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Abstract

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ON THE REACTION OF SODIUM HEXANITROCOBALTATE WITH PYRIDINE

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It is known that, when ammonia acts on a solution of $Na_3[Co(NO_2)_6]$, depending on the reaction conditions, both tetranitrodiammine and trinitrotriammine of the fac configuration may be isolated, since the nitro groups at the coordinates NO_2—Co—NO_2 are labilized owing to their large trans effect. It seemed highly probable that, when pyridine acts on $Na_3[Co(NO_2)_6]$, a dipyridine compound $[CoPy_2(NO_2)_4]^-$ and a tripyridine compound $[CoPy_3(NO_2)_3]$ could likewise be formed. Up to now only one compound of the tripyridine type has been known: $[CoPy_3Cl(NCS)_2]$, obtained by us ([1]).

In the present work an attempt was made to obtain new nitropyridine complex compounds of Co(III). When anhydrous pyridine is allowed to act on solid $Na_3[Co(NO_2)_6] \cdot 1/2H_2O$, even at room temperature, $[CoPy_3(NO_2)_3]$ is slowly formed over the course of 2–3 months.

On heating (2 g of $Na_3[Co(NO_2)_6] \cdot 1/2H_2O$ with 10 ml of anhydrous pyridine, taken in excess to dissolve the salt formed) at 50–60°, the solution gradually turns yellow and, after three hours, almost all the hexanitrite passes into solution. From the dark brown-orange filtered solution, on cooling, orange crystals of $CoPy_6(NO_2)_2$ precipitate; in air they rapidly lose pyridine. After separation of these crystals and evaporation of the mother liquor in the cold, cherry-red cubic, lustrous crystals precipitate. Analysis of these crystals, washed with methyl alcohol and ether and dried in air, established the following composition:

Found, %: Co 13.56; 13.65; N 19.17; 19.09; C 41.44; 41.35; H 3.62; 3.56.
$[CoPy_3(NO_2)_3]$. Calculated, %: Co 13.58; N 19.35; C 41.50; H 3.45.

The yield of $[CoPy_3(NO_2)_3]$ when the reaction is carried out at a higher temperature (70–75°) is markedly decreased because of reduction of Co(III) and formation of $CoPy_6(NO_2)_2$.

Crystals of $[CoPy_3(NO_2)_3]$ are insoluble in water, alcohol, and acetone. Their density is $D^{20} = 1.68$. The refractive indices are $N_g = 1.754$, $N_m = 1.720$, $N_p = 1.704$. The crystals melt with decomposition at 134–135°. Measurement of magnetic susceptibility showed that the substance is very weakly paramagnetic ($\chi_g \cdot 10^6 \simeq +0.1;\ +0.2$), which is in all probability explained by the presence of small impurities of Co(II). According to conductometric data in nitrobenzene, the compound behaves as a nonelectrolyte ($t = 25°$, $V = 5000$ l/mol, $\mu = 1.6\ \Omega^{-1} \cdot \text{cm}^2$).

The absorption spectrum of a solution of the complex in chloroform shows a maximum at 358 mμ.

Determination of the molecular weight in camphor bromide by the method of A. V. Babaeva and L. V. Gorshkova (^{2}) gave somewhat low results (Table 1), which may possibly be explained by partial reduction of the compound on melting in camphor bromide (m.p. of camphor bromide 76.5°; $K = 11.87$).

The theoretically calculated molecular weight is 434.25.

Hydrochloric acid at room temperature slowly reacts with $[\text{CoPy}_3(\text{NO}_2)_3]$, giving a green solution. The solution then becomes blue (reduction to Co(II)). Apparently this should be explained by the instability of the complex containing chlorine or water instead of nitro groups.

According to the method of preparation, $[\text{CoPy}_3(\text{NO}_2)_3]$ should have an inner-sphere structure. This is also confirmed by the fact that, on interaction with a solution of potassium nitrite on heating, $[\text{CoPy}_3(\text{NO}_2)_3]$ is converted into $K_3[\text{Co}(\text{NO}_2)_6]$, while 12% ammonia on heating converts $[\text{CoPy}_3(\text{NO}_2)_3]$ into the inner-sphere $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$.

Table 1

Weighed amount of bromoform, g	Weighed amount of substance, g	Observed ΔT, °C	Found mol. wt.
0.1437	0.0114	2.5	377
0.1301	0.0086	2.3	343
0.1248	0.0101	2.6	369

In aqueous solution the reaction between pyridine and $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ proceeds differently. When an aqueous solution of $\text{Na}_3[\text{Co}(\text{NO}_2)_6] \cdot \frac{1}{2}\text{H}_2\text{O}$ (1.3 g in 4-6 ml H_2O) is mixed with 0.8 g of pyridine (3 moles of pyridine per 1 mole of salt), a resinous suspension is formed, which after some time crystallizes. The crystalline precipitate is filtered off the next day, washed with a large amount of water, and dried over concentrated sulfuric acid. Found (%): Co 18.00, 18.05; N 18.00, 17.87; N_{NO2} 8.61, 8.71; C 36.78, 36.57; H 4.35, 3.88; H_2O 3.67, 3.81. Ratio of atoms in the molecule
$\text{Co} : \text{N} : \text{N}_{\text{NO2}} : \text{C} : \text{H} : \text{H}_2\text{O} = 1 : 4.2 : 2 : 9.7 : 13 : 0.7$.

