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Novel Trinuclear Mixed-metal Complexes Containing the Heteronuclear Ions $[M^{II}\{(OH)CrA_4(OH)\}_2(H_2O)_4]^{4+}$ and $[M^{II}\{(OH)CoA_4(OH)\}_2(H_2O)_4]^{4+}$ (A = Amine Ligand)

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In recent publications [1, 2] we have demonstrated the capability of cations of the general formula *cis*-$[M^{III}A_4(OH)_2]^+$ to act as chelate, bidentate ligands to bivalent and tervalent ions (M^{III} is Cr^{III} or Co^{III} and A_4 represents four ligating nitrogen atoms from ammonia, two bidentate or one tetradentate amine ligand). Consequently, series of tetranuclear and pentanuclear heterometallic compounds were synthesized and investigated.

We have now synthesized trinuclear compounds containing the bivalent metal ions Mg^{II}, Mn^{II}, Co^{II}, Ni^{II} and Zn^{II} as central metal ions and water and *cis*-$[M^{III}A_4(OH)_2]^+$ as ligands. The counter ion is dithionate. We here report the structural properties of the complexes formed where M^{III} is Cr^{III} and the central bivalent ions are Co^{II} and Mn^{II}. We also report the magnetic properties of several members of this series.

Experimental

Synthesis

The synthetic procedure is analogous to that which we have described previously [1, 2]. In all cases, the complexes separated when aqueous solutions of stoichiometric amounts of the appropriate metal chlorides and *cis*-dihydroxotetraminechromium(III) dithionates were mixed. The amine configuration in the starting material with 2-picolylamine was *cis*-α. The yields varied from 30–80%.

X-ray Data Collection and Structure Refinement

The manganese complex, $[MnCr_2C_{24}H_{44}N_8O_8](S_2O_6)_2\cdot\frac{1}{2}H_2O$, crystallizes as red–brown prisms. A crystal was mounted on a glass fiber in a random orientation, and this crystal was placed on a Nicolet R3m/V diffractometer equipped with a molybdenum tube ($\lambda\ K\alpha_1 = 0.70926$ Å; $\lambda\ K\alpha_2 = 0.71354$ Å) and a graphite monochromator. Preliminary examination suggested that the crystals belong to the monoclinic class; systematic absences of $h + k = 2n + 1$ for (hkl) and $l = 2n + 1$ for ($h0l$) data are consistent with the space groups $C2/c$ (No. 15) or Cc (No. 9). With four trinuclear complexes in the unit cell, C_2 symmetry is imposed on these species in the centrosymmetric space group. The centrosymmetric space group $C2/c$ was assumed, and this assumption was validated by the successful refinement of the structure. A total of 3573 data were collected in two shells, leading to 3179 unique reflections; the R index for merging was 0.009. The data were corrected for Lorentz–polarization and absorption effects; there is no evidence for secondary extinction. The 1849 independent data with $I \geqslant 3\sigma(I)$ were used in the refinement.

The structure was solved by Patterson methods, which revealed the locations of the Mn and Cr atoms. The remaining non-hydrogen atoms were located in difference Fourier summations. All hydrogen atoms were located in a difference Fourier map, but only their isotropic thermal parameters were varied, their positions being fixed at the locations indicated in the difference Fourier. Non-hydrogen atoms were refined anisotropically. In the final least-squares cycle, no parameter experienced a shift greater than 0.5σ, which is taken as evidence of convergence. Final residuals are $R = 0.037$, $R_w = 0.042$, $S(GOF) = 1.15$.

The cobalt complex $[CoCr_2C_{24}H_{44}N_8O_8](S_2O_6)_2\cdot\frac{1}{2}H_2O$, red–purple prisms, was treated in an entirely analogous manner. A total of 5128 data were collected, giving 4773 unique data; R for merging was 0.031. The 1183 data with $I \geqslant 2.5\sigma(I)$ were used in the refinement.

The structure was solved as above. Hydrogen atoms on the ligands were placed in calculated positions (C–H = 0.96 Å), while other H atoms were located in a difference Fourier map. Hydrogen atom parameters were not refined. In the final least-squares cycle, no parameter shifted by more than 0.5σ. Final residuals are $R = 0.069$, $R_w = 0.046$, $S = 1.35$. Programs used were from the SHELXTL system.

