Synthesis of molecular magnetics based on cobalt trisoxalate. Structural and magnetic properties of $NBu^n_4[Mn^{II}Co^{III}(C_2O_4)_3]$

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Bimetallic oxalate-bridged complexes $Q[M^{II}Co(C_2O_4)_3]$ ($Q = Me_4N^+$, $Bu^n_4N^+$, Ph_4P^+; M^{II} = Mn, Co, Ni, Cu, Zn) were synthesized. Single crystals of $[NBu^n_4][Mn^{II}Co^{III}(C_2O_4)_3]$ were studied by XRD. Unit cell parameters $a = b = 9.242(3)$ Å, $c = 54.524(13)$ Å; space group $R3c$. Magnetic measurements indicate the absence of a magnetic phase transition up to the temperature of liquid helium. The XRD data confirm the presence of Co^{III} ions with a low-spin configuration in the crystal.

Key words: synthesis, bimetallic oxalates, crystal and magnetic structure.

Development of spatially ordered (with respect to magnetic ions) high-dimensional structures is an important fundamental task. Polydentate ligands binding paramagnetic 3d-ions to form extended geometric structures play a specific role in the formation of these structures. Several compounds have been synthesized,[1,2] which compose a family of new metallocomplex ferromagnets with general formula $[NBu^n_4][M^{II}Cr^{III}(C_2O_4)_3]$, where M = Mn, Fe, Co, Ni, and Cu. Studies of these comp-ounds[3–6] have shown that they possess a layered structure and are two-dimensional ferromagnets by the character of their exchange interactions. A similar series of ferrimagnetic compounds based on $[MFe^{III}(C_2O_4)_3]^-$ (M = Mn, Fe, and Ni) has been synthesized and studied.[7–9] In this work, we synthesized and studied bimetallic complexes based on trisoxalatocobaltate(III) $Q[M^{II}Co(C_2O_4)_3]$, where $Q = Me_4N^+$, $Bu^n_4N^+$, and Ph_4P^+; M^{II} = Mn, Co, Ni, Cu, and Zn.

Experimental

The starting compound $K_3[Co(C_2O_4)_3] \cdot 3H_2O$ (**1**) was synthesized by the described method[10] using PbO_2 (analytical purity grade), glacial acetic acid (reagent grade), and $H_2C_2O_4 \cdot 2H_2O$ (reagent grade); $CoCO_3$ and $K_2C_2O_4 \cdot H_2O$ were prepared by the known procedures.[11] For synthesis of cobalt complexes, we used Bu^n_4NBr (Aldrich), Ph_4PBr (Fluka), methanol (reagent grade), $MnCl_2 \cdot 4H_2O$ (reagent grade), and $Co(NO_3)_2 \cdot 6H_2O$ (reagent grade); $CuCl_2 \cdot 2H_2O$ and $ZnCl_2 \cdot 1.5H_2O$ were obtained by the described procedures.[11]

Elemental analysis for C, H, N, and O was carried out as described previously.[12] The content of K, Co, and Mn was determined by atomic absorption spectroscopy on an AAS-3 instrument.

Synthesis of $Q[M^{II}Co(C_2O_4)_3]$ complexes. A mixture (20 mL) of aqueous solutions of the salt of a bivalent metal (2 mmol) and **1** (2 mmol) was stored for 2 h and filtered. A solution of the salt of an organic cation (2.2 mmol) was added to the filtrate: Bu^n_4NBr or Me_4NBr in 5 mL of water or Ph_4PBr in 5 mL of MeOH. The reaction mixture was stored for 5–8 h, the precipitate that formed was washed with ice-cold water or a $MeOH-H_2O$ mixture in a 1 : 2 ratio (for the systems with the tetraphenylphosphonium cation) and dried for 1 day *in vacuo* above P_2O_5. Data on the synthesis and element composition of the bimetallic cobalt trisoxalates synthesized are presented in Table 1.

X-ray diffraction analysis was carried out on a KM-4 single-crystal diffractometer (KUMA DIFFRACTION). The crystal structure was solved and refined using the X-ray package of the S86 and SHELXL 93 programs.[13]

Table 1. Conditions of synthesis and elemental analysis data of $Q[M^{II}Co(C_2O_4)_3]$ compounds

Q	M^{II}	Conditions of synthesis		Yield (%)	$\frac{\text{Found}}{\text{Calculated}}$ (%)		
		t/h	T/°C		C	H	N
Me_4N^+	Mn	24	12	74.70	26.50 26.57	2.70 2.66	3.11 3.10
	Co	24	12	72.50	26.28 26.34	2.65 2.63	3.10 3.07
$Bu^n_4N^+$	Mn	18	10	72.27	42.57 42.61	5.85 5.81	2.28 2.26
	Co	24	9	64.06	42.33 42.34	5.73 5.76	2.24 2.24
	Ni	66	9	9.17	42.33 42.35	5.75 5.77	2.23 2.24
	Cu	0.5	10	74.90	42.05 42.03	5.70 5.73	2.23 2.23
	Zn	0.75	10	77.00	41.93 41.91	5.70 5.71	2.20 2.22
Ph_4P^+	Mn	24	10	73.00	50.27 50.24	2.80 2.79	— —
	Co	24	10	71.00	50.00 49.97	2.80 2.78	— —

