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CONTRIBUTION TO CO(III) NITROCOMPLEXES CHEMISTRY. NEW ANALOGUES OF $NH_4[CO(NO_2)_4(NH_3)_2]$ COMPLEX WITH HEXAMETHYLENETETRAMINE

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ABSTRACT

The work presents experimental data about new analogues of ammonium tetranitro-diamine Co(III) complex (Erdmann complex) with hexamethyleneteramine (hta). The base complex obtained, $NH_4[Co(NO_2)_4(hta)_2]$, as well as the Erdmann complex, present practical importance for agriculture. They contain nitrogen under cationic, anionic and molecular form and Co(III) as micronutrient and can serve as source of other micronutrients through replacement of NH_4^+ with other complexes cations. Some of these complexes are soluble in water, others are hardly soluble and nonhygroscopic. Their efficiency in fertilizing was demonstrated by us experimentally.

KEYWORDS : Co(III) Nitrocomplexes, Hexamethylenetetramine, Micronutrients

RESUMO

O presente artigo apresenta dados originais obtidos para análogos novos do complexo de amônio e Co(III) com tetranitrodiamina (Complexo de Erdmann) com hexametilenotetramina (hta). O complexo obtido, $NH_4[Co(NO_2)_4(hta)_2]$, bem como o complexo de Erdmann tem importância prática na agricultura. Eles contém nitrogênio nas formas catiônica, aniônica e molecular e Co(III) como micronutrientes e podem servir como fontes de outros micronutrientes através da troca de NH_4^+ com complexos de outros cátions. Alguns destes complexos são solúveis em água, outros são pouco solúveis e nonigroscópicos. A sua eficiência como fertilizantes foi demonstrada experimentalmente.

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INTRODUCTION

There exists a wide range of complexes of nitroamine [1,2,3] as tetranitro-diamine ammonium Co(III) complex, a compound which was obtained for the first time by Erdmann [2]. This complex can serre as a fertilizer because it contains nitrogen and an element that can be a micronutrient. It has, however some disadvantages, we have extended the Co(III) nitrocomplexes series with fertilizing action to new nitrocomplexes with the general formula $(NH_4)_{n-3}[Co(NO_2)_{6-n}(N_4C_6H_{12})_n]$, where $N_4C_6H_{12}$ is hexamethylenetetramine noted *hta* [2,3] and n has the values of 2 or 3. These complexes are macrocrystalline substances, partially soluble in water, with red or yellow-orange colour. They decompose only at temperature between 138-175°C.

Starting from the base complex with two molecules of *hta* we have obtained a range of other ligands with or without nitrogen and also be replacing NH_4^+ ion with other simple complex ions.

EXPERIMENTAL PROCEDDURE

The procedure of preparing nitrocomplexes that have the general formula mentioned above consisted in treating $CoCl_2 \cdot 6H_2O$ dissolved in distilled water with a solution which contains NH_4Cl, $NaNO_2$ and $N_4C_6H_{12}$ taken in stoichiometrical ratios. The reaction took place in excess NH_4Cl and the oxidation of the reactions mixture is done by bubbling air 1.5 to 2 hours at room temperature. The product is obtained by crystallization for 12-24 hours.

The $NH_4[Co(NO_2)_4(hta)_2]$preparation

The Erdmann analogue preparation was done as follows: A sample of 91.5g $CoCl_2 \cdot 6H_2O$ (0.4mols) was dissolved in 200 mL distilled water which is the first solution and 100 g NH_4Cl (1.8 mols), 110.4 g $NaNO_2$ (1.6 mols) and 112 g $N_4C_6H_{12}$ (0.8 mols) in 1050 mL distilled water which is the second solution. The two solutions were mixed and a clear red with purple blue solution was obtained. The oxidation of the reactions mixture was done by bubbling air for 1.5-2 hours at room temperature. The solution was then allowed to crystallize for 12-24 hours. The reaction is as follows:

$$4CoCl_2 + 8NH_4Cl + 16NaNO_2 + 8N_4C_6H_{12} + O_2 \rightarrow 4NH_3 + 16NaCl + 4NH_4[Co(NO_2)_4(hta)_2] + 2H_2O \quad (1)$$

