Some Tetranuclear Nickel(II), Cobalt(II), and Mixed Cobalt(II)/Cobalt(III) Complexes of a Binucleating Ligand

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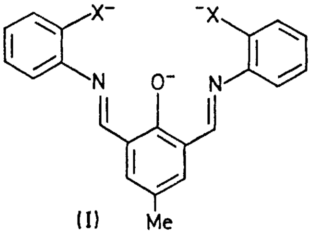
Summary Nickel(II), cobalt(II), and mixed cobalt(II)/cobalt(III) complexes of the binucleating ligand 4-hydroxy-bis-3,5-[*N*-(2′-hydroxyphenyl)formimidoyl]toluene, RH_3, contain the tetranuclear core $[RM_2(OH)]_2$.

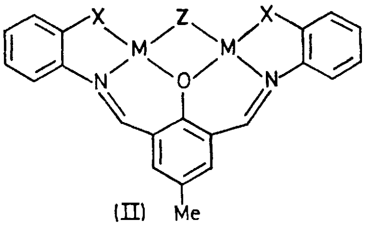
Some Cu^{II} complexes of the trianionic binucleating ligand (Ia) (hereafter R^{3-}) and a more extensive series of Cu^{II} and Ni^{II} complexes of (Ib) (hereafter L^{3-}), all of which were of the general form (II), where Z represents a range of mono-anionic bridging species, were described recently.[1,2] Reported here are some Ni^{II}, Co^{II}, and mixed Co^{II}/Co^{III} complexes of R in which two binuclear units associate to generate an unusual tetranuclear core.

A hygroscopic red-brown crystalline complex of empirical composition $RCo_2(CH_3CO_2),xH_2O$ is obtained from RH_3 and $Co(CH_3CO_2)_2,4H_2O$ in methanol under dinitrogen. This complex in methanolic solution reacts rapidly with dioxygen to yield black crystals of empirical composition $RCo_2(CH_3O)(CH_3CO_2)$. The dioxygen consumed in this reaction corresponds to only a quarter of that required for formation of the anticipated peroxy-bridged binuclear species [structure related to (II) with $Z = O_2^{2-}$, $M = Co^{III}$] but is consistent with conversion of only half the Co^{II} to Co^{III} with concomitant reduction of dioxygen to the water (or hydroxide) level. The compound has a magnetic moment of 3·58 B.M. per cobalt atom at room temperature and obeys the Curie–Weiss law from 287 to 95 K. This behaviour suggests equal numbers of diamagnetic Co^{III} and paramagnetic Co^{II}, the observed susceptibility implying a moment of 5·06 B.M. for the latter. The product is not amenable to *X*-ray crystallographic study but, after recrystallisation from aqueous ethanol, yields suitable crystals of empirical composition $RCo_2(OH)(CH_3CO_2)(H_2O)(EtOH)$ which were studied by *X*-ray diffraction.

Crystal data: $Co_2C_{25}H_{27}N_2O_8$, $M = 601{\cdot}4$, monoclinic, $a = 18{\cdot}657(2)$, $b = 12{\cdot}029(1)$, $c = 22{\cdot}616(3)$ Å, $\beta = 90{\cdot}10(2)°$, $U = 5076$ Å, $D_m = 1{\cdot}57$, $Z = 8$, $D_c = 1{\cdot}57$; space group, $C2/c$; $\mu = 105\ cm^{-1}$, absorption corrections applied. The 1673 independent reflections above background ($I > 2\sigma$) and within the sphere $\theta \leqslant 50°$ were measured on a Siemens automatic single-crystal diffractometer in the θ—2θ scan mode with Ni-filtered Cu-K_α radiation. The structure was solved by the heavy-atom method and after full-matrix least-squares refinement with individual isotropic thermal parameters, the value of the conventional R-factor was 0·104 on all observed data.



