

The Structure of Ammonium Hexaammine-tri- μ -hydroxo-dicobalt Tetrachloride*

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Ammonium hexaammine-tri- μ -hydroxo-dicobalt tetrachloride, $[(\text{NH}_3)_3\text{Co}(\text{OH})_3\text{Co}(\text{NH}_3)_3]^{3+} \cdot \text{NH}_4^+ \cdot 4\text{Cl}^-$, forms orthorhombic crystals, space group $Pnmm$, $a = 13.088$ (10), $b = 17.276$ (6), $c = 6.922$ (3) Å, and $Z = 4$. Least-squares refinement gave an R index of 0.041 for 1135 reflections collected with $\text{Co } K\alpha$ radiation in a 2θ scan mode. The two Co octahedra share one face, with a $\text{Co} \cdots \text{Co}$ distance of 2.565 (1) Å. The cations are disordered across the mirror plane such that there are two positions rotated with respect to each other. This disorder increases the strength and number of hydrogen bonds formed by the cations.

Introduction

The crystal structures of the tribromide and triiodide salts of hexaammine-tri- μ -hydroxo-dicobalt(III) were reported by Anderson (1967). These structures were derived from two-dimensional diffraction data and hence are of limited accuracy. In order to obtain more accurate structural data on this triply-bridged cation we have carried out a three-dimensional analysis of a trichloride compound, which crystallized as a mixed salt containing ammonium chloride. Unfortunately, the crystal structure shows disorder, and hence the accuracy of this determination is once again somewhat lower than desired.

Experimental

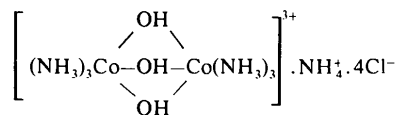
The compound was prepared by Dr Ulf Thewalt using the method of Werner (1907), and was crystallized by evaporation of a saturated ammonium chloride solution, yielding dark-red rectangular prisms elongated along c . The crystal used for data collection measured approximately $0.31 \times 0.23 \times 0.41$ mm. Weissenberg photographs showed orthorhombic diffraction symmetry and systematic absences ($0kl$, $k + l$ odd; $h0l$, $h + l$ odd) consistent with space groups $Pnmm$ or $Pnn2$; a satisfactory, albeit disordered, structure was derived in $Pnmm$. Crystal data are collected in Table 1.

Intensity data were collected on a Datex-automated General Electric quarter-circle diffractometer with Fe-filtered $\text{Co } K\alpha$ radiation, a θ - 2θ scan technique, a scan rate of 2° min^{-1} , and background counts of 30 s; the maximum value of 2θ was 150° . Three check reflec-

tions showed no unusual variation or decay. Data for two octants, hkl and $h\bar{k}l$, were collected and averaged to yield 1135 independent intensities, of which seven showed values less than zero and another 70 were below $3\sigma(I)$. Two reflections, 122 and 212, showed relatively poor agreement between the two measurements and were assigned weights of zero. Variances $\sigma^2(I)$ for the remaining intensities were assigned on the basis of counting statistics plus a term $(0.02S)^2$, where S is the scan count. The intensities and their standard deviations were corrected for Lorentz and polarization effects, and for absorption by the method of Gaussian quadrature (Busing & Levy, 1957); the transmission factors ranged from 0.113 to 0.284.

An ordered structure in space group $Pnmm$ was derived from Patterson and electron density maps and refined to an R index ($= \sum ||F_o| - |F_c|| / \sum |F_o|$) of 0.067. However, several of the atoms showed improbable anisotropic temperature parameters, and a difference map suggested that the cation and one of the chloride ions, $\text{Cl}(4)$, are disordered across the mirror plane perpendicular to c . The two disordered positions of the cation are related by a rotation of approximately 18° about the $\text{Co}-\text{Co}$ axis, which lies in the mirror plane.

