Crystal and Molecular Structure of a μ-Hyponitrito-bis[penta-amminecobalt(III)] Salt: the Nature of the Red Nitrosylpenta-amminecobalt(III) Cation

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The structure of the title cation, μ-hyponitrito-bis[penta-amminecobalt(III)], has been determined as a mixed bromide–nitrate salt from single-crystal three-dimensional *X*-ray photographic data, the stoicheiometry of the crystals used being $[Co(NH_3)_5NO]_2Br_{3-x}(NO_3)_{1+x},2H_2O$, where $x = ca.$ 0·5. The structure was solved by Patterson and Fourier methods, and refined by least-squares techniques to *R* 0·13 for 1264 independent reflections. The complex cation is binuclear with the two metal atoms bridged by a hyponitrito-group in a *cis*-asymmetric manner *via* a nitrogen atom and the oxygen atom bonded to the other nitrogen atom of the hyponitrite group. The unit cell is monoclinic with $Z = 4$, $a = 13{\cdot}72(3)$, $b = 7{\cdot}00(2)$, $c = 23{\cdot}65(4)$ Å, $\beta = 100{\cdot}4(2)°$, space group *A*2/*m*.

THERE has been much controversy about the nature of the red and black isomers of the nitrosylpenta-amminecobalt(III) ion since their initial preparation.[1] This has been due largely to misleading conclusions drawn from the magnetic data of impure samples of the black isomer, conflicting interpretations of the different chemical reactivities exhibited by the two isomeric forms, and the disputed assignments of the NO stretching frequencies in the i.r. spectra.‡ Crystals of the black chloride, which grow as intimate twins, were found to contain the mononuclear cation $[Co(NH_3)_5NO]^{2+}$.[2,3] A subsequent redetermination[4] of this structure, using improved refinement methods and data derived from counter techniques, showed that the arrangement of the Co–N–O atoms is not collinear as previously reported but such

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‡ An historical review of the many steps leading to the elucidation of the difference between the isomers is available from F. D. W.

[1] J. Sand and O. Genssler, *Ber.*, 1903, **36**, 2083; *Annalen*, 1903, **329**, 194.

[2] D. H. Dale and D. C. Hodgkin, *J. Chem. Soc.*, 1965, 1364; D. H. Dale, D. Phil. Thesis, Oxford University, 1962.

[3] D. Hall and A. A. Taggart, *J. Chem. Soc.*, 1965, 1359.

[4] C. S. Pratt, B. A. Coyle, and J. A. Ibers, Amer. Cryst. Assoc. Summer Meeting, 1970, Abs. *C* 8, 30; *J. Chem. Soc.* (*A*), 1971, 2146.

that the bond angle about the nitrogen atom is close to 120°.

Feltham[5] observed that the red nitrate behaved as a 4 : 1 electrolyte in aqueous solution providing conclusive evidence that the red isomer was binuclear. At the same time Dale and Hodgkin reported[2] a preliminary investigation of the crystal data for a red salt and we report here the completed crystal structure determination based on their data which they kindly made available to us. The complex cation of this red mixed bromide-nitrate salt is binuclear; the two metal atoms are bridged by a hyponitrito-group in a *cis*-asymmetric manner *via* a nitrogen atom and the oxygen atom attached to the other nitrogen atom of the hyponitrito-group as is shown in Figure 1.

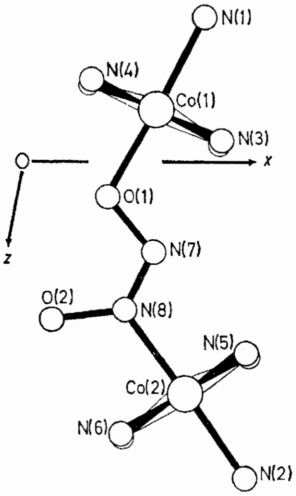

FIGURE 1 The cation viewed along the *b* axis

A preliminary account of this structure analysis has been given elsewhere.[6]

EXPERIMENTAL

Crystal Data.—$H_{34}Br_{3-x}Co_2N_{13+x}O_{7+3x}$, $x = 0{\cdot}44 \pm 0{\cdot}12$, $M = 678$, Monoclinic, $a = 13{\cdot}72(3)$, $b = 7{\cdot}00(2)$, $c = 23{\cdot}65(4)$ Å, $\beta = 100{\cdot}4(2)°$, $U = 2232$ Å^3, $D_m = 2{\cdot}04(2)$, $Z = 4$, $D_c = 2{\cdot}02$ g cm^{-3}, $F(000) = 4 \times 238$. Space group $A2/m$ (C^3_{2h}, No. 12). Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 180 cm^{-1}. Single-crystal oscillation and equi-inclination Weissenberg photographs.

