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EQUILIBRIUM STUDIES OF THE INTERACTIONS OF Zn(II) AND Cu(II) IONS WITH HUMIC ACID BY POTENTIOMETRIC TITRATION, IR AND FLUORESCENCE SPECTROSCOPY

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ABSTRACT:

The interactions of Zn(II) and Cu(II) with humic acids (HA) were characterized by potentiometric titration, IR and fluorescence spectroscopy. The equilibrium constants determined were: $\mathrm{Log([Zn(Cat)]/[Zn^{2+}][Cat])} = 15.25$, $\mathrm{Log([Zn(Cat)_2]/[ZnCat][Cat])} = 9.80$, $\mathrm{Log([Zn(Cat)(Sal)]/[Zn(Cat)][Sal])} = 8.59$, $\mathrm{Log([Zn(Cat)(Pht)]/[Zn(Cat)][Pht])} = 3.71$, $\mathrm{Log([Zn(OH)(Cat)_2][H^+]/[Zn(Cat)_2])} = -8.91$, for the Zn(II) system, and $\mathrm{Log([Cu(Cat)]/[Cu][Cat])} = 18.45$, $\mathrm{Log([Cu(Cat)_2]/[CuCat][Cat])} = 14.18$, and $\mathrm{Log([Cu(Cat)(Sal)]/[Cu(Cat)][Sal])} = 8.44$ for the Cu(II) system. The amounts of each group detected by potentiometric titration were: phenol = 0.666, carboxylic = 1.042, catechol = 0.540, phtalic = 1.163, and Salicylic = 0.810 mmoles per gram of HA, and the speciation curves were calculated.

KEYWORDS: Humic Acid, Zn(II), Cu(II), Speciation, Potentiometric Titration.

RESUMO:

As interações dos ions Zn(II) e Cu(II) com Ácidos Húmicos (HA) são caracterizadas por titulação potenciométrica, IV e Espectroscopia de Fluorescência. As constantes de equilíbrio determinadas são: $\mathrm{Log([Zn(Cat)]/[Zn^{2+}][Cat])} = 15{,}25$, $\mathrm{Log([Zn(Cat)_2]/[ZnCat][Cat])} = 9{,}80$, $\mathrm{Log([Zn(Cat)(Sal)]/[Zn(Cat)][Sal])} = 8{,}59$, $\mathrm{Log([Zn(Cat)(Pht)]/[Zn(Cat)][Pht])} = 3{,}71$, $\mathrm{Log([Zn(OH)(Cat)_2][H^+]/[Zn(Cat)_2])} = -8{,}91$, para o sistema Zn(II), e $\mathrm{Log([Cu(Cat)]/[Cu][Cat])} = 18{,}45$, $\mathrm{Log([Cu(Cat)_2]/[CuCat][Cat])} = 14{,}18$, e $\mathrm{Log([Cu(Cat)(Sal)]/[Cu(Cat)][Sal])} = 8{,}44$ para o sistema Cu(II). A quantidade de cada grupo detectada por titulação potenciométrica é: Fenol = 0,666; Carboxílico = 1,042; Catecol = 0,540; Ftálico = 1.163 e Salicílico = 0,810 mmoles por grama de HÁ, e as curvas de especiação foram calculadas.

PALAVRAS CHAVE: Ácido Húmico, Zn(II), Cu(II), Especiação, Titulação Potenciométrica.

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1. INTRODUCTION

Humic acids (HA) are a complex mixture of compounds, with different sizes, molar masses and several functional groups. The major groups are: carboxyl, phenol, catechol, phthalic and salicylic. Knowledge of the amount of each group present in this mixture is important in order to understand the interaction of humic substances (HS) with metal ions in the environment. The stability of complexes formed between HA and metal ions (HA-M) varies and is dependent on the pH, metal, ionic strength, and concentration of HA.[1,2,3]

A recent definition of the conformational nature of HA states that they should be regarded as supramolecular associations of self-assembling heterogeneous and relatively small molecules derived from the degradation and decomposition of biological material. A major aspect of the humic supramolecular conformation is that it is stabilized predominantly by weak dispersive forces instead of covalent linkages. Hydrophobic (van der Waals, π–π, CH-π) and hydrogen bonds are responsible for the apparent large molecular size of HA, the importance of the former increasing with pH.[2]

Metal complexation is important to understand the transport and availability of metals in soils and natural waters, and in the case of toxic metal contamination humic substances (HS) lower significantly the amount of free metal ion, reducing its toxicity to humans. This subject has gained considerable attention for many years and several methods have been employed to investigate HA-metal ion complexation.[4-18] However, none of these studies gives details regarding HA complexation.

Of the techniques available, potentiometric titration was selected since it allows the calculation of the amount of each functional group and it can also be used to measure the interaction of each group. In this study, the interactions of Cu(II) and Zn(II) were characterized by potentiometric titration, fluorescence and IR spectroscopy. The IR spectra are compared with those in the literature.[19-21]

2. EXPERIMENTAL

The potentiometric titration of HA (from Aldrich) in the absence and presence of copper(II) and zinc(II) was carried out with a Corning 350 pH/ion analyzer fitted with blue-glass and Ag-AgCl reference electrodes. The potentiometric apparatus was calibrated with standard HCl and KOH solutions to read $-\log [H^+]$ directly, and the pKw for water at $\mu = 0.100$ M was 13.78. Samples of 0.100 g of HA were diluted with 40 ml of bidistilled water (in the presence of $KMnO_4$) in a sealed thermostated vessel at 25.0 °C. The experimental solution of HA alone, adjusted to 0.100 M ionic strength with KCl, was titrated with 0.100 M standard CO_2-free KOH until the pH reached approximately 11, and back titrated with 0.100 M HCl. Solutions containing HA plus Cu(II) and HA plus Zn(II) were studied potentiometrically with 0.0350 mmol and 0.0700 mmol of metal ion. The argon was cleaned using two vessels of 0.100 M KOH solution and bubbled at the inlet and outlet of the thermostated cell. Computations of the triplicate experiments were all carried out with the BEST7 program, and the species diagrams were obtained with the aid of the SPECIES program.[22-25]

Infrared spectra of the humic acid fractions were recorded using samples in KBr pellets (1 mg of Aldrich humic acid per 100 mg of KBr) with a Shimadzu Resolution 1.04 FT-IR spectrometer. The KBr (FT-IR grade, Aldrich Co.) was dried by heating and kept under vacuum in desiccators prior to use.

In the fluorescence titration, stock solutions of HA were prepared by dissolving 0.0080 g of HA in 200 mL. Samples of 10 mL of stock solution were used to prepare the experimental solutions. Aliquots of 50 µL of $1.09\text{x}10^{-2}$ mol/L Cu(II) solution were added to the experimental solutions, and an interval of 30 minutes allowed the solutions to reach equilibrium.

The transmittance intensity of the experimental solutions was measured using a SimAminco SPF-500 spectrofluorometer. Emission and excitation slits were sets at a 10 nm band width. The wavelength emission was 510.5 nm and the excitation wavelength was 366 nm. Stern-Volmer graphics were obtained from these data for the HA-Cu(II) system at pH 9.

3. RESULTS AND DISCUSSION

3.1 The coordinating groups of humic acids

The potentiometric curve of HA is shown in Figure 1, together with the curves of the metal systems. In all the curves the buffers are not well defined. It can be seen that the curves of metal systems are below the curve of HA alone, indicating the coordination of the metal ions; copper(II) interacting more strongly than zinc(II). The amount of each group detected in the supramolecular structure of HA, as well as the pKa values, were determined with the help of the BEST7 program when possible, and the results are shown in Table 1.

3.2 Metal systems

The equilibrium constants determined (Table 2) allow the calculation of the distribution of the groups coordinated with the metal ions, showing the preference of each group for the metals. Figure 2 shows the distribution for the HA-Zn(II) system. Above pH 4, the Zn(II) ion coordinates to the catechol group, Zn(Cat), and also the phtalic group, Zn(Cat)(Pht), reaching a maximum at near neutral pH. A second catechol group coordinates to the Zn(II) ion resulting in $Zn(Cat)_2$ and a hydroxo species, $Zn(OH)(Cat)_2$. A mixed group interaction, catechol and salicylic, Zn(Cat)(Sal), also forms at higher pH.

The distribution of groups coordinated to Cu(II) is shown in Figure 3. Copper coordinates to the HA above pH 3. Its preference for the catechol group is shown, Cu(Cat), being 100 % coordinated at pH 5.0. Above this pH value a second catechol group coordinates, represented by Cu(Cat)2. A salicylic group also coordinates, and coordination of salicylic and catechol groups to Cu(II) is represented by Cu(Cat)(Sal).

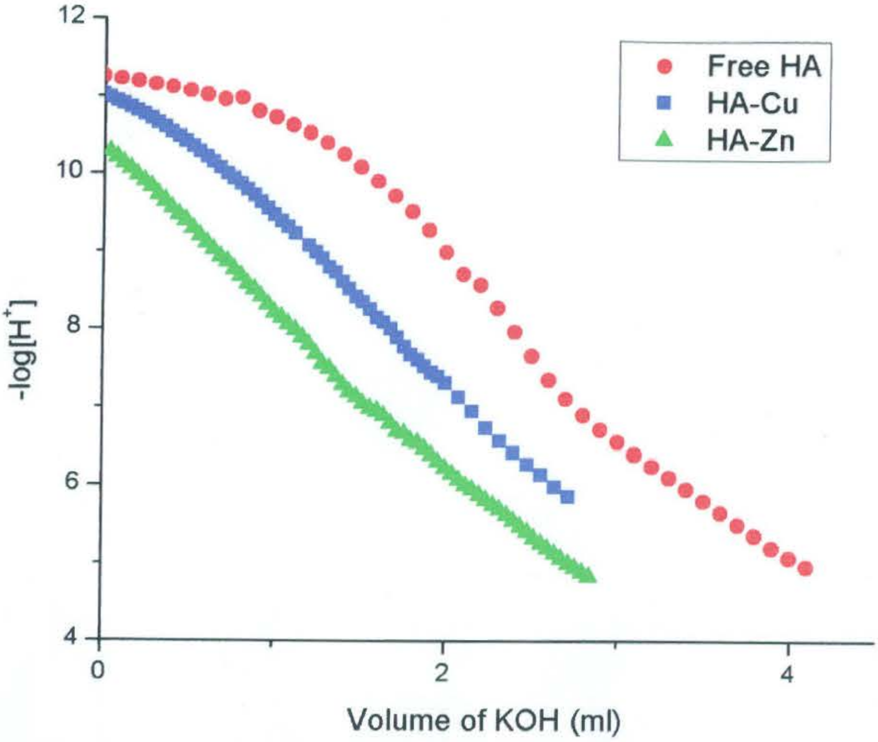

Figure 1 – Potentiometric titration curves of HA, HA in presence of Cu(II) and HA in presence of Zn(II); μ = 0.100 M (KCl), T = 25.0 °C.

Table 1 – Amounts of oxygenated groups detected in HAs obtained from Aldrich, and their pKa values, μ = 0.100 M (KCl), T = 25.0 °C.

Group	mmoles/g of HA*	pKa*
Phenol	0.666 (6)	9.66 (6)
Carboxylic	1.042 (19)	6.35 (2)
Catechol	0.540 (13)	7.97 (22) 13.30
Phtalic	1.163 (30)	2.76 (6) 4.71 (6)
Salicylic	0.810 (4)	3.29 (25) 13.40

*The number in parentheses is the average deviation of the measurement.

Table2: Equilibrium constants for the interactions of HA coordinating groups with Zn(II) and Cu(II) ions, $\mu = 0.100$ M (KCl), T = 25.0 °C.

Quotient	Log Q Zn(II)*	Log Q Cu(II)*
$[M(Cat)]/[M][Cat]$	15.25 (30)	18.45 (28)
$[M(Cat)_2]/[MCat][Cat]$	9.80 (05)	14.18 (08)
$[M(Cat)(Sal)]/[M(Cat)][Sal]$	8.59 (28)	8.44 (25)
$[M(Cat)(Pht)]/[M(Cat)][Pht]$	3.71 (02)	-
$[M(OH)(Cat)_2][H^+]/[M(Cat)_2]$	-8.91 (12)	-

*The number in parentheses is the average deviation of the measurement.

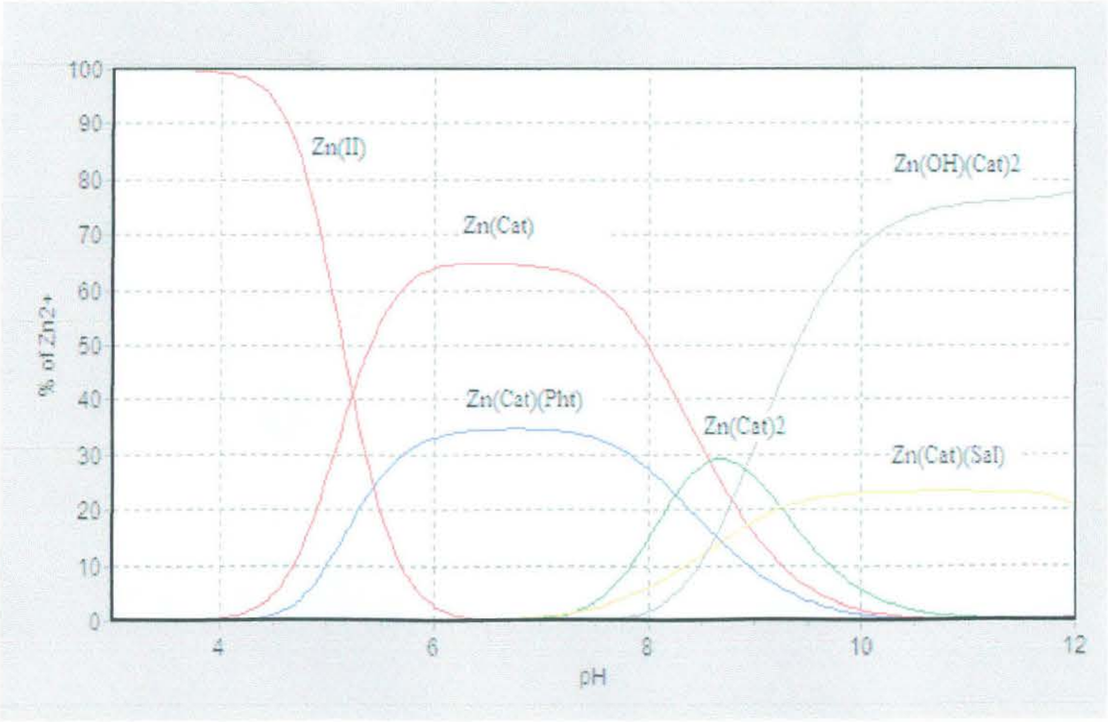

Figure 2 – Distribution curves of coordinated groups with Zn(II) ion.

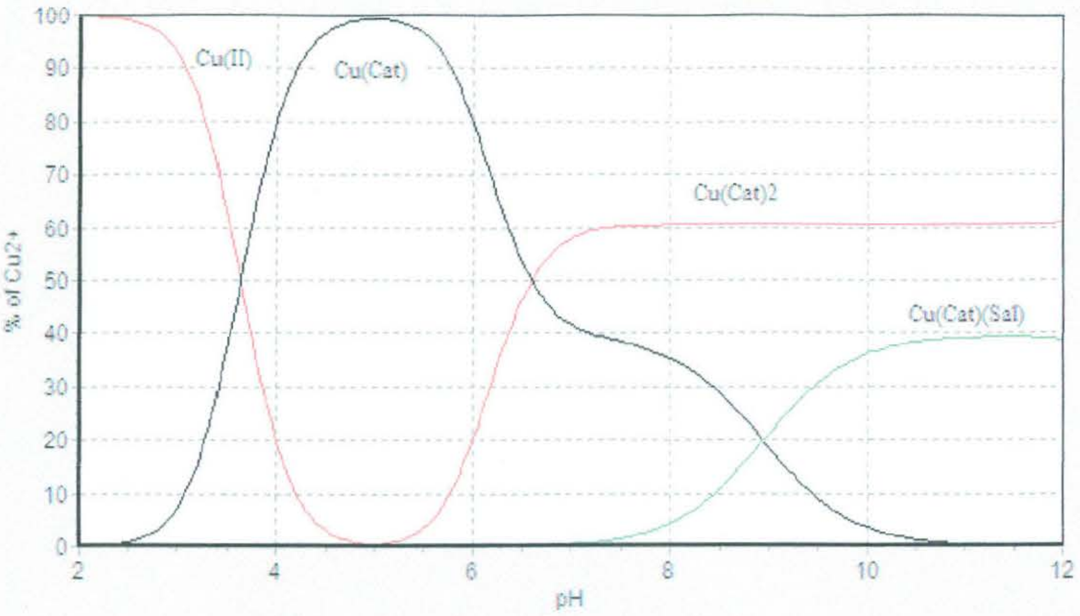

Figure 3 – Distribution curves of coordinated groups with Cu(II) ion.

3.3 IR studies.

The IR studies showed the complexation of the metal ions. On the IR spectrum of HA (Figure 4) a broad peak can be seen at 3400 cm^{-1} due to the axial stretching of the carboxylic and catechol O-H groups. The peaks between 2915 cm^{-1} and 2851 cm^{-1} are due to the CH_2CH_3 stretching, and at 1680 cm^{-1} there is a peak due to the stretching of deprotonated C=O.

The metal complexation can be evidenced through the increase in the intensity of the peaks at 1680 cm^{-1}, attributed to asymmetric stretching of the COO^-. For the HA-Zn(II) system the intensity of the peak at 1680 cm^{-1} is greater at pH 7, where Zn(II) is coordinated to phtalic and catechol groups (Figure 3). At higher pH values, Zn(II) is predominantly coordinated to catechol and salicylic groups, reducing the carboxylic environment in the Zn(II) ion, since the salicylic group has only one carboxylic group while phtalic has two. The peak at 1394 cm^{-1} is narrow due to the interaction with the metal ion and catechol group. At neutral pH it can be observed that there is also complexation of the metal ion with the catechol. At alkaline pH values, the tuning of the peaks 1680cm^{-1} and 1394cm^{-1} is attributed to the complexation of catechol and salicylic groups (Figure 4).

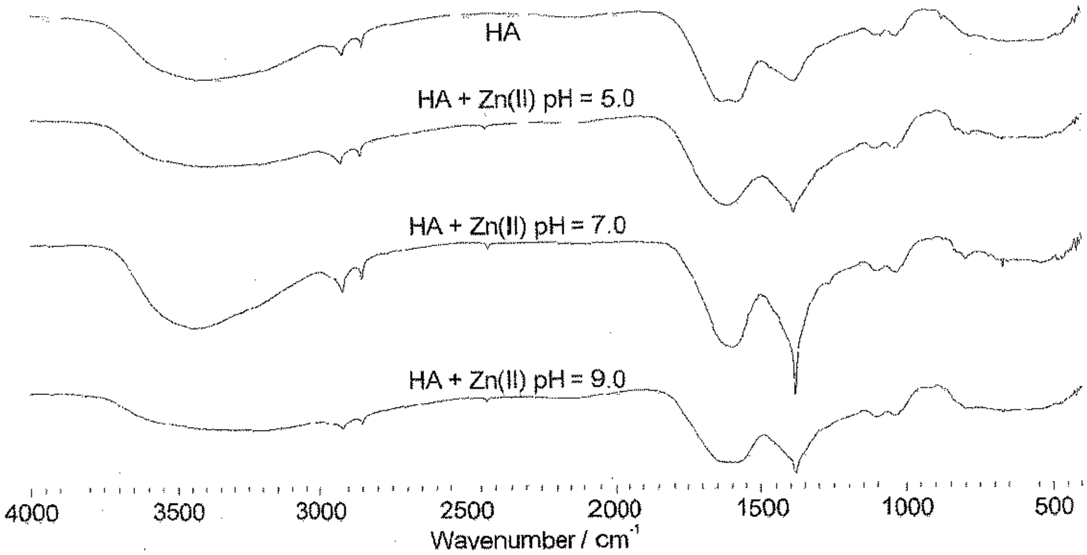

Figure 4 – IR spectra of HA-Zn(II) system.

The IR spectra of the HA-Cu(II) system is shown in Figure 5. The intensity of the peak at 1680 cm^{-1}, attributed to asymmetric stretching of the COO$^-$ group of HA remains constant at acid and neutral pH. A slight shift of this peak to a higher wave number (cm^{-1}) is observed at pH 9 (Figure 5), indicating the interaction of Cu(II) with the salicylic group, since this group has a carboxylic group. The peak at 1394 cm^{-1} is narrow due to the interaction with the metal ion and catechol group. Cu(II) is coordinated with catechol at all pH values above pH 3 (Figure 3), and in all IR spectra at pH values 5, 7 and 9 the peak at 1394 cm^{-1} is narrow, indicating that catechol is involved in the coordination sphere of Cu(II).

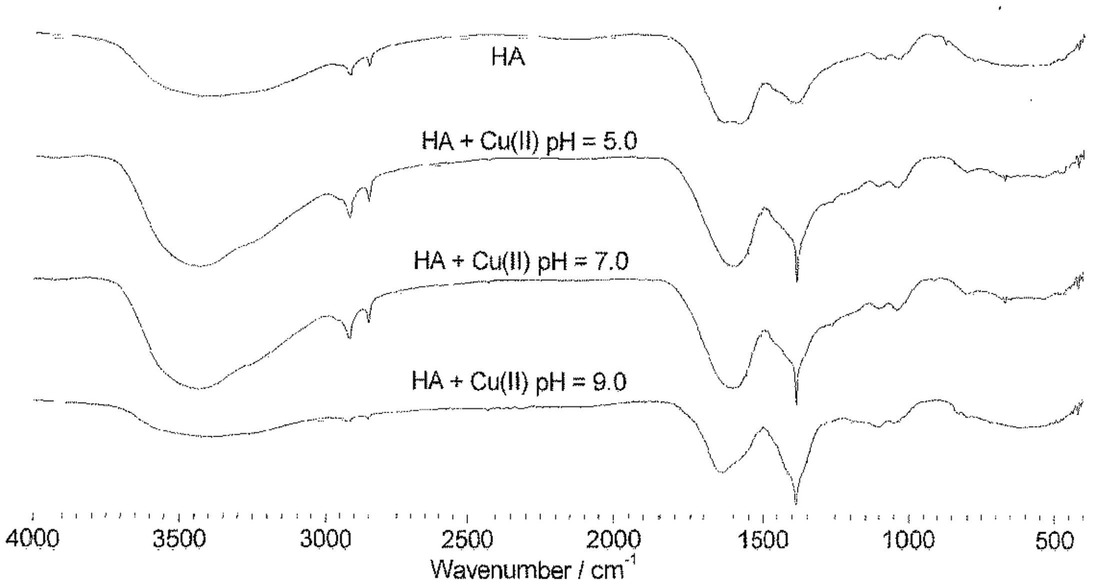

Figure 5 – IR spectra of HA-Cu(II) system.

3.4 – Fluorescence titration

Figure 6 shows the Stern-Volmer graph for the Cu(II) quenching titration of HA at 366/510.5 nm. As the amount of Cu(II) added in solution increases, the fluorescence intensity decreases due to Cu(II) binding, up to 2.1 μmol of Cu(II) per mg of HA, and further addition of Cu(II) does not affect the fluorescence intensity. At pH 9 most of the Cu(II) ion is coordinated in a 1:2 coordinating group:metal ion ratio (Figure 3). The saturation of the coordination groups with Cu(II) occurs with this amount of Cu(II). Thus, 2.1 mmol of Cu(II)/g of HA saturate approximately 4.2 mmol of coordinating groups per gram of HA. The sum of the mmoles for all groups in Table 1 is 4.221 mmol/g of HA. This result confirms the total amount of HA groups determined by potentiometric titration.

