

COORDINATION  
COMPOUNDS

## New Cobalt(II) Complexes with Cyanuric Acid

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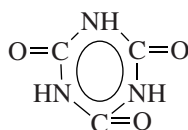
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**Abstract**—New cobalt(II) complexes with cyanuric acid  $C_3H_3N_3O_3$  (L), namely,  $[CoL_2(OH_2)_2]Cl_2 \cdot 4H_2O$ ,  $[CoL_2(OH_2)_2]SO_4 \cdot 3H_2O$ , and  $[CoL_2(OH_2)_2](NO_3)_2$ , were synthesized. The IR absorption spectra ( $400\text{--}4000\text{ cm}^{-1}$ ) of these compounds and the initial ligand, their X-ray diffraction patterns, thermograms, and thermogravigrams were examined. The electric conductivity of their aqueous and methanolic solutions was studied. The individual character of the synthesized complexes was proved. The coordination mode of the acido groups was determined.

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Compounds containing carbamide derivatives as ligands, which are biologically active and, as a rule, lowly toxic [1] neutral molecules, have been poorly studied. The search for new coordination compounds of microelements with carbamide derivatives is very urgent. Similar complexes are promising as microfertilizers and can be used as mineral additional forage for animals [2, 3] and drugs for the treatment of atherosclerosis, anemia, eczema, diabetes, and other diseases [4, 5]. They are also used as pesticides [6, 7], pigments [8], epoxide resin additives [9–11], etc. The number of such transition metal complexes described to date is small [12–14].

As a result of the studies performed, we developed procedures for the synthesis of new cobalt(II) complexes with cyanuric acid as a neutral ligand. The following new coordination compounds were obtained:  $[CoL_2(OH_2)_2]Cl_2 \cdot 4H_2O$ ,  $[CoL_2(OH_2)_2]SO_4 \cdot 3H_2O$ , and  $[CoL_2(OH_2)_2](NO_3)_2$  (L is cyanuric acid  $C_3H_3N_3O_3$ ).



Cyanuric acid

The properties of these complexes, their IR absorption spectra ( $400\text{--}4000\text{ cm}^{-1}$ ), and specific features of their thermal decomposition were characterized.

To determine the composition of the synthesized compounds, they were analyzed for cobalt by the trilonometric method [15], for sulfur by gravimetry (in the form of barium sulfate), for carbon chloride and hydrogen by the micromethod [16], and for nitrogen by the Dumas method [17].

The starting cobalt(II) salts (analytical grade) and cyanuric acid (L) were purified by recrystallization.

**Synthesis of  $[CoL_2(OH_2)_2]Cl_2 \cdot 4H_2O$  (1).** Hot aqueous solutions of  $CoCl_2 \cdot 6H_2O$  (2 g) and cyanuric acid (2.17 g) (molar ratio  $Co^{II} : L = 1 : 2$ ) acidified with hydrochloric acid (pH  $\sim 3$ ) were poured together. The resulting solution was placed in a vacuum desiccator over anhydrous  $CaCl_2$  and left at room temperature. Slow evaporation of the solvent for several days resulted in the precipitation of transparent pinkish needle crystals. They were filtered off; rapidly washed with cold distilled water acidified with hydrochloric acid (pH  $\sim 3$ ), acetone, and ether; and dried in a vacuum desiccator over anhydrous  $CaCl_2$ .

For compound **1** anal. calcd. (%): Co, 11.87; C, 14.52; Cl, 14.31; H, 3.58; N, 16.83;  $H_2O$ , 21.73.