Unit-cell dimensions were determined by use of single-film equi-inclination Weissenberg photographs of the $0kl$ and $h0l$ levels. Systematic absence (hkl $k + l$ odd, $h0l$ l odd, and $0k0$ k odd) indicated space groups $A2$, Am, or $A2/m$. The $N(z)$ distribution test[7] of the $h0l$ and $0kl$ reflections indicated that the (010) and (100) projections were both probably centrosymmetric favouring $A2/m$ as the space group; a satisfactory solution was achieved in the centrosymmetric space group.

Data Collection.—Crystals used in this structure determination were obtained by mixing saturated solutions of the red nitrosylpenta-amminecobalt(III) nitrate and potassium bromide.[8]

Equi-inclination Weissenberg photographs, were recorded by the multiple-film technique, for the layers $0kl$ and $h0$—$3l$, different crystals being used for each layer. All observations were placed on a common arbitrary scale by internal correlation of the $0kl$ with the $h0$—$3l$ layers. As this interlayer scaling was considered to be tentative because of a relatively small number of common hnl and $0kl$ reflections, it was decided to adjust the scaling, at different stages of the structure determination, so that for each layer $\Sigma|F_o| = \Sigma|F_c|$. Lorentz and polarisation corrections were applied; no corrections were made for either absorption or extinction. Some 1264 independent observed reflections were used in the structure determination.

Structure Determination and Refinement.—When a three-dimensional Patterson synthesis was calculated, it was found that the nineteen largest vector peaks lay on the sections at $V = 0$ and $b/2$, and that some smaller peaks lay close to the sections at $V = b/4$ and $3b/4$. Further, the only large peak on the Harker line $(0, V, 0)$ lay at the origin, suggesting that all the heavy atoms were situated on mirror planes at $y = 0$ and $b/2$. The only other vector peak along the Harker line was comparatively small; its position suggested that some light atoms might be *ca.* 1·3 Å from the mirror plane.

Assuming the empirical formula of the simple bromide $[Co(NH_3)_5NO]Br_2,2H_2O$, all attempts to locate the six unique heavy-atom positions (two cobalt and four bromine atoms) proved fruitless. A computer programme, written by F. D. W., calculated R for one or more heavy atoms placed in such a way as to be related by one of the largest vector peaks of the Patterson function. The atomic positions were varied systematically over the section $y = 0$ and the corresponding values of R were calculated by use of selected sets of structure factors. The results of these calculations, together with our interpretation of the Patterson function, indicated only five unique heavy-atom positions, and hence, the crystalline compound under investigation was not the simple bromide $[Co(NH_3)_5NO]Br_2,2H_2O$.

A structure-factor calculation based upon four possible heavy-atom positions (0·598,0,0·217; 0·177,0,−0·031; 0·215,0,0·369; and 0·275,0,0·199), using the bromide scattering-factor curve and an overall isotropic temperature factor, B, of 3 Å^2 gave a discrepancy factor of 0·44. In the subsequent difference-Fourier synthesis, the two crystallographically independent cobalt atoms were identified from the relative size of their electron-density peaks. This identification was substantiated in later calculations when the ligand atoms about each cobalt atom had been located as well as a further two atoms showing that the cobalt atoms were bridged by a *cis*-tetra-atomic grouping. Further, another four atom group was found which was approximately planar; its identification as a nitrate ion was based on the knowledge that the ' simple bromide ' was prepared originally from the red nitrate and potassium bromide. In later difference syntheses two more small peaks became definite; their positioning in the unit cell suggested that they were due to water molecules.

