# Crystal Structure of Di-μ-hydroxo-*trans*-diaquo-bis[triamminecobalt-(III)] Tetranitrate Dihydrate, and a Possible Mechanism for the Formation of the Cation

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The di-μ-hydroxo-bis[aquotriamminecobalt(III)]$^{4+}$ cation is formed in acidic solution from the tri-μ-hydroxo-bis-[triamminecobalt(III)]$^{3+}$ complex. The crystal structure of the hydrated nitrate salt of the di-μ-hydroxo-cation, $[Co_2(OH)_2(H_2O)_2(NH_3)_6](NO_3)_4,2H_2O$, has been reinvestigated and refined to $R$ 0·032 [space group $P2_1/n$, $a$ = 9·444(2), $b$ = 9·684(3), $c$ = 10·736(3) Å, β = 90·1(2)°, $Z$ = 2]. All hydrogen atom positions were found from a difference synthesis, which resulted in an unambiguous assignment of all hydrogen bonds, and enabled the $H_2O$ and $NH_3$ groups to be distinguished. The water molecules co-ordinated to the Co-atoms are *trans*. The ligands in the $Co^{3+}$ complex undergo rearrangement after breaking of the hydroxo-bridge, probably by formation of a reactive five-co-ordinate intermediate.

THE cation [1] tri-μ-hydroxo-bis[triamminecobalt(III)]$^{3+}$ reacts in acidic solution to form the complex cation di-μ-hydroxo-bis[aquotriamminecobalt(III)]$^{4+}$. The reaction is reversible, the equilibrium depending on the pH,[2] and involving protonation of the OH-group, the breaking of one hydroxide bridge, and the aquation of the co-ordination site which was freed by the hydroxide group [equation (1)]. The two water molecules can have four possible positions relative to each other, if it is assumed that the protonated hydroxide group remains in place (Figure 1). The water molecules can be easily replaced by anions, thus forming cations of type (I) where X is $NO_3^-$,[1] and $F^-$, $N_3^-$, or $NCS^-$.[2] The structures of these salts are not known. With other acids complexes of type (II) are formed where Y can be $AcO^-$,[3] $NO_2^-$,[3] $C_2O_4H^-$,[4]

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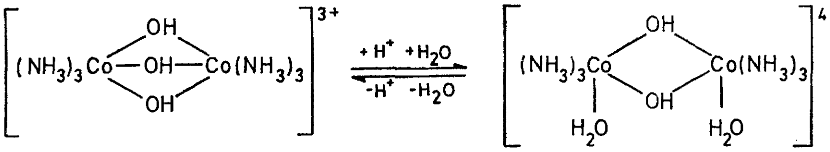
[1] A. Werner, *Ber.*, 1907, **40**, pp. 4834, 1908; **41**, 3879.

[2] M. Linhard and H. Siebert, *Z. anorg. Chem.*, 1969, **364**, 24.

[3] A. Werner, *Annalen*, 1910, **375**, 1.

[4] K. Wieghardt, *Z. anorg. Chem.*, 1972, **391**, 142.

or $HCO_2^-$.[5] Most likely the di-μ-hydroxo-bis[aquotriamminecobalt(III)] complex is an intermediate in such reactions. Therefore, and because of the ease of formation of type (II) cations, it is natural to assume that the two $H_2O$ molecules are in *cis*-positions.



(1)

A crystal structure determination of the nitrate salt[6] of this complex, $[Co_2(OH)_2(H_2O)_2(NH_3)_6](NO_3)_4,2H_2O$, however, did not succeed in establishing which isomer had been formed. Since a proof of the *cis*-structure, or of one of the other three possible isomers, is of obvious importance in elucidating the kinetic mechanism of aquation of a dinuclear cobalt–ammine complex, we reinvestigated the *X*-ray diffraction data on $[Co_2(OH)_2(H_2O)_2(NH_3)_6](NO_3)_4,2H_2O$ with a view toward differentiating between the aquo and the ammine groups on the basis of the hydrogen bonds donated by them.[7]