Table 1. Crystal data



Space group $Pnmm$
 $Z = 4$
 $a = 13.088$ (10) Å
 $b = 17.276$ (6)
 $c = 6.922$ (3)
 $V = 1565$ (2) Å³

F. W. 430.9
 $D_x = 1.83$ g cm⁻³
 $D_m = 1.829$
 $\text{Co } K\alpha$ ($\lambda = 1.7902$ Å)
 $F(000) = 880e$
 $\mu = 116.7$ cm⁻¹

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In the final calculations, the atoms which we presumed to be ordered – the two Co atoms, three of the Cl ions, and the N atom of the ammonium group – were assigned anisotropic temperature parameters; Cl(4) and the N and O atoms of the cation were presumed to be disordered and were assigned isotropic thermal parameters and half-populated sites. H atoms were located with the help of difference maps, but were not refined. Form factors for H were from Stewart, Davidson & Simpson (1965); those for N, O, Cl⁻ and Co were from *International Tables for X-ray Crystallography* (1962), values for Co being adjusted by $-2.19 e$ to account for the real component of anomalous dispersion (Cromer, 1965). A secondary-extinction parameter g (Larson, 1967) was included in the refinement; its final value was $(8.3 \pm 0.4) \times 10^{-6}$. Final values for the remaining parameters are given in Tables 2, 3 and 4. The R index is 0.041 for 1126 reflections with positive net intensity and the goodness-of-fit $\{= [\sum \omega(|F_o|^2 - |F_c|^2)^2 / (n - p)]^{1/2}\}$ is 3.50 for $p = 78$ parameters and $n = 1133$ observations of non-zero weight.*

At the conclusion of the refinement, the model was adjusted so as to conform to an ordered structure in space group $Pnn2$; the resulting structure factors showed an R index of 0.091, a goodness-of-fit of 18.6, and quite a number of very large discrepancies, especially among the weaker reflections. Least-squares refinement of this model was unsatisfactory: the structure approached the ordered, highly anisotropic model we originally derived in space group $Pnmm$, and singularities in the normal-equation matrix began to arise. We have no doubt that a disordered model in space group $Pnmm$ is the more appropriate description of the structure.

Discussion

Bond distances and angles within the cation are shown in Fig. 1. The formal e.s.d.'s of these values, evaluated

*A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32091 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

from the variances in the atomic coordinates (Tables 2 and 3) as obtained from the diagonal elements of the inverse least-squares matrix, are in the range 0.005–0.007 Å and 0.2–0.3°. However, covariance terms [those in the inverse matrix as well as those relating pairs of bond distances such as Co–O(2) and Co–O(3) (Waser, 1973)] are large because of the relatively small separation of the two sets of disordered sites. Thus, we believe that the e.s.d.'s as evidenced by the agreement between individual Co–N and Co–O

Table 3. *Coordinates ($\times 10^4$) and isotropic temperature factors for disordered atoms*

All sites have an occupancy factor of $\frac{1}{2}$.

	x	y	z	B (Å ²)
Cl(4)	4790 (1)	1361 (1)	-319 (3)	2.53 (4)
O(1)	761 (3)	947 (2)	-434 (7)	1.70 (9)
O(2)	2567 (5)	1109 (3)	-1608 (9)	1.66 (11)
O(3)	2204 (5)	1074 (3)	1908 (8)	1.37 (10)
N(1)	2813 (4)	2521 (3)	445 (9)	2.27 (13)
N(2)	1292 (5)	2380 (3)	-2250 (10)	1.83 (11)
N(3)	771 (5)	2333 (3)	1616 (10)	1.86 (11)
N(4)	3249 (4)	-201 (3)	423 (10)	2.43 (13)
N(5)	1689 (5)	-356 (3)	-2235 (10)	1.91 (11)
N(6)	1217 (5)	-405 (4)	1662 (10)	2.10 (11)

Table 4. *Coordinates ($\times 10^3$) for the H atoms*

These coordinates were derived from difference maps and were not refined. Because of the disorder, all sites except those of the ammonium ion [H(7), H(7') and H(7'')] have occupancy factors of $\frac{1}{2}$. An isotropic temperature factor with $B = 3.4$ Å² was assigned to all H atoms.