Least-squares refinement[9] was commenced in which the function minimised was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1$ for $|F_o| < 41$ and $(0{\cdot}067|F_o| - 1{\cdot}76)^{-1}$ for $|F_o| \geqslant 41$; nine reflections were given negligible weight in the final refinement

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[5] R. D. Feltham, *Inorg. Chem.*, 1964, **3**, 1038.

[6] B. F. Hoskins, F. D. Whillans, D. H. Dale, and D. C. Hodgkin, *Chem. Comm.*, 1969, 69.

[7] E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Cryst.*, 1950, **3**, 210.

[8] W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 38.

[9] W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory Report ORNL TM 305, Oak Ridge, Tennessee, 1962.

cycles as they appeared to suffer considerably from extinction effects. This scheme fitted the criteria [10] that the average value of $w(|F_o| - |F_c|)^2$ should be approximately constant over ranges of $|F_o|$ and sin θ.

All relevant positional parameters, all individual isotropic temperature factors and the overall scale factor were varied in the initial five cycles of the refinement. In order to test the validity of labelling the four atoms in the bridging group between the two cobalt atoms, a further two cycles of refinement were calculated in which only five parameters were varied, namely, the overall scale factor and the individual isotropic temperature factors of the four atoms. Here, each atom was assigned the scattering factor curve for an oxygen atom and an individual isotropic temperature factor, B, of 2·95 Å^2. If it is assumed that this group of four atoms contains two oxygen and two nitrogen atoms, it is possible that the individual atoms in the group could be identified with reasonable certainty from peaks in difference-Fourier syntheses and from the substantial increases in two of the four temperature factors; values of 2·3, 3·1, 3·9, and 4·9 Å^2 were obtained after two cycles for the atoms designated O(1), O(2), N(7), and N(8) respectively.

All the Fourier and difference-Fourier syntheses calculated during the course of the analysis indicated, from the relevant peak heights, that the lightest of the five heavy atoms possessed *ca.* 18 electrons.

The refinement had continued on the assumption that this position was occupied by a potassium ion since the compound was prepared from a potassium salt; when consideration was given to the formula of the compound under investigation all possible alternatives seemed unlikely. However, two independent analyses for potassium, by atomic absorption spectrometry, showed this element to be absent. A close examination of three small peaks, on the mirror plane, at distances of *ca.* 1·2 Å from the site of this atom and in an approximately triangular arrangement, led to the realisation that the peak corresponding to an atom of *ca.* 18 electrons could be explained sensibly if the site was partially occupied by bromide and nitrate ions. Hence the formula of the compound could be postulated as $[(NH_3)_5Co-N_2O_2-Co(NH_3)_5]Br_{3-x}(NO_3)_{1+x},2H_2O$ where x was *ca.* 0·5.

The temperature factor for the partially occupied nitrate ion nitrogen atom [N(10)] was estimated and its position was fixed arbitrarily at the centre of the three oxygen atoms [O(7), O(8), and O(9)] of the same nitrate ion. The occupancy appeared to be 0·5—0·6 bromide and 0·5—0·4 nitrate; the best value, considered to be 0·56(4) bromide and 0·44(4) nitrate, was used in the final refinement.

TABLE 1

Layer	Terms obs.	Final scale factor/original scale factor	R
0kl	80	1·00	0·185
h0l	295	1·00	0·100
h1l	311	0·82	0·161
h2l	333	1·03	0·139
h3l	298	1·18	0·132
hkl	1264	1·00	0·134

The final discrepancy factor for each layer photographed and a comparison of the original with the final scale-factor for each layer are given in Table 1. As a different crystal was used for each layer it seems likely that the anomalies seen in Table 1 can be explained in terms of the occupancy at the mixed bromide–nitrate site varying from crystal to crystal.

The scattering-factor curves used were those for trivalent cobalt, bromide ion, and neutral oxygen and nitrogen,[11] those for cobalt and bromine being corrected for anomalous dispersion.[11]

The final set of calculated structure factors and the set of observed structure amplitudes are listed in Supplementary Publication No. SUP 20604 (4 pp., 1 microfiche).* The final R was 0·134 and the weighed factor, R', was 0·17 $\{R' = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}$. Final fractional coordinates and the individual isotropic temperature factors are given in Table 2. All parameters converged in the refinement.