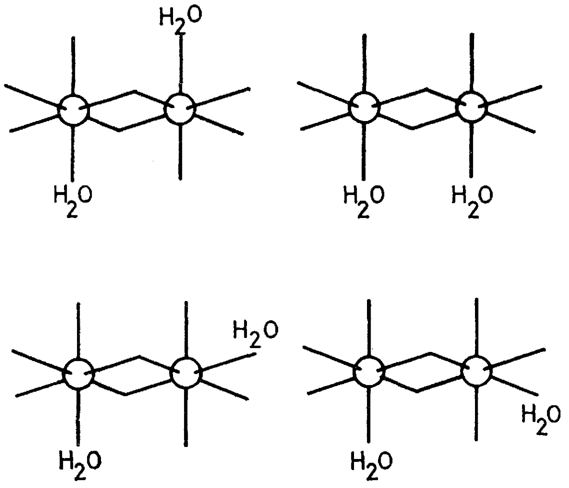
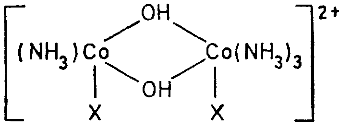
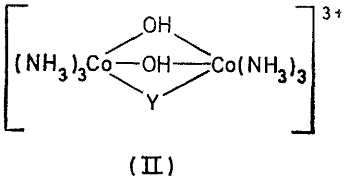


FIGURE 1 Four possible isomers of the di-μ-hydroxo-bis[aquotriamminecobalt(III)]$^{4+}$ cation, assuming that the protonated third hydroxo-group remains in position



(I)



(II)

EXPERIMENTAL

*Crystal Data*.—$[Co_2(OH)_2(H_2O)_2(NH_3)_6](NO_3)_4,2H_2O$, $M = 574·18$, Monoclinic Prismatic, $a = 9·444(2)$, $b = 9·684(3)$, $c = 10·736(3)$ Å, $\beta = 90·1(2)°$, $U = 981·9$ Å$^3$, $D_m = 1·92$ (by flotation), $Z = 2$, $D_c = 1·94$. Mo-$K_\alpha$ radiation, $\lambda = 0·71069$ Å, $\mu$(Mo-$K_\alpha$) = 30·9 cm$^{-1}$. Space group, $P2_1/n$.

*Structure Determination and Refinement*.—In the previous *X*-ray diffraction work[6] a total of 2248 symmetrically independent structure factors (of which 483 were zero) were measured on an automatic diffractometer.

We used the same structure factors and continued the refinement (from $R$ 0·047) in three steps employing unit weights. Examination of the hydrogen-bonding environment (see later) of atoms O(1) and O(2) (as numbered in ref. 6) suggested that O(1) is the nitrogen atom of an ammine group and O(2) the oxygen atom of a water molecule. Least-squares refinement which used the scattering curve of nitrogen[8] for O(1) [named N(5) in this paper] lowered $R$ in two cycles to 0·045. This change must be considered highly significant because it did not involve any additional parameters. The scattering curves of the neutral atoms were then replaced by those of partly ionized atoms:[8] $Co^{+1}$ for the cobalt atom, $N^{-1}$ for the ammine nitrogen atoms, and $O^{-1}$ for the oxygen atoms. This choice was based on the inspection of a difference synthesis and on a trial-and-error approach with different formal ionization states. $R$ was lowered subsequently by two further cycles of refinement to 0·043, again without the introduction of additional parameters. At this stage a difference-Fourier synthesis revealed fourteen maxima ranging in height from 0·72 to 0·53 eÅ$^{-3}$. Because of their locations relative to neighbouring oxygen and nitrogen atoms all these peaks could be interpreted as being hydrogen atom positions. The two next highest maxima (0·46 eÅ$^{-3}$) were found near the cobalt, while all other difference peaks had heights of $<0·38$ eÅ$^{-3}$. The inclusion of hydrogen atoms into the structure-factor calculation gave $R$ 0·037. Two additional refinement cycles with isotropic temperature factors for hydrogen lowered $R$ to 0·032, resulting in the positional and thermal parameters presented in Tables 1 and 2. At this stage the average shift-to-error ratio was 0·2. Further refinement (using a Hughes-type weighting scheme) did not change the parameters to any significant extent. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20823 (3 pp.).*

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full-size copies.)

