Acta Cryst. (1977). B**33**, 3185–3188

The Structure of Hexaammine-μ-acetato-di-μ-hydroxo-dicobalt Tribromide Trihydrate*

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(*Received* 21 *December* 1976; *accepted* 2 *April* 1977)

The structure of $(NH_3)_3Co(OH)_2C_2H_3O_2Co(NH_3)_3.3Br.3H_2O$ has been determined by single-crystal X-ray diffraction techniques. The compound forms orthorhombic crystals, space group $Pmn2_1$, with $a = 7{\cdot}252$ (1), $b = 12{\cdot}188$ (1), $c = 10{\cdot}790$ (1)Å, and $Z = 2$; the calculated density is 2·033 g cm^{-3}. Intensity data for 746 reflections were collected on a Datex-automated GE diffractometer using Co $K\alpha$ radiation. Patterson analysis gave the trial structure which was refined by least squares to a final R value of 0·045. The two Co octahedra share one face with the Co atoms 2·804 (6) Å apart. Although the cation is of $mm2$ symmetry chemically, its crystallographic symmetry is m.

Introduction

Werner (1910) originally reported the preparation of many triply-bridged dicobalt species, the bridging groups including NH_2, O_2, OH, NO_2, SO_4, and acetate. We have been investigating the structures of these cations to gain further understanding of the nature of the bonding about the Co atoms. As a part of these studies, we have prepared hexaammine-μ-acetato-di-μ-hydroxo-dicobalt tribromide trihydrate and carried out a crystal structure analysis.

The compound was made, as described by Werner (1910), by treating the iodide salt with fresh AgBr, filtering, and precipitating the bromide salt with ethanol. Recrystallization from water gave well formed acicular crystals, and preliminary precession and Weissenberg photographs showed Laue symmetry mmm with systematic extinctions $h0l$ with $h + l$ odd, indicating either the centrosymmetric space group $Pmnm$ or the non-centrosymmetric $Pmn2_1$. An approximately cubic crystal, 0·15 mm on an edge, was cut from a needle and mounted with its a axis slightly skew to the φ axis of a Datex-automated quarter-circle GE diffractometer. Unit-cell dimensions (Table 1) were obtained from a least-squares fit to the $\sin^2\theta$ values of 21 reflections. Intensity data were collected using Fe-filtered Co $K\alpha$ radiation, a θ–2θ scan technique, and 30 s background counts. Of the 746 reflections with 2θ less than 158°, 8 had negative values for their net intensity and were assigned weights of zero; all other reflections were assigned variances $\sigma^2(I)$ based on counting statistics plus the additional term (0·02 scan counts)^2. The data were corrected for Lorentz and polarization factors but not for absorption ($\mu = 155$ cm^{-1}). A single check reflection showed no systematic change in intensity.

A three-dimensional Patterson map yielded the coordinates of the Co atoms and two of the Br ions in positions consistent with space group $Pmnm$. Subsequent Fourier maps indicated the positions of the N, O, and C atoms of the cation and also indicated that the third Br ion, Br(3), as well as the water molecules O(4), O(5), and O(6) might be disordered between pairs of sites related by the mirror plane perpendicular to **c**. However, further refinement based on space group $Pmnm$ was unsatisfactory: many weighted residuals $w(F_o^2 - F_c^2)^2$ remained very large and difference maps showed unreasonable features, including large regions of negative electron density located at $z + \frac{1}{2}$ and $z + \frac{1}{4}$ relative to the heavy-atom (Co and Br) positions. The correlation between these holes and the heavy-atom positions led us to suspect that the mirror plane perpendicular to **c** is not present; accordingly, the structure was reformulated in space group $Pmn2_1$ with Br(3) and the three water molecules forming a more

Table 1. *Crystal data*

$(NH_3)_3Co(OH)_2C_2H_3O_2Co(NH_3)_3.3Br.3H_2O$
Space group $Pmn2_1$

$a = 7{\cdot}252$ (1) Å	$Z = 2$
$b = 12{\cdot}188$ (1)	$D_c = 2{\cdot}033$ g cm^{-3}
$c = 10{\cdot}790$ (1)	Co $K\alpha$ ($\lambda = 1{\cdot}7902$ Å)

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ordered array along **c**. Convergence was then smooth and rapid. H atom positions were obtained from difference maps and optimized to tetrahedral geometry; they were not refined.