	x	y	z		x	y	z
H(O1)	69	100	-170	H(4)	326	-64	-33
H(O2)	327	120	-134	H(4')	376	14	4
H(O3)	162	110	249	H(4'')	329	-33	175
H(1)	297	250	189	H(5)	150	-88	-173
H(1')	336	236	-16	H(5')	229	-38	-299
H(1'')	258	300	22	H(5'')	115	-12	-294
H(2)	191	245	-298	H(6)	58	-50	104
H(2')	99	284	-181	H(6')	160	-84	143
H(2'')	77	209	-290	H(6'')	109	-14	284
H(3)	13	230	109	H(7)	359	58	$\frac{1}{2}$
H(3')	78	211	288	H(7')	348	145	$\frac{1}{2}$
H(3'')	100	284	178	H(7'')	438	110	390

Table 2. *Coordinates and anisotropic temperature factors for ordered atoms*

Coordinates and U_{ij} values are $\times 10^4$; standard deviations are given in parentheses. The anisotropic temperature coefficients are of the form $\exp[-2\pi^2(h^2 a^{*2} U_{11} + \dots + 2klb^* c^* U_{23})]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)	1726 (1)	1782 (1)	0	220 (5)	143 (5)	156 (5)	6 (3)	0	0
Co(2)	1956 (1)	307 (1)	0	211 (5)	149 (5)	146 (5)	19 (3)	0	0
Cl(1)	3565 (2)	-810 (1)	$\frac{1}{2}$	963 (14)	251 (8)	398 (10)	49 (9)	0	0
Cl(2)	380 (1)	1016 (1)	$\frac{1}{2}$	662 (10)	326 (10)	163 (7)	-117 (7)	0	0
Cl(3)	3317 (1)	2848 (1)	$\frac{1}{2}$	608 (11)	265 (8)	569 (11)	-48 (7)	0	0
N(7)	3924 (6)	1047 (3)	$\frac{1}{2}$	806 (48)	350 (33)	769 (51)	-39 (31)	0	0

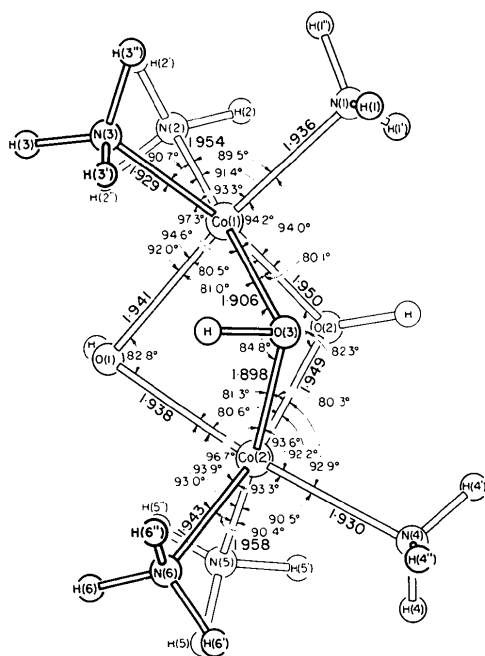


Fig. 1. Bond distances and angles in the cation. The Co—Co distance is 2.565 (1) Å.

distances, about 0.02 Å, are more valid estimates of the true uncertainties. This latter value is less than one-third the size of the corresponding e.s.d.'s reported by Anderson (1967) for the tribromide salt.

On this basis, the average values of the bond lengths, 1.942 for Co—N and 1.930 Å for Co—O, show e.s.d.'s of about 0.008 Å. This Co—N distance is appreciably shorter than the values of 1.968 Å obtained by Fronczek (1975) as an average Co—N distance in singly-bridged binuclear Co species containing pentaamminecobalt(III) groups, and 1.959 Å that we obtain as an average value in five doubly-bridged tetraammine species (Prout, 1962; Christoph, Marsh & Schaefer, 1969; Barro, Marsh & Schaefer, 1970; Thewalt & Marsh, 1970; Schaefer & Lighty, 1972); the average value in the unbridged hexaammine ion $\text{Co}(\text{NH}_3)_6^{3+}$ is 1.970 Å (Meek & Ibers, 1970; Iwata & Saito, 1973). Thus, as the number of $-\text{NH}_3$ ligands attached to a single Co atom decreases from six to three, the Co—N distances show a parallel decrease. While the effect is not large, it may be attributed to the increasing concentration of positive charge on the smaller number of ammine groups, leading to additional ionic character in the Co—N bonds. The average Co—O distance, 1.930 Å, is typical of values found in other