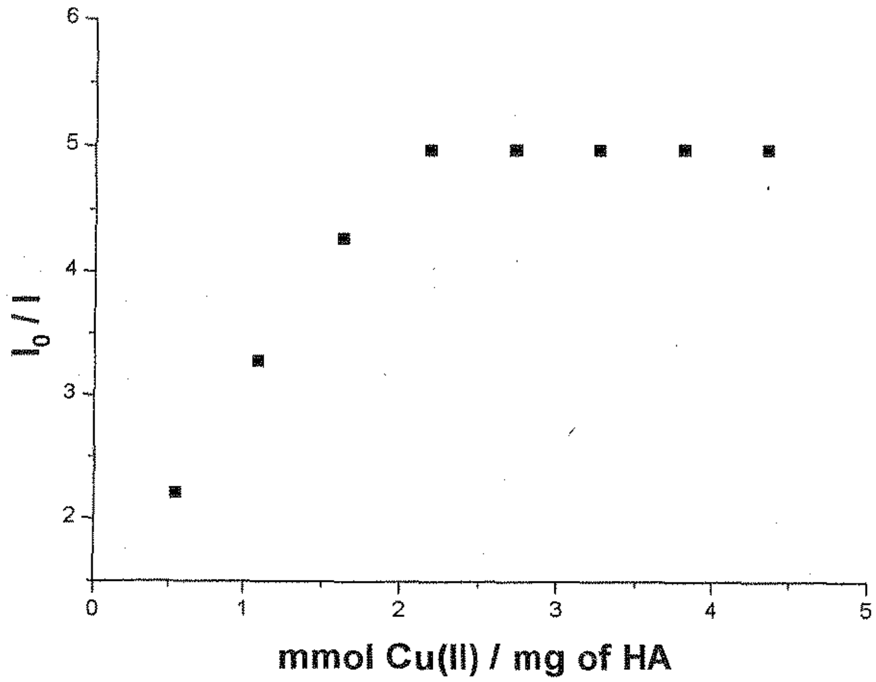

Figure 6 - Stern-Volmer graph of the HA-Cu(II) system at pH 9.

4. CONCLUSIONS

Potentiometric titration, used in conjunction with other techniques, is a powerful means to study the speciation of metals in the environment. The amount of each group present in HAs in significant quantities was determined by potentiometric titration and appropriate computer programs. Catechol, salicylic and phtalic are the major groups involved in the coordination of Zn(II) and Cu(II) and the equilibrium constants are determined for each group.

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SYNTHESIS AND ANTIMICROBIAL STUDIES OF NOVEL IMINES AND OXADIAZOLES

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ABSTRACT

N-benzylidene-2-(4-chloro-3-methylphenoxy)acetohydrazides **(3a-e)**, obtained by arylation of 2-(4-chloro-3-methyl phenoxy)acetohydrazide **(2)**, was cyclized with acetic anhydride to yield 1-(5-((4-chloro-3-methylphenoxy)methyl)-2-phenyl-1,3,4-oxadiazol-3(2H)-yl)ethanones **(4a-e)**. All the newly synthesized compounds were analytically and spectrally characterized and evaluated for anti-bacterial and anti-fungal activities.

KEYWORDS

Acetohydrazide, aryloxy acetate, imines, oxadiazoles, antimicrobial activity

RESUMO

N-benzilideno-2-(4-cloro-3-metilfenoxi)acetohidrazidas **(3a-e)**, obtidas pela arilação de 2-(4-cloro-3-metil fenoxi)acetohidrazida **(2)**, foram ciclizadas com anidrido acético para obter 1-(5-((4-cloro-3-metilfenoxi)metil)-2-fenil-1,3,4-oxadiazol-3(2H)-il)etanonas **(4a-e)**. Todos os compostos novos sintetizados foram caracterizados através de espectroscopia e outros métodos analíticos. A atividade antibacterial e antifúngica foram avaliadas.

PALAVRAS-CHAVE

Acetohidrazida, Ariloxi Acetato, Iminas, Oxodiazol, Atividade Antimicrobial

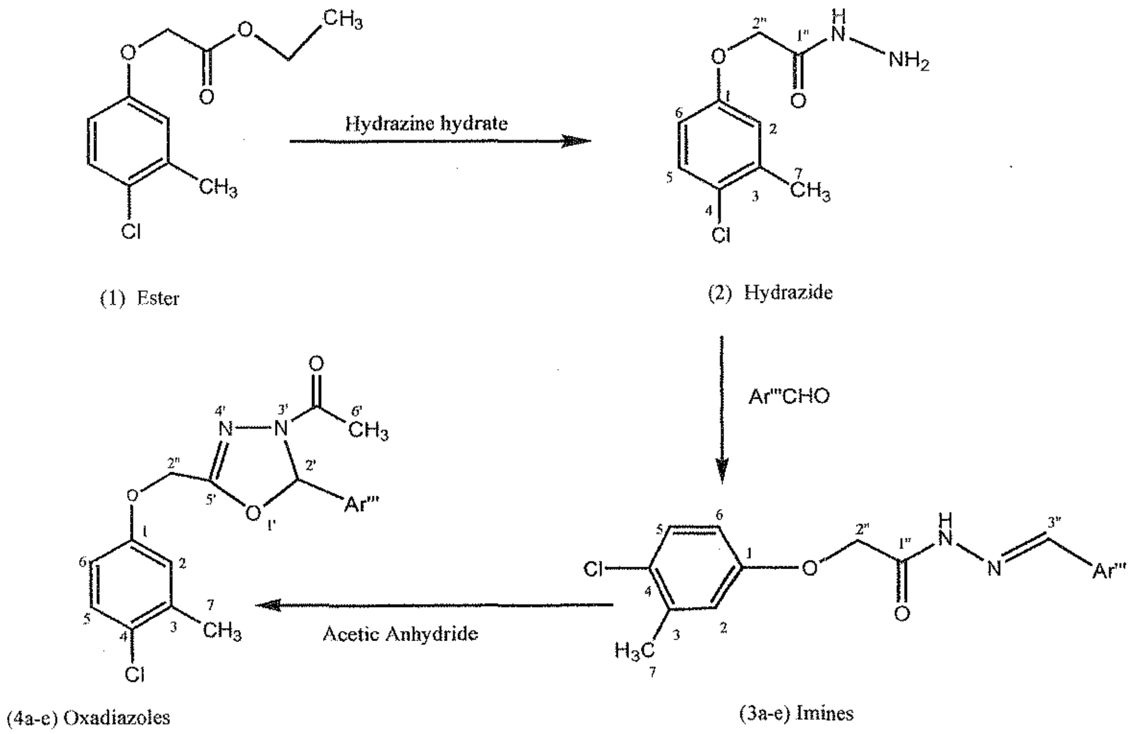
INTRODUCTION

It is an established fact that oxadiazoles, imines and phenolic moieties possess anti-convulsant[1,2], antiproteolytic[2], anantimitotic[3], anticancer[4], antikinetoplastid[5], antitussive[6], hybrid COX-2 inhibitor/nitric oxide donor[7], antimycotic[8], anti-tubercular[9], cosmetic biocide preservative[10], antimicrobial[11], antibacterial[12,13] activities. Phenolic moieties are known as precursor for imines [14], which are precursors for oxadiazoles[15]. As per literature, activities associated with oxadiazoles, imines and phenolic moieties, an attempt was made to synthesize novel potent antibacterial and antifungal by converting a phenolic ester moiety into some novel 1-(5-((4-chloro-3-methylphenoxy)methyl)-2-phenyl-1,3,4-oxadiazol-3(2H)-yl)ethanones **(4a-e)**, via synthesis of hydrazide **(2)** and imines **(3a-e)** as intermediates. The novel compounds were characterized and further evaluated for anti-bacterial and anti-fungal activities.

RESULTS AND DISCUSSION

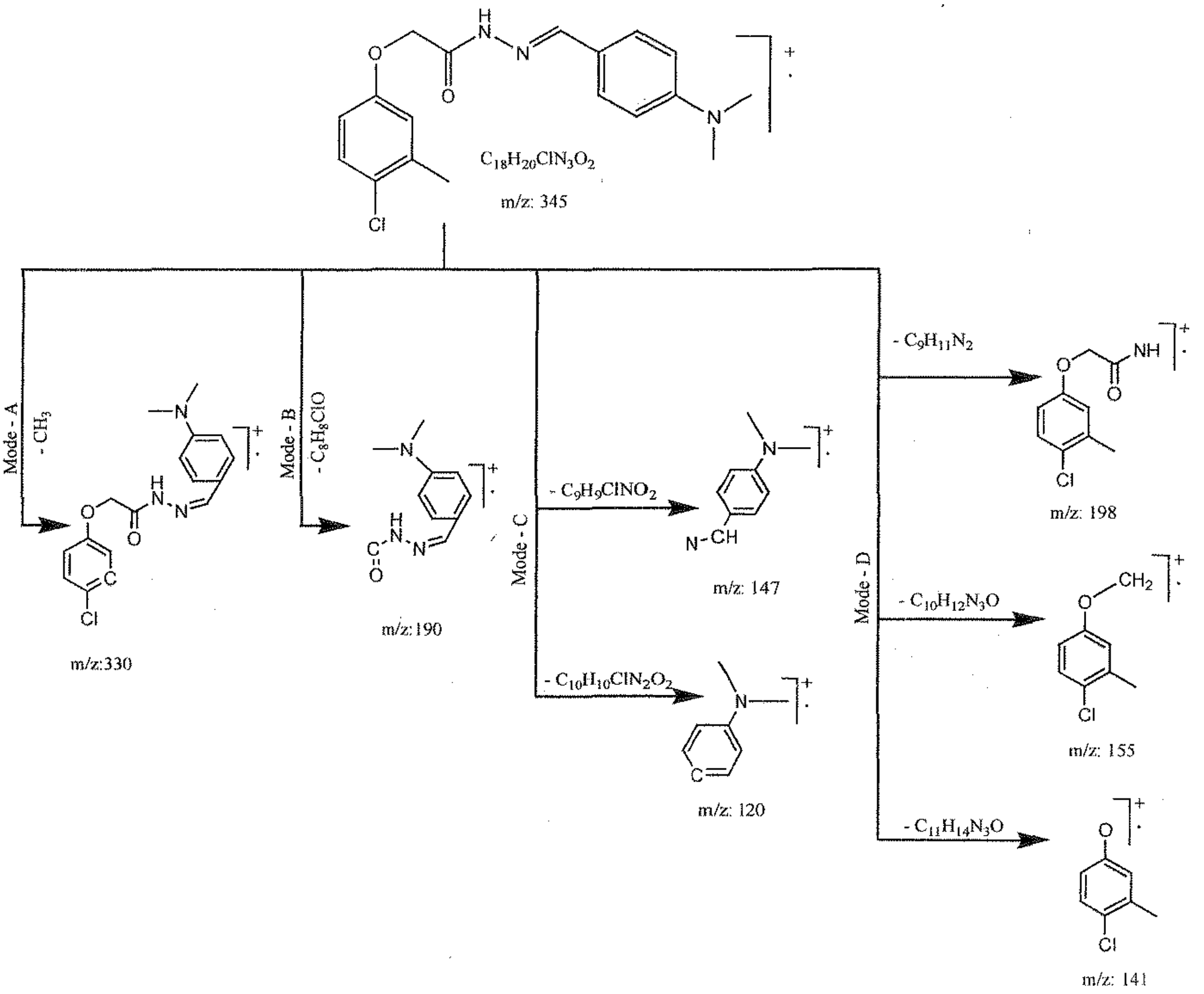
N-(substituted benzylidiene)-2-(4-chloro-3-methylphenoxy)acetamides **(3a-e)**, prepared from compound **1**, when cyclized with acetic anhydride leads to potent antibacterial and antifungal 1-(5-((4-chloro-3-methylphenoxy)methyl)-2-aryl-1,3,4-oxadiazol-3(2H)-yl)ethanones **(4a-e)**. Synthetic procedure for conversion of compound **1** to **2**, **3a-e** and **4a-e** is suggested in **Scheme-1**. Physical data of **1**, **2**, **3a-e** and **4a-e** are given in **Table-1**. The purity of all newly synthesized compounds was checked by TLC (Rf value given in **table-1)** and elemental analysis. The assigned structure, molecular formulae and the anomeric configuration of the newly synthesized compounds **2, 3a-e** and **4a-e** was further confirmed and supported by Mass, ^{1}H NMR and IR spectral data, arise as result of occurrence of molecular ion peak of the assigned structures, downfield shifting of protons and different stretching of bands of the compounds. The fragmentation pattern of compound **3a** and **4a** further supported the structure of newly synthesized compounds **3a-e** and **4a-e** given in **Scheme-II** and **III**. In general the IR spectra of newly synthesized compounds revealed NH, OH, CO (CONH), C-O-C peaks near 3256, 3510, 1645, 1253 cm^{-1} respectively. In the ^{1}H-NMR spectra, signals of respective protons of newly synthesized compounds showed the peaks for $-Co-CH_3$, $-CH_3$, $-O-CH_2$, -OH, aromatic protons, N=CH and NH near 2.06, 2.3, 4.8, 5.2, 6.1-7.4, 8.0 and 9.2 respectively. The general Mass fragmentation pattern for compound **3a** showed the m/z peaks at $345(M^+)$, 190(base Peak), 330, 198, 155, 147, 141, 120 as a result of loss of $-1e^-$, $-C_8H_8ClO$, $-CH_3$, $-C_9H_{11}N_2$, $-C_9H_{12}N_3O$, $-C_9H_9ClNO_2$, $-C_{11}H_{14}N_3O$, $-C_{10}H_{10}ClN_2O_2$ respectively and compound **4a** showed the m/z peaks at m/z: $387(M^+)$, 120(base peak), 372, 232, 155, 141 as a result of loss of $-1e^-$, $-C_{12}H_{12}ClN_2O_3$, $-CH_3$, $-C_8H_8ClO$, $-C_{12}H_{14}N_3O_2$, $-C_{13}H_{16}N_3O_2$ respectively. In the same way the fragmentation pattern of all newly synthesized compounds **3b-e** and **4b-e** was identified to further support the structure. The elemental analysis results were within ± 0.4% of the theoretical values. Both analytical and spectral data (IR, ^{1}H-NMR, Mass) of all the synthesized compounds were in full agreement with the proposed structure. The newly

SCHEME-I



Where Ar''' = 4-dimethyl amino phenyl, 4-chloro phenyl, 2,4-dihydroxy phenyl, phenyl and 4-hydroxyphenyl group

SCHEME-II : Fragmentation pattern of Imine (3a)



SCHEME-III : Fragmentation pattern of Oxadiazole (4a)

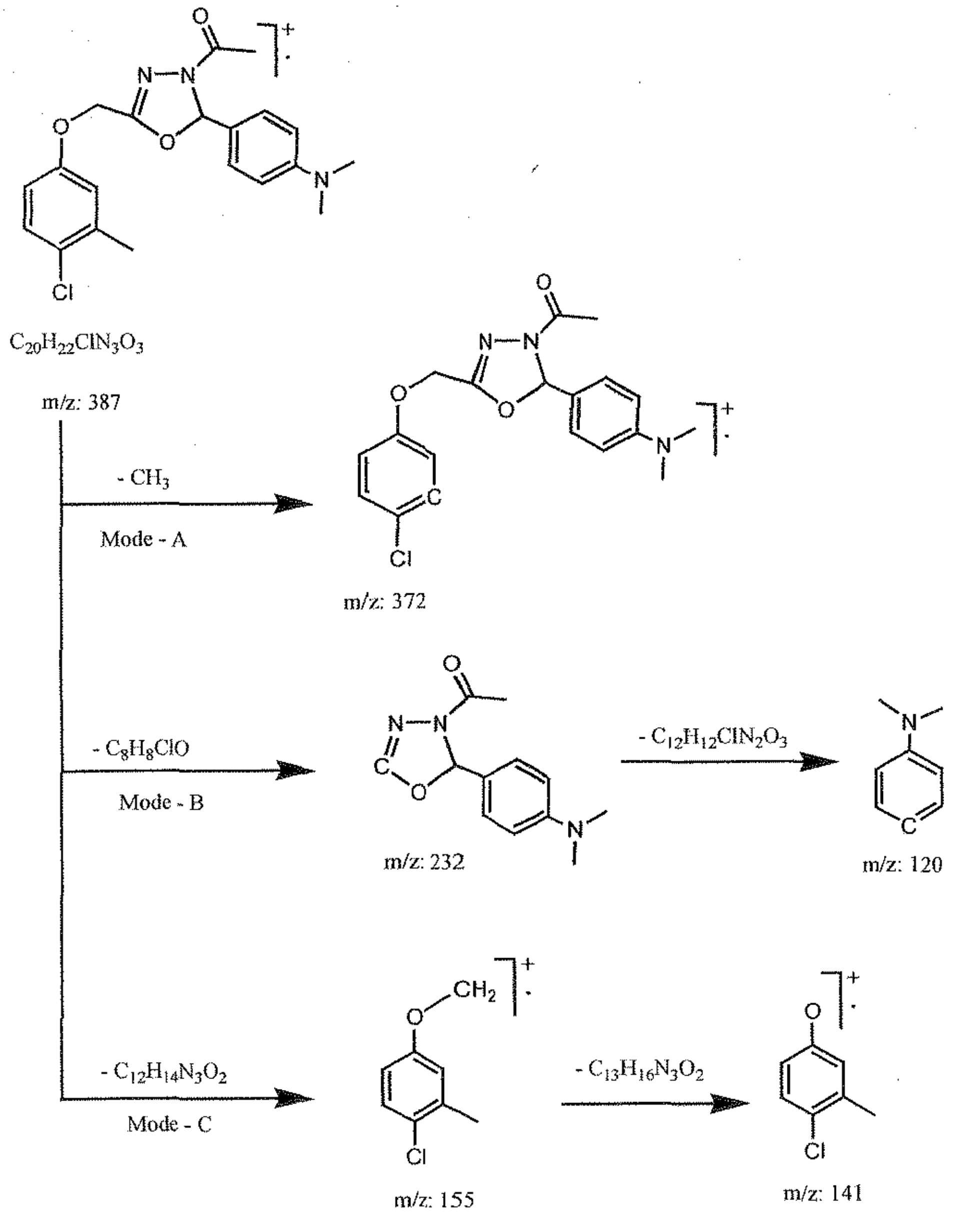
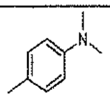
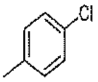
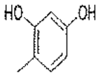
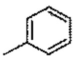
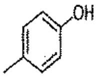
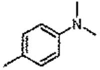
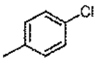
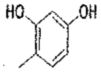
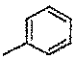
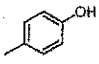


Table: 1 - Physical Data of compound 1, 2, 3(a-e) and 4(a-e)

Compd	Ar″	Physical Characteristics	Yield (%)	Molecular Formulae	Mol. Wt.	m.p. (°C)	Rf Value
1	-	Pale Brown liquid	70	$C_{11}H_{13}O_3Cl$	228.67	145 B.P.	-
2	-	White crystals	85	$C_9H_{11}ClN_2O_2$	214.64	160-161	0.57
3a		White crystals	72	$C_{18}H_{20}N_3O_2Cl$	345.82	194-195	0.59
3b		White crystals	63	$C_{16}H_{14}N_2O_2Cl_2$	337.2	212-213	0.52
3c		White crystals	65	$C_{16}H_{15}N_2O_4Cl$	334.75	220-221	0.55
3d		White cloggy crystals	59	$C_{16}H_{15}ClN_2O_2$	302.76	185-186	0.49
3e		White crystals	57	$C_{16}H_{15}N_2O_3Cl$	318.75	216-217	0.53
4a		Pale yellow crystals	72	$C_{20}H_{22}N_3O_3Cl$	387.86	218-219	0.49
4b		Orange Crystals	69	$C_{18}H_{16}N_2O_3Cl_2$	379.23	203-204	0.65
4c		Pale yellow crystals	70	$C_{18}H_{17}N_2O_5Cl$	376.79	215-216	0.52
4d		Pale yellow crystals	79	$C_{18}H_{17}N_2O_3Cl$	344.79	219-220	0.62
4e		Light brown crystals	75	$C_{18}H_{17}N_2O_4Cl$	360.79	210-211	0.68

synthesized compounds were tested for antibacterial activity against the freshly cultured strains of *S. aureus, E. coli, P. aeruginosa* using sterile Nutrient agar media and antifungal activity against the freshly cultured strains strains of *C. albicans, A. flavus, A. fumigatus* using sterile Sabouraud's agar medium. After comparing the antibacterial and antifungal results of newly synthesized compounds using ampicillin and fluconazole as standards it was found that compounds **3a-e** and **4a-e** possesses antibacterial and antifungal activities to certain extent. Among newly synthesized derivatives, compound **3c** and **4a** was found to be equipotent as ampicillin when tested against the strains of *E. coli,* where as tested compounds **3c, 4a and 4d** have shown good antibacterial and antifungal activity against *S. aureus, P. aeruginosa and C. albicans.,* where as remaining compounds have shown moderate antibacterial and antifungal activity when tested against the strains of *S. aureus, E. coli, P. aeruginosa A. flavus, A. fumigatus* given in **Table-2**. After comparing the antimicrobial results of compounds **3a-e** and **4a-e**, it was concluded that the incorporation of oxadiazole moiety in aryloxy derivatives enhances their antimicrobial activity and also para substitution in Ar″ group of oxadiazoles **4a-e** was found to enhance their potency especially in compound **4a**. Further studies to acquire more information about structure activity relationship are in progress in our laboratory

EXPERIMENTAL

Melting points of newly synthesized compounds were determined in open capillary tubes. IR spectra were recorded (in KBr) on Bruker PCIR, ^{1}H-NMR on bruker, DPX 300 and mass spectra on MASPEC (MSW/9629). Purity of synthesized compounds was checked by TLC aluminium sheets – silica gel 60 F254 (0.2 mm).

2-(4-chloro-3-methylphenoxy)acetohydrazide (2) :

A mixture of ethylaryloxyacetate **1** (0.05mol) and hydrazine hydrate (0.075mol) in ethanol was refluxed for 6 hours. The reaction mixture was distilled off to remove solvent and formed crystals were recrystallised from methanol to yield compound **2** (Physical data and Rf value found using ethyl acetate and petroleum ether in the ratio of 9.5:0.5 are given in **Table 1**). IR (KBr): ν (cm^{-1}) 3276, 3281 (NH and NH_2), 1740 (CO of ester); ^{1}H-NMR ($CDCl_3$): δ (ppm) 2.32 (s, 3H, CH_3), 4.83 (s, 2H, OCH_2), 6.38 (br, 2H, NH_2), 6.51 (d, 1H, J = 2.7 Hz, Ar-H2), 6.53 (dd, 1H, J = 2.7, 6.3 Hz, Ar-H6), 7.04 (d, 1H, J = 6.3 Hz, Ar-H5), 9.35 (s, 1H, NH); ^{13}C-NMR (100MHz, DMSO): δ (ppm) 19.83 (C-7), 66.48 (C-2''), 113.89 (C-6), 117.42 (C-2), 125.22 (C-4), 129.46 (C-5), 136.46 (C-3), 156.58 (C-1) and 166.56 (C-1''); Mass (%): m/z 214 (M^+, 12), 141 (base Peak, 100), 155 (52); Analysis (calculated) found: C (50.36) 50.32, H (5.17) 5.14, N (13.05) 13.02 %.

General procedure for synthesis of 2-{(4-chloro-3-methyl) phenoxy}-N-[substituted benzylidene]acetohydrazides (3a-e) :

A mixture of compound **2** (0.01mol) and aromatic aldehyde (0.01mol) in the presence of few drops of glacial acetic acid was refluxed for 6 hours. Formed products were isolated and recrystallised from methanol to yield compounds **3a-e** (Physical data and Rf values found using chloroform and methanol in the ratio of 9:1 are given in **Table 1**).