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Table 2. Coordinates of atoms (×10⁴) and their isotropic thermal parameters (U_{eq})* in crystal **2**

Atom	x	y	z	$U_{eq} \cdot 10^3/\text{Å}^2$
Co	0	0	2(2)	51(3)
Mn	3333	6667	−4(1)	42(3)
O(1)	−27(20)	1739(19)	179(3)	9(3)
O(2)	1525(25)	1734(23)	−190(4)	30(5)
O(3)	1303(31)	4447(41)	186(5)	71(8)
O(4)	2915(25)	4526(23)	−237(3)	28(4)
C(1)	1239(34)	3226(34)	104(5)	27(7)
C(2)	2058(66)	3113(74)	−106(8)	58(14)
N	0	0	1044(18)	76(22)
C(3)	0	0	1358(10)	126(33)

* U_{eq} were determined as 1/3 of the trace of orthogonalized tensor U_{ij}.

The [NBu^n_4][$MnCo(C_2O_4)_3$] crystal (**2**) has the form of a truncated pyramid with a maximum size of 0.1 mm. The positions of heavy atoms were determined by the Paterson method, and those of deficient atoms of the anionic part of structure and the N atom of the cation were found by a series of the difference Fourier syntheses. For determination of coordinates of C atoms of the cation, problems appeared that were similar to those for the solution of the structure of similar compounds.[7] As we mentioned in the previous works, they are due to the twinning of the crystals, whereas the experimental set of structural amplitudes is limited. The experimental set of data obtained in this work was small, which impeded the determination of the positions of the C atoms in the cationic part of the complex. The coordinates of the atoms of complex **2** are presented in Table 2. The coordinates of the C atoms of the cationic part are not presented, because they were not revealed adequately distinctly in the Fourier syntheses.

The static magnetic susceptibility $\chi(T)$ was carried out on a polycrystalline sample of **1** within the 78—300 K temperature range on a vibration magnetometer (PARC) in an external magnetic field H = 1 T. The dynamic magnetic susceptibility $\chi_{ac}(T)$ (ν = 111 Hz) was measured for the same sample within the 4.2—300 K temperature range.

Results and Discussion

Synthesis of bimetallic complexes with a building unit based on cobalt(III) trisoxalate has several specific features. Unlike chromium(III) and iron(III) trisoxalates, starting complex **1** is very photo- and thermosensitive. Therefore, all procedures of preparation, mixing, and filtration of the solutions and growing of crystals of magnetics from freshly prepared compound **1** were carried out in the dark in an inert atmosphere at 9—12 °C.

The nature of the bivalent metal plays a substantial role in the formation of bimetallic trisoxalates. Complex formation is most rapid in the case of Cu- and Zn-containing cobaltoxalates (see Table 1), and that of Mn- and Co-containing complexes requires somewhat longer time. The synthesis of the nickel complex is the slowest and gives a polycrystalline powder with a crystal size of <0.01 mm in a yield of 9%. According to the data of powder diffractometry, the spectra of the compounds obtained do not coincide with those of the diffraction patterns characteristic of trisoxalatocobaltates of other metals studied. We were not able to prepare the bimetallic complex of cobalt(III) trisoxalate with iron(II) because the initial building unit was destroyed during the reaction regardless of the synthesis conditions, and the more stable $Fe_2C_2O_4 \cdot 2H_2O$ compound was formed instead. We also established that a change in the size of the organic cation has no substantial effect on the course of the formation of bimetallic oxalates (see Table 1).

Our experiments showed that the following procedure is optimum for the synthesis of single crystals of **2**: compound **1** (0.3034 g) in water (15 mL) was mixed with an aqueous solution (5 mL) of manganese(II) salt (0.1319 g). The mixture was stored for 2 h, and an aqueous solution (5 mL) of Bu^n_4NBr (0.2362 g) was added to the filtrate. Two weeks later, dark-green single crystals of the main phase and a minor quantity of transparent pale-pink single crystals of the microadmixture were formed in the reaction flask. According to the data of powder diffractometry and elemental analysis, the admixture phase is $CoC_2O_4 \cdot H_2O$. Single crystals of **2** were washed with ice-cold water and dried *in vacuo* above anhydrous Na_2SO_4 for 24 h. The admixture phase was found in all polycrystalline samples of the synthesized bimetallic oxalates 2—4 months after storage in an inert atmosphere at 12—15 °C. Instability of the Q[$M^{II}Co(C_2O_4)_3$] compounds that formed is also indicated by their gradual transformation into $CoC_2O_4 \cdot H_2O$ during storage of the reaction mixture with the already formed magnetics precipitate for 2 weeks under the same conditions.