Table 5. Comparison of interatomic distances and angles in several hydroxyl-bridged cobalt compounds

Numbers in parentheses are e.s.d.'s in the average values, as obtained from the reported coordinate uncertainties; numbers in brackets, where appropriate, are r.m.s. deviations of the individual values from the average.

	Co—Co	Co—O	O—O	$\mu\text{O—Co—}\mu\text{O}$	Co— $\mu\text{O—Co}$	Reference
$\text{Co} \left[\begin{array}{c} \text{OH} \\ / \quad \backslash \\ \text{Co}(\text{en})_2 \\ \backslash \quad / \\ \text{OH} \end{array} \right]_3^{6+}$	2.89 (1){1} Å 2.890 (2){8}	1.92 (2){2} Å 1.921 (3){10}	2.54 (3){6} Å 2.531 (7){9}	82.7 (9){10}° 82.4 (2){4}	97.2 (10){7}° 97.6 (2){6}	a
$\left[\begin{array}{c} \text{OH} \\ / \quad \backslash \\ (\text{NH}_3)_4\text{Co} \quad \text{Co}(\text{NH}_3)_4 \\ \backslash \quad / \\ \text{OH} \end{array} \right]_2^{4+}$	2.932 (5)	1.912 (15){1}	2.46 (2)	79.9 (5)	100.1 (5)	b
$\left[\begin{array}{c} \text{OH} \\ / \quad \backslash \\ (\text{NH}_3)_3\text{Co} \quad \text{Co}(\text{NH}_3)_3 \\ \backslash \quad / \\ \text{CH}_3\text{CO}_2 \end{array} \right]_2^{3+}$	2.804 (6)	1.892 (11){28}	2.456 (9)	81.0 (4){15}	95.6 (3)	c
$\left[\begin{array}{c} \text{OH} \\ / \quad \backslash \\ (\text{NH}_3)_3\text{Co} \quad \text{Co}(\text{NH}_3)_3 \\ \backslash \quad / \\ \text{OH} \end{array} \right]_2^{3+}$	2.55 (2) 2.565 (1)	1.96 (7){5} 1.930 (8){23}	2.57 (10){6} 2.498 (16){17}	82 (3){3} 80.6 (3){4}	81 (3){1} 83.3 (3){13}	d

References: (a) Thewalt (1971), Dixon & Marsh (1977); (b) Prout (1962); (c) Mandel, Marsh & Wang (1976); (d) Anderson (1967), this work.

$\mu(\text{OH})$ systems (Table 5), including a tetranuclear species wherein a central Co atom is linked, by pairs of OH bridges, to three other Co atoms (Thewalt, 1971; Dixon & Marsh, 1977).

As noted by Anderson (1967), deviations from octahedral bonding about the Co atoms are presumably caused by repulsions between the Co atoms. If the two fused octahedra were regular, with Co—O distances of 1.93 Å, the Co...Co distance would be only 2.23 Å—appreciably less than, for example, the distance of about 2.51 Å found in the close-packed structures of elementary Co (*International Tables*, 1962; p. 282). This uncomfortable Co...Co contact is relieved by a pinching together of the $\mu(\text{OH})\text{—Co—}\mu(\text{OH})$ angles to a value of about 80°, compressing the $\mu(\text{O})\cdots\mu(\text{O})$ distance to about 2.5 Å (Table 5). This O...O distance is fairly constant in all these doubly- and triply-bridged

compounds. On the other hand, the Co—O—Co angles show a wide variation; the Co...Co distance ranges from a very short 2.56 in the present compound to a more comfortable 2.9 Å in doubly-bridged species.