N-(4-(dimethylamino)benzylidene)-2-(4-chloro-3-methylphenoxy)acetohydrazide (3a)

IR (KBr): ν (cm^{-1}) 1645 (CO of CONH), 3214(NH of CONH); ^{1}H-NMR ($CDCl_3$): δ (ppm) 2.39 (s, 3H, CH_3), 2.87 (s, 6H, N $(CH_3)_2$), 4.83 (s, 2H, OCH_2), 6.50 (d, 1H, J = 2.7

Table: 2 – Antimicrobial activity-sensitivity testing of 3(a-e) and 4(a-e)

Compd. No.	Zone of inhibition in mm					
	Antibacterial Activity			Antifungal Activity		
	SA	EC	PA	CA	AF	AFU
3a	18	18	13	10	8	9
3b	14	18	14	11	10	8
3c	22	24	22	12	13	10
3d	15	11	13	10	9	8
3e	22	21	21	13	11	12
4a	23	24	21	16	11	10
4b	19	18	14	15	10	8
4c	20	18	21	14	13	9
4d	24	20	23	16	12	8
4e	22	21	19	14	13	11
Ampicillin	25	24	24	-	-	-
Fluconazole	-	-	-	17	16	17

Where SA = *S. aureus*, EC = *E. coli*, PA= *P. aeruginosa*, CA = *C. albicans*, AF = *A. flavus*, AFU = *A. fumigatus*

Hz, Ar-H2), 6.53 (dd, 1H, *J* = 2.7, 6.3 Hz, Ar-H6), 6.62 (d, 2H, *J* = 6.3 Hz, Ar'''-H3''' & 5'''), 6.95 (d, 2H, *J* = 6.9 Hz, Ar'''-H2''' & 6'''), 7.04 (d, 1H, *J* = 6.3 Hz, Ar-H5), 8.00 (s, 1H, N=CH), 9.50 (s, 1H, NH); ^{13}C-NMR (100MHz, $CDCl_3$): δ (ppm) 19.56 (C-7), 40.29 ($N(CH_3)_2$), 68.82 (C-2''), 111.03 (C-6), 113.96 (C-3''' and C-5'''), 114.79 (C-2), 121.74 (C-1'''), 127.93 (C-4), 128.86 (C-5), 130.04 (C-2''' and C-6'''), 136.31 (C-3), 144.96 (C-3''), 150.03 (C-4'''), 156.84 (C-1) and 168.48 (C-1''); Mass : m/z 345 (M$^+$, 10), 190 (base Peak, 100), 330 (12), 198 (22), 155 (38), 147 (20), 141 (40), 120 (24); Analysis (calculated) found: C (62.52) 62.51, H (5.83) 5.82, N (12.15) 12.11 %

N-(4-chlorobenzylidene)-2-(4-chloro-3-methylphenoxy)acetohydrazide (3b)

IR (KBr): ν (cm^{-1}) 1648 (CO of CONH), 3256(NH of CONH); ^{1}H-NMR ($CDCl_3$): δ (ppm) 2.36 (s, 3H, CH_3), 4.80 (s, 2H, OCH_2), 6.50 (d, 1H, *J* = 2.8, Ar-H2), 6.53 (dd, 1H, *J* = 2.7, 6.3 Hz, Ar-H6), 7.04 (d, 1H, *J* = 6.2 Hz, Ar-H5), 7.10 (d, 2H, *J* = 6.3 Hz, Ar'''-H2''' & 6'''), 7.21 (d, 2H, *J* = 6.8 Hz, Ar'''-H3''' & 5'''), 8.00 (s, 1H, N=CH), 9.25 (s, 1H, NH); ^{13}C-NMR (100MHz, $CDCl_3$): δ (ppm) 19.92 (C-7), 69.05 (C-2''), 112.96 (C-6), 116.14 (C-2), 126.83 (C-4), 128.06 (C-3''' and C-5'''), 129.18 (C-5), 130.87 (C-2''' and C-6'''), 132.65 (C-1'''), 136.13 (C-4'''), 137.04 (C-3), 143.26 (C-3''), 157.78 (C-1) and 169.46 (C-1''); Mass : m/z 336 (M$^+$, 10), 198 (base Peak, 100), 321 (16), 181 (24), 155 (30), 141 (18), 138 (16), 111 (26); Analysis (calculated) found: C (56.99) 56.96, H (4.18) 4.16, N (8.33) 8.30 %

N-(2,4-dihydroxybenzylidene)-2-(4-chloro-3-methylphenoxy)acetohydrazide (3c)

IR (KBr): ν (cm^{-1}) 1646 (CO of CONH), 3310(NH of CONH), 3510 (OH); ^{1}H-NMR ($CDCl_3$): δ (ppm) 2.35 (s, 3H, CH_3), 4.80 (s, 2H, OCH_2), 5.16 (s, 1H, OH), 5.18 (s, 1H, OH), 6.20 (d, 1H, *J* = 2.8 Hz, Ar'''-H3'''), 6.30 (dd, 1H, *J* = 2.7, 6.7 Hz, Ar'''-H5'''), 6.50 (d, 1H, *J* = 2.7 Hz, Ar-H2), 6.53 (dd, 1H, *J* = 2.6, 6.3 Hz, Ar-H6), 7.03 (d, 1H, *J* = 6.6 Hz, Ar-H5), 7.31 (d, 1H, *J* = 6.6 Hz, Ar'''-H6'''), 8.01 (s, 1H, N=CH), 9.02 (s, 1H, NH); ^{13}C-NMR (100MHz, $CDCl_3$): δ (ppm) 18.84 (C-7), 68.43 (C-2''), 104.25 (C-3'''), 108.21 (C-5'''), 110.47 (C-1'''), 113.12 (C-6), 114.69 (C-2), 127.26 (C-4), 129.84 (C-5), 132.52 (C-6'''), 137.83 (C-3), 142.48 (C-3''), 158.06 (C-1), 161.91 (C-2'''), 162.02 (C-4''') and 169.42 (C-1''); Mass : m/z 334 (M$^+$, 6), 198 (base Peak, 100), 179 (34), 155 (50), 141 (30), 136 (24), 109 (28); Analysis (calculated) found: C (57.41) 57.40, H (4.52) 4.51, N (8.37) 8.34 %

N-benzylidene-2-(4-chloro-3-methylphenoxy)acetohydrazide (3d)

IR (KBr): ν (cm^{-1}) 1646 (CO of CONH), 3252(NH of CONH); ^{1}H-NMR ($CDCl_3$): δ (ppm) 2.36 (s, 3H, CH_3), 4.83 (s, 2H, OCH_2), 6.52 (d, 1H, *J* = 2.5 Hz, Ar-H2), 6.55 (dd, 1H, *J* = 2.7, 6.9 Hz, Ar-H6), 7.03 (d, 1H, *J* = 6.7 Hz, Ar-H5), 7.09 (t, 1H, *J* = 7.01, 7.02 Hz, Ar'''-H4'''), 7.14 (dd, 2H, *J* = 2.7, 6.5 Hz, Ar'''-H2''' & 6'''), 7.21 (m, 2H, Ar'''-H3''' & 5'''), 8.12 (s, 1H, N=CH), 9.50 (s, 1H, NH); ^{13}C-NMR (100MHz, $CDCl_3$): δ (ppm) 19.26 (C-7), 69.34 (C-2''), 113.08 (C-6), 114.10 (C-2), 126.56 (C-4), 127.28 (C-3''' and C-5'''), 128.75 (C-5), 129.98 (C-2''' and C-6'''), 131.09 (C-4'''), 132.45 (C-1'''), 137.54 (C-3), 143.64 (C-3''), 158.58 (C-1) and 170.23 (C-1''); Mass : m/z 302 (M$^+$, 6), 104 (base Peak, 100), 287 (18), 252 (30), 198 (28), 155 (24), 147 (22), 141 (26); Analysis (calculated) found: C (63.47) 63.44, H (4.99) 4.96, N (9.25) 9.23 %

N-(4-hydroxybenzylidene)-2-(4-chloro-3-methylphenoxy)acetohydrazide (3e)

IR (KBr): ν (cm^{-1}) 3508 (OH), 1640 (CO of CONH), 3310(NH of CONH); ^{1}H-NMR ($CDCl_3$): δ (ppm) 2.36 (s, 3H, CH_3), 4.84 (s, 2H, OCH_2), 5.00 (s, 1H, OH), 6.50 (d, 1H, J = 2.7 Hz, Ar-H2), 6.53 (dd, 1H, J = 2.7, 6.3 Hz, Ar-H6), 6.79 (d, 2H, J = 6.3 Hz, Ar'''-H3''' & 5'''), 7.04 (d, 1H, J = 6.37 Hz, Ar-H5), 7.40 (d, 2H, J = 6.6 Hz, Ar'''-H2''' & 6'''), 8.12 (s, 1H, N=CH), 9.28 (s, 1H, NH); ^{13}C-NMR (100MHz, $CDCl_3$): δ (ppm) 19.45 (C-7), 69.27 (C-2''), 111.76 (C-6), 113.45 (C-2), 116.73 (C-3''' & C-5'''), 125.11 (C-1'''), 126.62 (C-4), 128.26 (C-5) and 129.47 (C-2''' & C-6'''), 136.88 (C-3), 142.73 (C-3''), 157.36 (C-1), 161.71 (C-4''') and 169.88 (C-1''); Mass : m/z 318 (M^+, 6), 163 (base Peak, 100), 303 (10), 198 (18), 155 (22), 141 (24), 120 (22), 93 (20); Analysis (Calculated) Found: C (60.29) 60.27, H (4.74) 4.72, N (8.79) 8.76 %

1-(5-((4-chloro-3-methylphenoxy)methyl)-2-aryl-1,3,4-oxadiazol-3(2H)-yl) ethanone (4a-e) :

A mixture of compound **3a-e** (0.01mol) and acetic anhydride (0.02 mol) was refluxed for 6 hours. Formed product was isolated and recrystallized from methanol to yield compounds **4a-e**. (Physical data and Rf values found using chloroform and methanol in the ratio of 8:2 are given in **Table 1**).

1-(5-((4-chloro-3-methylphenoxy)methyl)-2-(4-(dimethylamino)phenyl)-1,3,4-oxadiazol-3(2H)-yl)ethanone (4a)

IR (KBr): ν (cm^{-1}) 1615 (C=N), 1682 (C=O), 1253 (C-O-C); ^{1}H-NMR (DMSO-D6) : δ (ppm) 2.04 (s, 3H, -CO-CH_3), 2.32 (s, 3H, CH_3), 2.88 (s, 6H, -N$(CH_3)_2$), 4.86 (s, 2H, -O-CH_2), 6.49 (d, 1H, J = 2.6Hz, Ar-H2), 6.54 (m, 3H, Ar-H6, Ar'''-H3''' & 5''), 6.60 (s, 1H, -N-CH-Ar''), 7.0 (d, 2H, J = 8.2Hz, Ar'''-H2''' & 6''), 7.04 (d, 1H, J = 8.3 Hz, Ar-H5); ^{13}C-NMR (100MHz, $CDCl_3$): δ (ppm) 18.56 (C-7), 24.44 (C-7'), 40.87 (C-7''' & C-8'''), 69.23 (C-2''), 74.14 (C-2'), 111.88 (C-6), 114.02 (C-3''' & C-5'''), 115.08 (C-2), 126.12 (C-4), 127.96 (C-2''' & C-6'''), 128.83 (C-5), 129.77 (C-1'''), 136.45 (C-3), 146.45 (C-4'''), 154.63 (C-5'), 157.89 (C-1) and 168.58 (C-6'); Mass : m/z 387(M^+, 4), 120 (base peak, 100), 372 (26), 232 (20), 155 (34), 141 (28), 112 (24); Analysis (Calculated) Found: C (61.93)61.91 , H (5.72)5.71 , N (10.83)10.80 %

1-(5-((4-chloro-3-methylphenoxy)methyl)-2-(4-chlorophenyl)-1,3,4-oxadiazol-3(2H)-yl)ethanone (4b)

IR (KBr): ν (cm^{-1}) 1605 (C=N), 1689 (C=O), 1254 (C-O-C); ^{1}H-NMR (DMSO-D6) : δ (ppm) 2.09 (s, 3H, -CO-CH_3), 2.38 (s, 3H, CH_3), 4.91 (s, 2H, -O-CH_2), 6.54 (d, 1H, J = 2.6Hz, Ar-H2), 6.56 (dd, 1H, J = 2.8, 7.9Hz, Ar-H6), 6.64 (s, 1H, -N-CH-Ar''), 7.04 (d, 1H, J = 8.3 Hz, Ar-H5), 7.13 (d, 2H, J = 8.1Hz, Ar'''-H2''' & 6'''), 7.22 (d, 2H, J = 8.3Hz, Ar'''-H3''' & 5'''); ^{13}C-NMR (100MHz, $CDCl_3$): δ (ppm) 19.25 (C-7), 23.68 (C-7'), 71.27 (C-2''), 73.65 (C-2'), 112.41 (C-6), 115.39 (C-2), 126.18 (C-4), 127.44 (C-2''' & C-6'''), 128.93 (C-3''' & C-5'''), 129.87 (C-5), 133.16 (C-4'''), 137.66 (C-3), 138.92 (C-1'''), 155.36 (C-5'), 158.74 (C-1), 168.45 (C-6'); Mass : m/z 378 (M^+, 6), 223 (base peak, 100), 363 (22), 155 (32), 141 (28), 112 (20), 111 (26); Analysis (Calculated) Found: C (57.01)57.00 , H (4.25) 4.21, N (7.39)7.36 %

1-(5-((4-chloro-3-methylphenoxy)methyl)-2-(2,4-dihydroxyphenyl)-1,3,4-oxadiazol-3(2H)-yl)ethanone (4c)

IR (KBr): ν (cm^{-1}) 3512 (OH), 1680 (C=O), 1610 (C=N), 1250 (C-O-C), ^{1}H-NMR (DMSO-D6) : δ (ppm) 2.08 (s, 3H, -CO-CH_3), 2.36 (s, 3H, CH_3), 4.89 (s, 2H, -O-CH_2), 5.20 (s, 1H, 4-OH), 5.26 (s, 1H, 2-OH), 6.12 (d, 1H, J = 2.7Hz, Ar'''-H3'''), 6.24 (dd, 1H, J = 2.73, 7.8Hz, Ar'''-H5'''), 6.50 (d, 1H, J = 2.7Hz, Ar-H2), 6.52 (dd, 1H, J = 2.6, 7.6Hz, Ar-H6), 6.62 (s, 1H, -N-CH-Ar''), 6.85 (d, 1H, J = 7.8 Hz, Ar'''-H6'''), 7.04 (d, 1H, J =

8.2 Hz, Ar-H5); ^{13}C-NMR (100MHz, $CDCl_3$): δ (ppm) 18.96 (C-7), 23.59 (C-7'), 65.37 (C-2'), 73.52 (C-2''), 103.66 (C-3'''), 109.51 (C-5'''), 112.33 (C-6), 114.68 (C-2), 122.77 (C-1'''), 125.36 (C-4), 128.43 (C-5), 129.65 (C-6'''), 137.21 (C-3), 155.08 (C-5'), 156.73 (C-2'''), 157.96 (C-1), 158.95 (C-4''') and 168.37 (C-6'); Mass : m/z 376 (M$^+$, 4), 141 (base peak, 100), 361 (20), 109 (22), 221 (24), 155 (30), 112 (32); Analysis (Calculated) Found: C (57.38)57.34, H (4.55)4.53 , N (7.43)7.42 %

1-(5-((4-chloro-3-methylphenoxy)methyl)-2-phenyl-1,3,4-oxadiazol-3(2H)-yl) ethanone (4d)

IR (KBr): ν (cm^{-1}) 1610 (C=N), 1686 (C=O), 1250 (C-O-C), ^{1}H-NMR (DMSO-D6) : δ (ppm) 2.02 (s, 3H, -CO-CH_3), 2.35 (s, 3H, CH_3), 4.87 (s, 2H, -O-CH_2), 6.51 (d, 1H, J = 2.6Hz, Ar-H2), 6.53 (dd, 1H, J = 2.5, 7.2Hz, Ar-H6), 6.64 (s, 1H, -N-CH-Ar'''), 7.04 (d, 1H, J = 8.1 Hz, Ar-H5), 7.19 (m, 5H, Ar'''-H2''', 3''', 4''', 5''' & 6'''); ^{13}C-NMR (100MHz, $CDCl_3$): δ (ppm) 19.51 (C-7), 23.67 (C-7'), 70.23 (C-2''), 73.81 (C-2'), 112.11 (C-6), 114.63 (C-2), 125.13 (C-4), 126.59 (C-4'''), 127.34 (C-2''' and C-6'''), 128.87 (C-3''' and C-5'''), 129.98 (C-5), 136.41 (C-3), 140.67 (C-1'''), 155.13 (C-5'), 158.23 (C-1) and 169.44 (C-7'); Mass : m/z 344 (M$^+$, 8), 189 (base peak, 100), 329 (18), 223 (28), 155 (36), 141 (32), 112 (28); Analysis (Calculated) Found: C (62.70)61.98 , H (4.97)4.95 , N (8.12)8.10 %

1-(5-((4-chloro-3-methylphenoxy)methyl)-2-(4-hydroxyphenyl)-1,3,4-oxadiazol-3(2H)-yl)ethanone (4e)

IR (KBr): ν (cm^{-1}) 3505 (OH), 1685 (C=O), 1618 (C=N), 1256 (C-O-C), ^{1}H-NMR (DMSO-D6) : δ (ppm) 2.06 (s, 3H, -CO-CH_3), 2.38 (s, 3H, CH_3), 4.84 (s, 2H, -O-CH_2), 5.24 (s, 1H, 4-OH), 6.51 (d, 1H, J = 2.8Hz, Ar-H2), 6.53 (dd, 1H, J = 2.6, 7.8Hz, Ar-H6), 6.61 (s, 1H, -N-CH-Ar'''), 6.7 (d, 2H, J = 7.6Hz, Ar'''-H3''' & 5'''), 7.02 (d, 2H, J = 7.8Hz, Ar'''-H2'''& 6'''), 7.04 (d, 1H, J = 8.1 Hz, Ar-H5); ^{13}C-NMR (100MHz, $CDCl_3$): δ (ppm) 19.86 (C-7), 24.08 (C-7'), 68.72 (C-2''), 74.66 (C-2'), 112.56 (C-6), 114.35 (C-2), 116.83 (C-3''' and C-5'''), 126.04 (C-4), 127.94 (C-2''' and C-6'''), 129.66 (C-5), 133.11 (C-1'''), 137.35 (C-3), 155.34 (C-5'), 157.02 (C-4'''), 158.61 (C-1) and 168.79 (C-6'); Mass : m/z 360 (M$^+$, 4), 155 (base peak, 100), 345 (20), 205 (22), 141 (34), 112 (30), 93 (24); Analysis (Calculated) Found: C (59.92)59.90, H (4.75) 4.72 , N (7.76)7.72 %

Screening for Biological activity :

The synthesized compounds **3a-e** and **4a-e** were screened for antibacterial (*S. aureus, E. coli, P. aeruginosa*) and antifungal (*C. albicans, A. flavus, A. fumigatus*) activities by disk diffusion method at a concentration of 2mg per ml. using DMF as solvent. The results were recorded in duplicate using ampicillin and fluconazole as standards given in **Table-2.**

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[BIS(D-ALANINATO)DIAQUA]NICKEL(II) DIHYDRATE:

PREPARATION AND CRYSTAL STRUCTURE

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ABSTRACT

The title complex of formula $[Ni(NH_2CH_3CHCOO)_2(H_2O)_2].2H_2O$ *has been prepared from nickel(II) chloride in aqueous solution by adding D-alanine and potassium hydroxide. It has been crystallized from aqueous solution and its structure was determined by X-ray structure analysis. The nickel(II) atom adopts distorted octahedral coordination geometry with two bidentate alanine molecules and two water molecules. The complex is neutral and dihydrated. The network crystal structure shows hydrogen bonding between water and amide hydrogens within the lattice, and each fragment of the complex contains two water molecules as hydrated water.*

KEY WORDS: **Alanine Complex, Crystal Structure, Hydrogen Bonding, Water of Hydration**

RESUMO

O complexo com a fórmula $[Ni(NH_2CH_3CHCOO)_2(H_2O)_2].2H_2O$ *foi preparado a partir de cloreto de níquel(II) em solução aquosa adicionando alanina e hidróxido de potássio. O composto foi cristalizado de solução aquosa e a sua estrutura foi determinada por análise de Raios-X. O níquel(II) tem uma geometria de coordenação octaédrica distorcida com duas moléculas de alanina bidentada e duas moléculas de água. O complexo esta neutro e desidratado. A rede cristalina indica pontes de hidrogênio entre a água e os hidrogênios da amida, e cada fragmento do complexo contém duas moléculas de água hidratada.*

PALAVRAS-CHAVE: **Complexos da Alanina, Estrutura Cristalina, Pontes de Hidrogênio, Água de Hidratação**

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INTRODUCTION

Complexes formed by metal cations and organic species are incorporated in many biochemical structures, such as cytochromes of mitochondrial membranes, hemoglobin and chlorophyll. Transition metal complexes with Schiff base ligand containing the carboxylate group have been of great interest due to their importance as essentially biologically active (1-3), models for metalloproteins (4) and their various geometry aspects (5). .Metals bound to amino acids are essential for the catalytic function of certain enzymes and their chemistry has received a great deal of research interest due to their significant interaction with enzymes and with different organic ligands (6-7). A number of complexes of amino acids with many transition metal ions have been prepared and thoroughly studied (8-16). Therefore, it was considered worthwhile and of great significant chemical interest to synthesize this complex and to study thoroughly its crystal structure. This paper describes the synthesis of bis(D-alaninato)(diaqua)nickel(II) dihydrate, $[Ni(NH_2CH_3CHCOO)_2(H_2O)_2].2H_2O$ and its characterization by X-ray crystallography.

EXPERIMENTAL

All chemicals were of reagent grade and used as purchased from commercial source. Crystallographic data for the structure reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and allocated deposition number CCDC 716012 for the title compound and can be obtained free of charge on application to CCDC 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

Preparation of $[Ni(NH_2CH_3CHCOO)_2(H_2O)_2].2H_2O$

The compound $NiCl_2.6H_2O$ (20 ml, 0.1 M), KOH (20 ml, 1.0 M) and D-alanine (20 ml, 0.2 M) were mixed. The mixture became basic with pH=8 and turned from green to pale blue. The flask solution was left at room temperature. After standing for two weeks blue/pale tablet-shaped crystals were obtained, removed and dried under vacuo. The isolated crystals were subjected to x-ray studies.

Crystal structure determination

Crystal data for $C_6H_{20}N_2NiO_8$; $M_r = 306.95$; monoclinic; space group C2; $a = 20.188(6)$ Å; $b = 6.4989(19)$ Å; $c = 9.666(3)$ Å; $\alpha = 90°$; $\beta = 94.482(4)°$; $\gamma = 90°$; $V = 1264.3(6)$ Å^3; Z = 4; T = 150(2) K; λ(Mo-Kα) = 0.71073 Å; μ(Mo-Kα) = 1.566 mm^{-1}; $d_{calc} = 1.613$g.cm^{-3}; 7185 reflections collected; 3064 unique ($R_{int} = 0.0223$); giving $R_1 = 0.0247$, $wR_2 = 0.0553$ for 2821 data with

[$I>2\sigma(I)$] and $R_1 = 0.0283$, $wR_2 = 0.0575$ for all 3064 data. Absolute structure (Flack) parameter 0.017(15). Residual electron density ($e^-.Å^{-3}$) max/min: 0.311/-0.225. An arbitrary sphere of data were collected on a pale blue prism-like crystal, having approximate dimensions of 0.80 × 0.21 × 0.06 mm, on a Bruker APEX-II diffractometer using a combination of ω- and φ-scans of 0.3°. Data were corrected for absorption and polarization effects and analyzed for space group determination. The structure was solved by direct methods and expanded routinely. The model was refined by full-matrix least-squares analysis of F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Water and amide hydrogen atoms were located from a difference Fourier map and included in refined positions with thermal parameters tied to that of the atom to which they are bonded. All other hydrogens were included in calculated positions with thermal parameters tied to that of the carbon to which they are bonded. The correct enantiomorph of the space group and handedness of the molecule were determined both by comparison of intensities of Friedel pairs of reflections and the known handedness of D-alanine. Both techniques agreed and the correct configuration is shown in the Figures.