The nitrocomplex was dissolved in warm water in order to recrystallize it and there was no danger of hydrolyzing. In the case of Erdmann's salt recrystallization was done from a 1M CH_3COOH solution with an efficiency of 91%. The complex obtained has macrocrystals under the form of red bright lamellae of different sizes within regular outlines. It is partially soluble in water (0.23g/100g water at 22°C) and it decomposes at 175°C.

The pentanitro- and trinitrocomplexes preparation with $N_4C_6H_{12}$

Modifying the stoichiometrical ratio between components (increasing $NaNO_2$ quantity and reducing the $N_4C_6H_{12}$ quantity) we obtained the pentanitrocomplex with the formula $(NH_4)_2[Co(NO_2)_5(hta)]$. It presented macrocrystals as bright lamellae with yellow- reddish colour a little different from the one of tetranitrocomplex.

As in the case of Erdmann's salt preparation, excess of $N_4C_6H_{12}$ leads to the formation of the nonelectrolyte form with the formula $[Co(NO_2)_3(hta)_3]$ during the bubbling of air. This is a precipitate with yellow – orange colour, with microcrystals and it is hardly soluble in water.

The three nitrocomplexes, which were obtained with hexamethylenetetramine (hta), were studied using many chemical and physical – chemical methods in order to establish their composition and structure.

The chemical analysis of the complexes

Cobalt was determined by complexonometrical titration using 0.01M complexon III with murexide [4]. For the calculation the following relation was used:

$$Co\% = \frac{0.5894n}{a} x100$$

where *n* is ml complexon used for titration, a is grams substance analyzed and 0.5894 is mg cobalt which corresponds to 1 ml complexon.

The measurement of NH_4^+ ion was done spectrometrically (λ=410 nm) using Nessler reagent. The total nitrogen was determined using the micro-Kjeldahl method. The difference between the total nitrogen and the ammnoniacal nitrogen represents the nitrogen, which is in the complex ion. This make possible to establish the number of NO_2^- groups and complexed *hta* molecules. In the Table 1 are presented the data obtained through chemical analysis for the three-synthetized complexes.

Table 1. The results of the chemical analyses.

Formulae	M_{calc}	η%	Content %					
			Co		NH_4^+		N_{total}	
			Found	Calc.	Found	Calc.	Found.	Calc.
$(NH_4)_2[Co(NO_2)_5(hta)]$	464.93	76.3	12.52	12.67	7.90	7.74	33.01	33.12
$NH_4[Co(NO_2)_4(hta)_2]$	536.93	91.0	10.87	10.97	3.52	3.35	33.70	33.89
$[Co(NO_2)_3(hta)_3]$	616.93	42.5	9.68	9.55	-	-	34.22	34.04

The thermal analysis

Using a Dr. Erdey derivatograph important data were obtained about the composition and the structure of the complexes synthesized. In Figures 1, 2 and 3 the penta-, tetra- and trinitrocomplexes thermograms are presented and in Figure 4 the thermogram of Erdmann's salt is presented.

