

## Crystal Structure of $\text{CoNi}(\text{OC}_2\text{H}_4\text{NH}_2)_3(\text{HOC}_2\text{H}_4\text{NH}_2)_3\text{I}_2$ : A Hydrogen-bonded Dinuclear Complex

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**Summary** A dinuclear complex containing 2-aminoethanol, cobalt(III), and nickel(II) has been prepared and the structure of its iodide salt has been determined by *X*-ray diffraction; the cation consists of octahedral tris-chelates of cobalt(III) and nickel(II) held together by three hydrogen bonds between the oxygen faces of the two octahedra, and the oxygen-oxygen distance is 2.51 Å.

CHELATE complexes containing 2-aminoethanol (EtaH) and its anion (Eta) have been reported: from the reaction of cobalt(II) salts with 2-aminoethanol Hieber and Levy<sup>1</sup> isolated compounds which they formulated as  $[\text{Co}(\text{EtaH})_3]\text{X}_2$ ,  $[\text{Co}(\text{EtaH})_2(\text{Eta})]\text{X}$  (X = Cl, Br, or I); in attempting to isolate tris-(2-aminoethoxido)cobalt(III), Yoneda and Kida<sup>2</sup> treated cobalt(III) ammine complexes with 2-aminoethanol and isolated crystals which they formulated as  $[\text{Co}(\text{EtaH})(\text{Eta})_2]\text{X}$ ,  $[\text{Co}(\text{EtaH})_2(\text{Eta})]\text{X}_2$  (X = Br, NO<sub>3</sub>, or ClO<sub>4</sub>); later studies<sup>3</sup> indicated that the two groups had isolated the same product and that it contained only cobalt(III). Although a double salt with discrete  $[\text{Co}(\text{EtaH})(\text{Eta})_2]^+$  and  $[\text{Co}(\text{EtaH})_2(\text{Eta})]^{2+}$  cations was considered,<sup>1,2</sup> the existence of dimeric units held together by hydrogen bridges was suggested as being more probable.<sup>3</sup>

In preparing a series of complexes of various metal ions with tris-(2-aminoethoxido)cobalt(III) groups as ligands,<sup>4</sup> a compound which analysed correctly for  $\text{CoNi}(\text{OC}_2\text{H}_4\text{NH}_2)_3(\text{HOC}_2\text{H}_4\text{NH}_2)_3\text{I}_2$  was isolated; the magnetic moment

of 3.12 B.M. indicated a paramagnetic nickel(II) ion and a diamagnetic cobalt(III) ion.

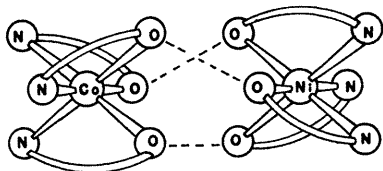
*Crystal data:*  $\text{C}_{12}\text{H}_{39}\text{CoI}_2\text{N}_6\text{NiO}_6$ ,  $M = 735.01$ , cubic,  $a = 13.60$  Å,  $D_m = 1.94$ ,  $Z = 4$ ,  $D_c = 1.93$ , space group =  $Pa\bar{3}$ .

Intensity data were collected on a Picker Four-circle Automated Diffractometer as previously described;<sup>5</sup> Zr-filtered Mo- $K_\alpha$  radiation was used. A total of 498 unique reflections were statistically above background and were used for the structure determination. The structure was solved by the heavy-atom method. The cobalt(III) and nickel(II) ions are disordered in an 8-fold set of positions; due to disorder, two sets of oxygen and nitrogen positions were located. Least-squares refinement, with the disordered oxygen and nitrogen atoms assigned occupancy factors of 0.5 and with anisotropic thermal parameters for Co, Ni, and I, converged to  $R = 0.069$  (weighted  $R = 0.045$ ).

The disorder in the oxygen and nitrogen positions probably results from the difference in size of the two metal ions; one set of M-O and M-N distances [1.93(3) and 2.06(3) Å, respectively] is identical to that found for the tris-(2-aminoethoxido)cobalt(III) unit of  $[\text{Co}_3(\text{Eta})_6]^{2+}$ ; the other set of M-O and M-N distances [2.08(2) and 2.15(2) Å, respectively] are reasonable values for a nickel(II) chelate. Although the carbon atoms are probably also disordered, the two sets are apparently not as well separated and only average positions are observed.

The structure of the cation is shown in the Figure. The two tris-chelates are joined face-to-face by hydrogen bonding as indicated by three equivalent oxygen-oxygen distances of 2.51(3) Å; this oxygen-oxygen distance indicates very strong bonding between the two tris-chelates.

The two tris-chelates are of opposite optical configurations because of the inversion centre between the two; the six oxygens of a dimeric unit form a distorted octahedron about



FIGURE

the inversion centre. As viewed down the three-fold axis, the distortion corresponds to a rotation of one triangular face of 19° from the position it would occupy for an undistorted octahedron. On the basis of this structure, it is probable that the cobalt(III) compounds,  $[\text{Co}_2(\text{EtaH})_3(\text{Eta})_3]\text{X}_3$ , and the corresponding chromium(III) compounds<sup>6</sup> contain the same type of hydrogen-bonded dinuclear unit; a structure study of the chloride salt of the cobalt(III) compound is in progress.

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