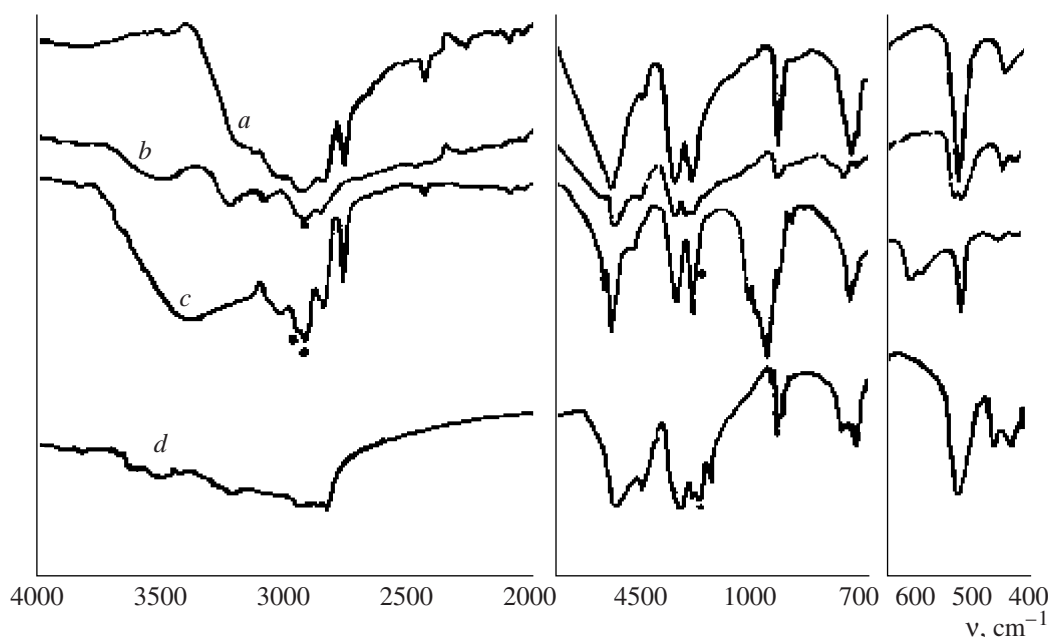
Found (%): Co, 11.81; C, 14.32; Cl, 14.12; H, 3.42; N, 17.21;  $H_2O$ , 22.11.

The crystals of **1** are stable in air; nonhygroscopic; readily soluble in hot water, methanol, and ethanol; poorly soluble in  $CCl_4$ ; insoluble in organic solvents, such as chloroform, benzene, toluene, acetone, ether, and hexane, indicating the polymeric structure of compound **1**.

On heating compound **1** to  $\sim 120\text{--}180^\circ C$ , hydration water and water of crystallization are lost, and the complex turns blue.

When an aqueous solution of silver nitrate is added to an aqueous solution of complex **1**, a silver chloride precipitate is formed, indicating that the  $Cl^-$  acido group is located in the outer sphere of the complex. This is also confirmed by IR spectral data and the results of measurements of the electric conductivity of a solution of complex **1**.

**Synthesis of  $[CoL_2(OH_2)_2]SO_4 \cdot 3H_2O$  (2).** Cobalt sulfate heptahydrate  $CoSO_4 \cdot 7H_2O$  (2 g) was dissolved in a minimum amount of hot distilled water. The solution was filtered off and acidified with sulfuric acid (to



**Fig. 1.** IR absorption spectra (in Nujol) of (a) cyanuric acid (L), (b)  $\text{CoL}_2\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ , (c)  $\text{CoL}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ , and (d)  $\text{CoL}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ .

pH ~ 4) in order to prevent cobalt(II) oxidation to cobalt(III). A hot aqueous solution containing cyanuric acid (1.84 g) (molar ratio  $\text{Co}^{\text{II}} : \text{L} = 1 : 2$ ) was added. The resulting solution was placed in a vacuum desiccator over anhydrous  $\text{CaCl}_2$  and left at room temperature. Upon slow evaporation of the solvent, reddish crystals precipitated within several days. The crystals were filtered off; rapidly washed with cold distilled water, acetone, alcohol, and ether; and dried in a vacuum desiccator over anhydrous  $\text{CaCl}_2$ .

For compound **2** anal. calcd. (%): Co, 11.72; C, 14.31; H, 3.18; N, 16.70; S, 6.36;  $\text{H}_2\text{O}$ , 17.89.

Found (%): Co, 11.12; C, 13.97; H, 3.02; N, 16.51; S, 6.35;  $\text{H}_2\text{O}$ , 18.

The resulting crystals are nonhygroscopic; readily soluble in hot water; poorly soluble in cold water, methanol, and ethanol; and insoluble in common organic solvents.

When a solution of barium chloride is added to an aqueous solution of complex **2**, a barium chloride precipitate is formed immediately (analytical reaction to the  $\text{SO}_4^{2-}$  ion), indicating that the  $\text{SO}_4^{2-}$  acido groups are located in the outer sphere of the complex.

Upon heating to ~120–210°C, compound **2** loses its hydration water and water of crystallization (the weight loss is ~18%, calcd. 17.89%  $\text{H}_2\text{O}$ ). The compound decomposes on heating to ~250°C.

