The Bis(biuretato)cobaltate(III) Ion: A Paramagnetic Planar CoN_4 Species

By J. J. BOUR, P. T. BEURSKENS, and J. J. STEGGARDA*

(Inorganic Chemistry Laboratory, University of Nijmegen, Nijmegen, The Netherlands)

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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 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-propbi)₂. 2(1-propbiH₂) (3-propbi = HN·CO·NPrⁿ·CO·NH, 1-propbiH₂ = PrⁿHN·CO·NH·CO·NH₂).

This compound forms small needle-shaped crystals (along *b*). Unit-cell parameters were determined from (*h*0*l*) 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 *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* = 0.13. All atoms except hydrogen were located.

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

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.

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.

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(biH₂)₂Cl₂.

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 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-propbi)₂L₂]⁻ 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 ${}^3B_{2g} + {}^3B_{2g}$ in D_{2h} symmetry. In the spectrum of the $\text{Co}(\text{bi})_3^{3-}$ 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_{xy}^2 and d_{xy} orbitals is near.

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