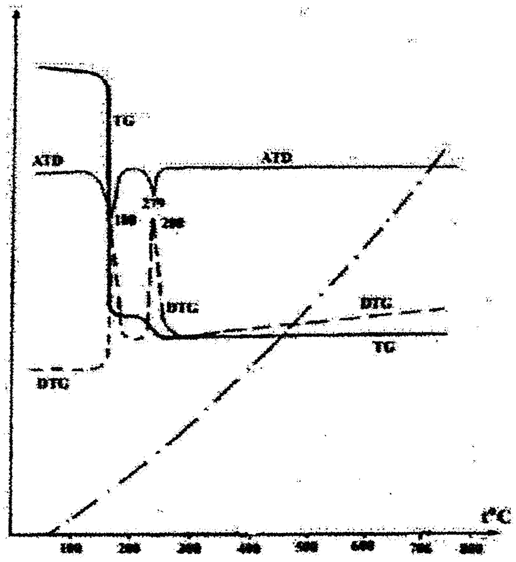


Figure 1. The thermogram of $(NH_4)_2[Co(NO_2)_5(hta)]$

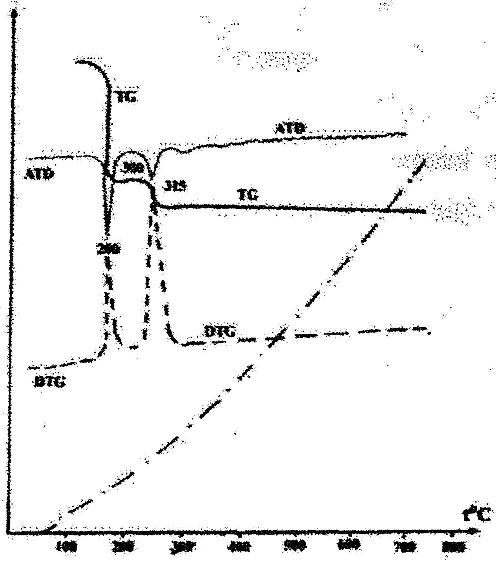


Figure 2. The thermogram of $NH_4[Co(NO_2)_4(hta)_2]$

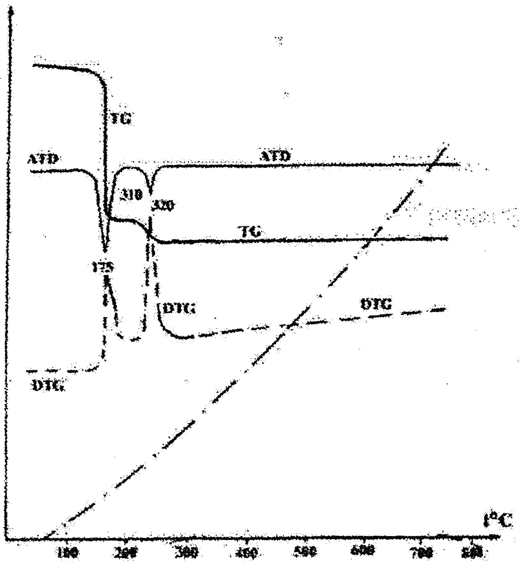


Figure 3. The thermogram of $[Co(NO_2)_3(hta)_3]$

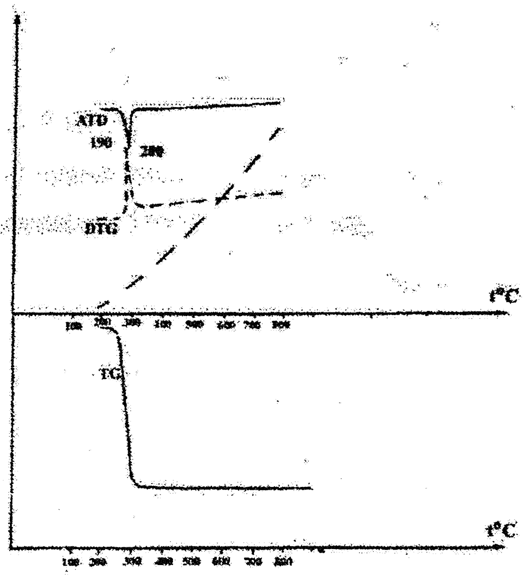


Figure 4. The thermogram of $NH_4[Co(NO_2)_4(NH_3)_2]$

Comparing these thermograms (Figures 1-3) with the thermogram of Erdmann's salt (Figure 4) we notice that:

- the endothermic effect which appears at 175-200°C, for Erdmann's salt, is due to NH_4^+, NH_3 and NO_2^- groups which leave the complex;
- the effect which appears at 275-320°C (Figures 1-3), which is not presented with Erdmann's salt, is due to *hta* which having a higher bond energy, needs a higher temperature in order to leave the complex.

