The Bis(biuretato)cobaltate(III) Ion: A Paramagnetic Planar CoN₄ Species

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Summary In the paramagnetic (3-5 B.M.) planar bis-(3-n-propylbiuretato)cobaltate(III) ion the cobalt is co-ordinated to four deprotonated amide nitrogen atoms, the u.v. spectrum being in accord with the assumption of a low-lying spin triplet term.

The bis(biuretato) complexes of CoIII, NiIII, and CuIII have been shown to have closely related structures,1 the last two compounds being reported to have planar co-ordination of four deprotonated amide nitrogen atoms.2 We now report on the bis-(3-n-propylbiuretato)cobaltate(III) ion, whose greater solubility allows a more detailed study. The compound can be prepared as described for the unsubstituted biuretato complex,1 using a mixture of 1- and 3-n-propylbiuret.2,3 A stable precipitate is formed with composition KCo(3-propbi)2·(2-propbiH5) (3-propbi = HN-CO-NPr-NH-CO-NH, 1-propbiH5 = Pr-NH-CO-NH-CO-NH).

This compound forms small needle-shaped crystals (along b). Unit-cell parameters were determined from (h00) Weissenberg, and diffractometer readings: a = 32-73 (2), b = 4-64 (1), c = 19-98 (1) Å, α = 94-50 (5), Z = 4, space group C2/c. A crystal of 0·07 mm diameter was used to collect 1068 intensities on an automatic Nonius diffractometer, using Mo-radiation. The structure was solved by Patterson and Fourier methods, and refined by least-squares methods until R = 0·13. All atoms except hydrogen were located.

The structural parameters of the biuretato ligand are almost the same as those found in the CuIII complex,4 the Co–N distances are like the amide –N–Co distance in the glycylglycinatocobaltate complex.5 The structure of the 1-n-propylbiuret molecules around the K+ ion is similar to that of the biuret molecules in Cd(biH2)Cl,.

Magnetic susceptibilities, measured between 120 and 300 K, follow closely the Curie–Weiss law with a Weiss constant of −26° and a moment of 3·51 B.M. A solution of the compound in Me2SO has a moment of 3·41 B.M. at room temperature. The only other example of such an unusual magnetic behaviour in a planar four-co-ordinated CoIII complex is in the bis(dithiolene)monoanion;7 some five-co-ordinated CoIII compounds, however, have similar properties.8 Upon addition of amines, diamagnetic ions of composition [Co(3-propbi)La]- are formed; their u.v. spectra can be interpreted assuming octahedral co-ordination.8

Figure 1. Projection along a. The biuret molecule and the propyl group of the biuret ion are omitted. Cobalt atoms are on centres of symmetry, potassium atoms are on a twofold axis (indicated by an arrow).

Figure 2. Projection along b. K–O bonds are indicated by heavily dashed lines; hydrogen bonds are indicated by dotted lines.
In the u.v. spectrum of a Me₂SO solution of the present compound two lines of low intensity occur at 11.4 (ε 50) and 13.0 kK (ε 100), which we assume to be the transitions \( ^3B_2g \rightarrow ^1A_2g \) and \( ^3B_2g \rightarrow ^1E_g \), respectively. In the spectrum of the solid compound the latter absorption is split into a doublet at 13.3 and 13.7 kK. This is probably due to the splitting of \(^3E_g\) in \( D_{4h} \) to \(^3B_{2g} + ^3B_{3g}\) in \( D_{4h} \) symmetry. In the spectrum of the Co(bi)₃⁺ ion the spin-forbidden transition \(^1A_{lg} \rightarrow ^3T_{1g}\) is observed at 12.8 kK (ε 1.5).

This indicates that in the planar bis-complex the \(^1A_{lg}\) and \(^3B_{lg}\) terms are very close and that the cross-over point of the \( d_{3z^2} \) and \( d_{xy} \) orbitals is near.

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