In the final full-matrix least-squares calculations, 73 parameters were adjusted: coordinates and anisotropic temperature factors for the Co and Br atoms, coordinates and isotropic temperature factors for C, N, and O, a scale factor, and a secondary extinction parameter (Larson, 1967). Form factors for Co, Br, C, N, and O were taken from *International Tables for X-ray Crystallography* (1962), and for H from Stewart, Davidson & Simpson (1965); anomalous dispersion corrections $\Delta f'$ and $\Delta f''$ for Br and Co were interpolated from the tables published by Cromer (1965). When convergence was reached, the polarity of the structure was reversed by changing the signs of the z coordinates; this model led to slightly lower values of the R index (0·045 *vs* 0·046) and goodness-of-fit (1·72 *vs* 1·80) and accordingly corresponds to the correct configuration of the structure (at the 0·005 significance level, Hamilton, 1965).

Final atomic parameters are given in Tables 2 and 3.* The final value of the secondary extinction parameter g (Larson, 1967) is 3·2 (0·3) × 10^{-6}.

Discussion

The structure as viewed along the a axis is shown in Fig. 1. The region between y = 0·15 and y = 0·85,

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32654 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Final coordinates* (× 10^4)*for the heavier atoms*

Values in parentheses are standard deviations obtained from the diagonal elements of the variance–covariance matrix.

	x	y	z
Co(1)	0	3137 (3)	6311 (4)
Co(2)	0	3149 (3)	3711 (4)
Br(1)	0	5218 (1)	−15 (5)
Br(2)	0	1895 (1)	0*
Br(3)	0	−1232 (2)	7646 (4)
N(1)	1924 (17)	3379 (8)	7530 (15)
N(2)	0	1583 (16)	6649 (20)
N(3)	0	1608 (15)	3360 (19)
N(4)	1993 (15)	3401 (7)	2536 (13)
O(1)	1693 (9)	2876 (4)	5034 (12)
O(2)	0	4697 (10)	6078 (14)
O(3)	0	4722 (12)	4011 (16)
O(4)†	−949 (30)	−533 (16)	4740 (21)
O(5)	0	−1694 (12)	2534 (21)
O(6)†	3439 (32)	614 (15)	5553 (18)
C(1)	0	5190 (10)	4993 (26)
C(2)	0	6404 (12)	5050 (26)

* The z coordinate of Br(2) was held fixed to define the origin.
† Half-occupied sites, disordered across the mirror plane.

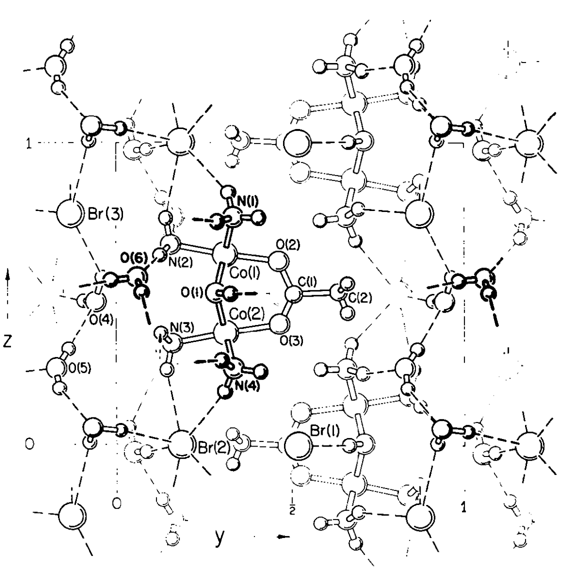


Fig. 1. The structure viewed down the a axis.