The analysis of the first three thermograms demonstrates that the endothermic effect, which is present because of the chemical bond break between the central ion and *hta*, is bigger than the one produced by of $Co-NO_2$ bond break. This can be explained both by the strength of bond and by the ligand nature and mass. The ligand with a larger mass and stronger band requires a larger quantity of heat in order to leave the complex. The sharp maximum of DTG curve proves that the effect is produced at a precise temperature (320°C) corresponding to the chemical bond break.

Analyzing the DTG curves of the three new combinations we can show that:
- the first maximum attributed to NO_2^- groups (175-200°C) decreases at the same time with the diminishing number of NO_2^- groups;
- the second maximum from 275 to 320°C, attributed to *hta* groups, increases in temperature and intensity simultaneously with the increase of number of the *hta* molecules.

This is the result of internal interactions, which are bigger when the complex contains more ionic ligands (NO_2^-) than neutral ligands *(hta)*. That is why the $Co-NO_2$ bond break occurs in the case of pentanitrocomplex at 175°C and the Co-hta bond break takes place at 275°C. In the case of tetranitrocomplex the temperature are higher: 200°C for the $Co-NO_2$ bond break and 315°C for the Co-hta bond break.

The higher stability of the tetranitrocomplex can also be explained by its octahedral configuration. There are two possible arrangements:
- the two bulky molecules of *hta* at the two tops of the octahedral:
- two NO_2^- ions at the two tops of the octahedral and the other two at the opposite diametrical corners if the base in order to assure a repulsion as small as possible among the NO_2^- ions.

The lamellar structure of pentanitro- and tetranitrocomplex suggests that the second variant is correct. In the case of trinitrocomplex it is not possible to find three bulky groups of *hta* in the base plane. One of the groups is found in one of the octahedral tops. For this reason:
- the macrocrystal lamellar structure disappears and a microcrystal structure appears;
- the solubility decreases;
- the colour is modified from red to yellow as compared to the other two complexes.

The TG curves, which show mass loss varying with temperature, confirm the conclusions drawn from the diagrams ATD and DTG analysis.

The IR spectral analysis

The absorption spectrum in IR of the complexes prepared was recorded with a UR 10 Jenna spectrometer. The tested sample was included into a KBr pellet at a pressure of 80 atm in dilution of 2-10 mg substance / 0.5g KBr. There frequencies were recorded in the range of 400-3600 cm^{-1} (Table 2).

Table 2. The IR spectra of the complexes

Band	$(NH_4)_2[Co(NO_2)_5(hta)]$	$NH_4[Co(NO_2)_4(hta)_2]$	$[Co(NO_2)_3(hta)_3]$
$\delta(NO_2)$	830 s, sh	830 s, sh	830 s, sh
$\nu_{sym.}(NO_2)$	1270 w	1250 w	1230 w
$\nu_{asym.}(NO_2)$	1465 w	1440 w	1420 m
$\gamma(CH_2)$	710 w	710 w	710 w
ν(C-N)	1065 s, sh	1065 s,sh	1065 s,sh
ν(Co-N)(l)	570 w	570 w	570 w
ν(Co-N)(ll)	510 w	510 w	510 w
$\nu(NH_4^+)$	3080-3300 w, br	3080-3300 w, br	-

s- strong; w- weak; sh- sharp; m- medium, br- broad
l: Co-N(NO_2); ll: Co-N(hta)

From Table 2 it can be noticed that generally with all three complexes there are the same absorption bands but they are shightly shifted and have different intensities. This is because of the resonance state of the atoms, which are fixed in a total correlation with the whole molecular structure, which is different from one substance to anoher.

