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Fig. 1. Light-absorption curves: a– 1,6-$[Co(DH)_2(H_2O)(H_2NC_6H_5)]NO_3 \cdot 2H_2O$ ($C = 0.001$ mol); b– 1,6-$[Co(DH)_2(H_2NC_6H_5)_2]NO_3 \cdot 2H_2O$, from ([6]).

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Abstract

Full Text

Chemistry

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Co(III) Dioximes Containing in the Inner Sphere a Molecule of Water and a Molecule of Ammonia or an Organic Amine

Complex Co(III) cations with dimethylglyoxime and ammonia or organic amines of the type $[Co(DH)_2A_2]^+$ were described by L. A. Chugaev as early as 1905 ([1]). As has now been shown, they have a trans configuration ([2,3]). Comparatively recently A. V. Ablov, M. P. Filippov, and N. M. Samus' synthesized salts of trans-bis-dimethylglyoximatodiaquocobalt $[Co(DH)_2 \cdot (H_2O)_2]X$ ([4]).

In the present communication we describe cobalt(III) dioximes containing in the inner sphere one molecule of water and one molecule of ammonia or an organic amine, of the general formula $[Co(DH)_2(H_2O)A]NO_3$. To obtain them, an exactly calculated amount of amine is added to a cooled aqueous solution of trans-bis-dimethylglyoximatodiaquocobalt nitrate. In the case of aniline, for example, brown crystals of $[Co(DH)_2(H_2O)(H_2NC_6H_5)]NO_3 \cdot 2H_2O$ separated. In aqueous solution this salt behaves as a binary electrolyte and shows an acidic reaction, but it is a weaker acid than the salts of trans-bis-dimethylglyoximatodiaquocobalt. The absorption curve of a dilute aqueous solution has two absorption bands (Fig. 1). The first band in the region of 350 nm is due to the coordinated aromatic amine; the second band at $\lambda = 250$ nm is characteristic of the planar $Co(DH)_2$ grouping ([5]).

Fig. 1. Light-absorption curves: a–1,6-$[Co(DH)_2(H_2O)(H_2NC_6H_5)]NO_3 \cdot 2H_2O$ ($C = 0.001$ mol); b–1,6-$[Co(DH)_2(H_2NC_6H_5)_2]NO_3 \cdot 2H_2O$, from ([6]).

When an excess of aniline acts on the nitrate obtained by us, a substance is

formed which, in crystal form and color, resembles bis-dimethylglyoximatodianilinecobalt nitrate
$[Co(DH)_2(H_2NC_6H_5)_2]NO_3 \cdot 2H_2O$ ([6]).

The nature of this compound was confirmed by recording the light-absorption curve ([5]) and by converting it, under the action of alkali, into the characteristic base
$[Co(D_2H)(H_2NC_6H_5)_2] \cdot 3H_2O$ ([7]).

On addition of one mole of hydrochloric acid to a concentrated aqueous solution of the salt obtained by us, a microcrystalline brown precipitate, sparingly soluble in water, immediately separates. In all its properties this compound is the nonelectrolyte
$[CoCl(DH)(H_2NC_6H_5)] \cdot 2H_2O$ ([8]). Similarly, on addition of one mole of hydrobromic or hydroiodic acid, the nonelectrolytes
$[CoBr(DH)_2(H_2NC_6H_5)] \cdot 2H_2O$ and $[CoI(DH)_2(H_2NC_6H_5)] \cdot \frac{1}{2}H_2O$ precipitated ([8]).

Since the dianilino and monoanilino dioximes $[Co(DH)_2(H_2NC_6H_5)_2]^+$ and $[CoHal(DH)_2(H_2NC_6H_5)]$, into which the aquoanilino complex is readily converted, have a trans configuration ([9]), the original cation must have the same structure. Therefore the reaction

trans-$[Co(DH)_2(H_2O)_2]^+ + H_2NC_6H_5 = [Co(DH)_2(H_2NC_6H_5)(H_2O)]^+ + H_2O$ is not accompanied by a change in spatial configuration.

By the method described above, cations of the type $[Co(DH)_2(H_2O)A]^+$ were synthesized with amines: aniline, *o*-, *m*-, and *p*-toluidines, *p*-anisidine, pyridine, and β-picoline.

To obtain the aquoammine dioxime, to a solution of trans-$[Co(DH)_2(H_2O)_2]NO_3 \cdot H_2O$ a calculated amount of ammonium acetate was added. Under these conditions there is no excess ammonia in the solution, and therefore the cation $[Co(DH)_2(NH_3)_2]^+$ is not formed.

Experimental Part

Nitrate of trans-bis-dimethylglyoximatoaquoanilinecobalt(III). $(Co \cdot (DH)_2(H_2O)(H_2NC_6H_5))NO_3 \cdot 2H_2O$.

To 2.0 g of trans-$[Co(DH)_2(H_2O)_2]NO_3 \cdot H_2O$ [(4)] 30 ml of water were added, the mixture was cooled to 5–10°, and a solution of 0.4 ml (5 mmoles) of aniline in 20 ml of alcohol was carefully poured in. From the filtered solution, after some time, a brown precipitate separates, which under the microscope has the appearance of rectangular plates. The substance is readily soluble in water and in alcohol, less readily in ether. Yield 70% of theory. The nitrate obtained was dissolved in water at 10° and precipitated with sodium nitrate. For analysis, the air-dried substance was taken.