Results and Discussion

The structures of the dithionate salts of both the Mn^{II} and Co^{II} complexes of the above formulation have been determined crystallographically.

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The two complexes are isomorphous, but since the crystals of the Mn^{II} complex were of superior quality to those of the Co^{II} complex, the structure of the Mn^{II} complex has been determined to greater precision.

The central metal ion [Mn^{II} or Co^{II}] sits on a crystallographic C_2 axis and is coordinated to four water molecules and to two *trans* hydroxo groups; these latter each link the central ion to a chromium atom, which is in turn coordinated to four nitrogen atoms from two ligands and to one (terminal) hydroxo group. A view of the entire manganese complex is given in Fig. 1, and a more detailed view of the inner coordination spheres is shown in Fig. 2. The coordination at the central metal is roughly octahedral, the *cis* angles at manganese ranging from 84.9(1)° to 88.6(1)° while those in the cobalt complex are from 84.3(4)° to 89.0(4)°.

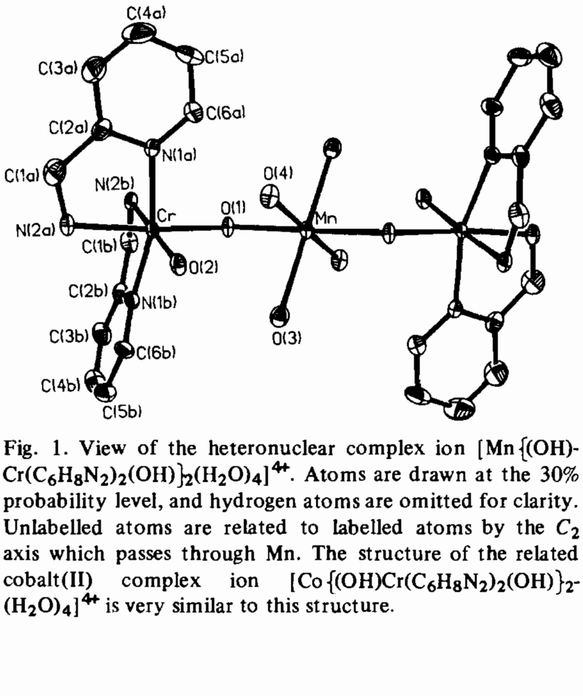

Fig. 1. View of the heteronuclear complex ion $[Mn\{(OH)Cr(C_6H_8N_2)_2(OH)\}_2(H_2O)_4]^{4+}$. Atoms are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity. Unlabelled atoms are related to labelled atoms by the C_2 axis which passes through Mn. The structure of the related cobalt(II) complex ion $[Co\{(OH)Cr(C_6H_8N_2)_2(OH)\}_2(H_2O)_4]^{4+}$ is very similar to this structure.

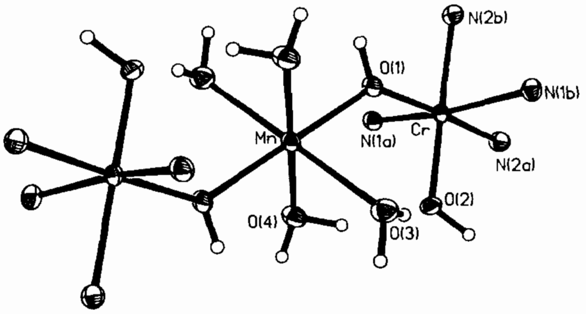

Fig. 2. View of the inner coordination spheres around the Mn and two Cr centers in $[Mn\{(OH)Cr(C_6H_8N_2)(OH)\}_2(H_2O)_4]^{4+}$.

In the manganese complex the Mn–Cr separation is 3.728(1) Å, the bridging Mn–O(1)–Cr angle being 134.3(2)°. The Mn–O(1) bond of length 2.110(4) Å is, as expected, considerably longer than the Cr–O(1) bond of 1.935(4) Å. In the cobalt complex the analogous values are 3.669(2) Å, 135.2(5)°, 2.034(10) and 1.934(10) Å. These values can be compared with those observed in μ-hydroxodichromium(III) complexes, where the Cr–Cr separations are in the range 3.677(2) to 3.878(2) Å, bridging Cr–O–Cr angles are from 135.4(2) to 165.6(9)°, and Cr–O bond lengths are from 1.941(16) to 1.989(4) Å [3–6].