**Synthesis of  $[\text{CoL}_2(\text{OH}_2)_2](\text{NO}_3)_2$  (**3**).** Aqueous solutions of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (2 g) and the ligand (1.76 g) (molar ratio  $\text{Co}^{\text{II}} : \text{L} = 1 : 2$ ) acidified with nitric acid

(pH ~ 4) were poured together. The resulting solution (pH ~ 4) was placed in a vacuum desiccator over anhydrous  $\text{CaCl}_2$  and left at room temperature. Slow evaporation of the solution resulted in the deposition of transparent pink-reddish crystals. They were filtered off; rapidly washed with cold distilled water, acetone, alcohol, and ether; and dried in a vacuum desiccator over anhydrous  $\text{CaCl}_2$ .

For compound **3** anal. calcd. (%): Co, 12.38; C, 15.08; H, 2.08; N, 23.47;  $\text{H}_2\text{O}$ , 7.53.

Found (%): Co, 12.15; C, 14.92; H, 2.051; N, 23.51;  $\text{H}_2\text{O}$ , 7.42.

The obtained crystals are stable in air; nonhygroscopic; readily soluble in hot water; poorly soluble in cold water, methanol, and ethanol; and insoluble in common organic solvents.

On heating to ~180°C, the weight loss is 7.42% (calcd. 7.53%). It is most likely that the water molecules are located in the inner sphere of the complex. The complex decomposes at ~300°C.

When a solution of diphenylamine in concentrated sulfuric acid is added to an aqueous solution of complex **3**, the solution immediately turns bright blue (qualitative reaction to the nitrate ion). This indicates that the  $\text{NO}_3^-$  acido groups are located in the outer sphere of the complex.

The IR absorption spectra (400–4000  $\text{cm}^{-1}$ ) of the synthesized complexes (Fig. 1) were recorded on a UR-20 spectrophotometer, and the samples were prepared as Nujol and fluorinated oil mulls (KBr plates). For comparison we also recorded the IR spectrum of

**Table 1.** Selected vibrational frequencies ( $\text{cm}^{-1}$ ) in the IR spectra of cyanuric acid (L) and complexes **1–3**

Compound	$\nu(\text{NH})$	$\nu(\text{C}=\text{O})$	$\delta(\text{CNH})$	$\nu(\text{CN})$	$\nu_{\text{ac}}(\text{CN})$	$\delta(\text{CNC})$	Some other frequencies
L	~3170* ~3130 ~3025 ~2940	1738 1725	1480	1410	1063	540	
<b>1</b>	3223 3182 3101	1726 1710	1483	1411	1068 1071	536 552	465 $\delta(\text{H}_2\text{O})$ 1622 $\nu(\text{H}_2\text{O})$ 3476–3500
<b>2</b>	3180 3034 2940	1730	1480	1410	1068	540	$\delta(\text{SO}_4^{2-})$ 615, 633, 643 $\nu_s(\text{SO}_4^{2-})$ 1014 $\nu_{\text{as}}(\text{SO}_4^{2-})$ 1114, 1156, 1184 $\delta(\text{H}_2\text{O})$ 1648 462 $\nu(\text{H}_2\text{O})$ 3318, 3420
<b>3</b>	3180 3140 2970	1721	1482 1471	1418	1067 1091	544	430, 474 $\delta(\text{NO}_3^-)$ 823 $\nu(\text{NO}_3^-)$ 1350, 1040 $\nu(\text{NO}_3^-)$ 1490 $\delta(\text{H}_2\text{O})$ 1620 $\nu(\text{H}_2\text{O})$ 3500–3600*

\* Broad composite band.

the initial ligand, which coincided with the spectrum described earlier [18, 19].

The IR spectra of the synthesized complexes ( $\text{cm}^{-1}$ ): **1**: 406, 438, 465, 501, 536, 552, 700, 1068, 1071, 1411, 1428, 1483, 1622, 1710, 1726, ~3101, ~3182, 3223, ~3476–3500  $\nu(\text{H}_2\text{O})$ ; **2**: 462, 540, 615, 633, 643, 760, 781, 1014, 1068, 1114, 1156, 1184, 1410, 1480, ~1648, 1730, 1763, 2940, ~3034, 3180, ~3318  $\nu(\text{H}_2\text{O})$ , ~3420  $\nu(\text{H}_2\text{O})$ ; **3**: 430, 474, 544, 823, 1067, 1091, 1324, 1418, 1471, 1482, 1620, ~1721, 1793, 2970, 3180, 3140, ~3500–3600  $\nu(\text{H}_2\text{O})$ .