[5] H. Siebert and G. Tremmel, *Z. anorg. Chem.*, 1972, **390**, 292.

[6] K. Wieghardt, *Z. Naturforsch.*, 1971, **26b**, 987.

[7] W. H. Baur, *Acta Cryst.*, 1972, *B*, **28**, 1456.

[8] 'International Tables for *X*-Ray Crystallography,' vol. 3, 1962, Kynoch Press, Birmingham, p. 202.

TABLE 1

Positional parameters in fractions of the cell edges and thermal parameters (all × $10^4$) * with standard deviations in parentheses † (For numbering system see Figure 2.)

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Co | 49692(4) | 45340(4) | 62736(4) | 462(4) | 388(4) | 286(3) | 1(4) | −22(2) | −10(3) |
| N(1) | 5799(4) | 5184(4) | 7835(3) | 99(4) | 80(4) | 48(3) | −1(3) | −13(3) | −13(3) |
| N(2) | 4136(4) | 2925(3) | 7057(3) | 88(4) | 58(3) | 48(3) | −10(3) | −3(3) | −7(3) |
| N(3) | 6835(3) | 0375(3) | 4633(3) | 94(3) | 67(3) | 64(3) | 0(3) | −17(2) | −11(2) |
| N(4) | 0738(3) | 3075(4) | 4839(3) | 71(3) | 117(4) | 84(3) | −10(3) | −4(3) | −28(3) |
| N(5) | 3302(3) | 5608(4) | 6607(3) | 69(3) | 64(3) | 49(2) | 12(3) | 9(2) | 0(2) |
| O(w1) | 3838(3) | 1637(3) | 2458(3) | 86(3) | 121(4) | 62(3) | 2(3) | −16(2) | 9(3) |
| O(w2) | 6676(3) | 3489(3) | 5937(2) | 63(3) | 64(3) | 53(2) | 14(2) | −16(2) | −10(2) |
| O(h3) | 5666(2) | 6052(2) | 5327(2) | 48(2) | 50(2) | 37(2) | −5(2) | −6(2) | −1(2) |
| O(4) | 6352(3) | 0714(3) | 5666(2) | 128(4) | 95(3) | 51(2) | −5(3) | 7(2) | −9(2) |
| O(5) | 7466(4) | −0730(3) | 4502(3) | 239(6) | 84(4) | 124(4) | 75(4) | −50(4) | −36(3) |
| O(6) | 6699(3) | 1151(3) | 3730(2) | 116(4) | 122(4) | 59(2) | 3(3) | 3(2) | 26(3) |
| O(7) | 1417(3) | 3311(4) | 3880(3) | 100(4) | 160(5) | 83(3) | −26(3) | 12(3) | 1(3) |
| O(8) | 1136(3) | 3602(4) | 5850(3) | 96(3) | 183(5) | 96(3) | −33(3) | −8(3) | −74(3) |
| O(9) | −0306(3) | 2307(4) | 4817(3) | 111(4) | 213(6) | 80(3) | −84(4) | 5(3) | −40(3) |

* Co × $10^5$.