Table 3. *Coordinates of the* H *atoms* (×10^3)

Isotropic temperature factors were set at B = 3·0 Å^2.

	x	y	z		x	y	z
N(1) H(1)	295	291	740	O(1) H	250	330	500
H(2)	347	411	751	C(2) H(1)	0	666	437
H(3)	149	324	835	H(2)	88	663	530
N(2) H(1)	0	144	752	*O(4) H(1)	−209	−87	477
H(2)	107	126	629	H(2)	−69	−35	554
N(3) H(1)	0	146	251	*O(5) H(1)	71	−161	185
H(2)	107	129	372	H(2)	62	−132	315
N(4) H(1)	311	305	280	*O(6) H(1)	382	1	542
H(2)	223	416	242	H(2)	444	73	505
H(3)	170	311	174				

* Half-occupied sites, disordered across mirror plane.

which includes the cation and two Br ions, Br(1) and Br(2), contains, within experimental error, mirror planes perpendicular to **c** and hence conforms to the space group *Pmnm*; it is the arrangement of the water molecules and the third Br ion, Br(3), that requires the lower symmetry of *Pmn*2_1. We have tried exhaustively, and unsuccessfully, to evolve a disordered arrangement of Br(3) and water molecules in space group *Pmnm* that would give satisfactory agreement with the measured intensities; the lowest values we were able to obtain for the R index and the goodness-of-fit were 0·103 and 4·41. The change from a disordered structure in *Pmnm* to an ordered structure in *Pmn*2_1 generates a component to the structure factors that, neglecting the small effect of anomalous dispersion, is 90° out of phase with the 'real' term due to the centrosymmetric, disordered structure. Since this out-of-phase component is due primarily to the asymmetric arrangement of Br(3), O(4), O(5), and O(6), it is a relatively small term and hence is important only when the 'real' term is also small. There are 133 reflections for which, in the final ordered structure in space group *Pmn*2_1, the out-of-phase component of F_c is greater than the 'real' term; for these 133 reflections, most of which are quite weak, the R index is 0·091 compared to 0·462 for the best *Pmnm* structure.

While the change from space group *Pmnm* to *Pmn*2_1 has removed the disorder along the **c** direction, disorder remains: the hydrogen-bonded chain of water molecules O(4), O(5), and O(6) (Fig. 1) is disordered with respect to the mirror plane perpendicular to **a**. Br(2) and Br(3), which accept hydrogen bonds from these water molecules, show relatively large U_{11} anisotropic temperature coefficients, suggesting that they may also participate, to a small degree, in the disorder, while Br(1), which is surrounded only by —OH and —NH$_3$ groups of the cation, shows smaller, more isotropic thermal motion. Since an ordered arrangement of water molecules in a lower-symmetry space group would require lower Laue symmetry, we have not pursued this possibility.

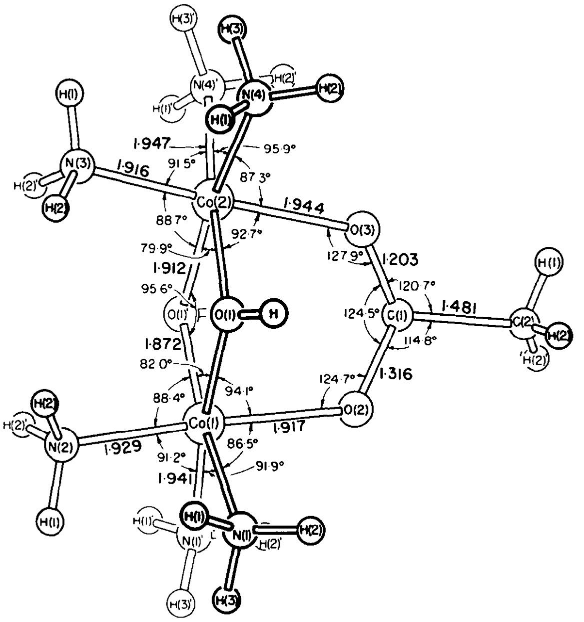


Fig. 2. Bond distances and angles within the cation. The Co···Co distance is 2·804 (6) Å.