Fig. 2 shows the structure as viewed down *c*. As noted earlier, the cation is disordered across a mirror plane such that the two orientations are related by a rotation of 17.9° about the Co...Co axis. Each of the two disordered positions results in significant improvement in the geometries of fourteen of the hydrogen bonds relative to their geometries in an intermediate, ordered position on the mirror plane. The arrangement of these fourteen hydrogen bonds is shown in Fig. 3 and they are noted in Table 6 (which gives the details of the hydrogen bonding). The symmetric arrangement of Cl⁻ ions apparently forces the cation to choose one of the two disordered positions rather than the average posi-

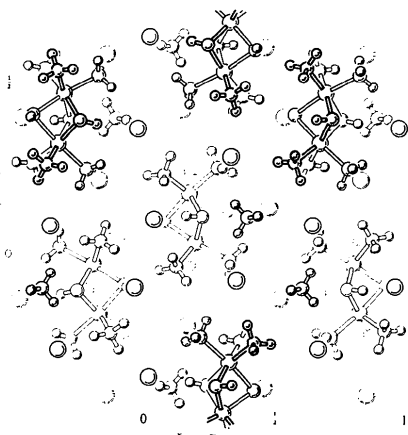


Fig. 2. The structure viewed along *c*. Each of the cations is shown in only one of its two disordered orientations.

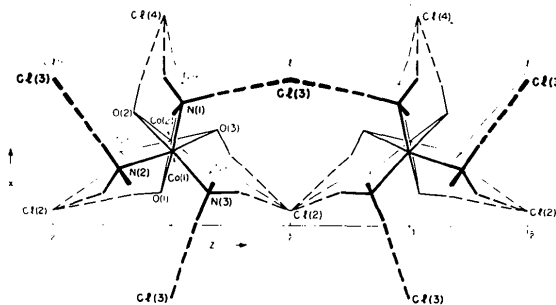


Fig. 3. The hydrogen bonds which are responsible for the disorder of the cation. The cation in the left half of the drawing is shown in one of the disordered positions, the cation in the right half in the other. Crystallographic mirror planes are located at $z = 0, \frac{1}{2}$, etc.

Table 6. Probable hydrogen bonds, $D\text{—H}\cdots A$

Distances indicated by an asterisk are shown in Fig. 3.

<i>D</i>	H	<i>A</i>	$d(D\cdots A)$	<i>D</i>	H	<i>A</i>	$d(D\cdots A)$	
O(1)	H(O1)	Cl(2) ⁽ⁱ⁾	3.20*	N(4)	H(4')	Cl(4)	3.41*	
O(2)	H(O2)	Cl(4)	3.07*		H(4'')	Cl(1)	3.36*	
O(3)	H(O3)	Cl(2)	3.21*	N(5)	H(5)	Cl(3) ^(iv)	3.47	
N(1)	H(1)	Cl(3)	3.27*		H(5')	Cl(1) ⁽ⁱ⁾	3.21*	
	H(1')	Cl(4)	3.32*		H(5'')	Cl(2) ⁽ⁱⁱ⁾	3.50*	
	H(1'')	Cl(1) ⁽ⁱⁱ⁾	3.42	N(6)	H(6')	Cl(3) ⁽ⁱⁱ⁾	3.28	
N(2)	H(2)	Cl(3) ⁽ⁱ⁾	3.36*		H(6'')	Cl(2)	3.55*	
	H(2')	Cl(1) ⁽ⁱⁱ⁾	3.50	N(7)	H(7)	Cl(1)	3.24	
	H(2'')	Cl(2) ⁽ⁱ⁾	3.26*		H(7')	Cl(3)	3.21	
N(3)	H(3)	Cl(3) ⁽ⁱⁱⁱ⁾	3.42*		H(H'')	Cl(1) ^(v)	3.31	
	H(3')	Cl(2)	3.30*		H(7'')	Cl(4) ^{(i),(vi)}	3.48	
	H(3'')	Cl(1) ⁽ⁱⁱ⁾	3.51					
Symmetry code								
	(i)	$x,$	$y,$	$-z$	(iv)	$\frac{1}{2} - x,$	$-\frac{1}{2} + y,$	$\frac{1}{2} - z$
	(ii)	$\frac{1}{2} - x,$	$\frac{1}{2} + y,$	$\frac{1}{2} - z$	(v)	$1 - x,$	$-y,$	$-z$
	(iii)	$-\frac{1}{2} + x,$	$\frac{1}{2} - y,$	$\frac{1}{2} - z$	(vi)	$x,$	$y,$	$1 + z$