The assignment of selected vibrational frequencies for cyanuric acid and the cobalt(II) complexes with cyanuric acid is presented in Table 1. The frequencies were assigned on the basis of the interpretation of the vibrational frequencies of free (noncoordinated) cyanuric acid [12, 14, 21]. The vibrational frequencies of free cyanuric acid and the acid incorporated in compounds **1–3** are close, and the absorption band intensities differ slightly. Therefore, we can conclude that the state of cyanuric acid does not undergo significant changes upon the formation of the considered cobalt(II) compounds with cyanuric acid.

The  $\nu(\text{NH})$  frequencies of stretching vibrations of the NH bonds of cyanuric acid in the cobalt(II) complexes are somewhat shifted to higher values. Therefore, the nitrogen atoms of the NH groups are not directly linked to the cobalt atoms, because otherwise

the  $\nu(\text{NH})$  frequencies would decrease rather than increase.

On the contrary, the  $\nu(\text{C}=\text{O})$  frequencies of stretching vibrations of the C=O bonds (at least some of them) somewhat decrease upon the formation of compounds **1–3**. Therefore, it can be concluded that the cyanuric acid molecules are coordinated through the oxygen atoms. It is most likely that the cyanuric acid molecules act as bridging groups.

The molar electric conductivity of aqueous and methanolic solutions of the synthesized complexes at room temperature (dilution 1000 L/mol) was measured both immediately and one hour after their preparation. The following results were obtained (aqueous (methanolic) solution,  $\Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ ): for complex **1**, 214 and 224 (98 and 211); for complex **2**, 93 and 102; for complex **3**, 228 and 232 (86 and 209) (the first value was for the freshly prepared solution, and the second value was obtained one hour after preparation).

The electric conductivity of aqueous solutions of complex **2** corresponds to the values for 1 : 1 electrolytes, and those for complexes **1** and **3** correspond to the values for 1 : 2 electrolytes.

The electric conductivity of freshly prepared methanolic solutions of complexes **1** and **3** is virtually equal to that of the solvent; i.e., the complexes behave as non-electrolytes. The electric conductivity of the methan-

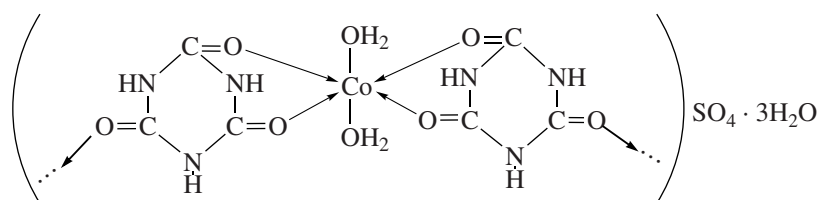


Fig. 2. Tentative structure of complex 2 (polymeric structure).

olic solutions increases with time and reaches the values characteristic of 1 : 2 electrolytes.

The electric conductivity of methanolic solutions of complex 2, both freshly prepared and stored for 2 h, is virtually equal to that of the solvent. This is due, most

Table 2. Relative intensities ( $I$ ) and interplanar distances ( $d$ ) in the structures of cyanuric acid (L) and complexes 1–3

L		1		2		3	
$I$	$d, \text{Å}$	$I$	$d, \text{Å}$	$I$	$d, \text{Å}$	$I$	$d, \text{Å}$
4	5.49	62	5.78	28	4.91	11	5.91
65	4.88	28	4.45	32	4.80	61	5.82
10	4.03	53	4.32	6	4.68	47	5.72
18	3.42	9	3.32	8	4.32	42	5.42
100	3.17	100	3.18	8	4.12	15	5.11
4	2.61	27	2.96	100	3.82	100	5.00
4	2.47	46	2.82	30	3.62	35	4.78
2	2.36	16	2.76	17	3.57	37	4.62
4	2.24	8	2.61	17	3.38	3	4.57
4	2.17	30	2.44	69	3.15	4	4.32
2	2.09	22	2.33	22	2.62	9	4.12
2	1.96	31	1.86	24	2.51	30	4.05
2	1.92	26	1.78	5	2.38	72	3.68
2	1.70	14	1.63	7	2.25	78	3.37
2	1.66	8	1.56	9	2.11	42	3.09
		7	1.50	13	1.95	10	2.98
		6	1.48	8	1.62	7	2.62
		6	1.42	9	1.30	7	2.41
		5	1.38	8	1.29	6	2.12
		4	1.32	9	1.28	5	1.95
		2	1.28	10	1.25	5	1.78
		2	1.25	5	1.21	4	1.62
				2	1.19	3	1.60
				2	1.18	2	1.55
				2	1.15	2	1.50

likely, to the strong electrostatic interaction between the  $\text{Co}^{2+}$  and  $\text{SO}_4^{2-}$  ions [22].