Bond distances in the cation are shown in Fig. 2. The Co···Co distance is 2·804 (6) Å. As pointed out by Mandel, Mandel, Marsh & Schaefer (1977), this distance is relatively flexible in bridged Co species, adjusting so as to satisfy relatively stringent requirements on the O···O distances between bridging hydroxyl groups. The O···O distance, 2·456 (9) Å, is similar to values in other triply- and doubly-bridged systems.

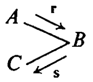
The e.s.d.'s in the bond distances, as calculated from diagonal terms of the inverse least-squares matrix, are approximately 0·015 Å for Co—O and Co—N and about 0·03 Å for C—O. On this basis the difference between the two C—O bond lengths, 0·113 Å, is probably significant, being nearly three times as large as its e.s.d. of 0·042 Å, and would imply that the bridging acetate ion is not symmetric, but should be represented as a $\mathrm{CH_3{-}C}\begin{smallmatrix}\nearrow\!\!\!\!\nearrow \mathrm{O}\\ \searrow \mathrm{O}\end{smallmatrix}$ group. Such a situation would be surprising because, even if the group is not bound symmetrically to the two Co atoms, it might be expected to be disordered between the two alternate bonding modes and hence appear symmetric to X-rays. However, if one includes the appropriate covariance terms (Waser, 1973), the e.s.d. in the difference between these two bond lengths becomes considerably larger, 0·053 Å. Details of the calculations of this revised e.s.d. are given in Table 4. Not surprisingly, the largest contribution to the important covariance term cov(r,s) comes from the variance in the z coordinate of C(1), which lies on the pseudo mirror plane; the second largest contribution arises from the correlation between the positions of O(2) and O(3) ($\mathbf{C}^{4C}$, Table 4) which are related to one another across the pseudo mirror plane.

Thus, the difference in the two C—O bond distances is 0·113 ± 0·053 Å, or 2·1σ. Although other asymmetric acetate bridges have been reported (Panattoni, Graziani, Bandoli, Zaili & Bombieri, 1969; Bandoli & Clemente, 1971; Bertrand & Hightower, 1973), these structures suffer either from disorder or from a lack of precision. The significance of this possibly asymmetric acetate bridge cannot be confirmed until it has been found in other high-precision structures.

Details of the probable hydrogen-bonding scheme are given in Table 5. While in poly-amminated species such as this it is not uncommon for the cation to be

Table 4. *Details of the calculation of the e.s.d. of the difference between the* C(1)—O(2) *and* C(1)—O(3) *bond lengths, including all covariance terms* (*Waser*, 1973)

Since the three atoms lie on a mirror plane perpendicular to **a**, all terms involving x vanish.



$A \equiv O(2)$
$B \equiv C(1)$
$C \equiv O(3)$

$\mathbf{r} = 0{\cdot}0493\mathbf{b} - 0{\cdot}1085\mathbf{c}$
$\mathbf{s} = -0{\cdot}0468\mathbf{b} - 0{\cdot}0982\mathbf{c}$
$\hat{\mathbf{r}} = \mathbf{r}/1{\cdot}316$
$\hat{\mathbf{s}} = \mathbf{s}/1{\cdot}203$

$$\sigma^2(r{-}s) = \sigma^2(r) + \sigma^2(s) - 2\,\mathrm{cov}(r,s),$$
$$\sigma^2(r) = \hat{\mathbf{r}}.\mathbf{C}^{AA}.\hat{\mathbf{r}} + \hat{\mathbf{r}}.\mathbf{C}^{BB}.\hat{\mathbf{r}} - 2\hat{\mathbf{r}}.\mathbf{C}^{AB}.\hat{\mathbf{r}},$$
$$\sigma^2(s) = \hat{\mathbf{s}}.\mathbf{C}^{BB}.\hat{\mathbf{s}} + \hat{\mathbf{s}}.\mathbf{C}^{CC}.\hat{\mathbf{s}} - 2\hat{\mathbf{s}}.\mathbf{C}^{BC}.\hat{\mathbf{s}},$$
$$\mathrm{cov}(r,s) = \hat{\mathbf{r}}.\mathbf{C}^{AB}.\hat{\mathbf{s}} - \hat{\mathbf{r}}.\mathbf{C}^{AC}.\hat{\mathbf{s}} - \hat{\mathbf{r}}.\mathbf{C}^{BB}.\hat{\mathbf{s}} + \hat{\mathbf{r}}.\mathbf{C}^{BC}.\mathbf{s}.$$

