Novel Tetranuclear Mixed-metal Complexes Containing the Heteronuclear Ions $[M^{II}\{(OH)_2CrA_4\}_3]^{5+}$ and $[M^{II}\{(OH)_2CoA_4\}_3]^{5+}$ (A = Amine Ligand)

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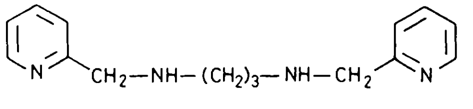
The synthesis and structural characterization of new tetranuclear complex ions with a central bivalent metal ion [Mg^{II}, Zn^{II}, Co^{II}, Mn^{II}, or Ni^{II}] octahedrally co-ordinated to six hydroxo groups which act as bridging ligands to three trivalent metal ions [Cr^{III} or Co^{III}], is reported.

We report the synthesis of the tetranuclear species $[M^{II}\{(OH)_2M^{III}A_4\}_3]^{5+}$, where M^{II} is Mg, Zn, Co, Mn, or Ni, M^{III} is Cr or Co, and A_4 is either four monodentate ammonia ligands, two bidentate 1,2-diaminoethane (en) ligands, or one tetradentate *N*,*N*′-bis(2-methylpyridyl)propane-1,3-diamine (bispictn) (**1**) ligand. The six-co-ordinate ionic radii of the M^{II} ions used are in the range 0.65—0.80 Å; in all cases the counter ion used was perchlorate. Our new compounds are somewhat analogous to Werner's 'brown salts,' which contain the homonuclear, tetranuclear ion $[Co^{III}\{(OH)_2$-



(**1**), bispictn

$Co(en)_2\}_3]^{6+}$,[1] and to the corresponding complexes where en is replaced by ammonia[2] and cobalt by chromium.[3] The compounds are unusual from a chemical viewpoint in that they contain bivalent metal ions octahedrally co-ordinated to six hydroxo groups; they are important because they offer a unique opportunity to study the intra-cluster interactions between the various metal ions. The amine ligands should provide adequate shielding to prevent inter-cluster interactions.

The complexes were prepared by mixing stoicheiometric amounts of concentrated (>0.1 M) aqueous solutions of the appropriate metal chloride and *cis*-dihydroxotetra-amine-chromium(III) perchlorate or its cobalt(III) analogue. The amine configuration in the starting material with bispictn was β. In some cases it was necessary to add sodium perchlorate to initiate precipitation. Yields varied from 20 to 70%. The NH_3 complexes crystallized with four to six moles of water, the en complexes with three, and the bispictn complexes with six.

The ammonia complexes are stereochemically the simplest since there is only one enantiomeric pair. Numerous configurations are theoretically possible for the en and bispictn compounds, but on the basis of *X*-ray powder diagrams it appears that the bispictn complexes actually fall into only two isomorphous series.

We have determined the three dimensional structure of one bispictn complex, in which M^{II} is Co^{II} and M^{III} is Cr^{III}, *i.e.* $[Co\{(OH)_2Cr(bispictn)_3\}]^{5+}$.† The complex cation has crystallographically imposed C_3 symmetry. The Co atom lies on the three fold axis and is surrounded by six hydroxo groups which serve as bridges to the three chromium atoms. The tetranuclear cation is shown in Figure 1 and a view of the crystallographically independent portion of the molecule is given in Figure 2. The configuration at both cobalt and chromium is Λ. The geometry at cobalt is distorted from octahedral, the (unique) O(1)–Co–O(2) angle being only 75.6(2)°, while the corresponding angle at chromium is 85.2(2)°. The isomer isolated was the β form in which the pyridine nitrogen atoms are *cis* (as expected, since we used the β form of the reactant). The absolute configuration at both N(1) and N(2) is *R*; using the notation we have described previously,[5,6] the isomer here is the Λ(β)*RR*′Λ-(β)*RR*′Λ(β)*RR*′ isomer. The Co–Cr distances in the tetramer [3.064(1) Å] are comparable to the value reported for the Cr–Cr separation in the binuclear bispictn complex $[Cr(bispictn)OH]_2^{4+}$ [3.054(2) Å][5] and to those in a variety of di-μ-hydroxo-chromium(III) complexes (2.950—3.059 Å).[7]

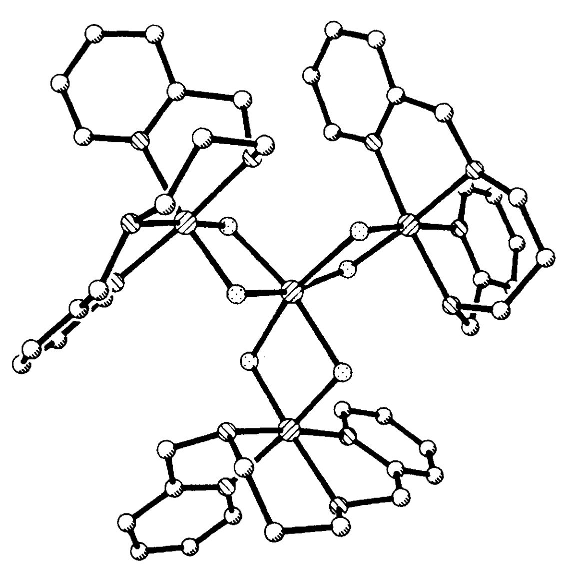


Figure 1. View of the tetranuclear complex ion $[Co\{(OH)_2Cr(bispictn)\}_3]^{5+}$. The Co, Cr, and N atom are cross-hatched, O atoms are dotted, and C atoms are shaded open ellipsoids.