tion. The disorder of the chloride ion [Cl(4)] probably acts cooperatively with that of the cation, since the hydrogen bonds to one of the mirror-related positions of Cl(4) are significantly shorter and more linear than those to the other position.

Finally, while we have been satisfied to depict only one of the chloride ions [Cl(4)] as accompanying the cation in its disorder, the high anisotropy of the thermal motions of the remaining chloride ions and the ammonium group (Table 2) suggests that they, too, may show some displacement disorder. In particular, the ammonium ion would find itself surrounded by a more regular tetrahedron of chloride ions if it were displaced by about 0.2 Å [corresponding to $(U_{33}-U_{22})^{1/2}$] to one or the other side of the mirror plane. However, many of the other anisotropies cannot be explained without assuming a very complicated pattern of disorder that certainly cannot be proven with the data at hand.

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References

- ANDERSON, P. (1967). *Acta Chem. Scand.* **21**, 243–256.
 BARRO, R., MARSH, R. E. & SCHAEFER, W. P. (1970). *Inorg. Chem.* **9**, 2131–2137.
 BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180–182.
 CHRISTOPH, G. G., MARSH, R. E. & SCHAEFER, W. P. (1969). *Inorg. Chem.* **8**, 291–297.
 CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
 DIXON, D. A. & MARSH, R. E. (1977). To be published.
 FRONCZEK, F. R. (1975). Thesis, California Institute of Technology, Pasadena.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–203. Birmingham: Kynoch Press.
 IWATA, M. & SAITO, Y. (1973). *Acta Cryst.* **B29**, 822–832.
 LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.
 MANDEL, G. S., MARSH, R. E. & WANG, B.-C. (1976). Unpublished.
 MEEK, D. W. & IBERS, J. A. (1970). *Inorg. Chem.* **9**, 465–470.
 PROUT, C. K. (1962). *J. Chem. Soc.* pp. 4429–4437.
 SCHAEFER, W. P. & LIGHTY, R. A. (1972). *Acta Cryst.* **B28**, 1777–1784.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 THEWALT, U. (1971). *Chem. Ber.* **104**, 2657–2669.
 THEWALT, U. & MARSH, R. E. (1970). *Inorg. Chem.* **9**, 1604–1610.
 WASER, J. (1973). *Acta Cryst.* **A29**, 621–631.
 WERNER, A. (1907). *Ber. dtsh. chem. Ges.* **40**, 4834–4844.

Acta Cryst. (1977). **B33**, 704–709

The Crystal and Molecular Structure of Briarein A, a Diterpenoid from the Gorgonian *Briareum asbestinum*

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The crystal structure of briarein A, a chlorine-substituted diterpenoid, isolated from *Briareum asbestinum*, has been determined and refined by three-dimensional least-squares techniques with data taken at -160°C . The molecule crystallizes in the space group $P2_12_12_1$, with unit-cell dimensions (at -160°C) $a = 11.661$ (4), $b = 26.26$ (2) and $c = 10.355$ (6) Å. The final R value for all 3668 reflections is 0.042. The molecule has fused 6- and 10-membered rings, a lactone ring, five acetate groups, chlorine substitution and a non-planar diene group. The absolute configuration has been determined.

Introduction

In 1960 we reported the occurrence, in octocorals from the Caribbean area, of a number of crystalline compounds which appeared to be lactones (Ciereszko, Sif-

ford & Weinheimer, 1960). The lactones isolated from gorgonians of the genera *Eunicea* and *Pseudoplexaura* are cembranolides, those from the genus *Pterogorgia*, polymethylene butenolides (Ciereszko & Karns, 1973; Schmitz, Lorange & Ciereszko, 1969). *Briareum*