The results of measuring the electric conductivity indicate that the acido groups are located in the outer sphere of the complexes. Dissociation in aqueous solutions occurs more rapidly than in methanolic solutions, which is quite explainable: water molecules are more efficient electron donors than methanol molecules.

The results obtained for the electric conductivity of solutions of complexes 1–3 agree with published data on other Co(II) complexes and some other metal complexes [22].

For additional confirmation of the individual character of the synthesized complexes, we obtained the X-ray diffraction patterns for compounds 1–3 and compared them with the X-ray diffraction pattern of the initial ligand (Table 2). The line intensity was estimated visually on a hundred-point scale. The Co(II) complexes with cyanuric acid were confirmed to be individual compounds. The tentative structure of complex 2 is shown in Fig. 2.

## REFERENCES

1. A. I. Adbukhakov, *Proceedings of X Scientific Conference of Tashkent Pharmaceutical Institute* (Tashkent, 1960), p. 30 [in Russian].
2. A. Kel'dibekov, *Reports of the Department of Chemistry, Kirgiz Agriculture Institute, 1953–1960*, p. 47.
3. D. I. Petriichuk, K. D. Aleitov, and A. G. Sadykov, *Byul. Nauchno-Tekh. Inf. Kirg. Nauchno-Issled. Inst. Zhivotnovod. Vet.*, Nos. 7-8, 44 (1963).
4. I. Z. Kochergina, in *Collected Works of Tashkent Medical Institute* (Tashkent, 1969), p. 52 [in Russian].
5. Kh. Kurotani, *Jpn. Application No. 55-57553, 20.01.78*, no. 53-129885, publ. 28.01.80.
6. H. Damm and B. Glaser, *GDR Patent 143 198, 07.01.81*.
7. L. J. Pomot, E. Lusarreta, and R. Becaine, *GB Patent 907 800, 10.10.61*.
8. G. T. Esayan, S. M. Kazaryan, and M. B. Ordyan, *Arm. Khim. Zh.* **33** (4), 290 (1980).
9. E. L. Smith and R. Hall, *US Patent 3 626 022, 07.01.58 3 22* (6260).
10. M. B. Ordyan, L. G. Rashidyan, G. B. Aivazyanyan, et al., *Arm. Khim. Zh.* **31** (10), 763 (1978).
11. G. T. Esayan, A. A. Babayan, V. P. Kukolev, et al., *USSR Inventor's Certificate No. 363 731, Byull. Izobret.*, No. 4 (1973).

12. Yu. Ya. Kharitonov and L. N. Ambroladze, *Koord. Khim.* **8**, 1431 (1982).
13. B. Ya. Shtenberg, Yu. I. Mushkin, and A. I. Finkel'shtein, *Opt. Spektrosk.* **34** (5), 615 (1974).
14. Yu. Ya. Kharitonov and L. N. Ambroladze, *Zh. Neorg. Khim.* **28**, 1206 (1983).
15. V. A. Rodko and E. N. Yakimets, *Tr. Ural'sk. Politekhn. Inst.*, No. 96, 166 (1969).
16. V. F. Klimova, *Basic Micromethods of Analysis of Organic Compounds* (Khimiya, Moscow, 1975) [in Russian].
17. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, *Applied Inorganic Analysis: With Special Reference to the Analysis of Metals, Minerals, and Rocks*, (Wiley, New York, 1953; Goskhimizdat, Moscow, 1957).
18. M. Z. Branzburg, M. Z. Gurevich, N. F. Shugal, and N. M. Dyatlova, *Proceedings of III All-Union Chugaev Conference on Coordination Chemistry* (Ivanovo, 1981), Part 1, p. 225 [in Russian].
19. Ts. N. Roginskaya, A. I. Finkel'shtein, and A. K. Ermoloeva, *Zh. Prikl. Spektrosk.* **14** (4), 654 (1971).
20. A. V. Babaeva and Yan Vei-Da, *Zh. Neorg. Khim.* **5** (12), 2735 (1960).
21. Yu. Ya. Kharitonov and I. Z. Babaevskaya, *Dokl. Akad. Nauk SSSR* **168** (3), 615 (1966).
22. A. Bittner, D. Mannig, and H. Noth, *Z. Naturforsch.* **41** (5), 587 (1986).