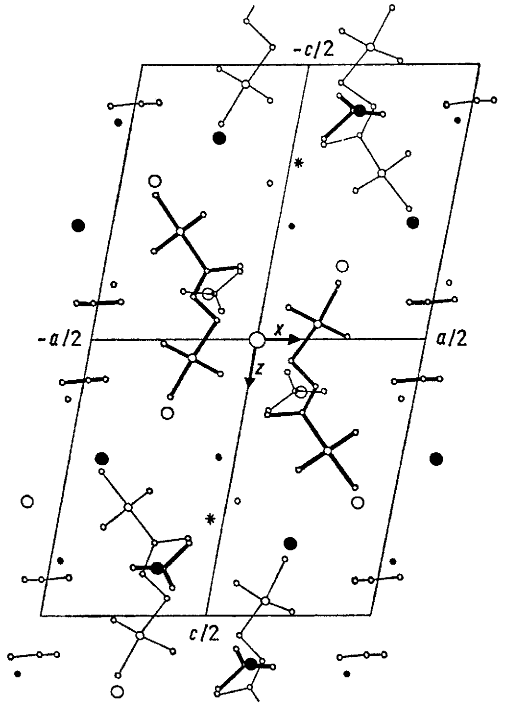

FIGURE 2 The arrangement of atoms in the unit cell viewed along the b axis. Note the partially occupied bromide–nitrate site above and below each hyponitrite bridge. Broad lines and shaded circles indicate those atoms at $y = 0$; other atoms are related by the symmetry transformation $x, \frac{1}{2} + y, \frac{1}{2} + z$

The final difference-Fourier synthesis gave no indication of the positions of the hydrogen atoms. The only peak, Y, was one which had been present from the initial stages of the structure determination at (−0·03,0·0,0·32) and situated 1·5 from the nitrate oxygen atom [O(8)], 3·1 from the bromide ion [Br(3)], and 2·5 Å from the water molecule [O(3)]; the angle Br(3)–O(8)–Y was 171°. The electron density of the peak (asterisked in Figure 2) was *ca.* 2 eÅ^{-3}, slightly less than those of the three oxygen atoms of the partially occupied nitrate, and could be attributed to the presence of a partially occupied water molecule which is hydrogen bonded both to Br(3) and O(3).

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[10] D. W. J. Cruickshank *et al.*, in 'Computing Methods and the Phase Problem in X-ray Crystal Analysis,' eds. R. Pepinsky, J. M. Robertson, and J. C. Speakman, Pergamon Press, Oxford, 1961, p. 45.

[11] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

TABLE 2

Final atomic (fractional) co-ordinates and thermal parameters

Atom	M*	$10^4 x/a$	$10^4 y/b$	$10^4 z/c$	$10^4\sigma_{\text{r.m.s}}$/Å	B/Å^2
Br(1)	$\frac{1}{2}$	5986(2)	0	2173(1)	25	3·79(7)
Br(2)	$\frac{1}{2}$	2140(2)	0	3687(1)	28	4·39(8)
Br(3)	$\frac{9}{32}$	−1562(4)	0	4176(2)	57	4·64(13) †
Co(1)	$\frac{1}{2}$	1744(2)	0	−326(1)	31	2·69(8)
Co(2)	$\frac{1}{2}$	2754(2)	0	1980(1)	32	2·79(8)
					$10^3\sigma$ r.m.s./Å	
N(1)	$\frac{1}{2}$	2169(14)	0	−1060(8)	18	3·4(4)
N(2)	$\frac{1}{2}$	3769(14)	0	2683(8)	19	3·5(4)
N(3)	1	2684(9)	200(3)	−61(5)	16	3·6(3)
N(4)	1	771(8)	200(3)	−571(5)	15	3·0(3)
N(5)	1	3471(9)	202(3)	1656(5)	16	3·4(3)
N(6)	1	2010(9)	199(3)	2299(5)	16	3·8(3)
N(7)	$\frac{1}{2}$	2036(13)	0	829(7)	17	2·8(4)
N(8)	$\frac{1}{2}$	1744(14)	0	1306(7)	18	3·4(4)
O(1)	$\frac{1}{2}$	1268(9)	0	371(6)	13	2·6(3)
O(2)	$\frac{1}{2}$	803(10)	0	1338(6)	14	3·0(3)
O(3)	$\frac{1}{2}$	−420(21)	0	2102(14)	31	11·9(12)
O(4)	$\frac{1}{2}$	5293(24)	0	4002(18)	37	11·8(12)
N(9)	$\frac{1}{2}$	5135(14)	0	677(8)	19	3·3(4)
O(5)	$\frac{1}{2}$	4306(13)	0	766(7)	18	4·5(4)
O(6)	1	5625(12)	137(3)	681(7)	19	6·7(5)
		$10^3x/a$	$10^3y/b$	$10^3z/c$		
N(10) ‡	$\frac{7}{32}$	−144	0	413		3·5
O(7)	$\frac{7}{32}$	−116(5)	0	459(3)	67	8·0(18)
O(8)	$\frac{7}{32}$	−82(4)	0	368(2)	55	6·6(14)
O(9)	$\frac{7}{32}$	−233(3)	0	413(2)	45	4·9(11)