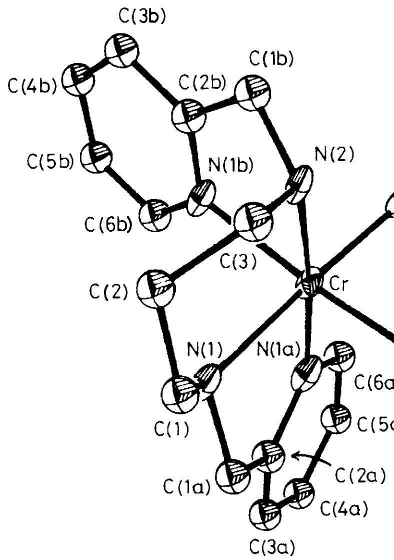


Figure 2. View of the co-ordination around the unique chromium(III) centre in the crystals of $[Co\{(OH)_2Cr(bispictn)\}_3](ClO_4)_5 \cdot 6H_2O$. Atoms are drawn at the 30% probability level, but hydrogen atoms are omitted for clarity.

The Cr–O–Co bond angles within the bridging unit are asymmetric, with Co–O(1)–Cr [101.6(2)°] larger than Co–O(2)–Cr [96.9(2)°], but both are within the normal range for di-μ-hydroxo metal complexes.[8] The Cr–O bond lengths [1.902(5) and 1.921(5) Å] are significantly shorter than the Co–O distances [2.050(5) and 2.166(5) Å], as expected for a complex containing Cr^{III} and Co^{II}.

All the compounds decomposed in dilute aqueous solutions to give absorption spectra identical with those of the parent *cis*-dihydroxo complexes. In dimethylformamide (DMF), however, the absorption spectra (λ_I 515—517 nm) were comparable to those obtained by diffuse reflectance from the solid samples (λ_I 514—516 nm).

The e.s.r. spectra of the complexes and the magnetic susceptibilities in the temperature range 2—300 K have been

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† *Crystal Data*: $[C_{45}H_{66}N_{12}O_6CoCr_3](ClO_4)_5 \cdot 6H_2O$, orange hexagonal prisms, M = 1691.4, trigonal, space group $P31c$ (No. 159), a = 16.144(5), c = 15.091(2) Å, U = 3406(4) Å^3, D_m = 1.60, D_c = 1.649 g cm^{-3}, $Z = 2$, $\mu(\text{Mo-}K_\alpha)$ = 9.82 cm^{-1}, T = 22 °C. Data were collected on an Enraf-Nonius CAD-4 diffractometer using Zr-filtered Mo-K_α radiation. 2747 Independent data were collected, of which 1604 with $I > 1.5\sigma(I)$ were used in the analysis. An empirical absorption correction was applied. The positions of the unique cobalt and chromium atoms were found by direct methods using MULTAN.[4] The structure was refined by least-squares methods to yield final values R = 0.063 and R_w = 0.046. All programs used were from the Enraf-Nonius SDP package. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

examined. The complexes with $M^{III} = Co^{III}$ and $M^{II} = Mg^{II}$ and Zn^{II} are diamagnetic, as expected, while those with $M^{III} = Co^{III}$ and $M^{II} = Mn^{II}$, Co^{II}, and Ni^{II} exhibit the ordinary magnetic properties of d^5 (high spin), d^7 (high spin), and d^8 configurations, respectively. Complexes with $M^{III} = Cr^{III}$ and $M^{II} = Mg^{II}$ or Zn^{II} show weak antiferromagnetic coupling among the three equivalent Cr^{III} centres, leading to doublet ground states, while those with $M^{III} = Cr^{III}$ and $M^{II} = Mn^{II}$, Co^{II} and Ni^{II} show complex variations of the magnetic moment with temperature which may be ascribed to magnetic interactions between the four paramagnetic centres.

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References

1 A. Werner, *Ber. Dtsch. Chem. Ges.*, 1914, **47**, 3037; U. Thewalt and J. Ernst, *Z. Naturforsch., Teil B.*, 1975, **30**, 818.

2 A. Werner, *Ber. Dtsch. Chem. Ges.*, 1907, **40**, 2103.

3 P. Andersen, T. Damhus, E. Pedersen, and A. Petersen, *Acta Chem. Scand., Ser. A*, 1984, **38**, 359; P. Andersen and E. Bang, *Acta Chem. Scand., Ser. A*, 1986, **40**, 476.

4 G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A.*, 1971, **27**, 368.

5 H. R. Fischer, D. J. Hodgson, K. Michelsen, and E. Pedersen, *Inorg. Chim. Acta*, 1984, **88**, 143.

6 M. A. Heinrichs, D. J. Hodgson, K. Michelsen, and E. Pedersen, *Inorg. Chem.*, 1984, **23**, 3174; M. A. Collins, D. J. Hodgson, K. Michelsen, and D. K. Towle, *J. Chem. Soc., Chem. Commun.*, 1987, 1659.

7 K. Michelsen, E. Pedersen, S. R. Wilson, and D. J. Hodgson, *Inorg. Chim. Acta*, 1982, **63**, 141, and references therein.

8 D. J. Hodgson, in 'Magneto-Structural Correlations in Exchange Coupled Systems,' eds. R. D. Willett, D. Gatteschi, and O. Kahn, Reidel, Dordrecht, pp. 497—522, 1985; D. J. Hodgson, *J. Mol. Catal.*, 1984, **23**, 219, and references therein.