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Synthesis and Structure of Novel Mixed-Metal Complexes containing the Heteronuclear Ions $[M^{III}\{(OH)_2Cr(NH_3)_4\}_4]^{7+}$ and $[M^{III}\{(OH)_2Co(NH_3)_4\}_4]^{7+}$

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The synthesis and structural and magnetic properties of new pentanuclear complex ions containing a central tervalent metal ion [Ce^{III}, Y^{III}, La^{III}, Pr^{III}, or Gd^{III}] co-ordinated to eight hydroxo groups which act as bridging ligands to four tervalent metal ions [Cr^{III} or Co^{III}], are described.

Previously[1] we have shown that cations of the general type *cis*-$[M^{III}A_4(OH)_2]^+$, where M^{III} is Cr^{III} or Co^{III} and A_4 represents four ligating nitrogen atoms from four monodentate, two bidentate, or one tetradentate amine ligand, can act as bidentate ligands to a variety of bivalent metal ions. Here, and in a forthcoming manuscript, we demonstrate that these new complex ligands are universal ligands, co-ordinating to virtually all metal ions with ionic radii between 0.5 and 1.1 Å. The number of these bidentate ligands surrounding the central metal depends upon the nature of the central metal ion, and may vary from one to four.[2] In the earlier publication, this value was three,[1] and here we describe complexes where there are four bidentate ligands.

As central metal ions we have chosen the lanthanides Ce^{III}, Y^{III}, La^{III}, Pr^{III}, and Gd^{III} because these ions are known to occur in a variety of heteronuclear species. As amine ligand we have primarily used ammonia, but some work has been done with the tetradentate ligand *N,N′*-bis(2-pyridylmethyl)-1,3-propanediamine (bispictn).

The complexes are prepared by mixing aqueous solutions of stoicheiometric quantities of the lanthanide chloride and the *cis*-dihydroxo complex; suitable crystals of the iodide or bromide salts are obtained by the addition of a large excess of aqueous potassium iodide or sodium bromide, respectively. In the case of ammonia as ligand, we have isolated two isomorphous series of complexes of the general formulas $[M\{(OH)_2Cr(NH_3)_4\}_4]I_7{\cdot}yH_2O$ and $[M\{(OH)_2Co(NH_3)_4\}_4]Br_7{\cdot}zH_2O$. The yields vary from 23%—36%. In the case of bispictn as ligand, the number of co-ordinating bidentate ligands is only three; this is also the case for a variety of other

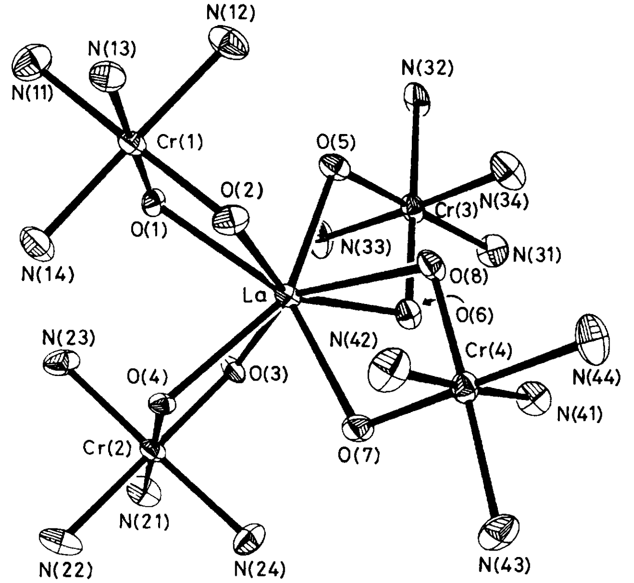

Figure 1. View of the heteronuclear complex ion $[La\{(OH)_2Cr(NH_3)_4\}_4]^{7+}$. Atoms are drawn at the 30% probability level; hydrogen atoms are omitted.

tervalent central metals including Fe^{III}, Cr^{III}, V^{III}, Co^{III}, Al^{III}, and In^{III}.[2]

The complexes are not stable in water, but are reasonably stable in dimethylformamide (DMF). The absorption spectra of the chromium lanthanide complex ions in DMF have maxima near 525 nm and 386—388 nm, which are comparable to their diffuse reflectance spectral maxima of 530—540 and 385—390 nm.