Data Collection

A fragment of a pale blue, prism-like crystal of $C_6H_{20}N_2NiO_8$ having approximate dimensions of 0.80 × 0.21 × 0.06 mm was mounted on a Kapton loop using Paratone N hydrocarbon oil. All measurements were made on a Bruker APEX-II (17) CCD area detector with graphite monochromated Mo-Kα radiation.

Cell constants and an orientation matrix, obtained from a least-squares refinement using the measured positions of 3363 centered reflections with $I > 10\sigma(I)$ in the range $3.30 < \theta < 28.14°$ corresponded to a Monoclinic cell with dimensions:

$a = 20.188(6)$ Å
$b = 6.4989(19)$ Å
$c = 9.666(3)$ Å
$V = 1264.3(6)$ Å^3

$\alpha = 90°$
$\beta = 94.482(4)°$
$\gamma = 90°$

For $Z = 4$ and F.W. = 306.95, the calculated density is 1.613 g.cm^{-3}.

Analysis of the systematic absences allowed the space group to be uniquely determined to be:

C2

The data were collected at a temperature of 150(2) K. Frames corresponding to an arbitrary sphere of data were collected using ω-scans of 0.3° counted for a total of 10 seconds per frame.The crystal data of the complex are shown in Tables 1,2 and 3.

[Bis(D-Alaninato)Diaqua]Nickel(II) Dihydrate

Table 1. Crystal data and structure refinement for the compound.

Empirical formula	$C_6H_{20}N_2NiO_8$	
Formula weight	306.95	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	C2	
Unit cell dimensions	a = 20.188(6) Å	α = 90°
	b = 6.4989(19) Å	β = 94.482(4)°
	c = 9.666(3) Å	γ = 90°
Volume	1264.3(6) $Å^3$	
Z	4	
Density (calculated)	1.613 $g.cm^{-3}$	
Absorption coefficient (μ)	1.566 mm^{-1}	
F(000)	648	
Crystal size	0.80 × 0.21 × 0.06 mm^3	
ω range for data collection	2.02 to 28.27°	
Index ranges	$-26 \leq h \leq 6$, $-8 \leq k \leq 8$, $-12 \leq l \leq 12$	
Reflections collected	7185	
Independent reflections	3064 [R_{int} = 0.0223]	
Completeness to θ = 28.27°	99.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9119 and 0.3672	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3064 / 3 / 192	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2σ(I)]	R_1 = 0.0247, wR_2 = 0.0553	
R indices (all data)	R_1 = 0.0283, wR_2 = 0.0575	
Absolute structure parameter	0.017(15)	
Largest diff. peak and hole	0.311 and -0.225 $e^-.Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for the compound. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

x	y	z	U(eq)	
Ni(1)	0.74664(1)	0.74526(11)	0.24736(3)	0.013(1)
O(1)	0.77203(7)	1.0241(3)	0.33744(15)	0.016(1)
O(2)	0.85325(6)	1.2549(5)	0.36350(14)	0.018(1)

O(3)	0.72239(7)	0.4674(2)	0.15836(15)	0.016(1)
O(4)	0.64087(7)	0.2403(5)	0.11909(14)	0.020(1)
O(5)	0.70662(8)	0.8869(3)	0.06409(16)	0.018(1)
O(6)	0.78539(9)	0.5982(3)	0.42583(19)	0.019(1)
N(1)	0.84249(9)	0.7728(4)	0.1885(2)	0.016(1)
N(2)	0.65052(8)	0.7264(5)	0.30809(19)	0.016(1)
C(1)	0.82682(10)	1.0997(4)	0.3067(2)	0.014(1)
C(2)	0.85997(10)	0.9947(3)	0.1878(2)	0.017(1)
C(3)	0.93413(11)	1.0309(4)	0.1906(3)	0.030(1)
C(4)	0.66387(11)	0.4027(4)	0.1738(2)	0.015(1)
C(5)	0.61846(11)	0.5285(4)	0.2595(2)	0.017(1)
C(6)	0.59699(12)	0.4027(4)	0.3811(2)	0.025(1)
O(10)	0.53355(9)	-0.0195(3)	0.13225(19)	0.032(1)
O(11)	0.53810(9)	0.0212(4)	0.6317(2)	0.032(1)
H(5OA)	0.6961(12)	1.009(4)	0.083(3)	0.021
H(5OB)	0.7314(11)	0.914(4)	-0.002(3)	0.021
H(6OA)	0.8020(14)	0.515(5)	0.416(3)	0.022
H(6OB)	0.7639(12)	0.592(4)	0.496(3)	0.022
H(1NA)	0.8673(11)	0.718(4)	0.254(2)	0.019
H(1NB)	0.8491(11)	0.732(7)	0.120(2)	0.019
H(2NA)	0.6233(11)	0.836(4)	0.269(2)	0.019
H(2NB)	0.6482(10)	0.746(6)	0.393(2)	0.019
H(2A)	0.8395	1.0541	0.0991	0.020
H(3A)	0.9522	0.9537	0.1150	0.045
H(3B)	0.9555	0.9843	0.2796	0.045
H(3C)	0.9427	1.1780	0.1789	0.045
H(5A)	0.5777	0.5635	0.1987	0.021
H(6A)	0.5665	0.4842	0.4331	0.037
H(6B)	0.6362	0.3654	0.4422	0.037
H(6C)	0.5744	0.2773	0.3462	0.037
H(10A)	0.5123(13)	-0.012(5)	0.197(2)	0.038
H(10B)	0.5567(13)	0.081(4)	0.117(3)	0.038
H(11A)	0.5167(13)	0.006(5)	0.569(2)	0.039
H(11B)	0.5624(13)	-0.067(4)	0.635(3)	0.039

Table 3. Anisotropic displacement parameters $(\AA)^2$ for the compound. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2 a^{*2} U_{11} + \ldots + 2\, h\, k\, a^*\, b^*\, U_{12}\,]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni(1)	0.0147(1)	0.0112(1)	0.0128(1)	-0.0003(1)	0.0038(1)	-0.0014(1)
O(1)	0.0166(8)	0.0145(9)	0.0162(8)	-0.0028(7)	0.0037(6)	-0.0024(6)
O(2)	0.0190(7)	0.0145(8)	0.0215(7)	-0.0061(11)	0.0034(5)	-0.0032(11)
O(3)	0.0170(8)	0.0135(9)	0.0170(8)	-0.0018(7)	0.0057(6)	-0.0024(6)
O(4)	0.0203(7)	0.0181(8)	0.0227(7)	-0.0018(12)	0.0037(6)	-0.0045(12)
O(5)	0.0228(9)	0.0149(9)	0.0152(8)	0.0020(7)	0.0054(6)	0.0020(7)
O(6)	0.0235(9)	0.0177(10)	0.0150(8)	0.0022(7)	0.0065(7)	0.0043(7)
N(1)	0.0189(9)	0.0152(16)	0.0147(9)	-0.0004(10)	0.0039(7)	-0.0002(9)
N(2)	0.0177(8)	0.0151(13)	0.0159(8)	-0.0014(11)	0.0062(7)	-0.0002(10)
C(1)	0.0163(11)	0.0126(11)	0.0132(10)	0.0019(8)	0.0004(9)	0.0018(8)
C(2)	0.0182(11)	0.0157(11)	0.0166(11)	-0.0012(8)	0.0050(9)	-0.0020(8)
C(3)	0.0235(13)	0.0286(13)	0.0395(15)	-0.0109(12)	0.0140(11)	-0.0086(10)
C(4)	0.0173(11)	0.0164(12)	0.0122(10)	0.0018(9)	-0.0012(8)	0.0007(9)
C(5)	0.0152(11)	0.0174(11)	0.0194(11)	-0.0020(9)	0.0005(9)	-0.0001(8)
C(6)	0.0289(13)	0.0249(12)	0.0210(11)	-0.0026(10)	0.0099(10)	-0.0093(10)
O(10)	0.0295(11)	0.0323(12)	0.0340(11)	0.0010(9)	0.0105(8)	-0.0099(8)
O(11)	0.0272(11)	0.0300(12)	0.0392(12)	-0.0014(10)	0.0005(8)	0.0103(8)

Data Reduction

Data were integrated by the program SAINT (18) to a maximum θ-value of 28.27°. The data were corrected for Lorentz and polarization effects. Data were analyzed for agreement and possible absorption using XPREP (19). An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS (20). (Tmax = 0.9119, Tmin = 0.3672). Of the 7185 reflections that were collected, 3064 were unique (R_{int} = 0.0223); equivalent reflections were merged. No decay correction was applied.

Structure Solution and Refinement

The structure was solved by direct methods (21) and expanded using Fourier techniques (22). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions but were not refined. The final cycle of full-matrix least-squares refinement (23) was based on 3064 reflections (all data) and 192 variable parameters and converged (largest parameter shift was 0.002 times its esd) with conventional unweighted and weighted agreement factors of:

$$R_1 = \Sigma||Fo| - |Fc|| / \Sigma|Fo| = 0.0247 \text{ for } 2821 \text{ data with } I > 2\sigma(I)$$

$$wR_2 = [(\Sigma w\ (|Fo|^2 - |Fc|^2)^2 / \Sigma w\ |Fo|^2)]^{1/2} = 0.0553$$

The standard deviation of an observation of unit weight (24) was 1.029. The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.311 and -0.225 $e^-.Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber (25). Anomalous dispersion effects were included in Fcalc; the values for Δf' and Δf" were those of Creagh and McAuley (26). The values for the mass attenuation coefficients are those of Creagh and Hubbel (27). All calculations were performed using the SHELXTL (17-22) crystallographic software package of Bruker Analytical X-ray Systems Inc. The drawing of the structures were made as ORTEP diagrams (28).

RESULTS AND DISCUSSION

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The title complex was prepared by the reaction of $NiCl_2.6H_2O$, KOH and D-alanine. The presence of KOH has two roles; first is to adjust the pH of the resulting solution from 6 to 8, and the second is to convert the carboxylic group of alanine to carboxylate ion in favor to bind readily with nickel(II) ion. The formation of the complex $[Ni(NH_2CH_3CHCOO)_2(H_2O)_2].2H_2O$ was proved by X-ray crystallography (Fig.1). It is crystallized from aquous solution as pale blue prismatic crystals. The present paper describes the synthesis and structure determination of nickel(II) ion coordinated by two D-alanine molecules and two water molecules, being to our knowledge the first time the x-ray crystal structure of this complex is described.

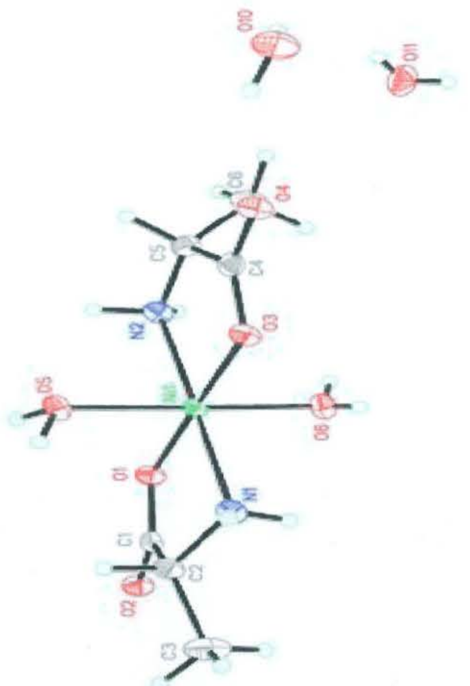

Figure 1.Illustration of the compound showing the atomic numbering scheme

The Structure (Fig.1) consists of an [Ni(D-alaninato)$_2$(H$_2$O)$_2$] and two water molecules. The nickel atom resides at the center of symmetry of the octahedron and is surrounded by two oxygen atoms of two D-alanine molecules, two oxygen atoms of two water molecules and two nitrogen atoms of the same two alanine molecules. The carboxylato oxygens and the amido nitrogens of the two D-alanine molecules define the equatorial positions, whereas the two oxygen atoms of the two water molecules occupy the axial ones. The complex is, then, built up of one nickel(II) ion, two D-alanine molecules and two coordinated and two hydrated water molecules. The octahedra is made up by two D-alanine molecules through their carboxylato and amido groups and two water molecules. It is observed that the axial Ni – O bond distances (Table 4) of 2.0712(19) Å and 2.1011(17) Å are significantly longer than the equatorial Ni-O bonds of 2.0433(18) Å and 2.0579(18) Å. All the Ni-O distances are in agreement with those found in six coordinate nickel(II) complexes (29). The Ni-N bond lengths are 2.0669(19) and 2.0744(18) Å that are longer than the equatorial N-O, and shorter than the axial counterparts. The average Ni – O and Ni – N bond length are in accordance to that known for nickel(II) distorted octahedral geometry. Therefore, two D-alanine molecules and two water molecules are directly involved in coordination. The coordination geometry around the nickel(II) ion is a six–coordinated tending towards distorted octahedral, with a metal center not lying exactly within the N_2O_2 plane because the bond angles (Tables 5, 6) are not perfect.

Table 4. Bond lengths [Å] for the compound.

atom-atom	distance	atom-atom	distance
Ni(1)-O(3)	2.0433(18)	Ni(1)-O(1)	2.0579(18)
Ni(1)-N(1)	2.0669(19)	Ni(1)-O(6)	2.0712(19)
Ni(1)-N(2)	2.0744(18)	Ni(1)-O(5)	2.1011(17)
O(1)-C(1)	1.267(3)	O(2)-C(1)	1.248(4)
O(3)-C(4)	1.274(3)	O(4)-C(4)	1.253(4)
O(5)-H(5OA)	0.84(3)	O(5)-H(5OB)	0.86(3)
O(6)-H(6OA)	0.65(3)	O(6)-H(6OB)	0.84(3)
N(1)-C(2)	1.485(4)	N(1)-H(1NA)	0.85(2)
N(1)-H(1NB)	0.73(3)	N(2)-C(5)	1.499(4)
N(2)-H(2NA)	0.96(2)	N(2)-H(2NB)	0.84(2)
C(1)-C(2)	1.534(3)	C(2)-C(3)	1.514(3)
C(2)-H(2A)	1.0000	C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800	C(3)-H(3C)	0.9800
C(4)-C(5)	1.521(3)	C(5)-C(6)	1.522(3)
C(5)-H(5A)	1.0000	C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800	C(6)-H(6C)	0.9800
O(10)-H(10A)	0.791(19)	O(10)-H(10B)	0.82(2)
O(11)-H(11A)	0.720(18)	O(11)-H(11B)	0.75(2)

Symmetry transformations used to generate equivalent atoms:

Table 5. Bond angles [°] for the compound.

atom-atom-atom	angle	atom-atom-atom	angle
O(3)-Ni(1)-O(1)	179.42(7)	O(3)-Ni(1)-N(1)	99.16(9)
O(1)-Ni(1)-N(1)	80.36(9)	O(3)-Ni(1)-O(6)	90.31(8)
O(1)-Ni(1)-O(6)	89.34(7)	N(1)-Ni(1)-O(6)	88.18(8)
O(3)-Ni(1)-N(2)	82.43(10)	O(1)-Ni(1)-N(2)	98.04(10)
N(1)-Ni(1)-N(2)	178.36(16)	O(6)-Ni(1)-N(2)	92.17(8)
O(3)-Ni(1)-O(5)	88.20(7)	O(1)-Ni(1)-O(5)	92.15(7)
N(1)-Ni(1)-O(5)	92.11(8)	O(6)-Ni(1)-O(5)	178.51(10)
N(2)-Ni(1)-O(5)	87.58(8)	C(1)-O(1)-Ni(1)	115.81(14)
C(4)-O(3)-Ni(1)	115.87(14)	Ni(1)-O(5)-H(5OA)	108.4(17)
Ni(1)-O(5)-H(5OB)	120.4(17)	H(5OA)-O(5)-H(5OB)	98(2)
Ni(1)-O(6)-H(6OA)	115(3)	Ni(1)-O(6)-H(6OB)	120.8(18)
H(6OA)-O(6)-H(6OB)	113(3)	C(2)-N(1)-Ni(1)	108.25(16)
C(2)-N(1)-H(1NA)	106.5(17)	Ni(1)-N(1)-H(1NA)	105.7(15)
C(2)-N(1)-H(1NB)	107(3)	Ni(1)-N(1)-H(1NB)	117.1(19)
H(1NA)-N(1)-H(1NB)	112(3)	C(5)-N(2)-Ni(1)	110.66(16)

Table 5. (cont.)

C(5)-N(2)-H(2NA)	107.1(15)	Ni(1)-N(2)-H(2NA)	111.2(14)
C(5)-N(2)-H(2NB)	113(3)	Ni(1)-N(2)-H(2NB)	113.2(15)
H(2NA)-N(2)-H(2NB)	101(3)	O(2)-C(1)-O(1)	124.1(2)
O(2)-C(1)-C(2)	119.48(19)	O(1)-C(1)-C(2)	116.33(19)
N(1)-C(2)-C(3)	112.7(2)	N(1)-C(2)-C(1)	108.10(17)
C(3)-C(2)-C(1)	114.00(19)	N(1)-C(2)-H(2A)	107.2
C(3)-C(2)-H(2A)	107.2	C(1)-C(2)-H(2A)	107.2
C(2)-C(3)-H(3A)	109.5	C(2)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5	C(2)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5	H(3B)-C(3)-H(3C)	109.5
O(4)-C(4)-O(3)	123.0(2)	O(4)-C(4)-C(5)	117.60(19)
O(3)-C(4)-C(5)	119.4(2)	N(2)-C(5)-C(4)	111.59(17)
N(2)-C(5)-C(6)	111.19(17)	C(4)-C(5)-C(6)	110.58(19)
N(2)-C(5)-H(5A)	107.8	C(4)-C(5)-H(5A)	107.8
C(6)-C(5)-H(5A)	107.8	C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5	H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5	H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5	H(10A)-O(10)-H(10B)	116(3)
H(11A)-O(11)-H(11B)	106(3)		

Symmetry transformations used to generate equivalent atoms:

Table 6. Torsion angles [°] for the compound.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
O(3)-Ni(1)-O(1)-C(1)	44(7)	N(1)-Ni(1)-O(1)-C(1)	8.07(16)
O(6)-Ni(1)-O(1)-C(1)	96.34(16)	N(2)-Ni(1)-O(1)-C(1)	-171.56(16)
O(5)-Ni(1)-O(1)-C(1)	-83.70(15)	O(1)-Ni(1)-O(3)-C(4)	145(7)
N(1)-Ni(1)-O(3)-C(4)	-179.17(16)	O(6)-Ni(1)-O(3)-C(4)	92.62(15)
N(2)-Ni(1)-O(3)-C(4)	0.47(16)	O(5)-Ni(1)-O(3)-C(4)	-87.33(16)
O(3)-Ni(1)-N(1)-C(2)	155.89(15)	O(1)-Ni(1)-N(1)-C(2)	-24.45(14)
O(6)-Ni(1)-N(1)-C(2)	-114.09(15)	N(2)-Ni(1)-N(1)-C(2)	-12(3)
O(5)-Ni(1)-N(1)-C(2)	67.38(16)	O(3)-Ni(1)-N(2)-C(5)	1.41(15)
O(1)-Ni(1)-N(2)-C(5)	-178.26(15)	N(1)-Ni(1)-N(2)-C(5)	169(3)
O(6)-Ni(1)-N(2)-C(5)	-88.62(16)	O(5)-Ni(1)-N(2)-C(5)	89.91(16)
Ni(1)-O(1)-C(1)-O(2)	-171.7(2)	Ni(1)-O(1)-C(1)-C(2)	10.8(2)
Ni(1)-N(1)-C(2)-C(3)	162.11(15)	Ni(1)-N(1)-C(2)-C(1)	35.2(2)
O(2)-C(1)-C(2)-N(1)	151.0(2)	O(1)-C(1)-C(2)-N(1)	-31.3(3)
O(2)-C(1)-C(2)-C(3)	24.9(3)	O(1)-C(1)-C(2)-C(3)	-157.5(2)
Ni(1)-O(3)-C(4)-O(4)	176.2(2)	Ni(1)-O(3)-C(4)-C(5)	-2.3(2)
Ni(1)-N(2)-C(5)-C(4)	-2.8(2)	Ni(1)-N(2)-C(5)-C(6)	121.18(17)
O(4)-C(4)-C(5)-N(2)	-175.1(2)	O(3)-C(4)-C(5)-N(2)	3.5(3)
O(4)-C(4)-C(5)-C(6)	60.5(3)	O(3)-C(4)-C(5)-C(6)	-120.8(2)

Symmetry transformations used to generate equivalent atoms:

It is observed that there are two water molecules not chemically bonded to Ni(II) and located at the opposite site of D-alanine group, and has no significant interaction with the metal atom. A hydrogen bonding is observed between the hydrogen atoms of coordinated and hydrated waters with the oxygen atoms of the carboxylato groups. Also, the hydrogen bonds are seen between the hydrogen of the amide nitrogen and the oxygen atoms of the hydrated water molecules and carboxylato groups (Table 7). The hydrogen bonding network structure of the compound is shown in Figure 2. These results are in good agreement with the X-ray structural studies, and in consistence with the previous investigations of amino acids complexses with metal ions (30-37).

Table 7. Hydrogen bonds for the compound [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5)-H(5OA)...O(4)#1	0.84(3)	1.92(3)	2.726(4)	159(2)
O(5)-H(5OB)...O(3)#2	0.86(3)	1.87(3)	2.726(2)	174(2)
O(6)-H(6OA)...O(2)#3	0.65(3)	2.07(3)	2.711(4)	175(3)
O(6)-H(6OB)...O(1)#4	0.84(3)	1.87(3)	2.688(2)	166(3)
N(1)-H(1NA)...O(11)#5	0.85(2)	2.49(2)	3.294(3)	159(2)
N(1)-H(1NB)...O(4)#2	0.73(3)	2.34(2)	3.026(3)	157(4)
N(2)-H(2NA)...O(10)#1	0.96(2)	2.35(2)	3.250(3)	155(2)
N(2)-H(2NB)...O(2)#4	0.84(2)	2.36(2)	3.187(2)	172(4)
O(10)-H(10A)...O(11)#6	0.791(19)	2.02(2)	2.808(2)	176(3)
O(10)-H(10B)...O(4)	0.82(2)	1.99(2)	2.758(3)	155(3)
O(11)-H(11A)...O(11)#6	0.720(18)	2.162(19)	2.870(4)	168(3)
O(11)-H(11B)...O(2)#7	0.75(2)	2.06(2)	2.792(3)	164(3)

Symmetry transformations used to generate equivalent atoms:

#1 x,y+1,z   #2 -x+3/2,y+1/2,-z   #3 x,y-1,z

#4 -x+3/2,y-1/2,-z+1   #5 -x+3/2,y+1/2,-z+1   #6 -x+1,y,-z+1

#7 -x+3/2,y-3/2,-z+1

The complex crystallizes as pale blue prismatic crystals from a water solution. There are four molecules of the nickel complex and eight waters of crystallization in the unit cell of the C-centered, acentric, monoclinic space group C2. The correct handedness of the molecule and enantiomorph of the space group were determined by comparison of the known handedness of the D-alanine molecule and by comparison of intensities of Friedel pairs of reflections [Flack parameter = 0.017(15), a value of zero indicates the correct handedness, a value of one the inversion isomer]. Both techniques agree and the correct enantiomer is depicted in the Figures.

