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Contribution to Co(III) nitro complexes chemistry. New analogues of $NH_4[Co(NO_2)_4(NH_3)_2]$ complex with hexamethylenetetramine

Research article

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Abstract
The article presents experimental data about new analogues of ammonium tetra nitro-di amine Co(III) complex (Erdmann complex) with hexamethylenetetramine (hta).The base complex $NH_4[Co(NO_2)_4(hta)_2]$, as well as the Erdmann complex analogues present practical importance for agriculture and their efficiency as fertilizers was demonstrated. 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 cations. Some of these complexes are soluble in water, others are hardly soluble and no hygroscopic.

Keywords: Co (III), nitrocomplexes, hehamethylenetetramine, micronutrients

1. INTRODUCTION

In recent years, numerous applications of the cobalt complex, which is synthesized by the complexation reaction of a cobalt salt with an ethylenediamine ligand, have been developed. These types of complexes containing nitrogen and oxygen in the structure have gained a lot of interest for usage in a wide range of practical applications because of their benefits of being easily synthesized, having stable chemical characteristics, and having good endurance.

There are a wide range of complexes of nitro amine [1-3] as tetra nitro-diamine ammonium Co(III) complex, a compound which was obtained for the first time by Erdmann [2]. This complex is used as a fertilizer because it contains nitrogen and an element that can be a micronutrient. It has, however some disadvantages, and for this reason we have extended the study of the Co(III) nitro complexes series with fertilizing action to new nitro complexes with the general formula $(NH_4)_{3-n}[Co(NO_2)_{6-n}(N_4C_6H_{12})_n]$, where $N_4C_6H_{12}$ in hexamethylenetetramine, noted hta [2,3] and n has the values of 2 or 3. These complexes are microcrystalline substances, partially soluble in water, with red or yellow-orange color. 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 complexes with or without nitrogen and also be replacing NH_4^+ with other simple complex ions.

2. MATERIALS AND METHODS

2.1. Materials

The procedure of preparing nitro complexes 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 stoichiometric ratios. The reaction took place in excess of NH_4Cl and the oxidation of the reaction mixture is done by bubbling air 1.5 to 2 hours at room temperature. The product is obtained by crystallization for 12-24 hours [4-6].

2.2. Analysis methods

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

The Erdmann analogue preparation was done as follows. A sample of 91.5 g $CoCl_2 \cdot 6H_2O$ (0,4 mols) was dissolved in 200 mL distilled water which is the first solution and 100 g NH_4Cl (1.6 mols), $NaNO_2$ (2 mols) and 112 g $N_4C_6H_{12}$ (0.8 mols), in 1050 mL distilled water is the second solution. The two solutions were mixed and a clear red with purple blue solution was obtained. The oxidation of the reaction mixture was done 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 nitrocomplexe was dissolved in warm water in order to recrystallize and there was no danger of hydrolysing. In the case of Erdmann's salt recrystallization was done from a 1 M 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^oC) and it decomposes at 175^0C.

2.2.2. The pentanitro and trinitrocomplexes preparation with $N_3C_6H_{12}$

Modifying the stoichiometric ratio between components (increasing $NaNO_3$ quantity and reducing the $N_4C_6H_{12}$ quantity) we obtained the pentanitrocomplexe with the formula $(NH_4)_2[Co(NO_2)_5(hta)]$. It presented bright lamellae with yellow-reddish colour, a little different from the one of tetranitro complex. 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. Cobalt was

determined by complexometric titration using 0.01M complexon III reagent and murexide as indicator.

The measurement of NH_4^+ ion was done spectrophotometric (λ=410 nm) using Nessler reagent and the total nitrogen was determined using the micro-Kejdahl method. The difference between the total nitrogen and the ammoniacal nitrogen represents the NO_2^- groups and complexed hta molecules. In 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

3. RESULTS AND DISCUSSION

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 synthetised.

