Synthesis of molecular ferromagnetics $[R_3R'X]MCr(C_2O_4)_3$ (X = N, R = Bu^n, R' = Pr^n, Et, Me; X = P, R = Ph, R' = Bu^n; M = Mn, Fe, Co, Ni, Cu)

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The synthesis, IR spectra, and the temperatures of the transition into a ferromagnetic state (T_c) of layered ferromagnetics $[R_3R'X]MCr(C_2O_4)_3$ (M = Mn, Fe, Co, Cu, and Ni) with the $[Ph_3BuP]^+$, $[Bu_3R'N]^+$ (R' = Pr, Et, and Me) cations capable of subsequently changing the distances between metallooxalate layers have been considered. The temperature T_c has been found to be independent of the size of the organic cation. It is believed that the determining factors in the transition to a ferromagnetic state are exchange interactions inside the metallooxalate layer.

Key words: tris(oxalato)chromates(III), synthesis; molecular ferromagnetics, temperature of the transition to a ferromagnetic state.

The metallooxalate complexes $[Bu_4N]MCr(ox)_3$ (**1**) (M^{2+} = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}; ox = $C_2O_4^{2-}$), which possess ferromagnetic properties, have been recently synthesized.[1] This work evoked great interest, and since then similar complexes have been obtained in several research groups.[2–5] The compounds described[1] were isolated as polycrystalline samples, which did not allow one to establish their structure.

We have obtained[6] single crystals of $[Bu_4N]MnCr(ox)_3$ to elucidate in detail the structure of complexes of this type. It is found that this compound has a layered structure, in which bimetallic metallooxalate networks alternate with layers of organic cations. This provides an ordered arrangement of the Mn^{2+} and Cr^{3+} ions both in the metallooxalate layer and in the direction perpendicular to the layers. This structure made it possible to assume that the distance between the metallooxalate layers exerts a substantial effect on the character of the interplanar Mn^{2+}—Cr^{3+} exchange and, hence, on the temperature of the transition of the substance into a ferromagnetic state (T_c). The $[Bu_4N]^+$ cations are arranged in the structure of compound **1** in such a way that three butyl substituents form an organic layer and the fourth one "penetrates" the cavities of the metallooxalate layer.[6]

The distance between the metallooxalate planes can probably be changed by varying the length of the alkyl substituent, which is present in the cavity of the metallooxalate layer. For this, we chose the $[R_3R'N]^+$ (R = Bu^n; R' = Pr^n, Et, and Me) cations with different lengths of the alkyl chain R'.

The purpose of the present work is to synthesize metallooxalate $[R_3R'X]MCr(ox)_3$ compounds with $[Bu_3R'N]^+$ and $[Ph_3BuP]^+$ cations, which are capable of subsequently changing the distance between the metallooxalate networks, and to study their ferromagnetic properties.

Experimental

The salt $K_3Cr(ox)_3 \cdot 6H_2O$ was obtained according to a known procedure.[7] The reagents $FeSO_4 \cdot 7H_2O$, $MnCl_2 \cdot 4H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ (chemically pure grade), $Co(NO_3)_2 \cdot 6H_2O$ (pure grade), and Bu_3MeNBr (Fluka) were used without additional purification; Ph_3BuPBr (pure grade) was recrystallized from methanol and ether; Bu_3EtNI and Bu_3PrNBr were synthesized by the standard procedure by the alkylation of tri(*n*-butyl)amine with the corresponding alkyl halide in methanol and recrystallized from methanol and ether.

Synthesis of $[R_3R'X]MCr(ox)_3$ salts. A solution of organic cation halide (1.1 mmol) in water (Ph_3BuPBr in 20 mL and Bu_3PrNBr in 5 mL of water) or in methanol (2.5 mL, Bu_3EtNI and Bu_3MeNBr) was added to a mixture obtained by pouring a solution of $K_3Cr(ox)_3 \cdot 3H_2O$ (1 mmol) in H_2O (6 mL) and a saturated aqueous solution of the salt of the corresponding bivalent metal (1 mmol) in an Ar atmosphere at ~20 °C. After 30 min, the precipitate that formed was filtered off. If no precipitate was formed immediately, the reaction mixture was kept at +5 °C for several hours or several days. The precipitates were washed with water or (when the reaction was carried out in a water—methanol solution) with a MeOH—H_2O (1 : 2) mixture and dried *in vacuo*. The conditions of the synthesis and the results of elemental analysis of the compounds obtained are presented in Table 1.