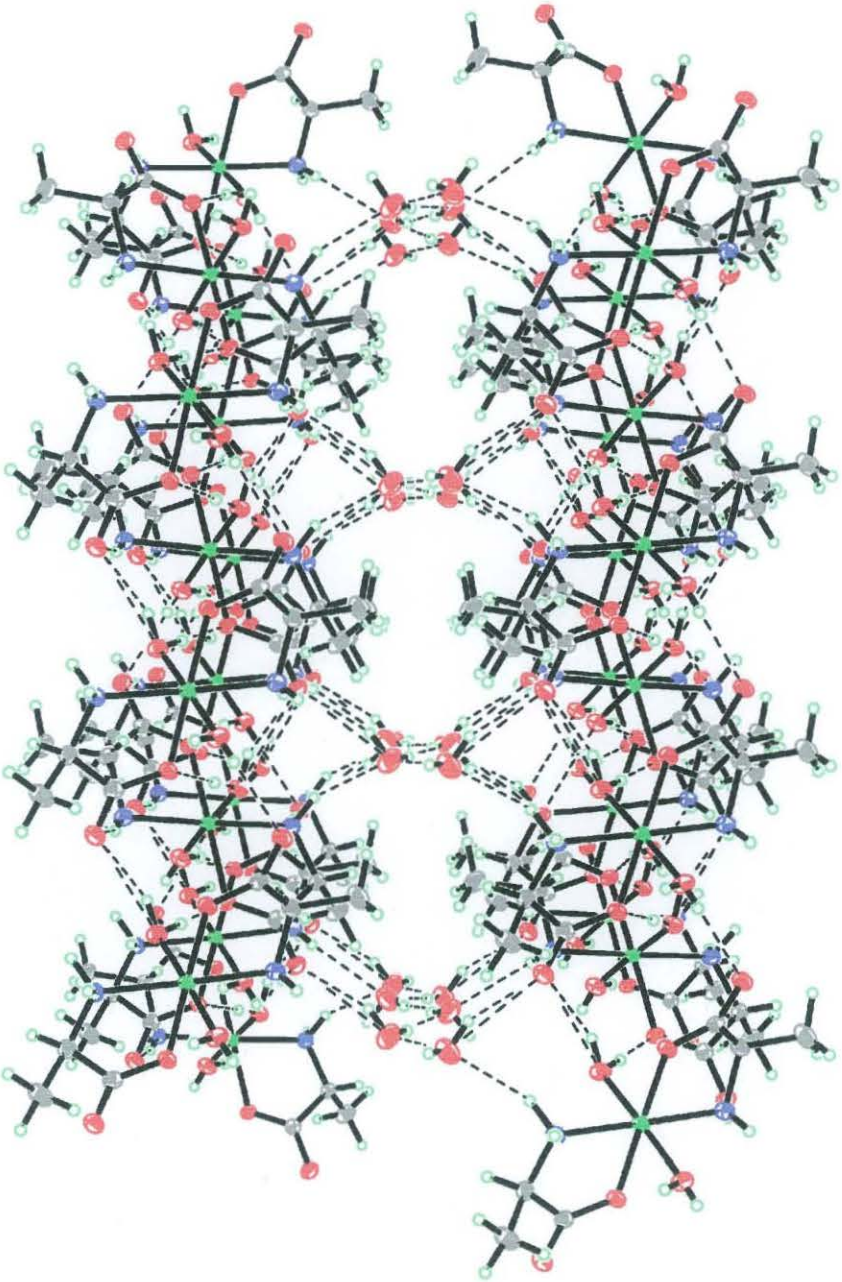

Figure 2 Hydrogen bonding network of D-alanine complex

The nickel is coordinated in a distorted octahedral geometry by the nitrogen and a carboxylate oxygen of each of two D-alanine moieties and two water molecules. The water molecules occupy the apical positions of the coordination sphere. The coordinating nitrogen atoms occupy positions *trans* to each other, as do the carboxylate oxygens [N1-Ni-N2 angle = 178.36(16)° and O1-Ni-O3 angle = 179.42(7)°]. The octahedral coordination geometry is necessarily distorted to accommodate the bonding and formation of two five-membered rings [N1-Ni-O1 and N2-Ni-O3 angles = 80.36(9) and 82.43(10)°, respectively]. The two coordinated waters have slightly different bonding contacts to the nickel center [Ni-O5 distance = 2.1011(17) and Ni-O6 distance = 2.0712(19) Å; the difference of 0.0299 Å is larger than the calculated statistically significant difference $(3.(\{(\sigma\ d_1)^2 + (\sigma\ d_2)^2\} = 0.0076$ Å)]. The D-alanine coordinating oxygens display a very small statistical difference in their respective bond distances while the nitrogens are not statistically different in distance. One of the D-alanine ligands has adopted an envelope geometry while the other has a largely planar geometry. Evidence for this is found in the deviations that the carbon atoms of the D-alanine chain exhibit from the Ni-O-N mean plane each ligand (Table 8).

Table 8. Deviations from the mean plane in Å.

	Deviation (Å)	s.u.	atom		Deviation (Å)	s.u.	atom
*	0.0000	(0.0000)	Ni1	*	0.0000	(0.0000)	Ni1
*	0.0000	(0.0000)	O1	*	0.0000	(0.0000)	O3
*	0.0000	(0.0000)	N1	*	0.0000	(0.0000)	N2
	-0.1602	(0.0031)	C1		-0.2636	(0.0055)	C3
	-0.5838	(0.0037)	C2		-0.0095	(0.0031)	C4

* *atom included in mean plane calculation*

The complex and the waters of crystallization form an extended three-dimensional network of hydrogen-bonded molecules. All of the located hydrogens (water and amide) are involved in a hydrogen-bond resulting in ten unique H-bonds within the lattice. The bond distances and angles within the molecules are otherwise typical for such interactions.

CONCLUSION

This paper describes the synthesis and crystallographic study of a complex of nickel(II), bis(D-alaninato)(diaqua), namely, $Ni(NH_2CH_3CHCOO)_2(H_2O)_2].2H_2O$ produced from aquous solution, which seems not to have been investigated before. The method illustrated for the preparation of this complex may be extended to other metal ions. In fact nickel(II) was chosen for our synthesis because it forms well-defined crystals that can be studies by x-ray crystallography. The complex is a chelate with two bidentate D-alanine ligands bonding through N and O and two water molecules. The oxygen of the carboxylato groups of D-alanine is deprotonated by removal of its hydrogen with the hydroxyl group of KOH producing water molecule. The crystal structure contains molecules of water, and many hydrogen bonds exist.

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23. Least-Squares:

Function minimized: $\Sigma w\,(|Fo|^2 - |Fc|^2)^2$

24. Standard deviation of an observation of unit weight:

$[\Sigma w(|Fo|^2 - |Fc|^2)^2/(N_o - N_v)]^{1/2}$

where: N_o = number of observations N_v = number of variables

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MICELLAR CATALYZED REACTION IN AQUEOUS GLYCEROL SOLUTIONS AND THE INTERNAL PRESSURE OF THE MEDIUM

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ABSTRACT

The experimental results obtained for the hydrolysis of p-nitrophenyl diphenyl phosphate (NPDPP) in the presence of sodium hydroxide (NaOH), micelles of cetyltrimethylammonium bromide (CTAB) and aqueous solution of glycerol were analyzed taking into consideration the internal pressure and the cohesive forces of the reaction medium. The effect of glycerol on micelle formation and also its influence on the internal pressure of the reaction medium are large enough to affect the micellar catalyzed alkaline hydrolysis of the phosphate ester.

KEY WORDS: Micellar Catalysis, Cetyltrimethylammonium Bromide (CTAB), Phosphate Esters, Solvent Effects, Internal Pressure of Liquids, Cohesive Forces, Glycerol

RESUMO

Os resultados experimentais obtidos para a hidrólise do p-nitrofenil difenil fosfato (NP DPP) na presença de hidróxido de sódio (NaOH), micelas de brometo de cetiltimetilamônio (CTAB) e soluções aquosas de glicerol foram analisados considerando a pressão interna e as forças de coesão do meio reacional. O efeito do glicerol sobre a formação de micelas e a sua influência sobre o meio da reação são suficientemente grandes para ter um efeito sobre a hidrólise alcalina do éster de fosfato na presença de micelas.

PALAVRAS CHAVE : **Catálise Micelar, Brometo de Cetiltrimetilamônio (CTAB), Éster de fosfato, Presssão Interna de Líquidos, Forças de Coesão**

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INTRODUCTION

Phosphate esters are compounds with interesting biological and pharmacological properties and are widely used as pesticides, drugs and nerve gases. Their accumulation and their effect in the environment are of paramount importance [1,9].

In previous studies, described in the literature [3,9], we have shown that the alkaline hydrolysis of di- and tri-substituted phosphate esters is catalyzed by micelles of various surfactants, have analyzed the effect of different additive on the reaction medium and have proposed mechanisms for the reaction.

Regardless of the models chosen for the liquid state, the consideration of cohesive forces or internal pressure is of primary importance. Starting with one of the basic thermodynamic relations that includes the first and the second laws of thermodynamics ($dE = TdS - PdV$) it can be shown, by standard methods that

$$(\partial E/\partial V)_T = T(\partial P/\partial T)_V - P \qquad (1)$$

where the term $(\partial E/\partial V)_T$ is called the internal pressure, P_i, and is related to cohesive or attractive forces in the system [10-15].

For real gases, this term is equal to the attraction term in the Van der Waals equation $[(\partial E/\partial V)_T = (an^2/V)]$. The "cohesive pressure" or internal pressure resulting from attraction forces is responsible for the negative deviation of real gases from ideal behavior and the larger the Van der Waals constant a, the larger the cohesive or internal pressure [10-15]. In general, the internal pressure of gases, P_i, is small compared to the real pressure.

In the case of liquids and solids, the internal pressure, P_i, is usually much greater than the real or external pressure, P. For example, for glycerol the internal pressure is 10,324 atm while for water $P_i = 22,355$ atm [14,15].

The analysis of the effect of solvents on the rate of chemical reactions is generally approached in two different ways. The first approach uses transition state theory and analyses the relative solvation between the initial state and the transition state. The solvation of either state reduces the free energy associated with it and increases its stability [14,16]. The change in the reaction medium leads to the reduction of the free energy of activation and to an increase in the rate of the reaction [16].

The second approach takes into consideration the structure of the solvent or the reaction medium, its cohesive or internal pressure and how the solvent-solvent interactions affect the reacting species. Clearly, both solvation and cohesion affects are manifestations of electrostatic interactions in the liquid medium and it is very difficult to separate the two.

For a reaction to take place in solution it is necessary to form cavities in the solvent in order to accommodate the reagents, activated complex and products. The facility with which solvent molecules can be separated from each other to form these cavities is a critical factor and determines the solubility of the solute. The use of internal pressure or "density of energy cohesion", as it has also been called, has been introduced originally by Hildebrand [10] to estimate solubility, and the square root of its value has been called the solubility parameter (δ).

Solvent molecules exhibit attractive and repulsion forces among themselves. In order to create a cavity in a liquid it is necessary to overcome the attractive forces that are responsible for the cohesion of the medium. For reactions where the products exhibit more cohesion than the reagents, the rate of the reaction is increased by solvents with higher internal pressure [17]. The activated complex of a reaction whose rate increases with the internal pressure of the medium occupies less volume than the reagents. In the present case, the reaction medium consists of water, glycerol, micelles and monomers of CTAB, and the nature of the micelle is affected by the amount of glycerol present.

EXPERIMENTAL

The p-nitrophenyl diphenyl phosphate (NPDPP) was prepared using standard methods [18-20]. A sample was also obtained from Prof. Fred Menger, Emory University, Atlanta, Georgia, USA. The surfactant cetyltrimethylammonium bromide (CTAB) was purchased from Aldrich Chemical Co. and recrystallized three times from absolute ethanol before use. Glycerol and sodium hydroxide were analytical reagent grade and were purchased from Merck Co.

The hydrolysis of p-nitrophenyl diphenyl phosphate was studied spectrophotometrically by measuring the rate of appearance of the p-nitrophenoxide anion at 4030 Å with a Varian DMS-80 spectrophotometer equipped with a temperature controlled cell compartment. The reaction was studied at 15, 25 and 35°C at various concentrations of NaOH, CTAB and glycerol. The pseudo-first order rate constant (k_ψ), in sec^{-1}, was determined from linear plots of logarithm of absorbance versus time and the second order rate constants (k_2), in $sec^{-1}.mol^{-1}$, were calculated from k_ψ and the hydroxide ion concentration. Activation parameters such as the activation energy (E_a), the activation Gibbs free energy ($\Delta G^{\neq}$), the activation entalphy ($\Delta H^{\neq}$) and the activation entropy ($\Delta S^{\neq}$) were determined from experimental k_ψ values measured at three different temperatures using the following equations.

$$\ln k_\psi = \ln A - (E_a/R)(1/T) \tag{2}$$

$$\Delta H^{\neq} = E_a - RT \tag{3}$$

$$\Delta S^{\neq} = 4.576 (\log k_\psi - 10.753 - \log T + E_a/4.576T) \tag{4}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\,\Delta S^{\neq} \tag{5}$$

where, R corresponds to the gas constant and T to the absolute temperature.

RESULTS AND DISCUSSION

The reaction under consideration is the hydrolysis of p-nitrophenyl diphenyl phosphate in aqueous solutions containing 0.010M NaOH, various concentrations of CTAB and glycerol ranging from 0 to 90% by volume and is illustrated in Figure 1.

Some typical profiles of the pseudo-first order rate constants, k_ψ, as a function of the concentration of CTAB for the hydrolysis of NPDPP at 25°C in aqueous solutions containing 0.010 M NaOH and concentrations of glycerol varying from 10 to 90% by volume are presented in Figure 2. The rate profiles obtained are characteristic of micellar catalyzed reactions in aqueous solutions. The addition of CTAB to the reaction medium causes an increase in the rate of hydrolysis up to a point where there is total incorporation of the substrate in the micellar phase. More addition of the surfactant causes a decrease in the reaction rate, probably due to the dilution of the reactive counter-ions in the Stern layer of a higher number of micelles. There is a maximum in all the rate profiles at 20×10^{-4}M CTAB. This maximum has the same value as that observed for CTAB-H_2O-NaOH. This behavior is totally different from that observed for solutions containing CTAB-H_2O-NaOH-DMSO (dimethylsulfoxide) and H_2O-NaOH-DMSO-DEHIES (diethyl heptadecyl imidazolinium ethylsulfate) where the maximum shifts for higher concentration of DMSO and the profiles exhibit three different types of behavior, indicating changes in the mechanism of the reaction [7,8,14,15].

For the case of CTAB-H_2O-NaOH-G (glycerol), the mechanism of the micellar catalyzed reaction apparently does not change, but the catalytic effect of CTAB (ratio of the reaction rate in the presence and absence of surfactant under the same experimental conditions) is reduced by the addition of glycerol.

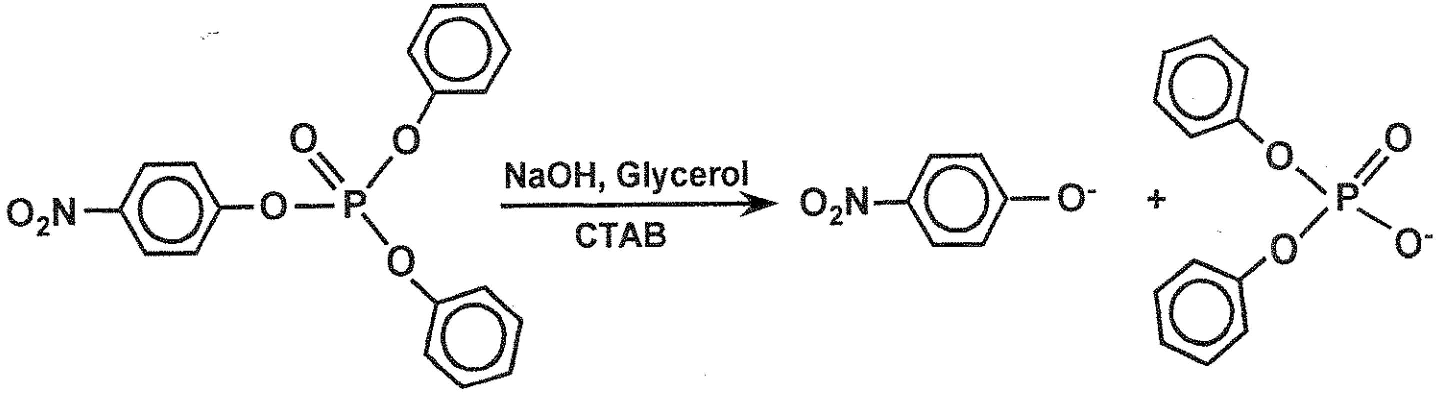

Figure 1 - Hydrolysis of p-nitrophenyl diphenyl phosphate (NPDPP) in aqueous solutions containing sodium hydroxide, glycerol and micelles of CTAB.

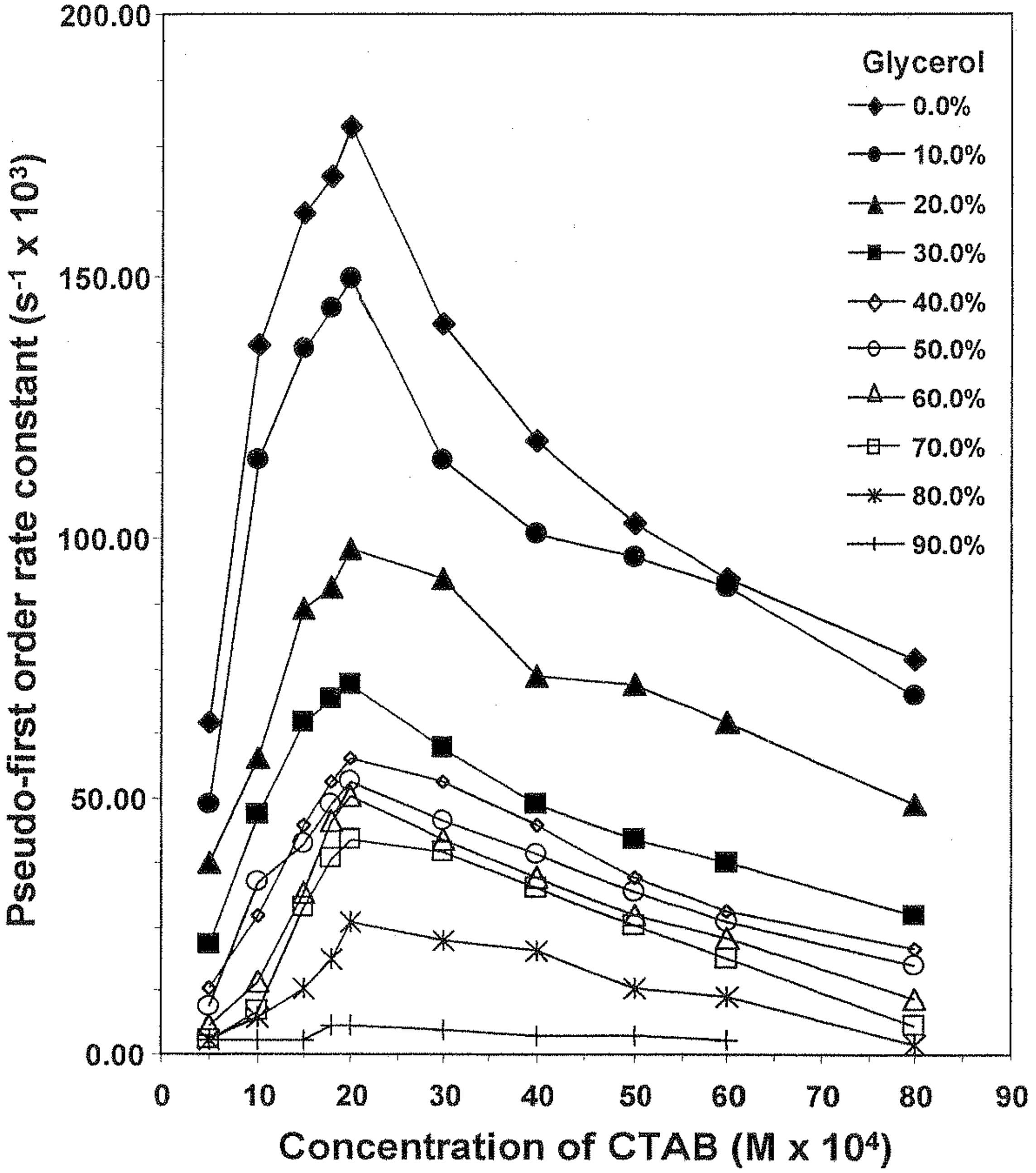

Figure 2 - Rate profiles for the hydrolysis of p-nitrophenyl diphenyl phosphate at 25°C in aqueous solutions containing 0.010 M NaOH in presence of CTAB and concentrations of glycerol varying from 0 to 90% by volume.

Figure 3 illustrates a plot of the pseudo-first order rate constant for the hydrolysis of p-nitrophenyl diphenyl phosphate at 25°C as a function of the mole fraction of glycerol for solutions containing 0.010M NaOH and 20 x 10^{-4} M CTAB. As can be seen, the pseudo-first order rate constant decreases exponentially as a function of the mole fraction of glycerol.

It is well known that glycerol decreases the spontaneity of the micellization process in water and that the critical micellar concentration (CMC) of the surfactant in aqueous solutions increases as a function of glycerol [21-25]. Figure 4 illustrates a plot of the dependence of the critical micellar concentration of CTAB at 25°C and 40°C ~~from~~ CTAB-H_2O-G solutions and clearly shows that the CMC increases exponentially as a function of the mole fraction of glycerol [23,24]. Formamide (F), ethylene glycol (EG) and glycerol (G) are solvents similar to water and micelle formation is common in these solvents, although it is less spontaneous than in water. The solvophobic effect per methylene group (-CH_2-) measured for acylcarnitines was -2.89 kJ.mol^{-1} for water, -0.75 kJ.mol^{-1} for glycerol, -0.71 kJ.mol^{-1} for ethylene glycol and -0.70 kJ.mol^{-1} for formamide [21,22].

