The Structure of the Red Nitrosylpenta-amminecobalt(III) Cation

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THERE has been much controversy about the nature of the black and the red isomers of the nitrosylpenta-amminecobalt(III) ion.[1,2] Crystal structure studies[3] have shown that the complex ion of the black chloride is monomeric and octahedral and that the atoms in the cobalt–nitrosyl group are colinear.

We report the crystal structure of one of the red nitrosylpenta-amminecobalt(III) salts, a mixed nitrate–bromide compound. We have found that the complex ion in these crystals is binuclear; the two crystallographically independent cobalt atoms, each surrounded by five ammonia molecules, are bridged asymmetrically through a hyponitrite ion. One cobalt atom is bonded to an oxygen atom and the other to a nitrogen atom (Figure). The hyponitrite is planar and *cis* in configuration. The dimeric nature of this ion is in accordance with the study of Feltham[4] who showed, by conductivity measurements, that the red nitrate is a 4:1 electrolyte, *i.e.* of composition $[(NH_3)_5Co-N_2O_2-Co(NH_3)_5](NO_3)_4$.

The crystals used for this study were obtained according to the method given by Griffiths *et al.*[1] for the preparation of the bromide. The crystal structure determination has shown that the crystals obtained were not those of the simple bromide but those of a mixed nitrate–bromide with a composition close to $[Co(NH_3)_5NO]_2Br_{2.5}(NO_3)_{1.5},2H_2O$. Of the anion sites in the unit cell, one is partially occupied by both nitrate and bromide ions, present in about equal weight.

Crystal data: $H_{34}O_{8.5}N_{13.5}Br_{2.5}Co_2$, $M = 677$, monoclinic, $a = 13.6_2$, $b = 6.95$, $c = 23.4_9$ Å, $\beta = 100.4°$, $U = 2187$ Å^3, $D_m = 2.04 \pm 0.04$ (flotation), $Z = 4$, $D_c = 2.05$ g.cm.$^{-3}$, space group $A2/m$, $(C^3_{2h}$; No. 12), Cu-K_α radiation, single crystal oscillation and equi-inclination Weissenberg photographs.

Attempts to solve the Patterson function on the basis of the simple bromide (six heavy atoms) were inconclusive. Eventually five possible heavy atoms were located by a trial and error method, with a computer programme developed by one of us (F.D.W.). The co-ordinates for the heavy-atom positions ultimately decided upon were consistent with the major peaks in the vector map. The positions of the nitrogen and oxygen atoms were located in

three-dimensional difference syntheses. Refinement is being achieved by the least-squares method, with individual
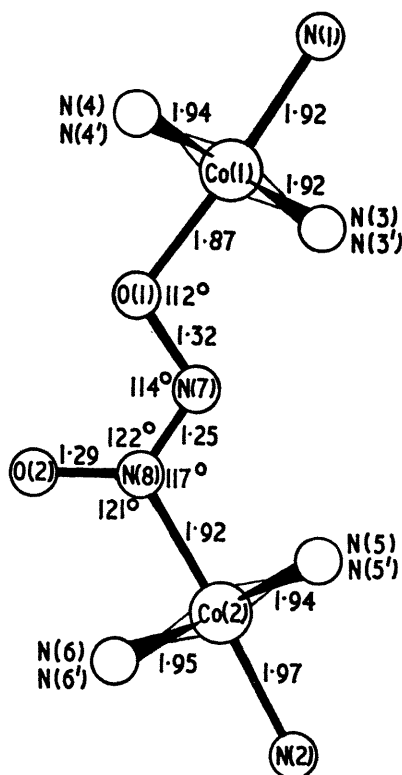
isotropic temperature factors; at present R is 0·16 for 1350 independent reflections. The relative sizes of the peaks in the difference synthesis and the temperature factors in the least-squares refinement have enabled us to identify the atoms in the hyponitrite group with reasonable certainty.

All the non-hydrogen atoms in the structure, except the equatorial nitrogen atoms of each co-ordination sphere of the two cobalt atoms and two oxygen atoms of the fully occupied nitrate ion, lie on mirror planes in the unit cell.

Each of the two crystallographically-independent cobalt atoms has an octahedral environment. The cobalt–ammonia-nitrogen bond distances range from 1·92 to 1·97 Å (current e.s.d. 0·024 Å), consistent with distances reported for similar bonds in other penta-amminecobalt (iii) complexes.[3,5] The sixth bonds of the two cobalt atoms are those to the hyponitrite ion. These are Co(1)–O(1) and Co(2)–N(8), (1·87 and 1·92 Å respectively, current e.s.d.'s 0·025 Å; these are normal covalent bond lengths). The bond angles around the cobalt atoms lie within the range 87°.—94°.

The dimensions of the hyponitrite ion are given in the Figure and seem to be of the order of magnitude expected for such a system. The current values of the e.s.d. of the bond lengths is 0·03 Å. The cis-configuration is probably adopted for steric reasons, this being the only configuration which will allow the bridging of the two $Co(NH_3)_5$ groups without steric interference between them.

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