* M, the multiplicity of the atom, equals $\frac{1}{2}$ if the atom lies on a mirror plane. † B for the atom Br(3) changes *ca.* 0·1 Å^2 for every 1% change in occupancy. The value of 4·64(13) is that obtained from an unvaried occupancy of 9/16. ‡ The atom N(10) was assigned arbitrarily chosen parameters (see text).

RESULTS AND DISCUSSION

Intermolecular Structure.—The crystals of the salt, hitherto called the red nitrosylpenta-amminecobalt(III) salt, consist of complex binuclear cations of μ-*cis*-hyponitrito(*N*,*O*′)-bis[penta-amminecobalt(III)], anions of bromide and nitrate, and molecules of water (Figure 2). Most of the non-hydrogen atoms of the structure are positioned on the mirror planes of the unit cell. The five unique atoms not located on these planes are the nitrate oxygen atom [O(6)] and the four equatorial nitrogen atoms, [N(3)—(6)] of the co-ordination spheres about the two crystallographically independent cobalt atoms.

The cation of the asymmetric unit makes contact with one cation, related by the symmetry transformation $(\bar{x}, \bar{y}, \bar{z})$, in such a way that the two cations lie side by side on the same mirror plane (see Figure 2). This pair of cations is positioned between two pairs of fully occupied nitrate anions such that the complex cation pair and the nitrate anion pair alternate in the x direction at intervals of a.

The anion site, which is partially occupied by both bromide and nitrate ions, is situated 3·5 Å (b/2) above and below the hyponitrite group of the complex cation (see Figure 2). Viewed down the b axis through the hyponitrite grouping of the complex cation, the complex cation and this mixed bromide–nitrate site are seen to alternate at intervals of b. Although the sum of the van der Waal's radii[12] (1·95 + 1·54 = 3·49 Å) indicates that the bromide–nitrogen contacts should be considered as quite weak van der Waal's interactions, the apparent influence of the bromide ion on the i.r. stretching frequencies of the hyponitrite group is to be noted. Griffith *et al.* reported[8] the NO stretch was 1045, 1080, 1150, 1173, and 1195 cm^{-1} for the red nitrate, sulphate, chloride, bromide, and iodide. Mercer *et al.* reported[13] that the NN stretch in the red nitrate (1136 cm^{-1}) was different from that in the red bromide (1165 cm^{-1}). These differences suggest that some interaction is occurring. The nitrate atoms at the mixed bromide–nitrate site lie in a plane parallel to the mirror plane containing the hyponitrite grouping. They appear to be positioned so as to minimise electrostatic repulsion forces from the atoms of the hyponitrite group, and to facilitate hydrogen bonding.