The effect of these three cosolvents on the micellization process in water can be explained in terms of their breaking up the structure of water and diminishing the hydrophobic effect in the ternary systems (surfactant-water-cosolvent). The breaking up of the water structure results from the formation of complexes of the type EG.$2H_2O$, F.H_2O and G-$2H_2O$ through hydrogen bonding. Experimental studies involving various techniques, including NMR, for aqueous solutions of ethylene glycol and glycerol, have shown the existence of inter and intramolecular hydrogen bonding and have indicated

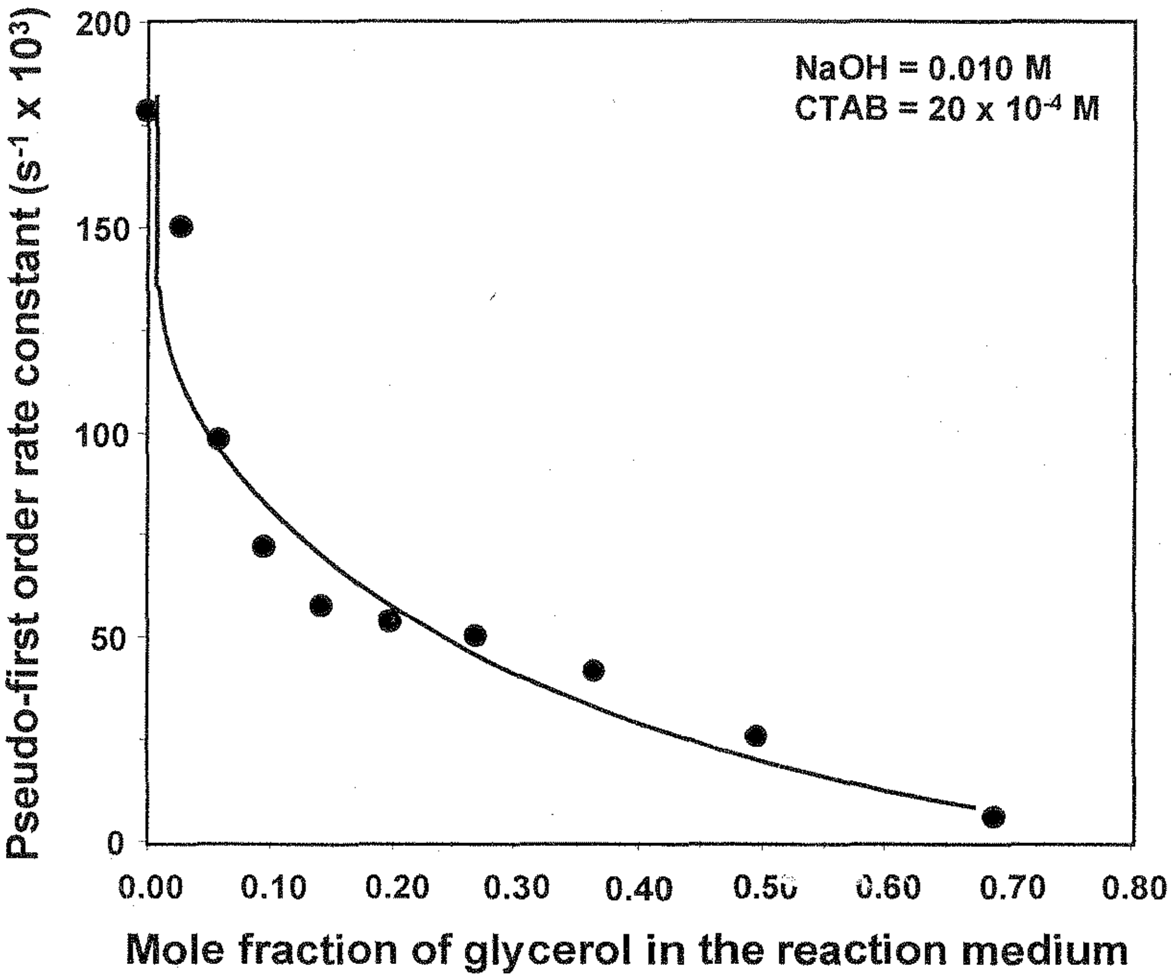

Figure 3- Plot of the pseudo-first order rate constant for the hydrolysis of p-nitrophenyl diphenyl phosphate at 25°C as a function of the mole fraction of glycerol.

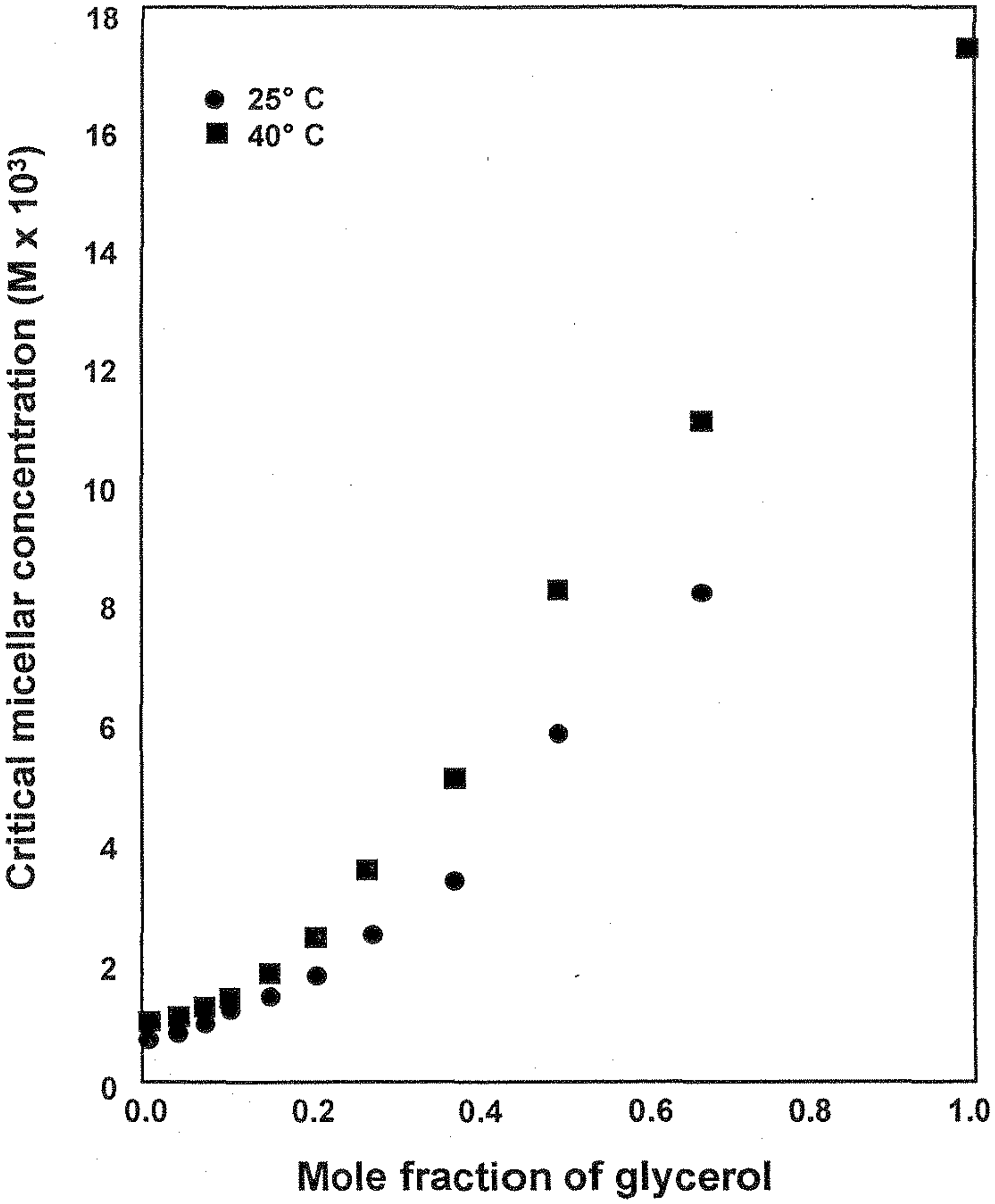

Figure 4 - Dependence of the critical micellar concentration (CMC) of CTAB in aqueous solutions as a function of the mole fraction of glycerol.

that the hydrogen bonds between either one of the two and water are stronger than those among themselves [26-28].

Table I shows some typical activation parameters for the reaction at 25°C in the presence and absence of CTAB and cosolvents such as glycerol and dimethylsulfoxide. As can be seen, addition of CTAB in the form of micelles in the reaction medium reduces the activation energy, E_a, of about 5 kcal/mole as compared to aqueous solutions containing only NaOH. The entropy of activation under the same conditions varies from -22.2 to -29.9 e.u., indicating that the presence of micelles leads to a more structured transition state. The addition of glycerol and dimethylsulfoxide (10% by volume) decreases slightly more the activation energy. When the reaction is carried out in the presence of 10% cosolvent by volume, the entropy of activation is reduced even more (-31.6 e.u. for glycerol and -33.5 e.u. for dimethylsulfoxide).

The internal pressure, Pi, of the reaction medium was calculated according to Equation (6) using the appropriate mole fraction of water and glycerol [15].

$$P_i\,(\text{medium}) = X_{\text{water}}\, P_{i\ \text{water}} + X_{\text{glycerol}}\, P_{i\ \text{glycerol}} \qquad (6)$$

The internal pressure used for water was 22,355.0 atm and for glycerol was 10,324.2 atm. Figure 5 illustrates a plot of the logarithm of the pseudo-first order rate constant versus the internal pressure of the medium for the hydrolysis of p-nitrophenyl diphenyl phosphate at 25°C in the presence of 0.010 M NaOH and 20 x 10^{-4} M CTAB. As can be seen, the plot of log k_ψ versus internal pressure gives essentially a straight line and the rate of the reaction increases with the internal pressure. This indicates that the products

Table 1 - Activation parameters for the hydrolysis of p-nitrophenyl diphenyl phosphate at 25°C in aqueous solutions of 0.010 M NaOH in the presence and in the absence of CTAB and of glycerol or DMSO .

Concentrations		**E_a**	**$\Delta H^{o\neq}$**	**$\Delta S^{o\neq}$**
Cosolvent	**CTAB**			
(% by volume)	**($M \times 10^4$)**	**($kcal.mole^{-1}$)**	**($kcal.mole^{-1}$)**	**(e.u.)**
-	-	+15.2	+14.6	-22,2
-	15	+11.4	+10.8	-26.6
-	20	+10.5	+ 9.9	-29.9
Glycerol (10%)	18	+10.3	+9.7	-30.1
Glycerol (10%)	20	+10.0	+9.4	-31.6
Glycerol (10%)	30	+9.4	+8.8	-34.2
DMSO (10%)	-	+18.7	+18.2	- 9.4
DMSO (10%)	20	+ 9.3	+ 8.7	-33.5

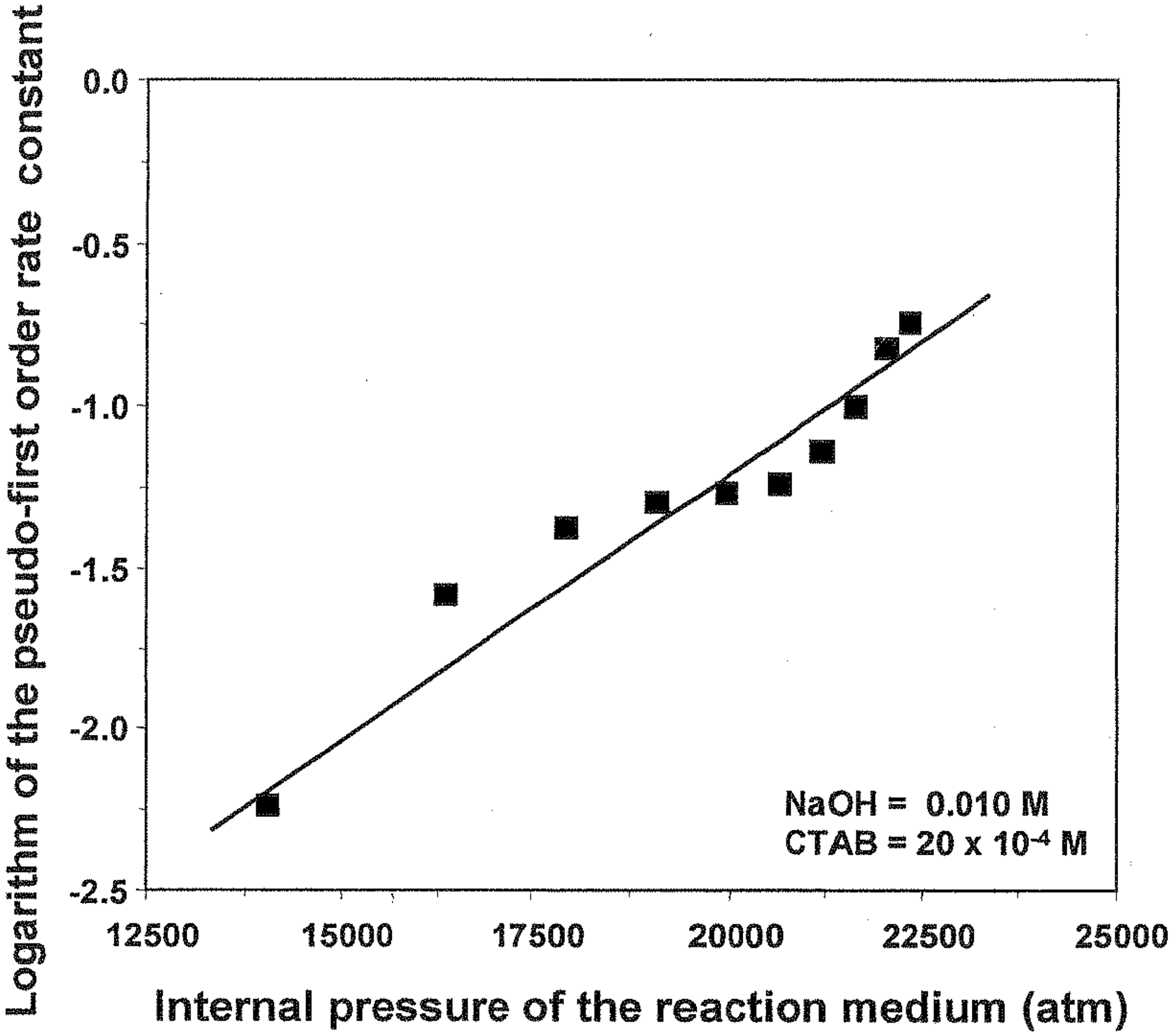

Figure 5 - Plot of the logarithm of the pseudo-first order rate constant for the hydrolysis of p-nitrophenyl diphenyl phosphate at 25°C in 0.010 M NaOH and 20 x 10^{-4} M CTAB as a function of the internal pressure of the reaction medium.

exhibit more cohesion than the reagents and that the activated complex occupies less volume than the reagents. In the presence of micelles (as is the case in consideration) the activated complex is in the interior or near the surface of the micelle. The addition of glycerol to the H_2O-CTAB medium that contains the micelles leads to the diminution of the internal pressure and the aggregates. The activated complex now formed occupies a smaller volume than the reagents and the rate of the reaction continues to decrease as long as micelles are still present in the liquid medium. This is in fact what is being observed for the case of micellar catalysis in aqueous solutions containing glycerol.

CONCLUSIONS

The addition of glycerol to the reaction medium has a effect on micellar catalyzed alkaline hydrolysis of p-nitrophenyl diphenyl phosphate which is caused not only by the formation of the complex $G.2H_2O$ and reduction of CTAB micellization but also by the changes in the internal pressure of the medium.

ACKNOWLEDGEMENTS

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THE PERIODIC TABLE OF THE ELEMENTS AND THE ASSOCIATED MINERALS: URANIUM

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ABSTRACT

Uranium is silvery-white metal of the actinide series. It is the heaviest of naturally occurring elements and it is found in low concentrations in soil, water and rocks. Uranium is relatively reactive and combines with oxygen, sulfur, chlorine, fluorine, phosphorus, bromine and other elements. This article describes some of the properties and uses of uranium and presents a synopsis of the two hundred and four (204) uranium minerals known at the present time.

KEY WORDS: Uranium, Mineralogy of Uranium, Properties of Uranium, Uses of Uranium

RESUMO

O urânio é um metal branco-prateado da série dos actinídeos. É o mais pesado dos elementos que estão presentes na natureza e encontra-se em concentrações baixa no solo, na água e nas rochas. O urânio é relativamente reativo e combina com oxigênio, enxofre, cloro, flúor, fósforo, bromo e outros elementos. Este trabalho descreve algumas das propriedades e usos do urânio e apresenta uma rápida sinopse dos duzentos e quatro (204) minerais nos quais o urânio encontra-se presente, conhecidos até o momento..

PALAVRAS-CHAVE: Urânio, Mineralogia do Urânio, Propriedades do Urânio, Usos do Urânio

INTRODUCTION

Uranium is a silvery, shiny metal and is both ductile and malleable, slightly paramagnetic and poor electrical conductor. It is a member of the actinide series and the heaviest naturally occurring element. Uranium metal has a very high density and approximately 70% denser than lead and slightly less dense than gold.

Uranium is a relatively rare element and is present in water, soil and rocks with an estimated abundance of approximately 1 to 2 parts per million.The most common ore of uranium is pitchblende. Other common minerals are uraninite, carnotite, uranophane and coffinite. [1,179-190]

The most common way of mining uranium is similar to iron. The ore is treated with nitric acid to form uranyl nitrate ($UO_2(NO_3)_2$) that is converted to uranium dioxide (UO_2). Treatment with hydrogen leads to uranium metal. The metal reacts with almost all nonmetallic elements. Acids like HCl and HNO_3 dissolve uranium and nonoxidizing acids attack the metal very slowly. Finely divided uranium can react with cold water and the uranium metal becomes coated with a dark layer of uranium oxide.[181-190]

The discovery of uranium is usually credited to Martin Heinrich Klaproth in 1789. He actually isolated a powder of uranium oxide. The first sample of uranium metal was obtained by Eugène Melchior Peligot in 1841 by heating uranium tetrachloride with potassium. The Romans used uranium oxide to obtain the yellow color of glasses and ceramic glazes, a practice continued during the Middle Ages with oxide obtained from pitchblende from the silver mines of Joachimstahl, Bohemia (Jáchymow, Czech Republic).[180]

All three naturally occurring isotopes of uranium, U-234 (0.0056%), U-235 (0.711%) and U-238 (99.284%) are radioactive. The radioactive properties of uranium were discovered by A.H. Becquerel in 1896 and Enrico Fermi and his collaborators were mainly responsible for the use of the element as a fuel in the nuclear power industry and in nuclear weapons. Uranium-238 has a half-life of approximately 4.47 billion years and uranium-235 of about 704 million years and both are used in dating the age of the Earth.[182-186]

Some properties of uranium are given in Table I.

Uranium has 15 isotopes, three of them, as mentioned above, occur in nature and the others are synthetic. Table II describes some of the most stable isotopes.[185-190]

Table I. Some Properties of Uranium.

Atomic weight	**238.0289 g/mol**
Electronic configuration	**(Rn) $5f^3 6d^1 7s^2$**
Density	**19.1 g/cm^3**
Melting point	**1132.3 °C**
Boiling point	**4131°C**
Heat of vaporization	**417.1 kJ/mol**
Heat of fusion	**9.14 kJ/mol**
Oxidation states	**6,5,4,3**
Van de Waals radius	**186 pm**
Electrical resistivity	**0.280 microOhm-m**

Table II. Most Stable Isotopes of Uranium

Isotope	Nat. abund.	Half-life	Decay Modes	DE (Mev)	DP
^{232}U	synthetic	68.9 y	α, SF	5.414	^{228}Th
^{233}U	synthetic	159,200 y	SF, α	4.909	^{229}Th
^{234}U	0.0054%	245,500 y	SF, α	4.859	^{230}Th
^{235}U	0,7204%	$7.038x10^{8}$ y	SF, α	4.679	^{231}Th
^{236}U	synthetic	$2.342x10^{7}$ y	SF, α	4.572	^{232}Th
^{238}U	99,2742%	$4.468x10^{9}$ y	SF, α	4.270	^{234}Th

Uranium compounds are still used today to color glass and ceramics. The tones of color produced range from orange-red to lemon yellow. Uranium has been used for tinting and shading in photography and as a mordant in dyeing operations of textile. Mordants are compounds that help dyes stick to cloth. Uranium oxide has a limited use as an attachment to filaments in light bulbs. It reduces the speed at which an electric current enters the bulb and the possibility of the filament heating too fast and breaking.

The most important application of uranium today is in nuclear weapons and nuclear power plants.

Uranium -235 is the only naturally occurring fissile isotope.Uranium-238 is both fissionable by fast neutrons and fertile. In a nuclear rector it can be converted to fissile ^{238}Pu. The artificial fissile isotope ^{233}U can be produced from thorium in high power breeder reactors and is important in nuclear technology. Uranium-238 has a small possibility to undergo fission spontaneously when bombarded with fast neutrons.[179]

On the other hand, ^{235}U and also ^{233}U undergo fission relatively easy when bombarded with slow neutrons. The heat generated is used in nuclear reactors as a source of power and the fissile material for the production of nuclear weapons. Both of these uses depend on the ability of uranium to produce a sustained nuclear reaction. Depleted uranium (^{238}U) is used in armor plating and kinetic energy penetrators.

Most nuclear weapons produced between 1945 and 1991 employed enriched uranium or uranium derived plutonium. They are both fission bombs. A more powerful fusion bomb (hydrogen bomb), developed later uses plutonium in an uranium casing to produce fusion between a mixture of tritium and deuterium.

There are approximately five hundred (500) commercial nuclear power plants in the world and they produce about 20% of the electrical energy. Most reactors use enriched uranium as a fuel (approximately 3% of ^{235}U). The only commercial reactor capable of using un-enriched uranium is the CANDU reactor. Military nuclear reactors used for propulsion and other purposes employ highly enriched ^{235}U. The use of uranium as a nuclear fuel produces a large amount of nuclear residue and the disposal of nuclear waste is still a major problem today.

Depleted uranium (DU) is employed widely for high density penetrators. The ammunition consists of depleted uranium alloyed with other metals. At high impact velocity, the projectile leads to the destruction of heavily armored targets because of its hardness, density and flammability. Depleted uranium is also used to make tank armor, removable armor plates on combat vehicles, shielding material for missile re-entry vehicles, special containers and counterweight for aircraft control surfaces. Depleted uranium ammunition was widely used in the Persian Gulf and Yugoslavia in the recent past.

Most uranium compounds are poisonous if ingested. Being a radioactive element, exposure to uranium compounds for a prolonged period of time leads to serious health problems with most organ systems. In addition, uranium metal in powdered form is pyrophoric and tends to catch fire spontaneously.[179-190]

Uranium ingested via dust into the lungs tends to accumulate in bone because of uranium's affinity for phosphates. Uranium has a deleterious effect on the reproductive system and uranyl ions (UO2+) from uranyl nitrate, uranium trioxide and other hexavalent compounds cause defects and damage to the immune system.

URANIUM MINERALS

Of the 4271 mineralogical species validated by IMA (International Mineralogical Association) until 2008, two hundred and four (204) contain uranium. Of these, there are 50 phosphates, 44 oxides, 25 arsenates , 24 carbonates, 20 silicates, 13 sulfates, 10 vanadates, 7 molybdates, 5 selenites, 3 tellurites and one species of arsenites, tungstates and vanadium oxysalts, respectively. The only mineral discovered after 2008 is uramarsite ($(NH_4,H_3O)_2(UO_2)_2[(AsO_4,PO_4)_2]_2.6H_2O$), a arsenate complex , found as encrustations on a fracture surface in sub-betuminous coal and uranium coal deposits(178). A synopsis of the minerals follows.

a) Arsenids

a_1) Acid and normal arsenides

1. Chadwickite $H(UO_2)(AsO_3)$ – Tetragonal system; 60.42% U. A secondary mineral found in dump material from granite rocks of the uranium mines(1,30).

b) Arsenates

b_1) Anhydrous arsenates

1. Hallimondite $Pb_2(UO_2)(ASO_4)_2$ – Triclinic system; 24.74% U. Secondary mineral of Pb-Zn veins(1,62).

b_2) Halogenarsenates

1. Chistyakovaite $Al(UO_2)_2(AsO_4)_2F.6.5H_2O$ – Monoclinic system; 48.53% U. Hidrothermalism in uranium deposits(1,32).

b_3) Hydrated arsenates

1. Abernathyite $K_2(UO)_2(AsO_4)_2.8H_2O$ – Tetragonal system; 45.77% U. Rare secondary mineral in the uraniferous sandstones deposits(1,2).

2. Arsenuranospathite $HAl(UO_2)_4(AsO_4)_{4\cdot40}H_2O$ – Tetragonal system; 39.93% U. A very rare secondary mineral in uraniferous deposits(1,8).

3. Arsenuranylite $Ca(UO_2)_4(AsO_4)_2(OH)_4.6H_2O$ – Orthorhombic system; 60.48% U. Occurs in oxidation zone of sulfide deposits rich in As(1,9).

4. Asselbornite $(PbBa)(UO_2)_6(BiO)_4(AsO_4)_2.(OH)_{12}.3H_2O$ – Cubic system; 44.24% U. Occurs in quartz gangue from an uranium mines(1,10).

5. Arsenovanmeersscheite $U(UO_2)_3(AsO_4)_2(OH)_6.4H_2O$ – Orthorhombic system; 63.47% U. Secondary mineral in the uraniferous deposits(1,14).

