The Bis(biuretato)cobaltate(III) Ion: A Paramagnetic Planar CoN$_4$ Species

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Reprinted from
Journal of The Chemical Society
Chemical Communications
1972

The Chemical Society, Burlington House, London WIV OBN
The Bis(biuretato)cobaltate(III) Ion: A Paramagnetic Planar CoN 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-propbi)2(1-propbiHs) (3-propbi = HN-CO-NPr"-CO-NH, 1-propbiHs = Pr"HN-CO-NH-CO-NHs).

This compound forms small needle-shaped crystals (along b). Unit-cell parameters were determined from (h0l) Weissenberg, and diffractometer readings: a = 32.73 (2), b = 4.64 (1), c = 19.98 (1) Å, \( \alpha = 94.50^\circ \) (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 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

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

\[ \text{Figure 2. Projection along } b. \text{ K-O bonds are indicated by heavily dashed lines; hydrogen bonds are indicated by dotted lines.} \]

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 biuret 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)Cl2.

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)L4]− are formed; their u.v. spectra can be interpreted assuming octahedral co-ordination. 8
In the u.v. spectrum of a Me$_2$SO 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 $^3B_{3g} \rightarrow ^3E_g$, 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 $D_{4h}$ symmetry. In the spectrum of the Co(bi)$_2^2-$ ion the spin-forbidden transition $^1A_{1g} \rightarrow ^3T_{1g}$ is observed at 12-8 kK (ε 1-6). 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 $d_3^3$ and $d_{xy}$ orbitals is near.

We thank Dr. G. L. Gartland and Dr. W. P. J. H. Bosman and Mr. J. M. M. Smits for help with the X-ray work. The investigations were supported by SON with financial aid from ZWO.

(Received, 8th December 1971; Com. 2094.)