A substance of the same composition is also obtained with other ratios of pyridine and hexanitrocobaltate. The compound is a microcrystalline brick-red powder, insoluble in water, poorly soluble in alcohol, and better soluble in acetone and chloroform. From a chloroform solution, after evaporation of the solvent in air, a transparent film is formed.

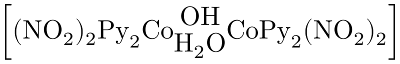
The compound melts with decomposition at 94-96°. According to measurements by V. I. Belova it is weakly paramagnetic ($\chi_g \cdot 10^6 = +2.00; +2.09; \mu_{\text{eff}} = 1.28$). This supports the view that the compound apparently represents a combination of compounds of divalent and trivalent cobalt. Measurement of the electrical conductivity in methyl alcohol showed that it is a nonelectrolyte ($V = 1000$ l/mol, $t = 25°$).

τ, min.	10	40	60	90	120	180	240
μ, $\text{ohm}^{-1} \cdot \text{cm}^2$	16.2	19.5	21.2	23.1	25.1	26.7	27.9

On treatment of this compound with conc. HCl, a brown powdery precipitate and a greenish-blue solution are formed. With time the precipitate passes entirely into a blue solution, from which crystals of $(PyH)_2[CoCl_4]$ separate on evaporation. Thus the result of the action of hydrochloric acid is analogous to the result of the action of $[CoPy_3(NO_2)_3]$.

If the compound is dissolved in ammonia under a nitrogen atmosphere (to prevent oxidation), the solution is neutralized with HCl, and then potassium rhodanide and pyridine are added, crystals of $CoPy_4(NCS)_2$ precipitate in small amount, which confirms the presence of divalent cobalt in the compound.

On the basis of all that has been said, it may be assumed that the product of the reaction of hexanitrite with pyridine in aqueous solution is or binuclear



$$\left[(NO_2)_2Py_2Co\underset{H_2O}{\overset{OH}{}}CoPy_2(NO_2)_2\right]$$

or a supercomplex compound $[CoPy_2(NO_2)][CoPy_2(NO_2)_2H_2OOH]$, for which the following was calculated (in %): Co 18.05; N 17.15; N_{NO2} 8.58; C 36.88; H 3.54; H_2O 4.12 (provided that, according to Elishuru, OH can be determined as $^1/_2H_2O$).

It was not possible to determine the molecular weight in nitrobenzene, since on freezing the solution the compound underwent some change (the freezing temperature of the solution decreased more and more with each freezing).

To study this phenomenon, 1 g of the compound was dissolved in 5-7 ml of nitrobenzene and the solution was frozen several times. After several days (up to 10), small reddish crystals separated from the solution; these were filtered off and washed with nitrobenzene and ether. The compound exhibited strong paramagnetism and, consequently, was a Co(II) complex.

The crystals were recrystallized from CH_3OH and analyzed:

$$CoPy_2(NO_3)_2 \cdot 2H_2O \quad (3).$$

Found, %: Co 15.69; 15.67; N 14.30; 14.83; H_2O 10.12
Calculated, %: Co 15.62; N 14.85; H_2O 9.55

Thus, in the present case, oxidation of the nitro group bound in the complex to a nitrato group occurred in nitrobenzene. The oxidizing agent in this process may be nitrobenzene, being reduced to azoxybenzene. But the Co(III) compound may prove to be an accelerator of this reaction. To clarify the latter question, the dinitrodipyridine compounds of Co(II) described in the literature were prepared. According to measurements by V. I. Belova, all of them are strongly paramagnetic.

$$\begin{aligned} Co(NO_2)_2 \cdot 2Py \quad &(4) \quad \chi_r \cdot 10^6 = +17.8; \\ Co(NO_2)_2 \cdot 2Py \cdot 2H_2O \quad &(5) \quad \mu_{\text{eff}} = 4.39,\ 4.14; \\ Co(NO_2)_2 \cdot 2Py \cdot H_2O \quad &(5) \quad \mu_{\text{eff}} = 3.80,\ 3.69. \end{aligned}$$

These compounds are decomposed by water; in nitrobenzene no visible changes occur when their solutions are frozen, but on prolonged standing of a solution of $Co(NO_2)_2 \cdot 2Py \cdot 2H_2O$ in nitrobenzene, the separation of a small amount of crystals of $CoPy_2(NO_3)_2 \cdot 2H_2O$ is observed. If, however, a little $[CoPy_3(NO_2)_3]$ and 1-2 drops of water are added to a solution of $CoPy_2(NO_2)_2$ in nitrobenzene, then after several days crystals of $CoPy_2(NO_3)_2 \cdot 2H_2O$ separate in appreciable quantity. This fact confirms the supposition that the substance obtained by the interaction of $Na_3[Co(NO_2)_6] \cdot {}^1/_2H_2O$ with pyridine in aqueous solution contains both Co(II) and Co(III).

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