The Bis(biuretato)cobaltate(III) Ion: A Paramagnetic Planar CoN_4 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(biureto) complexes of Co^{III}, Ni^{III}, and Cu^{III} 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 $KCo(3\text{-propbi})_2 . 2(1\text{-propbiH}_2)$ (3-propbi = $HN{\cdot}CO{\cdot}NPr^n{\cdot}CO{\cdot}NH$, 1-propbiH$_2$ = $Pr^nHN{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$).

This compound forms small needle-shaped crystals (along *b*). Unit-cell parameters were determined from (*h0l*) Weissenberg, and diffractometer readings: $a = 32{\cdot}73$ (2), $b = 4{\cdot}64$ (1), $c = 19{\cdot}98$ (1) Å, $\alpha = 94{\cdot}50$ (5), $Z = 4$, space group *C*2/*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 $R = 0{\cdot}13$. All atoms except hydrogen were located.

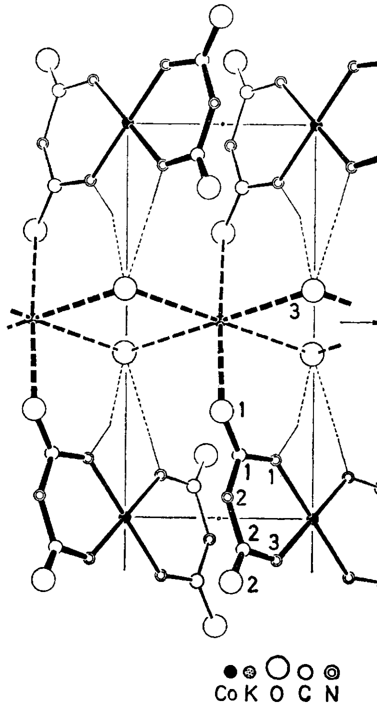

Figure 1. *Projection along* a. *The biuret molecule and the propyl group of the biuret ion are omitted. Cobalt atoms are on centres of symmetry, potassium atoms are on a twofold axis (indicated by an arrow).*

The structure is shown in the Figures. Cobalt is in square-planar co-ordination with four nitrogen atoms. Co–N(1) = 1·88, Co–N(3) = 1·88 (2) Å, N(1)–Co–N(3) = 88·5 ± 1·0°. The complex ion is planar, except for the atoms C(4) and C(5). Distances and angles in N(1)–C(1)–N(2)–C(2)–N(3) are 1·29, 1·42, 1·42, 1·28 (3) Å and 120, 123, 124 ± 2°, respectively. C(1)–O(1) = 1·22, C(2)–O(2) = 1·24 (3) Å. These ions are piled along the *b* axis; the shortest interionic distance is Co–N(2) = 3·40 Å. Potassium is in slightly-distorted octahedral co-ordination with six oxygen atoms.

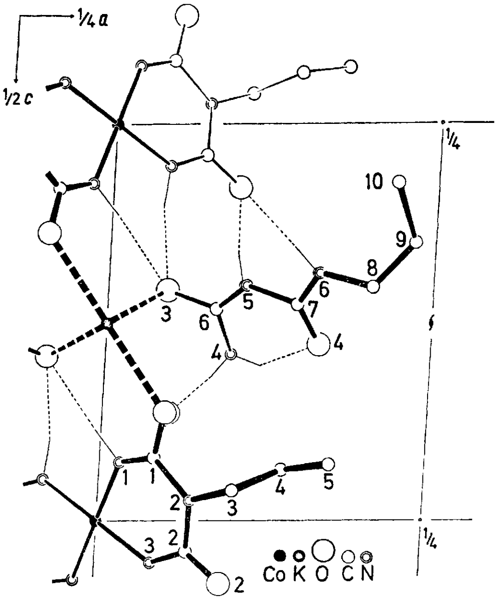

Figure 2. *Projection along* b. *K–O bonds are indicated by heavily dashed lines; hydrogen bonds are indicated by dotted lines.*

The structural parameters of the biuretato ligand are almost the same as those found in the Cu^{II} 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 $Cd(biH_2)_2Cl_2$.

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 Me_2SO 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 Co^{III} complex is in the bis(dithiolene)monoanion;[7] some five-co-ordinated Co^{III} compounds, however, have similar properties.[8] Upon addition of amines, diamagnetic ions of composition $[Co(3\text{-propbi})_2L_2]^-$ are formed; their u.v. spectra can be interpreted assuming octahedral co-ordination.[3]

In the u.v. spectrum of a Me_2SO 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 $^3B_{2g} \rightarrow {}^3A_{2g}$ and $^3B_{2g} \rightarrow {}^3E_g$, 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_{2h} symmetry. In the spectrum of the $Co(bi)_3{}^{3-}$ ion the spin-forbidden transition $^1A_{1g} \rightarrow {}^3T_{1g}$ is observed at 12·8 kK (ϵ 1·5). This indicates that in the planar bis-complex the $^1A_{1g}$ and $^3B_{2g}$ terms are very close and that the cross-over point of the d_{z^2} and d_{xy} orbitals is near.

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