† The definition of the temperature factor is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

TABLE 2

Positional (× $10^3$) and thermal parameters of the hydrogen atoms as deduced from the least-squares refinement and geometrically calculated hydrogen atom co-ordinates (from CALHPO). The distance from the least-squares position to the corresponding geometrical one is indicated under Δ.

| | Least-squares | | | | Geometrical | | | |
|---|---|---|---|---|---|---|---|---|
| | $x$ | $y$ | $z$ | $B$/Å$^2$ | $x$ | $y$ | $z$ | Δ |
| H(N1a) | 665(7) | 512(7) | 783(6) | 5·7(1·7) | 683 | 491 | 785 | 0·26 Å |
| H(N1b) | 510(6) | 510(6) | 845(5) | 5·3(1·5) | 534 | 489 | 864 | 0·36 |
| H(N1c) | 597(7) | 592(7) | 789(6) | 4·5(1·9) | 572 | 622 | 774 | 0·34 |
| H(N2a) | 381(5) | 239(5) | 655(5) | 3·2(1·2) | 380 | 220 | 645 | 0·22 |
| H(N2b) | 348(5) | 324(6) | 755(5) | 3·7(1·2) | 331 | 324 | 758 | 0·16 |
| H(N2c) | 471(6) | 259(6) | 748(5) | 4·4(1·5) | 489 | 252 | 761 | 0·23 |
| H(N5a) | 303(4) | 558(4) | 741(4) | 1·1(0·8) | 304 | 551 | 752 | 0·13 |
| H(N5b) | 345(5) | 633(5) | 644(4) | 2·2(1·2) | 334 | 662 | 638 | 0·31 |
| H(N5c) | 256(7) | 533(7) | 615(6) | 4·3(1·6) | 257 | 513 | 608 | 0·21 |
| H(O1a) | 389(5) | 134(5) | 312(5) | 2·6(1·2) | 375 | 090 | 307 | 0·45 |
| H(O1b) | 462(5) | 140(5) | 198(5) | 3·5(1·2) | 466 | 147 | 194 | 0·09 |
| H(O2a) | 654(5) | 279(5) | 578(4) | 1·5(1·1) | 655 | 250 | 583 | 0·29 |
| H(O2b) | 732(6) | 362(6) | 637(5) | 3·6(1·3) | 747 | 366 | 650 | 0·20 |
| H(O3) | 641(4) | 614(4) | 536(4) | 0·5(0·8) | 657 | 645 | 560 | 0·42 |

## DISCUSSION

The new refinement gave positional parameters for the heavy atoms very close to those determined previously:[6] for 30 of the 45 parameters the ratio of shift-to-σ is $\leqslant 1$. However, some of the shifts are systematic, because the mean cobalt–ligand distance is now 0·009 Å shorter than before (Table 3). The shifts in parameters which accomplished this, took place when the structure was refined with the scattering curves for partly ionized atoms. The replacement of the nitrogen scattering curve, and the introduction of the hydrogen atoms into the refinement did not affect the heavy-atom positions to any noticeable degree. The thermal parameters in the two refinements are very similar for all atoms except of course N(5) [previously O(1)], which previously had β values *ca.* 50% higher than those of the other atoms co-ordinated to the cobalt.

In view of the experimental difficulty of establishing hydrogen atom positions in the presence of heavy atoms the evidence was carefully scrutinized by applying the eight criteria for the prediction of hydrogen bonds.[7] Specifically all angles Co–D–H (D is the hydrogen-bond donor) were found to be >100° and all H ··· H distances

TABLE 3

Interatomic distances and angles in the dinuclear octahedral group and in the nitrate groups

(*a*) Distances (Å)

| | | | |
|---|---|---|---|
| Co–O(h3) | 1·905(2) | N(3)–O(5) | 1·233(4) |
| Co–O(h3) | 1·906(2) | N(3)–O(6) | 1·233(4) |
| Co–N(5) | 1·922(3) | N(3)–O(4) | 1·244(4) |
| Co–O(w2) | 1·938(3) | N(4)–O(7) | 1·235(4) |
| Co–N(2) | 1·939(3) | N(4)–O(9) | 1·236(5) |
| Co–N(1) | 1·953(3) | N(4)–O(8) | 1·256(5) |
| Co–Co | 2·880(1) | | |