The extensive scheme of weak oxygen–nitrogen hydrogen bonding appears to play a part in the stabilisation of the *cis*-configuration of the complex cation. For example, the oxygen atom [O(5)] of the fully occupied nitrate ion seems to form a hydrogen bond with two of the ammine nitrogen atoms [N(3) and N(5)] of the complex cation; these contacts are 3·03 and 2·94 Å respectively. The angles N(9)–O(5)–N(3) and N(9)–O(5)–N(5) of 120 and 129° and the angles Co(1)–N(3)–O(5) and Co(2)–N(5)–O(5) of 104 and 103° suggest hydrogen bonding in which a hydrogen atom of each of the two ammine ligands is attracted to the nitrate oxygen atom. Similarly, the oxygen atom [O(9)] of the partially occupied nitrate appears to be hydrogen bonded to the same two ammine nitrogen atoms and their equivalent atoms related by the symmetry transformation $(x, 1-y, z)$; these contacts, N(3) ··· O(9$^{\text{II}}$) and N(5) ··· O(9$^{\text{II}}$) [II

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[12] L. Pauling, in 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1963, pp. 228—229, 260—263.

[13] E. E. Mercer, W. A. McAllister, and J. R. Durig, *Inorg. Chem.*, 1967, **6**, 1816.

represents atoms at $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$], are 3·15 and 3·03 Å respectively. The angles Co(1)–N(3)–O(9^{II}) and Co(2)–N(5)–O(9^{II}) (122 and 120°) and N(10^{II})–O(9^{II})–N(3) and N(10^{II})–O(9^{II})–N(5) (106 and 114°) are also consistent with the presence of weak hydrogen bonding.

Finally, the intermolecular contacts, O(1) $\cdots$ N(4^{III}) (3·24 Å) and O(2) $\cdots$ N(4^{III}), (2·92 Å) (III denotes atoms at $\bar{x}, y, \bar{z}$), between the hyponitrite oxygen atoms and the ammine nitrogen atom strongly suggest that hydrogen bonding is responsible for the association of the binuclear complex cations described previously. This latter contact is the shortest nitrogen–oxygen contact observed in the structure and it is consistent with the oxygen atom, O(2), possessing a residual negative charge; the angle of 103° for O(2)–N(4^{III})–Co(1^{III}) suggests a reasonably direct hydrogen bond.

TABLE 3

Intramolecular covalent bond lengths and bond angles

(*a*) Bond lengths (Å)

Co(1)–N(1)	1·93(2)	Co(2)–N(5)	1·96(2)
Co(1)–N(3)	1·93(2)	Co(2)–N(6)	1·96(2)
Co(1)–N(4)	1·95(2)	Co(2)–N(2)	1·97(2)
Co(1)–O(1)	1·88(2)		
O(1)–N(7)	1·37(2)	N(9)–O(5)	1·19(3)
N(7)–N(8)	1·26(2)	N(9)–O(6)	1·17(2)
N(8)–O(2)	1·31(2)		
		N(10)–O(7)	1·07(20)
Co(2)–N(8)	1·92(2)	N(10)–O(8)	1·47(20)
		N(10)–O(9)	1·22(15)

(*b*) Bond angles (deg.) *

N(1)–Co(1)–N(3)	90·0(6)	N(3)–Co(1)–O(1)	91·9(5)
N(1)–Co(1)–N(4)	92·0(5)	N(4)–Co(1)–O(1)	86·2(5)
N(3)–Co(1)–N(3^{I})	93·0(11)	N(5)–Co(2)–N(8)	90·7(6)
N(4)–Co(1)–N(4^{I})	92·0(10)	N(6)–Co(2)–N(8)	88·4(6)
N(3)–Co(1)–N(4)	87·5(8)		
N(3)–Co(1)–N(4^{I})	178·0(5)	Co(1)–O(1)–N(7)	110·8(11)
N(1)–Co(1)–O(1)	177·4(7)	O(1)–N(7)–N(8)	112·6(17)
N(2)–Co(2)–N(5)	90·1(6)	N(7)–N(8)–O(2)	121·8(17)
N(2)–Co(2)–N(6)	90·7(6)	N(7)–N(8)–Co(2)	116·5(14)
N(5)–Co(2)–N(5^{I})	92·6(11)	O(2)–N(8)–Co(2)	121·7(13)
N(6)–Co(2)–N(6^{I})	90·6(11)	O(5)–N(9)–O(6)	124·3(13)
N(5)–Co(2)–N(6)	88·4(8)	O(6)–N(9)–O(6^{I})	110·0(26)
N(5)–Co(2)–N(6^{I})	178·7(7)	O(7)–N(10)–O(8)	125(10)
N(2)–Co(2)–N(8)	178·8(8)	O(7)–N(10)–O(9)	101(10)
		O(8)–N(10)–O(9)	134(10)

* The transformation I ($x, \bar{y}, z$) is that due to the mirror plane.