This explain why the bands at 1270 and 1465 cm^{-1}, which were assigned to the symmetrical and unsymmetrical stretching vibrations of NO_2^- groups [4-6], from the pentanitrocomplex, are shifted ~ 40 cm^{-1} with tetra- and trinitrocomplexes. It can be noticed that the $\delta(NO_2)$ and $\gamma(CH_2)$ vibrations at 830 and 710 cm^{-1} are constant respectively in all three complexes. The C-N stretching vibration characteristic of the C-N bond of *hta* appears at 1065 cm^{-1} and decreases in intensity from pentanitro- to trinitrocomplex.

The Co-N(l) and Co-N(ll) stretching vibrations appear in all three complexes at 570 and 510 cm^{-1} respectively. The vibrations at 3080-3300 cm^{-1}, characteristic of NH_4^+ ion, do not appear for the trinitrocomplex, which demonstrates that it is a nonelectrolyte.

The UV spectra

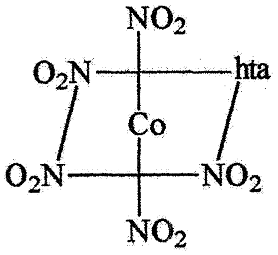
A UNICAM SP 8000 spectrometer was used for recording the absorption spectra in UV. Depending on the number of the NO_2^- and *hta* groups two maxima of absorption were obtained in UV domain.

Analysing these spectra one can notice that the three complexes present the first maximum at 253 nm (with Erdmann's salt λ_1=254 nm) and the second at 350 nm (with Erdmann's salt λ_1=348 nm). From the absorption maxima there were determined the maxim absorbance:

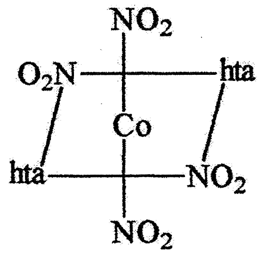
- in the case of pentanitro- and tetranitrocomplexes they are very close (0.30 and 0.33 respectively 0.12 and 0.12);
- in the case of the nonelectrolyte they are very different (0.12 and 50 respectively for the second maximum of absorption);

From the chemical analyses and the other physical-chemical methods which were used we proposed the following structure and the composition of the three nitrocomplexes synthezised:

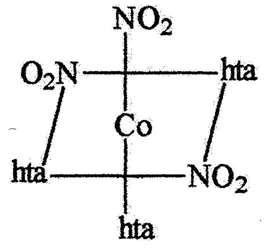
$(NH_4)_2[Co(NO_2)_5(hta)]$



$NH_4[Co(NO_2)_4(hta)_2]$



$[Co(NO_2)_3(hta)_3]$



NEW DERIVATIVES OF $NH_4[Co(NO_2)_4(hta)_2]$

The $NH_4[Co(NO_2)_4(hta)_2]$ complex is an Erdmann analogue as well as all the derivatives resulting from partial or total substitution of *hta* groups. Starting from this base combination we synthetized numerous Erdmann analogues. They contain a useful element for the plant, within the complex ion or they contain instead of the NH_4^+ cation another complexed microelement of the type $[Me(NH_3)_6]^{n+}[Co(NO_2)_4(hta)_2]_n^-$.

Thus, the $NH_4[Co(NO_2)_4(NH_3)(hta)_2]$ complex was studied. It was obtained by introducing into the mixture of reaction both *hta* (according to the stoichiometrical reaction) and NH_3, in small excess. The favourable efficiency was obtained by mixing two solutions as follows:

- the first solution was obtained by dissolving $CoCl_2 \cdot 6H_2O$ (0.4 mols) in 200 mL distilled water:
- the second solution by dissolving NH_4Cl (1.8 mols), *hta* (0.4 mols), $NaNO_2$ (2 mols) and NH_3 25% (2 mL) in 950 mL distilled water;