6. **Heinrichite** $Ba(UO_2)_2(AsO_4)_2.10\text{-}12H_2O$ – Tetragonal system – 41.27% U. Secondary mineral present in uraniferous deposits on silicified rhyolite tuffs(1,63).

7. **Hügelite** $Pb_2(UO_2)_3(AsO_4)_2.(OH)_4.3H_2O$ – Monoclinic system; 43.96% U. Secondary mineral of Pb-U deposits(1,65).

8. **Kahlerite** $Fe^{2+}(UO_2)_2(AsO_4)_2.10\text{-}12H_2O$ – Tetragonal system; 44.41% U. Rare secondary mineral in the oxized zone in hydrothermal uraniferous deposits (1,69).

9. **Metaheinrichite** $Ba(UO_2)_2(AsO_4)_2.8H_2O$ – Tetragonal system – 43.30% U. Mineral formed by alteration of heirichite(1,63).

10. **Metakahlerite** $Fe^{2+}(UO_2)_2(AsO_4)_2.8H_2O$ – Tetragonal system; 46.77% U. Rare secondary mineral which occurss in the oxized zone from the hydrothermal uraniferous deposits (1,81).

11. **Metakirchheimerite** $Co(UO_2)_2(AsO_4)_2.8H_2O$ – Tetragonal system; 46.63% U. Rare secondary mineral which occurss in the oxized zone from the hydrothermal uraniferous deposits on pitchblende (uraninite) crystals(1,82).

12. **Metanovacekite** $Mg(UO_2)_2(AsO_4)_2.4\text{-}8H_2O$ – 50.10% U. Rare secondary mineral which occurss in the oxized zone from the hydrothermal deposits of uranium ores(1,84).

13. **Metauranospinite** $Ca(UO_2)_2(AsO_4)_2.8H_2O$ – Tetragonal system; 47,50% U. Secondary uranium mineral which occurss in the oxidation zone of U deposits(1,93).

14. **Metazeunerite** $Cu^{2+}(UO_2)_2(AsO_4)_2.8H_2O$ – Tetragonal system; 46.42% U. Rare secondary mineral in the oxidized zones of As-bearing hydrothermal uranium deposits(1,97).

15. **Natrouranospinite** $(Na_2,Ca)(UO_2)_2(AsO_4)_2.5H_2O$ – Tetragonal system; 47.89% U. Secondary mineral psudomorphous after metazeunerite(1,104).

16. **Novacekite I** $Mg(UO_2)_2(AsO_4)_2.12H_2O$ – Triclinic system; 44.98% U. Rare secondary mineral which occurss in the oxized zone from the hydrothermal deposits of uranium ores (1,84).

17. **Novacekite II** $Mg(UO_2)_2(AsO_4)_2.10H_2O$ – Triclinic system; 46.57% U. Rare secondary mineral which occurss in the oxized zone from the hydrothermal deposits of uranium ores (1,84).

18. **Orthowalpurgite** $(UO_2)Bi_4O_4(AsO_4)_2.2H_2O$ – Orthorhombic system; 16.04% U. Secondary mineral formed by weathering of Bi-bearing ore minerals(1,110).

19. **Seelite** $Mg(UO_2)_2(As^{3+}O_3)_{1.4}(As^{5+}O_4)_{0.6}.7H_2O$ – Monoclinic system; 38.34% U. Secondary mineral of oxidization zone of U-bearing ores(1,138).

20. **Trogerite** $(H_3O)[(UO_2)(AsO_4)](H_2O)_3$ – Tetragonal system; 49.38% U. Secondary mineral found as crusts or aggregates of microscopic crystals and growing with zeunerite(1,157).

21. **Uramarsite** $NH_4(UO_2)AsO_4.3H_2O$ – Tetragonal system; 20.21% U. Secondary mineral which occurs in fractures of uraniferous igneous rocks associated with meta-autunite (1,161).

22. **Metauranospinite** $Ca(UO_2)_2(AsO_4)_2.10H_2O$ – Tetragonal system; 45,86% U. Secondary uranium mineral which occurss in the oxidation zone of U deposits(1,93).

23. Zeunerite $Cu^{2+}(UO_2)_2(AsO_4)_2.10\text{-}16H_2O$ – Tetragonal system; 44.84% U. Secondary mineral in the oxidized zones of As-bearing hydrothermal uranium deposits(1,97).

c) Carbonates

c₁) Anhydrous carbonates

1. Cejkaite $Na_4(UO_2)(CO_3)_3$ – Triclinic system – 44.87% U. A secondary mineral formed by decomposition of uraninite crystals in dry condictions and alkaline pH(1,29).

2. Rutherfordine $UO_2(CO_3)$ – Orthorhombic system – 76.12% U. Secondary mineral product of alteration from uraninite(1,130).

3. Widenmannite $Pb_2(UO_2)(CO_3)_3$ – Orthorhombic system; 27,54% U. Mineral found in alteration zone of uranium ores (1,174).

c₂) Compound carbonates

1. Lepersonnite-(Gd) $Ca(Gd,Dy)_2(UO_2)_{24}O_{12}(CO_3)_8(SiO_4)_4.60H_2O$ – Orthorhombic system; 66.83% U. Secondary mineral present in basal portion of the oxidation zone of uranium ores(1,74).

2. Schrockingerite $NaCa_3(UO_2)(CO_3)_3(SO_4)F.10H_2O$ – Triclinic system; 26.79% U. Secondary mineral found in uranium-bearing ores on matrix rock(1,136).

c₃) Halogencarbonates

1. Albrechschraufite $Ca_4Mg(UO_2)_2(CO_3)_6F_2.17H_2O$ – Triclinic system; 32.92% U. Secondary mineral in the silver deposit of Jáchimov, Czech Republic(1,5).

c₃) Hydrated carbonates

1. Andersonite - $Na_2Ca(UO_2)(CO_3)_3.6H_2O$ – Trigonal system; 36.95% U. Occurs as efflorescenses in uranium mines(1,7).

2. Bayleyite $Mg_2(UO_2)(CO_3)_3.18H_2O$ – Monoclinic system; 28.92% U. Very rare radioactive mineral; occurs as eflorescenses in uranium mines(1,17).

3. Blatonite $UO_2CO_3.H_2O$ – Hexagonal/trigonal systems; 68.39% U. Typical mineral of sedimentary rocks(1,23).

4. Grimselite $K_3Na(UO_2)(CO_3)_3.H_2O$ – Hexagonal system; 39.13% U. Mineral found in granite-aplites and veins of mineralized zones(1,59).

5. Kamotoite-(Y) $Y_2U^{6+}{}_4(CO_3)_3O_{12}.14.5H_2O$ – Monoclinic system; 53.19% U. Mineral found in the oxidation zone of Cu-Co deposits (1,6).

6. Liebigite $Ca_2(UO_2)(CO_3)_3.11H_2O$ – Orthorhombic system; 32.68% U. Secondary mineral in the oxidized zone of uraniferous deposits associated with carbonates and sulfates(1,75).

7. Metazellerite $Ca(UO_2)(CO_3)_2.3H_2O$ – Orthorhombic system; 49.16% U. Typical mineral which occurss in sediments of the uranium mines in oxidized zones(1,96).

8. Swartzite $CaMg(UO_2)(CO_3)_2.12H_2O$ - Monoclinic system; 32.58% U. Secondary mineral which occurs as efflorescence in wall of mines(1,148).

9. Voglite $Ca_2Cu^{2+}(UO_2)(CO_3)_4.6H_2O$ (?) – Monoclinic system; 31.24% U. Mineral found as alteration product of uraninite(1,172).

c$_4$) Hydroxylcarbonates

1. Astrocyanite-(Ce) $Cu_2(Ce,Nd,La)_2(UO_2)(CO_3)_5(OH).1.5H_2O$ – Triclinic system; 25.02% U. Mineral found in the oxidation zone of Cu-Co deposits(1,11).

2. Bijvoetite-(Y) $(Y,Dy)_2(UO_2)_4(CO_3)_4(OH)_6.11H_2O$ – Orthorhombic system; 53.88% U. Occurs in the basal zone of the oxidation uranium deposits(1,21).

3. Oswaldpeetersite $(UO_2)_2CO_3(OH)_2.4H_2O$ – Monoclinic system; 67.42% U. Secondary mineral which occurs in sandstone and conglomerate rocks rich in organic matter(1,111).

4. Rabbittite $Ca_3Mg_3(UO_2)_2(CO_3)_6(OH)_4.18H_2O$ – Monoclinic system; 32.05% U. Secondary mineral found as efflorescenses in wall of uranium mines(1,124).

5. Roubaultite $Cu_2(UO_2)_3(CO_3)_2O_2(OH)_2.4H_2O$ – Triclinic system; 59.74% U. Secondary mineral found on uraninite ore(1,129).

6. Shabaite-(Nd) $Ca(Nd,Sm,Y)_2(UO_2)(CO_3)_4(OH)_2.6H_2O$ – Monoclinic system; 24.54% U. Secondary mineral found in Cu-Co deposits(1,140).

7. Sharpite $Ca(UO_2)_6(CO_3)_5(OH)_4.6H_2O$ – Orthorhombic system; 66.85% U. Secondary mineral found in Cu-Co deposits (1,141).

8. Urancalcarite $Ca(UO_2)_3(CO_3)(OH)_6.3H_2O$ – Orthorhombic system; 66.97% U. Secondary mineral found on uraninite crystals(1,163).

9. Wyartite $CaU^{5+}(UO_2)_2(CO_3)O_4(OH).7H_2O$ – Orthorhombic system; 67.77% U. Orthorhombic system; 66.97% U. Secondary mineral found as alteration product of uraninite(1,167).

d) Molybdates

d$_1$) Anhydrous molybdates

1. Deloryite $Cu^{2+}{}_4(UO_2)(MoO_4)_2(OH)_6$ – Monoclinic system; 25.16% U. A secondary mineral found in oxized zone of U-Mo deposits(1,47).

2. Mourite $U^{4+}Mo^{6+}{}_5O_{12})(OH)_{10}$ – Monoclinic system; 22.04% U. Secondary minerals present in U-Mo deposits(1,101).

3. Sedovite $U^{4+}(MoO_4)_2$ – Orthorhombic system; 42.66% U. Secondary mineral found in suoergene zone of U-Mo deposits.(1,137).

d$_2$) Hydrated molybdates

1. Calcurmolite $Ca(UO_2)_{3-4}(MoO_4)_3(OH)_{2-5}.7\text{-}12H_2O$ – (?); 45.71% U. Secondary mineral found in oxized zone of U-Mo deposits(1,27).
2. Molurarite $H_4U^{4+}(UO_2)_3(MoO_4)_7.18H_2O$ – Amorphous; 38.15% U. Secondary mineral found in the oxidation zone of uranium ores(1,99).
3. Tengchongite $Ca(UO_2)_6(MoO_4)_2O_5.12H_2O$ – Orthorhombic system; 62.74% U. Secondary mineral which occurss in oxidized zone of uranim mineralizations(1,150).
4. Umohoite $[(UO_2)MoO_4(H_2O)](H_2O)$ – Triclinic system; 53.13% U. Secondary mineral found in U-Mo deposits(1,160).

e) Oxides

e$_1$) Multiple oxides

1. Betafite $U^{4+}(Nb,Ti)_2O_6OH$ – Cubic system; 17.20% U. Common primary mineral in granite pegmatites, and rare in carbonatites. It's a secondary source of U(1,20,40).
2. Bismutopyrochlore $(Bi,U,Ca,Pb)_{1+x}(Nb,Ta)_2O_6(OH).nH_2O$ – Cubic system; 12.69% U. Mineral strongly radioactive formed on lepidolite in cavities of pegmatite veins(1,22).
3. Brannerite $(U,Ca,Y,Ce)(Ti,Fe)_2O_6$ – Monoclinic system; 33.54% U. Secondary mineral found in gold placers(1,108).
4. Davidite-(Ce) $(Ce,La)(Y,U,Fe^{2+})(Ti,Fe^{3+})_{20}(O,OH)_{38}$ – Trigonal system; 3.18% U. Occurs in pegmatites(1,45).
5. Davidite-(La) $(La,Ce)(Y,U,Fe^{2+})(Ti,Fe^{3+})_{20}(O,OH)_{38}$ – Trigonal system; 3.20% U. Occurs in pegmatites(1,45).
6. Dessauite-(Y) $Sr(Y,U,Mn)Fe_2(Ti,Fe^{3+},Cr,V)_{18}(O,OH)_{38}$ – Trigonal system; 3.85% U. Occurs in cavities of calcite veins(1,50).
7. Euxenite-(Y) $(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$ – Orthorhombic system; 16.10% U. Acessory mineral in granite-pegmatites and detrital in black sands(1,53).
8. Orthobrannerite $U^{4+}U^{6+}Ti_4O_{12}(OH)_2$ – Orthorhombic system; 53.28% U. Secondary mineral found in the weathering residue of biotite pyroxene syenites(1,109).
9. Petscheckite $U^{4+}Fe^{2+}(Nb,Ta)_2O_8$ – Trigonal system; 36.52% U. Secondary mineral, product of oxidation zones of U deposits(1,114).
10. Tanteuxenite-(Y) $(Y,Ce,Ca,U)(Ta,Nb,Ti)_2O_6$ – Orthorhombic system; 52.37% U. Mineral component of the tin placers(1,149).
11. Thorutite $(Th,U,Ca)Ti_2(O,OH)_6$ – Monoclinic system; 24.36% U. Acessory mineral of nepheline-syenites normally as veins of microcline(1,152).
12. Uranmicrolite $U_{0.5}Ca_{0.5}Ta_2O_6(OH)$ – Cubic system; 27,37% U. Typical mineral of U oxidized zones(1,165).
13. Uranopolycrase $(U,Y)(Ti,Nb)_2O_6$ – Orthorhombic system; 34.35% U. Mineral found in zoned pegmatite vein near contact with granodirites(1,168).

14. Uranosphaerite $Bi(UO_2)O_2(OH)$ – Orthorhombic system; 45.08% U. Mineral found in alteration zone of uraninite(1,167).

15. Uranpyrochlore $Ca_{0.5}U_{0.5}Nb_2O_6(OH)$ – Cubic system; 17.59% U. Mineral found in calcareous tuffs associated with carbonatites(1,165).

16. Yttrocrasite-(Y) $(Y,Th,Ca,U)(Ti,Fe^{3+})_2(O,OH)_6$ – Orthorhombic system; 7.99% U. Mineral present in granites, pegmatites and metamorphic rocks(1,177).

e_2) Simple Oxides

1. Agrinierite $(K_2,Ca,Sr)U_3O_{10}.4H_2O$ – Orthorhombic system; 71.48% U. Typical mineral of oxidation zones in the uraniferous deposits in association with uranophane in small cavities of this rocks(1,3,4).

2. Bauranoite $BaU_2O_7.4\text{-}5H_2O$ – Triclinic system; 59.03% U. Secondary mineral replacing uraninite crystals(1,16).

3. Becquerelite $Ca(UO_2)_6O_4(OH)_6.8H_2O$ – Orthorhombic system; 72.48% U. Secondary mineral which occurss in sedimentary uranium deposits in the oxidization zones(1,18).

4. Billietite $Ba(UO_2)_6O_4(OH)_6.8H_2O$ – Orthorhombic system; 71.57% U. Rare mineral, product of alteration from the uraninite(1,18).

5. Calciouranoite $(Ca,Ba,Pb)U_2O_7.5H_2O$ – Amorphous; 60.58% U. Rare mineral found in felsitic rocks, and oxidation zones of U-Mo deposits(1,25).

6. Clarkeite $(Na,K,Ca,Pb)(UO_2)O(OH).0\text{-}1H_2O$ – Trigonal system; 67.21% U. A secondary mineral occurs as hydrothermal alteration product (1,34).

7. Cleusonite $Pb(U^{4+}U^{6+})(Fe^{2+})_2(TiFe^{2+}Fe^{3+})_{18}(O,OH)_{38}$ – Trigonal system; 7.51% U. A rare mineral present in greenchist facies from gneissic rocks(1,35).

8. Compreignacite $K_2(UO_2)_6O_4(OH)_6.7H_2O$ – Orthorhombic system; 71.11% U. The mineral is a product of oxidation from pitchblende (uraninite) ores(1-41).

9. Curite $Pb_2U^{6+}{}_5O_{17}.4H_2O$ – Orthorhombic system; 63.34% U. Occurs associated with torbernite in the oxidation zone of uranium ores(1,44).

10. Fourmarierite $PbU^{6+}{}_4O_{13}.4H_2O$ – Orthorhombic system; 64.53% U. Secondary Pb-U mineral, product of alteration from uraninite(1,54).

11. Holfertite $(UO_2)_{1.75}[TiO_4[(H_2O)_3Ca_{0.25}]$ – Hexagonal system; 63,31% U. Acessory mineral in rhyolite(1,64).

12. Ianthinite $U^{4+}{}_2(UO_2)_4O_6(OH)_4.9H_2O$ – Orthorhombic system; 78.29% U. Mineral occurss in sedimentary uranium deposits(1,66).

13. Metacalciouranoite $(Ca,Na,Ba)U_2O_7.5H_2O$ – Orthorhombic system; 69.58% U. Rare mineral found in oxidation zones of U-Mo deposits(1,80).

14. Metaschoepite $[(UO_2)_8O_2(OH)_{12}].10H_2O$ – Orthorhombic system; 76.04% U. Secondary mineral which occurss in the oxized zone of U deposits(1,86).

15. Metastudtite $UO_2(OH)_4$ – Orthorhombic system; 70.41% U. Secondary mineral which occurss in uranium deposits associated with uranium-lead oxides(1,87).

16. Metavandendriesscheite $PbU_7O_{22}.nH_2O$ - Orthorhombic system; 69.56% U. Secondary mineral present in gummitic zone of the uranium deposits(1,86,167).

17. Paraschoepite $UO_3.2H_2O$ (?) – Orthorhombic system; 73.91% U. Secondary mineral which occurss on pichblende (uraninite) crystals in uranium mines(1,112).

18. Protasite $Ba(UO_3)O_3.3H_2O$ – Monoclinic system; 61.91% U. Secondary mineral found in copper and uranium deposits(1,121).

19. Rameuauite $K_2CaU^{6+}{}_6O_2.9H_2O$ – Monoclinic system; 70.40% U. Secondary mineral found in uranium mines on uraninite(1,125).

20. Richetite $Pb_9(UO_2)_{36}(OH)_{24}O_{36}$ – Triclinic system; 66.15% U. Secondary mineral which occurss on needles of uranophane(1,128).

21. Sayrite $Pb_2(UO_2)_5O_6(OH)_2.4H_2O$ – Monoclinic system; 60.52% U. Secondary uranium mineral which occurss associated with becquerelite and uranophane(1,133).

22. Schoepite $(UO_2)_8O_2(OH)_{12}.12H_2O$ – Orthorhombic system; 72.89% U. Secondary mineral product of alteration of uraninite(1,135).

23. Spriggite $Pb_3[(UO_2)_6O_8(OH)_2](H_2O)_3$ – Monoclinic system; 59.10% U. Secondary mineral found in alteration zone of hydrothermal hematite-U-Nd-REE(1,143).

24. Studtite $UO_4.4H_2O$ – Monoclinic system; 63.63% U. Secondary mineral found in percolation waters of uranium mines(1,146).

25. Uraninite UO_2 – Cubic system; 88.15% U. Occurs in granite and syenites pegmatites, conglomerates, and colloform crusts in hydrothermal veins of high temperatures[164]. Its a major industrial source of uranium. Also called pitcblende.

26. Vandenbrandeite $Cu^{2+}(UO_2)(OH)_4$ – Triclinic system; 59.27% U. Secondary mineral on pitchblende (uraninite) ores(1,165).

27. Vandendriesscheite $Pb_{1.5}(UO_2)_{10}O_6(OH)_{11}.11H_2O$ – Orthorhombic system; 67.76% U. Secondary mineral of gummite alteration zones(1,86,167).

28. Wolsendorfite $Pb_7(UO_2)_{14}O_{19}(OH)_4.12H_2O$ – Orthorhombic system; 59.99% U. Mineral found in fissures of fluorite veins(1,86,167).

f) Phosphates

f$_1$) Compound phosphates

1. Coconinoite $Fe^{3+}{}_2Al_2(UO_2)_2(PO_4)_4(SO_4)(OH)_2.20H_2O$ – Monoclinic (?) system; 30.91% U. Typical mineral of the sedimentary rocks (arkosic and sandstones)(1,3).

2. Xiangjiangite $(Fe^{3+},Al)(UO_2)_4(PO_4)_2(SO_4)_2(oh).22H_2O$ – Tetragonal (?) sytem; 49.67% U. Secondary mineral of the oxidized zones of uranium deposits(1,176).

f$_2$) Hydrated phosphates

1. Autunite $Ca(UO_2)_2(PO_4)_2.10\text{-}12H_2O$ – Tetragonal system; 48.27% U. Secondary mineral in oxidation zone in the pegmatites and uraniferous deposits. It's an important source of U(1,12,40).

2. Bassetite $Fe^{2+}(UO_2)_2(PO_4)_2.8H_2O$ – Monoclinic system; 51.19% U. Rare secondary mineral in the oxized zone in hydrothermal uraniferous deposits(1,15).

3. Bergenite $Ca_2Ba_4[(UO_2)_3O_2(PO_4)_2]_3.16H_2O$ – Monoclinic system; 43.28% U. A secondary uranium mineral(1,19).

4. Chernikovite $(H_3O)_2(UO_2)_2(PO_4)_2.6H_2O$ – Tetragonal system; 54.34% U. Occurs in granite pegmatites(1,31).

5. Dewindtite $Pb_3[(UO_2)_3O(PO_4)_2(OH)]_2.12H_2O$ – Orthorhombic system; 49.18% U. Rare secondary mineral formed by alteration from uraninite(1,51).

6. Dumontite $Pb_2(UO_2)_3O_2(PO_4)_2.5H_2O$ – Monoclinic system; 46.47% U. Secondary mineral of Pb-U deposits(1,52).

7. Fritzscheite $Mn^{2+}(UO_2)_2[(PO_4)_2].10H_2O$(?) – Tetragonal system; 47.65% U(1).

8. Lehnerite $Mn^{2+}(UO_2)_2(P,V)O_4)_2.8H_2O$ – Monoclinic system; 51.24% U. Secondary mineral formed by decomposition of zwieselite crystals(1,73).

9. Meta-ankoleite $K_2(UO_2)_2(PO_4)_2.6H_2O$ – Tetragonal system; 51.96% U. Mineral found in pegmatites(1,78).

10. Meta-autunite $Ca(UO_2)_2(PO_4)_2.2\text{-}6H_2O$ – Tetragonal system; 56.53% U. Typical mineral which occurss in fractures in uraniferous igneous rocks associated with autunite(1,79).

11. Metanatroautunite $Na_2(UO_2)_2(PO_4)_2.6\text{-}8H_2O$ – Tetragonal system; 48.06% U. Secondary mineral in granite-quarries rich in uranium(1,83).

12. Metasalleite $Mg(UO_2)(PO_4).8H_2O$ – Monoclinic system; 44.62% U. Secondary mineral occursed in silicious rocks associated with uranium ores(1,85).

13. Metatorbernite $Cu^{2+}(UO_2)_2(PO_4)_2.8H_2O$ – Tetragonal system; 50.77% U. Secondary mineral product of weathering and dehydratation of torbernite(1,88).

14. Metauranocircite I $Ba(UO_2)_2(PO_4)_2.6H_2O$ – Tetragonal system; 47.92% U. Secondary mineral derived from phosphatic uraninite deposits(1,90).

15. Metauranocircite II $Ba(UO_2)_2(PO_4)_2.6H_2O$ – Tetragonal system; 47.92% U. Secondary mineral derived from phosphatic uraninite deposits(1,90,91).