The crystal structure of compounds **2** is layered and consists of alternating anionic and cationic layers (see Fig. 1, Tables 3 and 4). The crystal structure of similar compounds has been discussed in several works[3—7]; there-

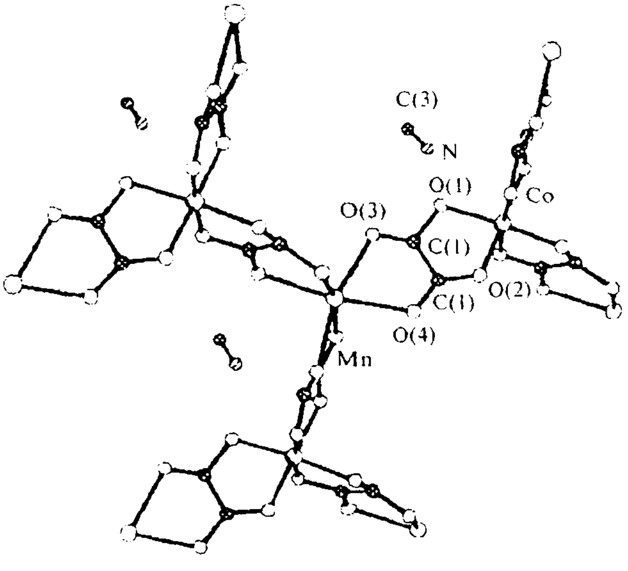

Fig. 1. Fragment of the bilayer of complex **2**.

Table 3. Interatomic distances (d) in $[MO_6]$ polyhedra of complex **2**

Bond	d/Å	Bond	d/Å
Co—O(2)	1.84(2)	Mn—O(3)^c	2.23(3)
Co—O(2)^a	1.84(2)	Mn—O(3)	2.23(3)
Co—O(2)^b	1.84(2)	Mn—O(3)^d	2.23(3)
Co—O(1)^a	1.887(14)	Mn—O(4)^c	2.22(2)
Co—O(1)	1.887(14)	Mn—O(4)^d	2.22(2)
Co—O(1)^b	1.887(14)	Mn—O(4)	2.22(2)
O(1)—C(1)	1.35(3)	O(2)—C(2)	1.20(6)
O(3)—C(1)	1.19(4)	O(4)—C(2)	1.35(6)
C(1)—C(2)	1.40(4)		

^{a} $-x + y, -x, z$.
^{b} $-y, x - y, z$.
^{c} $-x + y, -x + 1, z$.
^{d} $-y + 1, x - y + 1, z$.

Table 4. Bond angles (ω) in $[MO_6]$ polyhedra of complex **2**

Angle	ω/deg	Angle	ω/deg
O(2)—Co—O(2)^a	91.0(9)	O(3)—Mn—O(4)^c	165.3(9)
O(2)—Co—O(1)^a	89.9(9)	O(4)^d—Mn—O(4)	90.4(7)
O(2)—Co—O(1)	83.1(9)	O(3)—C(1)—O(1)	117(3)
O(2)—Co—O(1)^b	174.0(10)	O(3)—C(1)—C(2)	127(4)
O(1)—Co—O(1)^b	96.1(7)	O(1)—C(1)—C(2)	113(3)
O(3)—Mn—O(3)^c	100.0(9)	O(2)—C(2)—O(4)	124(3)
O(3)—Mn—O(4)	75.8(9)	O(2)—C(2)—C(1)	116(5)
O(3)—Mn—O(4)^d	94.6(9)	O(4)—C(2)—C(1)	116(4)

^{a} $-x + y, -x, z$.
^{b} $-y, x - y, z$.
^{c} $-y + 1, x - y + 1, z$.
^{d} $-x + y, -x + 1, z$.

fore, we will not describe their structure. Its distinctive feature is a short interatomic cobalt—oxygen distance, which indicates the low-spin state of Co^{III}.

The Weiss constant determined from the temperature dependence of the inverse static susceptibility $\chi^{-1}(T)$ is close to zero, which indicates the absence of noticeable spin-spin interactions in complex **2**. According to measurements of $\chi_{ac}(T)$, no maxima were observed on the plot of the $\chi_{ac}(T)$ function, which indicates the absence of the magnetic phase transition down to the temperature of liquid helium. This result is consistent with the crystallographic data on the Co—O distance of 1.85 Å, which confirms the low-spin configuration of the Co^{III} ions in the octahedral field and, correspondingly, the nonmagnetic ground state ($S = 0$). The magnetic Mn^{II} ions ($S = 5/2$) are separated by the nonmagnetic Co^{III} ions, and the weak $Mn^{II}—Mn^{II}$ interactions of the second neighbors are the only significant interactions inside the layer.

Thus, the nature of the metal in starting complex **1** substantially affects the properties of the magnetics obtained. Unlike ferromagnets formed in the system where $M = Cr^{3+}$ [14] and ferrimagnets in the system where $M = Fe^{3+}$,[7] the three-dimensional structural ordering of cobalt and manganese ions in the system under consideration does not result in magnetic ordering down to helium temperatures due to the nonmagnetic ground state of the cobalt atom.

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