Environment of the Cobalt Atoms.—Each of the crystallographically independent cobalt atoms has an octahedral environment (Figure 1). The N–Co–N and N–Co–O angles about these cobalt atoms range from 86·2 to 93·0°; none of these angles is significantly different from 90°.

The cobalt–ammine nitrogen bond lengths range from 1·927 to 1·966 Å, mean 1·947 Å. These distances, which differ by only 2σ, verify that each cobalt atom has a formal oxidation state of +3; they compare well with previously reported values for cobalt(III) ammine complexes, in particular with the Co^{III}–NH_3 distance (1·936 Å) in $[Co(NH_3)_6]I_3$, and differ markedly from the Co^{II}–NH_3 distance (2·114 Å) in $[Co(NH_3)_6]Cl_2$.[14] The values of the cobalt–hyponitrite bond distances, Co(1)–O(1) and Co(2)–N(8) [1·881(15) and 1·915(18) Å] are as expected.

The Hyponitrite Bridge.—The N(7)–N(8), O(1)–N(7), and N(8)–O(2) bond distances [1·264(23), 1·366(21), and 1·307(23) Å] suggest that the most important valence representation for the group is that of a hyponitrite ion, namely $^{-}O{\cdot}N{:}N{\cdot}O^{-}$. Furthermore, some of the bond angles within the hyponitrite group also substantiate the identification of its atoms. The O(1)–N(7)–N(8) bond angle [112·6(17)°] suggests that N(7) is a nitrogen atom, as similar values have been found for the corresponding angles in N_2F_2 (115°) and Me_2N_2 (110°).[15] The Co(1)–O(1)–N(7) angle [110·8(11)°] is consistent with a formulation of the grouping as a hyponitrite ion.

There is a strong resemblance between the conformation of the hyponitrite group and that of the anion of potassium methanediazoate, $K^+[^{-}O{\cdot}N{:}NMe]$, which has also a *cis*-configuration.[16] The nitrogen–nitrogen and nitrogen–oxygen distances of the anion of the latter (1·246 and 1·306 Å) agree closely with those for the hyponitrite: N(7)–N(8) 1·264(23) and N(8)–O(2) 1·307(23) Å. In addition, the CH_3–N–N and N–N–O angles (116·2 and 119·8°) compare satisfactorily with the O(1)–N(7)–N(8) and N(7)–N(8)–O(2) angles [112·6(17) and 121·8(17)°]. This close resemblance suggests that the oxygen atom, O(2), possesses a considerable residual negative charge. In support of this, there appears to be a moderately strong hydrogen bond between the hyponitrite oxygen atom, O(2), and the oxygen atom, O(3), of a water molecule; the distance of 2·68 Å between these two atoms falls within the range (2·49—3·15, mean 2·75 Å) quoted[17] for hydrogen bonds of this type in hydrated inorganic salts and the range (2·42—2·84 Å) quoted for fifteen determinations by neutron diffraction.[18] Hence, the formation of the acid cation, $[(NH_3)_5Co$–N_2O_2H–$Co(NH_3)_5]^{5+}$, prepared by the addition of concentrated nitric acid to the red nitrate,[19,20] can be accounted for satisfactorily.

We thank Dr. J. C. B. White and Dr. S. A. Mason for computing assistance, Mr. C. G. Baird and Mrs. H. Andrews for chemical analyses, Professor D. P. Mellor for first suggesting this problem and, Professor Dorothy Crowfoot Hodgkin for passing it on to us. We also thank the Education Department of Victoria and the Australian Research Grants Committee for financial support.

[2/2161 *Received, 18th September*, 1972]

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