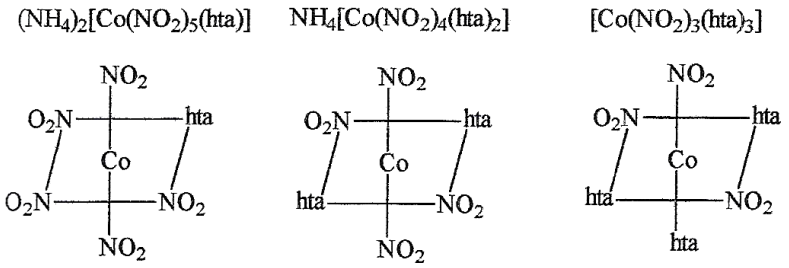

Figure 1. Structure and composition of formed nitrocomplexes

The $NH_4[Co(NO_2)_4(hta)_2]$ complexe is an Erdmann analogue as well as all the derivatives resulting from partial or substitution of hta groups. 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 stoichiometric reaction) and NH_3 in small exces. 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 noneelectrolyte $[Co(NO_2)_4(hta)_2]$ is formed in a small quantity.It need 2-3 days for crystallizing after filtering.Crystalls with bright red lamellae are obtained.The chemical and physical-chemical studies confirm the $NH_4[Co(NO_2)_4(hta)_2]$ complex composition and structure.The fact that Erdmann salt does not appear even in traces (it can be seen with naked eye), because it has dark-brown prismatic crystalls, proves that act as a ligand a higher affinity for cobalt than for NH_3.

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 complexe ion is $[Co(NO_2)_4(hta)X]^-$ where X is the ligand which is introduced by synthesis.

Table 2 presents examples of such derivatives, which are considered Erdmann's analogues which are obtained by replacing the NH_4^+cation with metallic cations such as Ag^+, Hg_2^{2}.They are obtained by a simple precipitation of $[Co(NO_2)_4(hta)_2X]^-$ion with metal salts or with ammonia complex cations or derivatives[7-9].

Tabel 2. New analogues of $NH_4[Co(NO_2)_4(hta)_2]$

No	Complex compound	Molecular Weight calc.	Yield %	Appearance	Analysis Co(III)	
					Calculated	Found
I	II	III	IV	V	VI	VII
1	$NH_4[Co(NO_2)_4(hta)_2SCN]$	476.73	68.20	Irregular plates Microcrystals Pink-lilas coloured	12.35	12.5
2	$NH_4[Co(NO_2)_4]_2(hta)(py)]$	480.03	71.10	Rhombic plates Microcrystals Pink coloured	12.27	12.38
3	$Ag[Co(NO_2)_4(hta)_2(NH_3)]$	507.83	•	Plates microcrystals Dark-yellow coloured	11.60	11.32
4	$Hg[Co(NO_2)_4(hta)(NH_3]_2$	1201.04	•	Plates microcrystal redish coloured	4.91	5.18
5	$Tl[Co(NO_2)_4(hta)(NH_3)]$	604.3	•	Plates microcrystal Dark-yelow coloured	9.75	9.60
6	$(NH_3)_2[Co(NO_2)_4(hta)(NH_3)]$	444.93	64.50	Irregular plates Microcrystals , red-brick coloured	13.24	13.11
7	$[Cu(NH_3)_4]A_2$	931.41	•	Plates microcrystals Greenish coloured	6.33	5.98
8	$[Zn(NH_3)_4]A_2$	933.23	•	Plates microcrystals Yellow-golden coloured	6.31	6.14
9	$[Co(NH_3)_4CO_3]A$	586,86	•	Plates microcrystals Brown coloured	10.04	10.41
10	$[Co(NH_3)_4C_2O_4]A$	702.86	•	Plates microcrystals Chocolate coloured	8.38	8.02

where: $A=[Co(NO_2)_4(hta)(NH_3)]$ and the symbol „•” is for total precipitating of complexe.

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 [10,11].

4. CONCLUSION

The Erdmann complexe presents properties of fertilizing for plants because it contains both nitrogen under different forms and Co(III) as a microelement. But this combination has many disadvantages for use.Amog 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 article presents the way for obtaining and studying the composition and structure of the above mentioned analogue and a number of other derivatives.

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