(*b*) Angles

| | | | |
|---|---|---|---|
| O(h3)–Co–O(h3) | 81·8(1) | N(5)–Co–N(1) | 89·6(1) |
| O(h3)–Co–N(5) | 88·0(1) | O(w2)–Co–N(2) | 90·0(1) |
| O(h3)–Co–O(w2) | 90·9(1) | O(w2)–Co–N(1) | 89·8(1) |
| O(h3)–Co–N(2) | 173·1(1) | N(2)–Co–N(1) | 92·8(1) |
| O(h3)–Co–N(1) | 94·0(1) | Co–O(h3)–Co | 98·2(1) |
| O(h3)–Co–N(5) | 94·2(1) | O(5)–N(3)–O(6) | 119·3(3) |
| O(h3)–Co–O(w2) | 86·4(1) | O(5)–N(3)–O(4) | 120·6(3) |
| O(h3)–Co–N(2) | 91·4(1) | O(6)–N(3)–O(4) | 120·2(3) |
| O(h3)–Co–N(1) | 174·3(1) | O(7)–N(4)–O(9) | 120·7(3) |
| N(5)–Co–O(w2) | 178·7(1) | O(7)–N(4)–O(8) | 119·4(3) |
| N(5)–Co–N(2) | 91·2(1) | O(9)–N(4)–O(8) | 119·9(3) |

were observed to be $>$2·0 Å. Four of the hydrogen atoms [H(N1a), H(N2c), H(N5a), and H(N5b)] are possibly involved in bifurcated bonds (Table 4). Atom H(N1b) appears to form a very weak hydrogen bond (possibly such a long contact should not be called a hydrogen bond at all). As a further test of the reasonableness of the hydrogen-bonding scheme (Figures 2 and 3) theoretical hydrogen-atom positions were calculated using the program CALHPO,[7] assuming O–H to be 0·98 in the hydroxide group and 0·97 in the water molecule, N–H 1·01 Å, and the H–O–H and H–N–H angles 109·5°. In the case of atom O(w1) which is not co-ordinated to cobalt the hydrogen-bond donors were assumed to play the role of co-ordinating metal atoms.[9] The geometrical positions (Table 2) agree on average within 0·26 Å with the experimental positions. Therefore, the suggested hydrogen-bonding scheme and the assignment of oxygen and nitrogen atoms to the Fourier maxima is based on (*a*) the results of the least-squares refinement, (*b*) the maxima in the difference-Fourier synthesis, and (*c*) the calculation of theoretical hydrogen atom positions.

TABLE 4

Postulated hydrogen-bond geometries. For every donor acceptor pair the upper value is that calculated for the experimental hydrogen positions (from least-squares refinement), and the lower is based on the hydrogen positions calculated by CALHPO. The donor atom is D, the acceptor atom of the hydrogen bond is A