$$\mathbf{C} \times 10^6\ (\text{Å}^2)$$

$$\begin{array}{c|ccc|}
 & \begin{matrix} Y_A & Z_A \end{matrix} & \begin{matrix} Y_B & Z_B \end{matrix} & \begin{matrix} Y_C & Z_C \end{matrix} \\
\begin{matrix} Y_A \\ Z_A \end{matrix} & \mathbf{C}^{AA} = \begin{bmatrix} 152 & -15 \\ -15 & 221 \end{bmatrix} & & \\
\begin{matrix} Y_B \\ Z_B \end{matrix} & \mathbf{C}^{AB} = \begin{bmatrix} 8 & -9 \\ -36 & 79 \end{bmatrix} & \mathbf{C}^{BB} = \begin{bmatrix} 152 & 0 \\ 0 & 806 \end{bmatrix} & \\
\begin{matrix} Y_C \\ Z_C \end{matrix} & \mathbf{C}^{AC} = \begin{bmatrix} -114 & 4 \\ -12 & 177 \end{bmatrix} & \mathbf{C}^{BC} = \begin{bmatrix} -14 & 55 \\ 2 & 55 \end{bmatrix} & \mathbf{C}^{CC} = \begin{bmatrix} 219 & -2 \\ -2 & 283 \end{bmatrix} \\
\hline
\end{array}$$

$$\sigma^2(r) = 219 + 670 - 2(82{\cdot}5) = 724 \times 10^{-6}\ \text{Å}^2,$$
$$\sigma^2(s) = 659 + 267 - 2(63{\cdot}3) = 799 \times 10^{-6}\ \text{Å}^2,$$
$$\mathrm{cov}(r,s) = 70 - 170 - 598 + 69 = -629 \times 10^{-6}\ \text{Å}^2,$$
$$\sigma(r - s) = 0{\cdot}0527\ \text{Å}.$$

Table 5. *Hydrogen-bonded distances* (D—H···A)

D	H	A	$D\cdots A$	D	H	A	$D\cdots A$
N(1)	H(1)	O(5)	3·032 Å	O(1)	H	Br(1)	3·339 Å
	H(2)	Br(1)	3·740*	O(4)	H(1)	Br(2)	3·386
		Br(1)	3·930*		H(2)	Br(3)	3·321
	H(2)	Br(2)	3·510	O(5)	H(1)	O(6)	2·753
N(2)	H(1)	Br(2)	3·636		H(2)	O(4)	2·853
	H(2)	O(6)	3·002	O(6)	H(1)	H(2)	3·315
N(3)	H(1)	Br(2)	3·642		H(2)	Br(3)	3·420
	H(2)	Br(3)	3·735				
N(4)	H(1)	Br(3)	3·429				
	H(2)	Br(1)	3·817*				
		Br(1)	3·818*				
	H(3)	Br(2)	3·598				

* These interactions are too long and too non-linear to represent true hydrogen bonds; they are not shown in Fig. 1.

surrounded by a rather irregular array of electronegative species without a well-defined hydrogen-bonding pattern, in the present case the ammonia groups appear to form several relatively linear N—H···Br and N—H···O bonds. Exceptions are H(2) atoms attached to N(1) and N(4), each of which is approximately equidistant from two neighboring Br(1) ions, and two of the H atoms on N(2), each having an acceptor, O(6), only one-half of the time because of the disorder.

We thank Dr Jürg Waser for his assistance in the variance–covariance analysis. The investigation was supported in part by Research Grant No. 12395 from the National Heart and Lung Institute, National Institutes of Health.

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