The dithionate anions in the structures are very regular, with approximate D_{3d} geometry. Thus, in the manganese complex the S(1)–S(2) separation is 2.130(2) Å while the S–O bonds fall in the range 1.418(5) to 1.445(5) Å [average 1.435(10) Å]. The ideally ±60° torsion angles range from ±58.0 to ±62.0°, while the ideally 180° torsion angles are from 178.3 to 179.2°. These structural parameters are consistent with those found in previous determinations [6, 7].

In the previous, apparently related, series of complexes which we have described [1, 2], the *cis*-dihydroxo complexes act as bidentate chelating ligands. In the present complexes, however, each *cis*-dihydroxo complex behaves as a monodentate ligand with one bridging hydroxo group. The terminal hydroxo groups, on the other hand, are involved in hydrogen bonding with the water molecules ligated to the central metal ion. This type of bonding is present in some binuclear complexes of Cr(III) with ethanediamine (en) [5, 8].

For the series of compounds with *cis*-$[Cr\,en_2(OH)_2]^+$ and *cis*$[Co\,en_2(OH)_2]^+$, it still remains an open question as to whether we have singly or doubly bridged coordination corresponding to general formulations like $[M^{II}\{(OH)Cr(NH_3)_4(OH)\}_2(H_2O)_4](S_2O_6)_2\cdot 1–2H_2O$ or $[M^{II}\{(OH)_2Cr(NH_3)_4\}_2(H_2O)_2](S_2O_6)_2$. For the compounds with *cis*-$[Cr(NH_3)_4(OH)_2]$, however, two series of compounds with different water contents were isolated, one with analyses fitting the general formula $[M^{II}\{(OH)Cr(NH_3)_4(OH)\}_2(H_2O)_4](S_2O_6)_2\cdot 4–5H_2O$ and another fitting the general formula $[M^{II}\{(OH)_2Cr(NH_3)_4\}_2(H_2O)_2](S_2O_6)_2\cdot H_2O$.

Diffuse reflectance spectra were measured for the chromium compounds with 2-picolylamine ($\lambda_1 = 567–579$, $\lambda_2 = 373–379$ nm) and ethanediamine ($\lambda_1 = 495–504$, $\lambda_2 = 359–375$ nm), respectively.

The magnetic susceptibilities of the complexes were measured in the temperature range 2–300 K at 13000 Oe. Here we report some of the results for 2-aminomethylpyridine complexes of Cr^{III} with the central ions $M^{II} = Zn^{II}$, Mn^{II}, Co^{II} and Ni^{II}. Data fittings were performed using programs and parameters as earlier described [9]. Magnetic interactions were assumed according to the spin Hamiltonian

$$\mathcal{H} = \sum_{i<j\leqslant 3} J_{ij}\hat{S}_i\cdot\hat{S}_j$$

The values of S in our fittings were set to 0, 5/2, 3/2, 1 and 3/2 for Zn^{II}, Mn^{II}, Co^{II}, Ni^{II} and Cr^{III}, respectively. For Co^{II} this is obviously a crude approximation since the ground state for Co^{II} is expected to be a $^4T_1(O_h)$ state in the analogous Co^{III}–Co^{II}–Co^{III} complex with no interactions. The resulting exchange parameters are shown in Table 1.

TABLE 1. Exchange Parameters, J_{ij}, in the Complexes $[M^{II}\{(OH)Cr(C_6H_8N_2)_2(OH)\}_2(H_2O)_4](S_2O_6)_2\cdot H_2O$

	Zn^{II}	Mn^{II}	Co^{II}	Ni^{II}
$J_{12} = J_{23}$ (cm^{-1})		9.93(3)	16(1)	8.43(3)
J_{13} (cm^{-1})	0.29(3)	1.5(2)		2.94(4)

The spins of the ground states in the Zn^{II}, Mn^{II} and Co^{II} complexes were found to be 0, 1/2 and 3/2, respectively. In the Ni^{II} complex three states with $S = 0$, 1 and 2 were found below 2.5 cm^{-1}. Their positions depend on the number of parameters fitted.

Supplementary Material

Atomic coordinates, bond lengths and angles, and thermal parameters for both complexes are available from D.J.H.

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