Air was bubbled in the two solutions for 2 hours after mixing. The purple colour of the solution becomes red and it is turbid because the nonelectrolyte $[Co(NO_2)_3(hta)_3]$ is formed in a small quantity. It need 2-3 days for crystallizing after filtering. Crystals with bright red lamellae are obtained. The chemical and physical-chemical studies confirm the $NH_4[Co(NO_2)_4(NH_3)(hta)]$ complex composition and structure. The fact that the Erdmann salt does not appear even in traces (it can be seen with naked eye), because it has dark-brown prismatic crystals, proves that *hta* as a ligand a higher affinity for cobalt than for NH_3. The IR spectrum of this complex confirms the presence of the NH_3 groups by the presence of the weak band at 1620 cm^{-1} (δ_{asym} NH_3 vibrations) [7-9] and the band at 1310 cm^{-1} (δ_{sym} NH_3 vibrations).

In the same way we obtained new derivatives, which contain, another ligand ion or molecule in the complex ion besides the four NO_2^- groups and one *hta* molecule. The formula of the new complex ion is $[Co(NO_2)_4(hta)X]^-$ where W is the new ligand which is introduced by synthesis [10-13].

Table 3 presents examples of such derivatives, which are considered Erdmann's analogues. In the same table are presented analogues, which are obtained by replacing the NH_4^+ cation with metallic cations such as Ag^+, Hg_2^{2+} and Tl^+. They are obtained by a simple precipitation of $[Co(NO_2)_4(hta)X]^-$ ion with the metal salts or with ammonia complex cations or derivatives [14-16].

Table 3. New analogues of $NH_4[Co(NO_2)_4(hta)]$

Complex combination	M (calculated)	η%	Aspect	Co(III)%	
				Calculated	Found
$NH_4[Co(NO_2)_4(hta)(SCN)]$	476.93	68.20	irregular plates, microcrystals, pink-lilas coloured	12.35	12.5
$NH_4[Co(NO_2)_4(hta)(py)]$	480.03	71.10	rhombic plates macrocrystals, pink coloured	12.27	12.38
$Ag[Co(NO_2)_4(hta)(NH_3)]$	507.83	*	plates microcrystals, dark-yellow coloured	11.60	11.32
$Hg_2[Co(NO_2)_4(hta)(NH_3)]_2$	1201.04	*	plates microcrystals, reddish coloured	4.91	5.18
$Tl[Co(NO_2)_4(hta)(NH_3)]$	604.3	*	plates microcrystals, dark-yellow coloured	9.75	9.60
$(NH_4)_2[Co(NO_2)_4(hta)(CN)]$	444.93	64.50	irregular plates microcrystals, red-brick coloured	13.24	13.11
$[Cu(NH_3)_4]A_2$	931.41	*	plates microcrystals, greenish coloured	6.33	5.98
$[Zn(NH_3)_4]A_2$	933.23	*	plates microcrystals, yellow-golden coloured	6.31	6.14
$[Co^{III}(NH_3)_4(CO_3)]A$	586.86	*	plates macrocrystals, brown coloured	10.04	10.41
$[Co^{III}(NH_3)_4(C_2O_4)]A$	702.86	*	plates macrocrystals, chocolate coloured	8.38	8.02

*- total precipitating; $A=[Co(NO_2)_4(hta)(NH_3)]$

The latter compounds are hardly soluble and they have different colours due to the presence of the second complexed metal which could be used as a microelement for fertilizing plants.

CONCLUSIONS

The Erdmann complex presents properties of fertilizing plants because it contains both nitrogen under different forms and Co(III) as a microelement. But this combination has many disadvantages for use. Among them we mention: decomposing under action of light and unstable character in water solution.

The analogue obtained by us, $NH_4[Co(NO_2)_4(hta)_2]$, eliminates these disadvantages because *hta* is tied more strongly to Co(III) and has a higher stability. The paper presents the way for obtaining and studying the composition and structure of the above mentioned analogue and a number of other derivatives. The general formula of the complex ion is $[Co(NO_2)_4(hta)X]^-$ and its charge is neutralized by monovalent metallic cations or complex ions.

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