| D–H ··· A | D–H/Å | H ··· A/Å | D ··· A/Å | (D–H ··· A)/deg. |
|---|---|---|---|---|
| N(1),H(N1a),O(w1$^{I}$) | 0·81(6) | 2·71(6) | 3·394(5) | 144(6) |
| | 1·01 | 2·45 | 3·394 | 155 |
| N(1),H(N1a),O(4$^{II}$) | 0·81(6) | 2·54(6) | 3·175(5) | 136(6) |
| | 1·01 | 2·47 | 3·175 | 127 |
| N(1),H(N1b),O(9$^{I}$) | 0·94(6) | 2·78(6) | 3·383(5) | 123(4) |
| | 1·01 | 2·55 | 3·383 | 140 |
| N(1),H(N1c),O(w1$^{III}$) | 0·72(7) | 2·42(7) | 3·114(5) | 163(7) |
| | 1·01 | 2·13 | 3·114 | 164 |
| N(2),H(N2a),O(5$^{IV}$) | 0·81(5) | 2·31(5) | 3·098(5) | 166(5) |
| | 1·01 | 2·12 | 3·098 | 162 |
| N(2),H(N2b),O(6$^{V}$) | 0·87(5) | 2·19(5) | 3·056(5) | 174(5) |
| | 1·01 | 2·05 | 3·056 | 177 |
| N(2),H(N2c),O(7$^{I}$) | 0·78(6) | 2·37(6) | 3·145(5) | 175(6) |
| | 1·01 | 2·14 | 3·145 | 177 |
| N(2),H(N2c),O(9$^{I}$) | 0·78(6) | 2·51(6) | 3·016(4) | 124(5) |
| | 1·01 | 2·38 | 3·016 | 120 |
| N(5),H(N5a),O(5$^{V}$) | 0·90(4) | 2·31(4) | 3·210(5) | 174(4) |
| | 1·01 | 2·21 | 3·210 | 169 |
| N(5),H(N5a),O(6$^{V}$) | 0·90(4) | 2·53(4) | 3·225(4) | 134(3) |
| | 1·01 | 2·43 | 3·225 | 135 |
| N(5),H(N5b),O(6$^{III}$) | 0·73(5) | 2·45(5) | 3·160(5) | 162(5) |
| | 1·01 | 2·16 | 3·160 | 169 |
| N(5),H(N5b),O(w2$^{III}$) | 0·73(5) | 2·56(5) | 2·868(4) | 108(4) |
| | 1·01 | 2·49 | 2·868 | 102 |
| N(5),H(N5c),O(8) | 0·89(6) | 2·18(6) | 2·935(5) | 143(5) |
| | 1·01 | 2·02 | 2·935 | 150 |
| O(w1),H(O1a),O(4$^{IV}$) | 0·77(5) | 2·39(5) | 3·045(5) | 144(5) |
| | 0·97 | 2·08 | 3·045 | 177 |
| O(w1),H(O1b),O(8$^{I}$) | 0·93(5) | 1·88(5) | 2·785(5) | 165(5) |
| | 0·97 | 1·82 | 2·785 | 171 |
| O(w2),H(O2a),O(4) | 0·71(5) | 2·03(5) | 2·720(4) | 169(5) |
| | 0·97 | 1·75 | 2·720 | 179 |
| O(2w),H(O2b),O(w1$^{I}$) | 0·78(5) | 1·86(5) | 2·616(4) | 163(6) |
| | 0·97 | 1·68 | 2·616 | 160 |
| O(h3),H(O3),O(7$^{III}$) | 0·71(4) | 2·27(4) | 2·947(4) | 161(4) |
| | 0·98 | 1·99 | 2·947 | 164 |

Roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at $x, y, z$:

I $1/2 + x, 1/2 - y, 1/2 + z$
II $3/2 - x, 1/2 + y, 3/2 - z$
III $1 - x, 1 - y, 1 - z$
IV $1 - x, - y, 1 - z$
V $-1/2 + x, 1/2 - y, 1/2 + z$

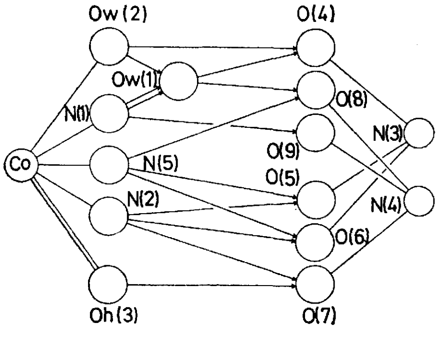

FIGURE 2 Hydrogen bonding scheme in $[Co_2(OH)_2(H_2O)_2(NH_3)_6](NO_3)_4,2H_2O$; arrows point towards the acceptor atoms of the hydrogen bonds

The most important result of the refinement and of the hydrogen-bond assignment is that the atomic positions N(5) and O(w2), which were both thought originally[6] to be possibly statistically occupied by ammine groups and water molecules can now be shown to be distinct. Atom O(w2) donates two short hydrogen bonds (2·62 and 2·72

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[9] W. H. Baur and A. A. Khan, *Acta Cryst.*, 1970, *B*, **26**, 1584.