16. Metavanmeersscheite $U^{6+}(UO_2)_3(PO_4)_2(OH)_6.2H_2O$ – Orthorhombic system; 69.19% U. Secondary uranium mineral found in pegmatites(1,94).

17. Ningyoite $(U,Ca)_2(PO_4)_2.1\text{-}2H_2O$ – Orthorhombic system; 51.50% U. Seconadary mineral wchich occurss in an unoxidized zone of uranium deposits (1,106).

18. Parsonsite $Pb_2(UO_2)[PO_4]_2.2H_2O$ – Triclinic system; 26.15% U. Secondary mineral of Pb-Zn veins(1,115).

19. Phosphowalpurgite $(UO)_2Bi_4O_4(PO_4)_2.2H_2O$ – Triclinic system; 15.56% U. Secondary mineral formed by the supergene alteration of bismuth sulfides and uraninite(1,116).

20. Phophuranylite $KCa(H_3O)_3(UO_2)_7(PO_4)_4O_4.8H_2O$ – Orthorhombic system; 63.73% U. Secondary mineral typical occursring in weathered zones of granite pegmatites(1,117).

21. Phurcalite $Ca_2(UO_2)_3O_2(PO_4)_2.7H_2O$ – Orthorhombic system; 57.67% U. Secondary mineral of the iron deposits associated with hematite(1,119).

22. Przhevalskite $Pb(UO_2)_2(PO_4)_2.4H_2O$ – Orthorhombic system; 41.17% U. Secondary mineral found in oxidized zone of sulfide and uraninite ore deposits(1,122).

23. Sabugalite $H_{0.5}Al_{0.5}(UO_2)_2(PO_4)_2.8H_2O$ - Monoclinic system; 53.60% U. Secondary mineral found associated with salleite, meta-autunite and phophuranylite(1,131).

24. Saleeite $Mg(UO_2)_2(PO_4)_2.10H_2O$ – Monoclinic system; 50.94% U. Secondary mineral found disseminated in carnotite-bearing sandstones and uranium phosphates(1,132).

25. Torbernite $Cu^{2+}(UO_2)_2(PO_4)_2.8\text{-}12H_2O$ – Tetragonal system; 48,00% U. Secundary mineral of granites in uranium ores(1,154).

26. Triangulite $Al_3(UO_2)_4PO_4)_4(OH)_5.5H_2O$ – Triclinic system; 55.48% U. Secondary mineral found in pegmatites(1,155).

27. Tristramite $(Ca,U^{4+})(PO_4).2H_2O$ – Hexagonal system; 30.74% U. Secondary mineral which occurss in intergrown with goethite in fine fractures in uraninite crystals(1,156).

28. Ulrichite $CaCu^{2+}(UO_2)(PO_4)_2.4H_2O$ – Monoclinic system; 37.45 U. Secondary mineral found in granites(1,159).

29. Uramphite $(NH_4)_2(UO_2)_2(PO_4)_2.6H_2O$ – Orthorhombic system; 54.46% U. Mineral found as encrustions on a fracture surface in sub-betuminous coal and uranium coal deposits(1,162).

30. Uranocircite $Ba(UO_2)_2(PO_4)_2.12H_2O$ – Tetragonal system; 46.82% U. Secondary mineral derived from phosphatic uraninite deposits(1,90,91).

31. Uranospathite $Al_{1-x}\square_x[(UO_2)(PO_4)]_2(H_2O)_{20+3x}F_{1-3x}$ – Orthorhombic system; 43.11% U. A very rare secondary mineral in uranium deposits(1,8).

32. Vanmeersscheite $U^{6+}(UO_2)_3(PO_4)_2(OH)_6.4H_2O$ – Orthorhombic system; 67.42% U. Secondary uranium mineral found in pegmatites(1,94).

33. Vyachelavite $U^{4+}(PO_4)(OH)._nH_2O$ – Orthorhombic system; 60.25% U. Mineral found on quartz crystals associated with pyrite(1,173).

34. Walpurgite $(BiO)_4(UO_2)(AsO_4)_2.2H_2O$ – Triclinic system; 18.20% U. Mineral found in oxidized polymetallic ore deposit(1,167).

35. Yingjiangite $K_2Ca(UO_2)_7(PO_4)_4(OH)_6.6H_2O$ – Orthorhombic system; 63.90% U. Secondary mineral of the oxidation zone of uraninite and uranothorite(1,175).

f_3) Hydrated phosphates containing hydroxyl

1. Althupite $AlTh(UO_2)[(UO_2)_3O(OH)(PO_4)_2]_2(OH)_3.15H_2O$ – Triclinic system; 57.77% U. Secondary mineral in the uraniferous zone of the pegmatites(1,6).

2. Françoisite-(Ce) $Ce(UO_2)_3(PO_4)_2O(OH).6H_2O$ – Monoclinic system; 59.44% U. Rare mineral in uranium deposits(1,56).

3. Françoisite-(Nd) $Nd(UO_2)_3(PO_4)_2O(OH).6H_2O$ – Monoclinic system; 61.26% U. Secondary mineral, product of alteration in Cu-Co sedimentary deposits(1,57).

4. Furongite $Al_2(UO_2)(PO_4)_2(OH)_2.8H_2O$ – Triclinic system; 30.24% U. Secondary mineral found in the oxidation zone of uranium deposits(1,58).

5. Kamitugaite $PbAl(UO_2)_5[(P,As)O_4]_2(OH)_9.9.5H_2O$ – Triclinic system; 56.71% U. Secondary mineral found in pegmatites(1,70).

6. Moreauite $Al_3(UO_2)(PO_4)_3(OH)_2.13H_2O$ – Monoclinic system; 26.33% U. Secondary mineral found in the oxidation zone of uranium deposits(1,100).

7. Mundite $Al(UO_2)_3(PO_4)_2(OH)_3.5.5H_2O$ – Orthorhombic system; 61.13% U. Secondary mineral found in the oxidation zone of uranium deposits(1,102).

8. Phuralumite $Al_2(UO_2)_3(PO_4)_2(OH)_6.10H_2O$ – Monoclinic system; 53.44% U. Secondary mineral found in pegmatites associated with others U-phophates(1,118).

9. Ranunculite $HAl(UO_2)(PO_4)(OH)_3.4H_2O$ – Monoclinic system; 46.12% U. Secondary mineral found in U-rich pegmatites(1,126).

10. Sreinite $Pb_2(UO_2)_{11}(BiO)_8(PO_4)_5(OH)_{19}.6H_2O$ – Cubic system; 25.59% U. Secondary mineral found in fissures of quartz crystals in a bismuth deposit from Krusne Hory Mountais, Czech Republic(1,144).

11. Threadgoldite $Al(UO_2)_2(PO_4)_2(OH).8H_2O$ – Monoclinic system; 51.85% U. Mineral which occurss in pegmatites on uraninite(1,152).

12. Upalite $Al(UO_2)_3O(OH)(PO_4)_2.7H_2O$ – Monoclinic system; 60.20% U. Secondary mineral found in pegmatites(1,153).

13. Vochtenite $(Fe^{2+},Mg)Fe^{3+}(UO_2)_4(PO_4)_4(OH).12\text{-}13H_2O$ – Monoclinic system; 52.72% U. Secondary mineral with occurss in oxidized of the uranium mines(1,171).

g) Selenites

g_1) Anhydrous selenites

1. Derriksite $Cu_4(UO_2)(SeO_3)_2(OH)_6$ – Orthorhombic system; 27.04% U. Mineral found in basal portion of Cu-Co deposits(1,49).

g_2) Hydrated selenites

1. Demesmaekerite $Pb_2Cu^{2+}{}_5(UO_2)_2(Se^{4+}O_3)_6(OH)_6.2H_2O$ – Triclinic system; 21.92% U. Mineral found in basal portion of Cu-Co deposits(1,48).

2. Guilleminite $Ba(UO_2)_3(SeO_3)_2O_2(H_2O)_3$ – Orthorhombic system; 55,47% U. Mineral occurss in the oxidized zone of the Cu-Co deposits(1,60).

3. Larisaite $Na(H_3O)(UO_2)_3(SeO_3)_3O_2.4H_2O$ – Monoclinic system; 59,52% U. Secondary mineral in sedimentary rocks(1,72).

4. Piretite $Ca(UO_2)_3(SeO_3)_2(OH)_4.4H_2O$ – Orthorhombic system; 45,6% U. Secondary mineral in uranium and copper deposits(1,120).

h) Silicates

h_1) Cyclosilicates

1. Arapovite $(U,Th)(Ca,Na)_2(K_{1-x}\square_x)Si_8O_{20}.H_2O$ – Tetragonal system; 16.45% U. Mineral found in rocks of maraines in Tajikistan in association with turkestanite(1,13).

h_2) Inosilicates

1. Ciprianiite $Ca_4[(Th,U)(REE)](Al,\square)_2(Si_4B_4O_{22})(OH,F)_2$ – Monoclinic system; 17.24% U. Mineral found in pyroclastic rocks in miarolitic cavities(1,33).

h_3) Nesosilicates

1. Boltwoodite $HK(UO_2)SiO_4.1.5H_2O$ – Monoclinic system; 55.45% U. Surrouding hydrated uranyl oxides incrusting uraninite crystals(1,24).
2. Calciouranilite $Ca_4(UO_2)_4(Si_2O_5)_5(OH)_6.15H_2O$ – (?); 41.51% U. Rare mineral formed in a granite-porphyry(1,26).
3. Coffinite $USiO_4.nH_2O$ – Tetragonal system; 72.63% U. Typical mineral of the sedimentary rocks. It's an important source of U(1,39,40).
4. Coutinhoite $Th_x(Ba_{1-2x})(H_2O)_y(UO_2)_2Si_5O_{13}.H_2O$ – Orthorhombic system; 67.40% U. Secondary mineral of pegmatites, product from the oxidation of uraninite(1,42).
5. Cuprosklodowskite $Cu(UO_2)_2Si_2O_7.6H_2O$ – Triclinic system; 55.24% U. Secondary mineral formed by alteration from uranium ores(1,24).
6. Haiweeite $Ca(UO_2)_2Si_5O_{12}(OH)_2.4.5H_2O$ – Orthorhombic system; 47.58% U. Secondary mineral formed by alteration from uranium ores.(1,61).
7. Kasolite $Pb(UO_2)SiO_4.H_2O$ – Monoclinic system; 40.53% U. Mineral found in uranium mines, oxidation product of uraninite. A source of U(1,40,71).
8. Metahaiweeite $Ca(UO_2)_2Si_6O_{15}.nH_2O$ – Monoclinic system; 46.05% U. Secondary mineral formed by alteration from uranium ores.(1,61).
9. Natroboltwoodite $(H_3O)(Na,K)(UO_2)SiO_4.H_2O$ – Orthorhombic system; 51.60% U. Secondary mineral occurss in small amounts in soils of arid regions(1,103).
10. Oursinite $Co[(UO)_2)(Si_3OH)].4H_2O$ – Orthorhombic system; 54.61% U. Secondary mineral found in oxidation zones of U ores(1,10).
11. Sklodowskite $Mg(UO_2)_2Si_2O_7.6H_2O$ – Monoclinic system; 55.44% U. Secondary mineral of oxidization zone of uranium ores commonly associated with uraninite(1,142).
12. Soddyite $(UO_2)_2SiO_4.2H_2O$ – Orthorhombic system; 71.25% U. Secondary mineral found in oxidized uranium ores associated with curite(1,142).
13. Swamboite $U^{6+}H_6(UO_2)_6(SiO_4)_6.30H_2O$ – Monoclinic system; 56.34 % U. Secondary mineral which occurs as alteration product of others uranium minerals(1,147).
14. Thorite $(Th,U)SiO_4$ – Tetragonal system; 2.36% U. Mineral acessory of augite-syenites(1,151).
15. Uranophane-alpha $Ca(UO_2)_2[SiO_3(OH)]_2.5H_2O$ – Monoclinic system; 40.59% U. Occurs as alteration product of gummites(1,166).
16. Uranophane-beta $Ca(UO_2)_2[SiO_3(OH)]_2.H_2O$ – Monoclinic system; 60.70% U. Occurs as alteration product of uraninite in oxidized zones and pegmatites(1,166).
17. Uranosilite $U^{6+}CaSi_7O_{17}$ – Orthorhombic system; 33.69% U. Occurs as intergrowth with studtite and uranophane on quartz and hematite(1,169).

18. Weeksite $(K,Na)_2(UO_2)_2(Si_5O_{13}).3H_2O$ – Orthorhombic system; 48.58% U. Mineral with occurs in veins of ryolites, conglomerates, limestones and sandstones(1,167).

i) Sulfates

i_1) Anhydrous sulfates

1. Magnesiumzippeite $Mg(H_2O)_{3.5}[(UO_2)_2(SO_4)(O_2)]$ – Monoclinic system; 63.01% U. Secondary mineral from the oxidation zone of sulfides in the uranium deposits(1,76).

i_2) Hydrated sulfates containing hydroxyl

1. Cobaltzippeite $Co_2(UO_2)_6(SO_4)_3(OH)_{10}.16H_2O$ – Orthorhombic system; 57.86% U. Mineral found in oxidized zone of copper ores.(1,37).
2. Deliensite $Fe^{2+}(UO_2)_2(SO_4)_2(OH)_2.3H_2O$ – Orthorhombic system; 54.34% U. Secondary mineral of oxidization zone from uranium deposits(1,46).
3. Jáchymovite $(UO_2)_8(SO_4)(OH)_{14}.13H_2O$ – 69.79% U. Mineral found in dolomitic veins(1,67).
4. Johannite $Cu(UO_2)_2(SO_4)_2(OH)_2.8H_2O$ – Triclinic system; 48.88% U. Secondary mineral, product from the oxidation of uraninite in gypsiferous deposits(1,68).
5. Metauranopilite $(UO_2)_6(SO_4)(O_2)(OH)_{10}.5H_2O$ – Orthorhombic (?) system; 72.19% U – Secondary mineral from an uranium–bearing hydrothermal ore deposits (1,92).
6. Natrozippeite $Na_5(H_2O)_{12}[(UO_2)_8(SO_4)_4O_5(OH)_3]$ – Orthorhombic system; 63.34% U. Secondary mineral of the uranium deposits(1,105).
7. Nickelzippeite $Ni_2(UO_2)_6(SO_4)_3(OH)_{10}.16H_2O$ – Orthorhombic system; 57.49% U. Secondary mineral of the uranium deposits(1,106).
8. Pseudojohannite $Ni_{6.5}[(UO_2)_4O_4(SO_4)_2]_2(OH)_5.25H_2O$ – Triclinic system; 51.93% U. Secondary mineral found in uranium deposits(1,123).
9. Rabejacite $Ca(UO_2)_4(SO_4)_2(OH)_6.6H_2O$ – Orthorhombic system; 62.54% U. Secondary mineral of uranium deposits associated with gypsum(1,124).
10. Uranopilite $(UO_2)_6(SO_4)(OH)_{10}.12H_2O$ – Monoclinic system; 67.93% U. Secondary mineral found on altering uraninite(1,167).
11. Zinczippeite $Zn_2(UO_2)_2(SO_4)(OH)_3.H_2O$ – Monoclinic system; 59.93% U. Mineral common in underground uranium mines(1,167).
12. Zippeite $K(UO_2)_2(SO_4)(OH)_3.H_2O$ – Monoclinic system; 61.91% U. Mineral common in underground uranium mines(1,167).

j) Tellurites

1. Cliffordite $UTe^{4+}{}_3O_9$ – Cubic system; 31.12% U. Mineral found in oxidized zones of hydrothermal Au-Ag telluride deposits(1,36).

2. Moctezumite $Pb(UO)_2(TeO_3)_2$ – Monoclinic system; 28.73% U. Secondary mineral in uranium-bearing ores(1,98).

3. Schmitterite $(UO_2)TeO_3$ – Orthorhombic system; 53.41% U. Secondary mineral found in the oxidized parts of a telluride-bearing deposit(1,134).

k) Tungstates

k$_1$) Basic and hydrated tungastates

1. Uranotungstite $(Fe^{2+},Ba,Pb)(UO_2)_2(WO_4)(OH)_4.12H_2O$ – Orthorhombic system; 40.77% U. Mineral found as crusts on quartz, meta-uranocircite and meta-heirichite in uranium deposits(1,170).

l. Vanadates

l$_1$) Hydrated vanadates

1. Carnotite $K_2(UO_2)_2(VO_4)_2.3H_2O$ – Monoclinic system; 52.77% U. A secondary mineral product from the alteration of uranium minerals (uraninite, davidite or montroseite), occurs principally in sandstones, fossil carbonaceous matter, and calcretes(1,28,40).

2. Curienite $Pb(UO_2)_2(V_2O_8).5H_2O$ – Orthorhombic system; 44.61% U. Secondary mineral in sedimentary rocks (sandstones) rich in U-V(1,43).

3. Francevillite $Ba(UO_2)_2(V_2O_8).5H_2O$ – Orthorhombic system; 48.64% U. Secondary mineral occurss as impregnations in sandstones(1,55).

4. Margaritasite $(Cs,K,H_3O)_2(UO_2)_2V_2O_8.H_2O$ – Monoclinic system; 48.84% U. (1,77).

5. Metatyuyamunite $Ca(UO_2)_2(VO_4)_2.3H_2O$ – Orthorhombic system; 55.10% U. Secondary mineral which occurss as product of dehydration of tyuyamunite(1,89).

6. Strelkinite $Na_2(UO_2)_2V_2O_8.6H_2O$ – Orthorhombic system; 51.52% U. Mineral found in carbonaceous-siliceous shales(1,145).

7. Tyuyamunite $a(UO_2)_2V_2O_8.5\text{-}8H_2O$ – Orthorhombic system; 51.85% U. Secondary mineral found in U-V sandstones deposits(1,158).

l$_2$) Hydrated vanadates containing hydroxyl

1. Metavanuralite $Al(UO_2)_2(VO_4)_2(OH).3H_2O$ – Triclinic system; 49.69% U. Secondary mineral stable in humidity between 28-47%; the less hydrated form of varuralite(1,95).

2. Sengierite $Cu_2(UO_2)_2(VO_4)_2(OH)_2.6H_2O$ – Monoclinic system; 47.36% U. Secondary mineral found in uranium-bearing copper deposits(1,139).

3. Metavanuralite $Al(UO_2)_2(VO_4)_2(OH).11H_2O$ – Triclinic system; 47.04% U. Secondary mineral stable in humidity between 28-47%; the less hydrated form of varuralite(1,95).

m) Vanadium Oxysalts

1. Rauvite $Ca(UO_2)_2V^{5+}_{10}O_{28}.16H_2O$ – Amorphous; 26.07% U. Secondary mineral found in oxized zone of U-V ores(1,127).

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BOOKS / LIVROS

PAULO CÉSAR PEREIRA DAS NEVES, FLÁVIA SCHENATO FLÁVIO ANTÔNIO BACHI, "***Introdução à Mineralogia Prática***", 2ª edição, Revisada e Atualizada, Editora da ULBRA, Canoas, RS, Brasil, 2008, 335 páginas.

A 2ª edição deste excelente livro apresenta além de um acréscimo no número de páginas uma melhoria significativa com respeito à 1ª edição. Ver a nossa resenha original (***South. Braz. J.Chem.,Vol.11, No.12***, 21-22, 2003).O conteúdo científico e a qualidade gráfica, especialmente das imagens das espécies de minerais, podem ser considerados de primeira categoria. Os autores estão de parabéns.

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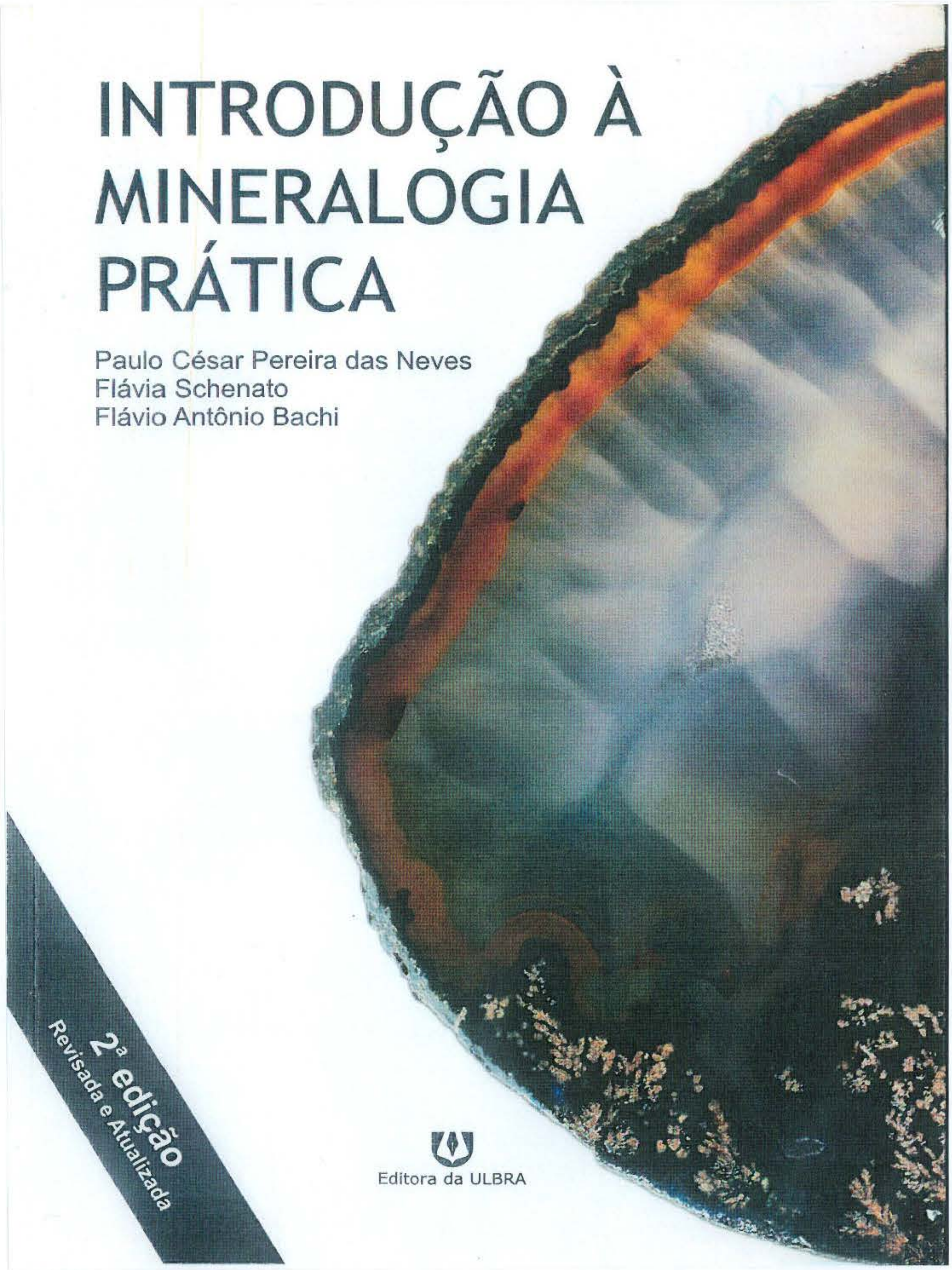

INTRODUÇÃO À MINERALOGIA PRÁTICA

Paulo César Pereira das Neves
Flávia Schenato
Flávio Antônio Bachi

2ª edição
Revisada e Atualizada

Editora da ULBRA

Sumário

The 2nd edition of "*Introdução à Mineralogia Prática*" (in Portuguese) is a considerable improvement compared to the first edition. See our previous review (*South. Braz. J. Chem., Vol.11, No.12,* 23 , 2003). The scientific content has been expanded and improved significantly and the quality of the photographs of the minerals is first class. We congratulate the authors.

Recomendamos altamente este livro para todos os interessados nas Ciências da Terra.

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Lavinel G. Ionescu, B.S., M.S., Ph.D.(Physical Chemistry/Astrophysics)

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