Found, %: Co 11.86; 11.88; N 16.63; 16.70; C 33.61; 33.54; H 5.23; 5.31; H_2O 7.30

$CoC_{14}H_{23}N_6O_8 \cdot 2H_2O$. Calculated, %: Co 11.82; N 16.87; C 33.73; H 5.46; H_2O 7.23

The substance may also be obtained in the following manner. 1.7 g (5 mmoles) of trans-hydroxo-bis-dimethylglyoximatoaquocobalt $[Co(OH)(DH)_2 \cdot (H_2O)]$ [4,10] was covered with 30 ml of water cooled to 5–10°, and 0.4 ml (5 mmoles) of aniline dissolved in 20 ml of ethanol was added, after which the hydroxoaquo compound rapidly dissolves. To the filtered solution, a calculated amount of concentrated nitric acid was added dropwise. A brown precipitate separated, which was transferred to a filter and washed with cold water, a small amount of alcohol, and finally with ether.

Found, %: Co 11.90; N 16.65

$CoC_{14}H_{23}N_6O_8 \cdot 2H_2O$. Calculated, %: Co 11.82; N 16.87

Below are given the electrical conductivity and pH of solutions of nitrate of bis-dimethylglyoximatoaquoanilinecobalt:

V, l • mole^{-1}	μ, ohm^{-1} • l • cm^{-2}	pH
250	100.1	5.00
500	102.2	5.10
1000	106.4	5.22

Nitrate of bis-dimethylglyoximatoaquo (*p*-toluidine)cobalt(III) $[Co(DH)_2(H_2O)(H_2NC_6H_4(CH_3))]NO_3$.

The substance was obtained analogously to the preceding one, with a yield of 80% of theory. Under the microscope it has the appearance of yellow plates.

Found, %: Co 12.37; 12.39; N 17.34; 17.40

$CoC_{15}H_{25}N_6O_8$. Calculated, %: Co 12.36; N 17.65

Nitrate of bis-dimethylglyoximatoaquo (*m*-toluidine)cobalt(III) $[Co(DH)_2(H_2O)(H_2NC_6H_4(CH_3))]NO_3$.

Under the microscope it has the appearance of long thin needles.

Found, %: Co 12.24; 12.30; N 17.66; 17.58

$CoC_{15}H_{25}N_6O_8$. Calculated, %: Co 12.36; N 17.65

Bis-dimethylglyoximatoaquo(o-toluidine)cobalt(III) nitrate $[Co(DH)_2(H_2O)(H_2NC_6H_4CH_3)]NO_3$.

A light-yellow substance; under the microscope it has the appearance of long rectangular plates.

$CoC_{15}H_{25}N_6O_8$.	Found, %:	Co 12.33; 12.30; N 17.55; 17.48
	Calculated, %:	Co 12.36; N 17.65

Bis-dimethylglyoximatoaquo(*p*-anisidine)cobalt(III) nitrate $[Co(DH)_2(H_2O)(H_2NC_6H_4OCH_3)]NO_3 \cdot 2H_2O$.

A reddish substance. Under the microscope it has the appearance of square plates.

$CoC_{15}H_{25}N_6O_9 \cdot 2H_2O$.	Found, %:	Co 11.27; 11.20; N 15.78; 15.75; H_2O 6.95
	Calculated, %:	Co 11.16; N 16.92; H_2O 6.82

Bis-dimethylglyoximatoaquopyridinecobalt(III) nitrate $[Co(DH)_2(H_2O)Py]NO_3$.

A light-brown substance, which under the microscope has the appearance of long prisms.

$CoC_{13}H_{21}N_6O_8$.	Found, %:	Co 13.02; 13.10; N 18.88; 18.90; C 34.96; 35.00 H 4.79; 4.79
	Calculated, %:	Co 13.14; N 18.75; C 34.81; H 4.72

Bis-dimethylglyoximatoaquo(*β*-picoline)cobalt(III) nitrate $[Co(DH)_2(H_2O)(C_5H_4NCH_3)]NO_3$.

Under the microscope it has the appearance of yellow long prisms.

$CoC_{14}H_{23}N_6O_8$.	Found, %:	Co 12.74; 12.78; N 18.06; 17.75
	Calculated, %:	Co 12.75; N 18.19

Bis-dimethylglyoximatoaquoamminecobalt(III) nitrate $[Co(DH)_2(H_2O)(NH_3)]NO_3$.

2.0 g (5 mmoles) of $[Co(DH)_2(H_2O)_2]NO_3 \cdot H_2O$ was dissolved in 30 ml of water cooled to 5–10°; to the filtered solution, 0.35 g (5 mmoles) of ammonium acetate was added. On standing, and more rapidly upon addition of alcohol, brown crystals separated from the solution; under the microscope they have the appearance of squares. The substance is readily soluble in water, somewhat less so in alcohol and ether.

$CoC_8H_{19}N_6O_8$.	Found, %:	Co 15.30; 15.31; N 21.80; 21.78
	Calculated, %:	Co 15.26; N 21.77;

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Note: Figure translations are in progress. See original paper for figures.