Å), as can be expected of a water molecule bonded to a trivalent cation,[7] while N(5) forms three long hydrogen bonds (2·94, 3·16, and 3·21 Å), similar to the situation found around atoms N(1) and N(2). The number and lengths of these contacts leave no doubt that O(w2) is the oxygen atom of a water molecule, while N(5) is the nitrogen atom of an ammine group. Therefore, the *trans*-positions of the water groups in $(NH_3)_3H_2OCo{\cdot}(OH)_2{\cdot}Co(NH_3)_3(H_2O)$ are established (Figure 4).

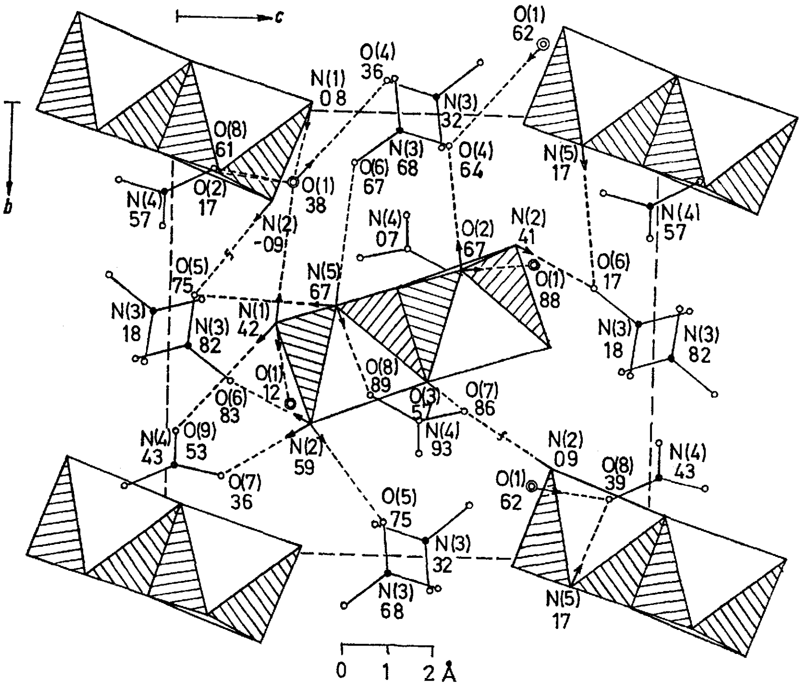

FIGURE 3 A view of the molecule parallel to [100]. The complex is shown as two octahedra with a shared edge (the central one centred at 1/2, 1/2, 1/2, other ones at 0, 0, 0 *etc.*). Nitrogen atoms are represented as small solid circles, nitrate group oxygens as small open circles, water oxygens as double circles. Hydrogen bonds are indicated by arrows pointing towards the acceptor atoms. The complete hydrogen-bonding co-ordination is displayed only once for every crystallographically different atom in the unit cell. For some atoms the height ($\times 10^2$) in fractional co-ordinates is given

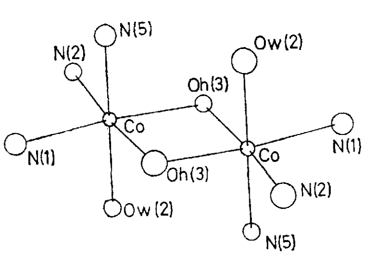

FIGURE 4 View of the cation

Contrary to the expectation based on the ease of formation of type (II) complexes the water molecules in the di-μ-hydroxo-bis[aquotriamminecobalt(III)]$^{4+}$ cation are *trans*. Any attempt to postulate a possible mechanism for the formation of this complex must take into account the fact that upon dissolving the nitrate salt of the compound in water, the solution becomes acid within a few minutes. On addition of $NaClO_4$ the starting compound crystallizes again as its perchlorate salt. It is therefore obvious that the rearrangements of the ligands must be accomplished easily. A possible mechanism of formation would involve, as a first step, the protonation of one of the bridging hydroxide groups, which would weaken the Co–$OH_2$ bonds. From the extended electrostatic valence rule[10] it can be estimated that the distances Co–$OH_2$ should be 2·1 Å, *ca.* 0·2 Å longer than Co–OH. At this point one of the two Co–$OH_2$ bonds must break, because this bonding situation is energetically unfavourable: in a crystal structure a water molecule has never been observed to be simultaneously bonded to two octahedrally co-ordinated three-valent cations. After the rupture of one of the Co–$OH_2$ bonds, one cobalt atom in the dinuclear cation is only five-co-ordinate (Figure 5). It is necessary to assume a reactive, intermediate five-co-ordinate product because one ammine group must be relocated in order to arrive at the *trans*-arrangement of the water molecules. Following the reasoning outlined by Basolo and Pearson[11] the five-co-ordination should be in the shape of a trigonal bipyramid. The five-co-ordinate cobalt would have no preferred site for the addition of the $H_2O$ molecule, and four isomers should be expected: *cis*, *trans*, and two additional ones, which are