(I)
a; X = O
b; X = S



(II)

The crystal is composed of discrete molecules of the neutral centrosymmetric tetranuclear complex $[RCo^{II}Co^{III}(OH)(CH_3CO_2)]_2$, situated about a site of symmetry $\bar{1}$ together with two molecules each of water and ethano which participate in an intricate H-bonded chain. The molecular geometry, with some relevant dimensions, is represented in the Figure. Noteworthy features of the structure are: (*a*) the coplanar array of four cobalt centres which fall into two distinct pairs of Co^{III} ions [Co(1) and Co(1′)] and Co^{II} ions [Co(2) and Co(2′)], which can be clearly differentiated on the basis of cobalt–ligand bond lengths, (*b*) the μ_3-hydroxo-group, O(4), and (*c*) the unusually long Co(2)–O(2′) bond of 2·24 Å which appears to result from steric repulsion between the benzene ring bearing N(1′) and O(2′) and the chelate ring system [Co(2), O(3), N(2)] immediately beneath it. In accord with the latter view the ligand side arm bearing N(1′), O(2′) is buckled so that the aromatic ring is directed away from the associated binuclear unit. This structure bears some resemblance to that, reported very recently,[3] of $Co_4(CH_3O)_4(CH_3CO_2)_2(C_5H_7O_2)_4$, in which two Co^{II} and two Co^{III} ions occupy the corners of a tetrahedron.

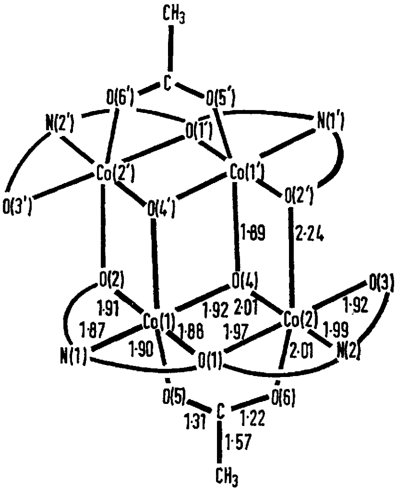


FIGURE *Representation of the geometry around the tetranuclear core of* $[RCo^{II}Co^{III}(OH)(CH_3CO_2)]_2$. *Estimated standard deviations of the metal-donor atom bond lengths vary from* 0·009 *to* 0·103 Å *and those of the* C–O (*acetato*) *bond lengths, near* 0·02 Å.

$[RCo^{II}Co^{III}(OH)(CH_3CO_2)]_2 2H_2O,2EtOH$ shows only broad absorption in the O–H stretching region of the i.r. spectrum but, after being dried *in vacuo*, a weak sharp band appears at 3565 cm^{-1} assigned to the μ_3-hydroxo-group The related material formulated as $[RCo^{II}Co^{III}(CH_3O)(CH_3CO_2)]_2$ with μ_3-methoxo-groups, significantly, shows no absorption above 3100 cm^{-1} after drying.

LH_3 with $Ni(OAc)_2,4H_2O$ in methanol yields $[LNi_2(OMe)]$.[2] By contrast, RH_3 with either $Ni(OAc)_2,4H_2O$ or $Co(OAc)_2,4H_2O$ under similar conditions in methanol yields the acetate-containing products $[RM_2(OH)]_2(CH_3CO_2)_2(H)_2$ ($M = Co^{II}$ or Ni^{II}) presumed to have a tetranuclear core analogous to that in the Figure. The nickel compound is readily converted into $[RNi_2(OH)]_2(CH_3CO_2)(NO_2)(H)_2$ and $[RNi_2(OH)]_2(CH_3CO_2)_2(H)_2(C_5H_5N)_2$ by reaction with sodium nitrite and pyridine respectively. All three nickel complexes show molecular weights in 2-methoxyethanol at 59 °C close to the theoretical values for the tetranuclear species. Under the same conditions in 2-methoxyethanol the complexes behave as non-electrolytes. Two 'additional' protons [represented $(H)_2$ above] required for electrical neutrality by the presence of the anions external to the neutral $[RM^{II}_2(OH)]_2$ core are observed for all four complexes of divalent metals by potentiometric titration with lithium hydroxide in 2-methoxyethanol. The most likely basic sites for the titratable protons are the aminophenol oxygen atoms of R.

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[1] R. Robson, *Austral. J. Chem.*, 1970, **23**, 2217.
[2] W. D. McFadyen, R. Robson, and H. Schaap, *Inorg. Chem.*, 1972, **11**, 1777.
[3] J. A. Bertrand and T. C. Hightower, *Inorg. Chem.*, 1973, **12**, 206.