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Table 1. Conditions for the synthesis of $[R_3R'X]MCr(ox)_3$ compounds and elemental analysis data

M^{II}	Conditions of formation of the precipitate		Yield (%)	Found/Calculated (%)		
	t/h	T/°C		C	H	N
			$[Ph_3BuP]MCr(ox)_3$			
Mn	0.5	5	86	48.70 48.70	3.83 3.48	
Fe	6	5	58	48.09 48.60	3.88 3.47	
Ni	15 48	−15 5	34	48.33 48.42	3.52 3.46	
Cu	0.5	17	85	48.25 48.10	3.68 3.44	
Co	0.5	5	60	48.49 48.42	3.62 3.46	
			$[Bu_3PrN]MCr(ox)_3$			
Mn	0.5	17	15	42.13 42.35	5.98 5.68	2.80 2.34
Fe	48	5	12	41.72 42.00	5.13 5.67	2.25 2.33
Ni	15 72	−15 5	21	41.00 41.81	5.60 5.64	2.33 2.32
Co	48	5	12	41.91 41.80	5.38 5.64	2.26 2.32
Cu	0.5	17	67	40.67 41.48	6.07 5.60	2.70 2.30
			$[Bu_3EtN]MCr(ox)_3$			
Mn	3	5	11	41.18 41.03	5.46 5.47	2.44 2.39
Fe	48	5	44	40.25 40.95	5.44 5.46	2.61 2.38
Co	3	5	8	39.77 40.75	5.55 5.43	2.49 2.38
Ni	24	5	7	40.01 40.77	5.54 5.44	2.43 2.38
			$[Bu_3MeN]MCr(ox)_3$			
Mn	0.5	17	20	39.99 39.93	5.33 5.25	2.20 2.45
Fe	24	5	23	39.44 39.86	5.10 5.24	2.75 2.45
Ni	24	5	14	39.33 39.67	5.23 5.22	2.49 2.45
Co	0.5	17	51	39.83 39.66	5.08 5.22	2.34 2.44
Cu	24	5	42	39.59 39.34	5.08 5.18	2.35 2.42

IR spectra of the compounds synthesized were recorded on a Specord 75 IR spectrophotometer. Since the IR spectra of all $[R_3R'X]MCr(ox)_3$ salts are very similar, we present here the IR spectrum of $[Bu_3MeN]MnCr(ox)_3$ as an example. This spectrum includes the following components: (1) the spectrum of the anion $[MnCr(ox)_3]^-$ (KBr), ν/cm^{-1}: 1630, 1430 (ν_{as}(C=O), ν_s(C=O)); 1295, 905 (ν_s(C=O) + δ(OCO)); 815, 800 (δ(OCO) + ν(MnO)); 540, 475, 420 (ν(MnO) + ν(CC), δ of the ring + δ(OCO), ν(MnO) + δ of the ring);[8] (2) the spectrum of the cation $[Bu_3MeN]^+$, ν/cm^{-1}: 2965, 2935, 2870 (ν_{as}(Me), ν_{as}(CH$_2$), ν_s(Me)); 1455, 1450, 1335 (δ_{as}(Me), δ(CH$_2$), δ_s(Me)).[9]

Results and Discussion

The general method for the synthesis of the $[R_3R'X]MCr(ox)_3$ complexes is to mix aqueous solutions of $K_3Cr(ox)_3 \cdot 3H_2O$, metal(II) salt, and tetraalkylammonium salt, as has been described previously[1] for the $[Bu_4N]MCr(ox)_3$ complex. It can be assumed that the first stage in the aggregation is the association of the $[Cr(ox)_3]^{3-}$ anion with an organic cation followed by the binding of the "blocks" formed through metal(II) cations to form networks. This assumption is based on the fact that in the structure of the $[Bu_4N]MnCr(ox)_3$ [6] and $[Ph_4P]MnCr(ox)_3$ [3] salts of the equilibrium positions above Cr^{III} and Mn^{II} atoms, organic cations occupy only positions above Cr^{III} atoms.

Obviously, this explains that the time of formation and the yield of the product $[R_3R'X]MCr(ox)_3$ depend on the nature of both the $[R_3R'X]^+$ cation and the metal(II). On the whole, the salts with the $[R_3R'X]^+$ cations precipitate less than $[Bu_4N]^+$-containing compounds. The reaction mixture must be cooled down to 5 °C, sometimes for a long time (from several hours to several days), to isolate the reaction products. This makes it possible to obtain the $[Ph_3BuP]MCr(ox)_3$ compounds in higher yields than the salts containing the $[Bu_4N]^+$ cation (*cf.* Ref. 1). The attempts to isolate the compounds with $[Bu_3EtN]^+$ and $[Bu_3MeN]^+$ cations from aqueous solutions failed. Crystals of $K_4[Cr(ox)_3][Mn(OH)_6]_{0.25}H_2O$ are formed when methanol is added to these aqueous solutions as they cool.

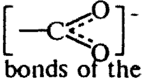
Metallooxalate complexes $[Bu_3EtN]MCr(ox)_3$ and $[Bu_3MeN]MCr(ox)_3$ were obtained by mixing aqueous solutions of $K_3Cr(ox)_3 \cdot 3H_2O$ and the metal(II) salt with methanol solutions of halides of the corresponding organic cations.