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[10] W. H. Baur, *Trans. Amer. Cryst. Assoc.*, 1970, **6**, 129.

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enantiomorphic (Figure 1). Because the reaction is reversible the four configurations should be in equilibrium. Presumably, because the di-μ-hydroxo-*trans*-diaquo-bis[triamminecobalt(III)] nitrate is the least soluble of these forms, it is the one which crystallizes, and therefore the reaction leads to a complete transformation into the *trans*-configuration. There is no direct evidence for the existence of the five-co-ordinate cobalt or of the other forms of Figure 1, and our mechanism is therefore speculative.

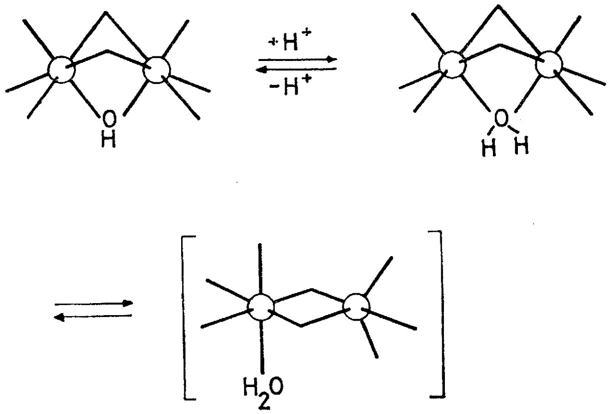

FIGURE 5 Possible steps in the protonation of the tri-μ-hydroxo-cation and the formation of a five-coordinate intermediate, $(NH_3)_3(H_2O)Co(OH)_2Co(NH_3)_3$, which can lead to the isomers shown in Figure 1

Schwarzenbach *et al.*[12] have recently investigated the formation of various dinuclear μ-hydroxo-cobalt(III) complexes including those of *cis-cis*-1,3,5-triaminocyclohexane (= tach). They report that upon addition of strong acids $(tach)Co(OH)_3Co(tach)^{3+}$ is transformed almost instantaneously into $(tach)Co(H_2O)(OH)_2Co(H_2O)(tach)^{4+}$ (this reaction is analogous to the formation of the di-μ-hydroxo-bis[aquotriamminecobalt(III)]$^{4+}$ complex from the tri-μ-hydroxo-bis[triamminecobalt(III)]$^{3+}$ cation [2]). These authors favour the *cis*-arrangement of the water molecules in the di-μ-hydroxo-complex because this would enable formation of two hydrogen bonds from the co-ordinated $H_2O$ groups to a third water molecule to be attached to the complex in the outer sphere. In view of the rigidity of the triaminocyclohexane, which can only co-ordinate facially to the Co atoms, this may be a reasonable assumption.

Further information about the reaction pathways of these and similar cations will be obtained from kinetic studies [13] and from *X*-ray investigations on substitution products of the di-μ-hydroxo-bis[aquotriamminecobalt-(III)]$^{4+}$ complex. The establishment of the *trans*-configuration of the water molecules in the present complex indicates the difficulty of making correct predictions about the geometry of these complexes and suggests that some internal rearrangements may be more easily accomplished than is usually thought to be possible.

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