The structure of the iodide salt of the complex ion $[La\{(OH)_2Cr(NH_3)_4\}_4]^{7+}$ has been determined crystallographically.† There is no crystallographically-imposed symmetry on the complex ion, which consists of a central 8-co-ordinate La^{III} ion linked by eight hydroxo groups to four Cr^{III} ions. The four chromium atoms form an almost perfect tetrahedron around the central lanthanum ion. A view of the complex ion is given in Figure 1. The geometry at La is necessarily distorted because of the constraints due to the bidentate ligands, but is well described as a dodecahedron in which each bidentate ligand occupies one A site and one B site. Thus, the unique axis bisects the edges formed by O(1) $\cdots$ O(4) and O(6) $\cdots$ O(8), the overall structure closely resembling that described by Cartmell and Fowles.[3]

The La–Cr separations are in the range 3.511(3)—3.536(3) Å, with an average value of 3.525(11) Å. The eight bridging La–O–Cr angles are from 102.7(5)—106.8(5)° [average, 105(2)°], which can be compared with the corresponding Co–O–Cr angle of 101.6(2)° found[1] in the analogous tetrameric cluster $[Co\{(OH)_2Cr(bispictn)\}]^{5+}$. The La–O distances of 2.45(1)—2.55(1) Å [average 2.50(4) Å] are longer than the Cr–O separations of 1.909(12) to 1.949(12) Å [average 1.931(13) Å], as anticipated, but both appear to be within the expected ranges.[4,5]

The compounds $[M\{(OH)_2M'(NH_3)_4]X_7\cdot nH_2O$ with M = Y^{III}, La^{III}, and M′ = Co^{III} exhibit almost temperature independent paramagnetism in the temperature range 2—300 K. Compounds with M = Y^{III}, La^{III}, and M′ = Cr^{III} are paramagnets with weak antiferromagnetic interactions between the Cr^{III} centres. $[La\{(OH)_2Cr(NH_3)_4\}_4]I_7\cdot 5H_2O$, for example, has the effective magnetic moments, calculated for the formula unit, of 7.682 μ_B and 6.527 μ_B at 198.44 K and 4.27 K, respectively. The magnetic data for this compound were fitted by procedures described elsewhere[6] to the Hamiltonian (1), using two variable parameters g and $J = J_{12} = J_{13} = J_{14} = J_{23} = J_{24} = J_{34}$. The result was g = 1.986(4) and J = 0.73(4) cm^{-1}. The variance per degree of freedom was 86 for 165 measurements which shows that more elaborate models are warranted. The small value of J is in accordance with the fact that the centre atoms M have no orbitals available with appropriate symmetry to allow long distance π-overlaps between the Cr^{III} atoms.[7]

$$H = \sum_{i>j}^{4} J_{ij}\hat{S}_i\cdot\hat{S}_j + \beta g H\cdot\hat{S} \qquad (1)$$

Compounds with M = Ce^{III}, Pr^{III}, and Gd^{III} and M′ = Cr^{III} are also paramagnets with weak antiferromagnetic interactions. $[Gd\{(OH)Cr(NH_3)_4\}_4]I_7\cdot 5H_2O$, for example, has the effective magnetic moments, calculated for the formula unit, of 10.994 μ_B and 10.180 μ_B at 300.83 K and 4.13 K, respectively. Data fittings are in progress for this type of compound with interactions between five magnetic centres. The weakness of these interactions indicates that the overlaps between d-orbitals on M′ and f-orbitals on M are very small, as expected, and dipolar couplings through space may be relatively important for this class of compounds.

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† *Crystal data*: $[LaCr_4N_{16}O_4H_{56}]I_7\cdot 3H_2O$, red prisms, M = 1633.8, monoclinic, space group $C2/c$ (No. 15), a = 16.828(4), b = 18.363(4), c = 32.009(1) Å, β = 99.70(2)°, U = 9750(4) $Å^3$, D_m = 2.24, D_c = 2.226 g cm^{-3}, Z = 8, μ(Mo-K_α) = 61.2 cm^{-1}, T = 22 C. Data were collected on a Nicolet R3m/V diffractometer using Mo-K_α radiation and a graphite monochromator. 5877 Independent intensities were measured, of which 4041 with $I > 3\sigma(I)$ were used in the refinement. An empirical absorption correction was applied. The positions of the one lanthanum and seven iodine atoms were located by direct methods. The structure was refined by least-squares methods to yield final values of R = 0.059 and R_w = 0.064. All programs used were from SHELXTL. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.