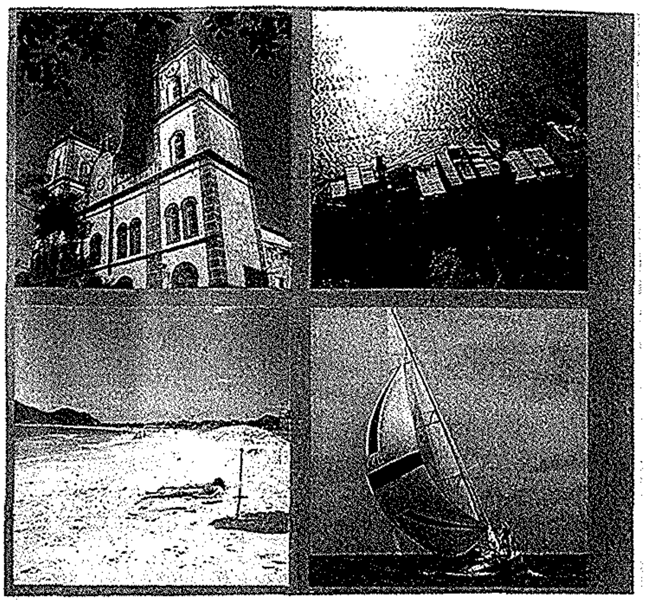

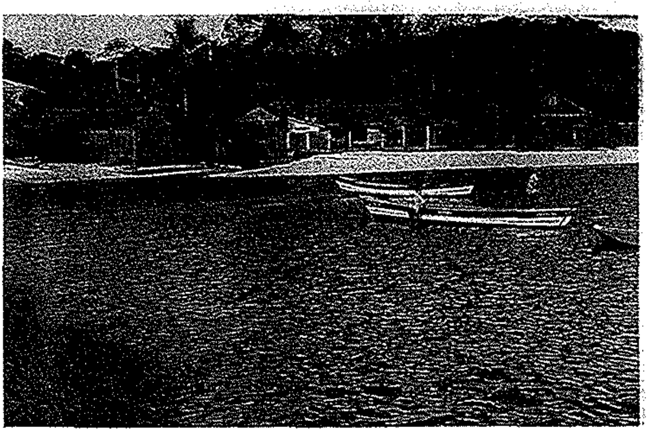
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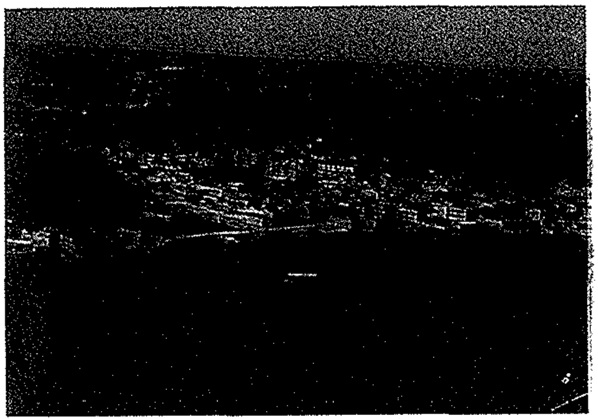
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CENTRO

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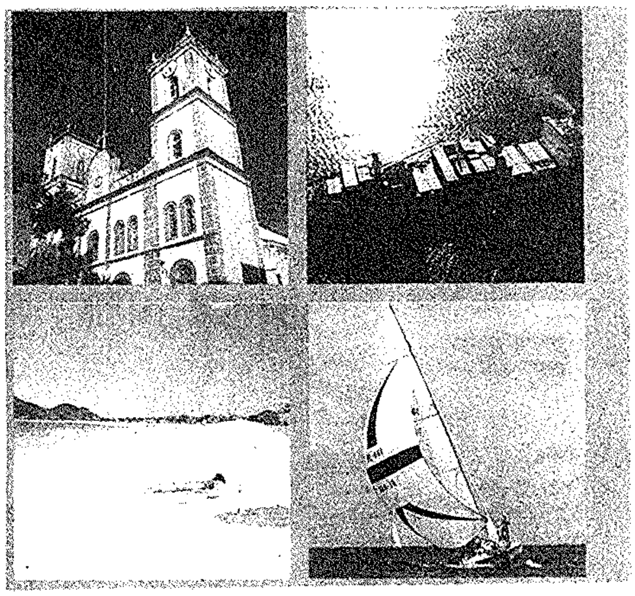

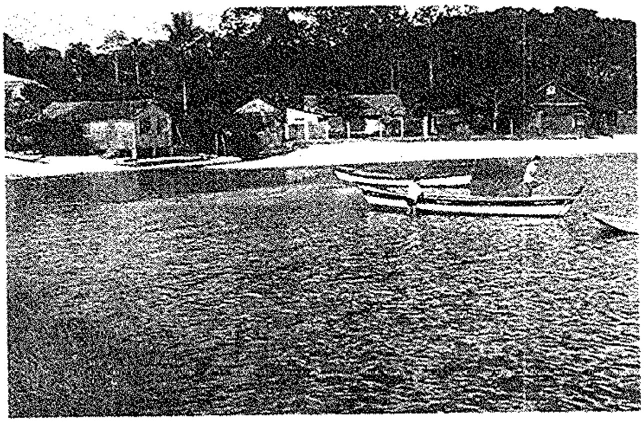
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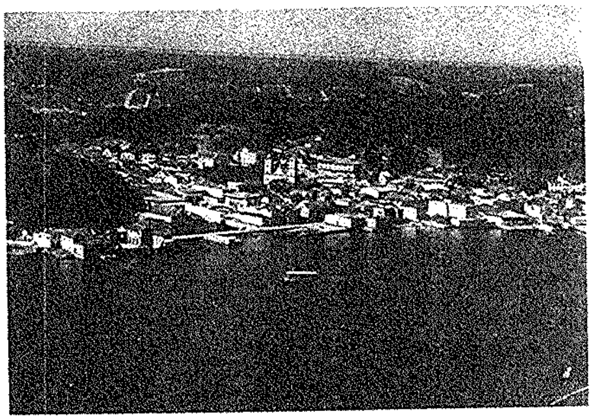
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