It has been established that for the same organic cation complexes form most rapidly (see Table 1) in the case of Cu- and Mn-containing chromooxalates, a somewhat longer time is required for Co- and Fe-containing compounds, and the formation of Ni-chromooxalates is most difficult. According to the published data,[1] the yield of $[Bu_4N]NiCr(ox)_3$ is 6%. We found that the Ni-containing compounds $[R_3R'X]NiCr(ox)_3$ with nonsymmetric Bu_3PrN^+ and $BuPh_3P^+$ cations can be isolated in 20—35% yields if the reaction mixture is kept for 10—15 h at −15 °C and then for 2—3 days at +5 °C.

The use of iodides of alkylammonium salts, in particular, Bu_3EtNI, for the preparation of Cu-containing chromooxalates results in a reaction product $[Bu_3EtN]CuCr(ox)_3$ that contains up to 35% CuI formed by the reduction of Cu^{II} with the iodide anion. The similar "contaminated" sample also undergoes a ferromagnetic transition (Table 2).

Table 2. Temperatures of transition to the ferromagnetic state (T_c/K) for $[R_3R'X]MCr(ox)_3$ compounds

M^{II}	$[Bu_3MeN]^+$	$[Bu_3EtN]^+$	$[Bu_3PrN]^+$	$[Bu_4N]^+$	$[Ph_3BuP]^+$	$[Pr_4N]^+$
Mn	6.3	6.4	6.5	6	6	6.4
Cu	8	7	7.2	7	6	
Fe	10	12	10	12	11	10
Co	15	12	10	10	5	
Ni	12—18	19.6	14	18	11	18

The IR spectra of the $[R_3R'X]MCr(ox)_3$ salts are the superposition of the spectra of the cations and anions. The spectra of the $[MCr(ox)_3]^-$ anions for M = Mn, Fe, Cu, Co, and Ni are identical in the number of bands and their relative intensity. No unambiguous effect of the nature of the metal on the frequencies and intensities of vibrations in the bimetallic oxalate networks is observed. Since there are only two absorption bands corresponding to the antisymmetric and symmetric stretching vibrations of the  $\left[-C\begin{smallmatrix}O\\ O\end{smallmatrix}\right]^-$ group, it can be concluded that all C=O bonds of the oxalate bridges are equivalent. The effect of the metallooxalate network manifests itself as a restriction of the amplitudes of the stretching vibrations: ν_{as}(C=O) shifts to 1630 cm^{-1}, and ν_s(C=O) and (ν_s(C=O) + δ(OCO)) increase to 1430 and 1290 cm^{-1}, respectively. In the low-frequency region, the absorption band of the mixed vibration caused by the stretching vibration of the M—O bond and the deformation of the ring shifts monotonically from 405 to 430 cm^{-1} in the following order: Fe, Mn, Co, Cu, Ni. It is evident that the equilibrium M—O distance becomes shorter in the same order. The scatter of the frequencies of the other low-frequency vibrations, whose shapes are also noncharacteristic, is chaotic within 5 cm^{-1}.

The spectra of the $[Bu_3R'N]^+$ (R' = Me, Et, Pr, and Bu) and $[Ph_3BuP]^+$ cations are also identical. No effect of the chain length of the alkyl substituent was observed. The broadening of the absorption bands of the stretching vibrations of the Me and CH_2 groups at 2965, 2935, and 2970 cm^{-1} compared to the similar vibrations in the salts $[R_3R'X]$Hal should be mentioned. This is related to the possibility of conformational transitions in the aliphatic chains of the cations, because the arrangement of the latter in the organic layer is not compact.[6]

For all compounds obtained, the temperature dependences of the magnetic susceptibility with alternating current (χ_{ac}) were studied using methods similar to the one described previously.[1] The temperatures of the transition to the ferromagnetic state determined by the position of the maximum are presented in Table 2. As can be seen from the data of Table 2, for Mn^{2+}- and Cu^{2+}-containing chromooxalates, whose T_c are very low (6 and 7 K for the salts with Bu_4N^+, respectively), the temperature of the transition remains unchanged within the experimental error. In the case of Fe^{2+}-, Co^{2+}-, and Ni^{2+}-containing chromooxalates, for which high values of the intralayer hyperexchange parameters and, hence, higher T_c, were expected, no dependence of T_c on the size of a cation was revealed.

The absence of this dependence may mean that either the contribution of interplanar exchange interactions is rather weak, or the asymmetric $[R'R_3X]^+$ cations in the structure of $[R_3R'X]MCr(ox)_3$ are disordered; therefore, the shortening of one alkyl group does not result in a decrease in the interlayer distances in the structure, and these distances are almost the same as those for the salt $[Bu_4N]MnCr(ox)_3$.[6] Therefore, we synthesized the $[Pr_4N]MCr(ox)_3$ compounds (M = Mn, Fe, and Ni) with the symmetric $[Pr_4N]^+$ cation, whose size is less than that of $[Bu_4N]^+$. The shortening of the interlayer distances was expected *a fortiori* for the $[Pr_4N]^+$ cations. However, no increase in T_c is observed in this case as well (see Table 2). Thus, it can be assumed that the T_c values for the synthesized compounds with different organic cations are determined rather by differences in the geometry of the exchange bonds inside the layer than by the interlayer M—Cr distances.

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