2·95 Å, $c=18·25$ Å and $Z=3$, in the hexagonal description (Hahn & de Lorent, 1957). The hexagonal unit cell consists of three hexagonal sub-units, which are related to each other by the threefold screw axis parallel to the c axis, as shown in Fig. 3. The dimensions of the sub-unit are 2·95 Å along the a axis, and 6·08 Å along the c axis. The structure of this sub-unit is quite similar to that of δ-AgFeO$_2$. The structures of CuFeO$_2$ (Soller & Thompson, 1935; Pabst, 1946) and CuCrO$_2$ (Dannhauser & Vaughan, 1955) are also analogous to that in AgCrO$_2$.

Although the structure of α-AgFeO$_2$ has not been determined, we can build a model structure of it, in which three sub-units of AgFeO$_2$ found in δ-AgFeO$_2$ are stacked along the c axis in a similar fashion as in AgCrO$_2$. The observed cell dimensions of α-AgFeO$_2$, $a=3·041$ and $c=18·55$ Å (Croft et al., 1964), are in good agreement with those of the model structure, $a=3·039$ and $c=18·59$ Å.

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The Structure of Octammine-μ-amido-μ-hydroxodicobalt Disulfate Dihydrate*
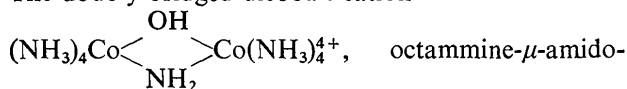
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The structures of two closely related compounds, octammine-μ-amido-μ-hydroxodicobalt disulfate dihydrate (the 'pure' compound) and the same compound with the hydroxo bridge partially substituted by chlorine (the 'mixed' compound), have been determined by X-ray diffraction techniques. The compounds form isostructural triclinic crystals: for the 'pure' compound, $a=9·066$ (4), $b=8·601$ (4), $c=6·977$ (3) Å, $\alpha=106·92$ (3), $\beta=111·72$ (4), and $\gamma=68·62$ (4)°. The observed density is 1·86 (2) g.cm^{-3} and that calculated for one formula weight in the unit cell is 1·848 (2) g.cm^{-3}. The space group is $P\bar{1}$; 1229 reflections were measured on a GE diffractometer and used to solve the structure. Refinement by full-matrix least-squares methods gave a final R index of 0·027. For the 'mixed' compound, $a=9·151$ (6), $b=8·633$ (6), $c=6·910$ (3) Å, $\alpha=106·66$ (7), $\beta=111·94$ (4), and $\gamma=68·95$ (9)°. The measured density is 1·88 (2) g.cm^{-3} and the calculated density 1·853 (2) g.cm^{-3}. The structure was solved using 1106 reflections and refined to an R index of 0·036. In both compounds, the cation is disordered about a center of symmetry; bond distances and angles in the cation and the sulfate groups are normal.

Introduction

The doubly-bridged dicobalt cation

$$(NH_3)_4Co\underset{NH_2}{\overset{OH}{\diagup\diagdown}}Co(NH_3)_4^{4+},$$ octammine-μ-amido-

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μ-hydroxodicobalt[4+], is obtained from Vortmann's (1885) sulfate and is a convenient starting material for the preparation of many other di-bridged dicobalt ions. The amide bridge is difficult to break, but the hydroxo bridge can be easily hydrolyzed, or substituted to give other di-bridged ions. The structure of this ion has not yet been reported. We intended to determine the structure several years ago, but instead of preparing the correct material, we made the μ-amido, μ-chloro compound (Barro, Marsh & Schaefer, 1970). We have now

prepared two more compounds – including the one we wanted – and have determined their structures.

The octammine-μ-amido-μ-chlorodicobalt chloride we made earlier came from a concentrated hydrochloric acid reaction mixture. We wanted to determine the crystal structure of the μ-amido, μ-hydroxo compound with no bridging chloride: unfortunately, our first preparation had been once-recrystallized from dilute HCl and some Cl had become incorporated in the bridge. We found this out only after the structural analysis was nearly complete. We therefore began again, crystallizing our starting material from dilute sulfuric acid with no chloride present at all. We obtained well-formed crystals and again performed an X-ray structural analysis. We present the results of this in detail here, along with a brief description of the structure of the partially chloro-substituted salt. These two determinations, along with the earlier report on the fully substituted μ-NH$_2$, μ-Cl compound (Barro *et al.*, 1970), give a complete picture of structural changes with substitution at the bridging OH-group in these dicobalt compounds.

Experimental

Vortmann's sulfate was prepared according to Werner's (1907) directions. The material was transformed to the nitrate, and the green μ-O$_2$, μ-NH$_2$ compound,

$$(NH_3)_4Co\underset{NH_2}{\overset{O_2}{\diagup\!\!\!\diagdown}}Co(NH_3)_4(NO_3)_4$$ (Christoph, Marsh
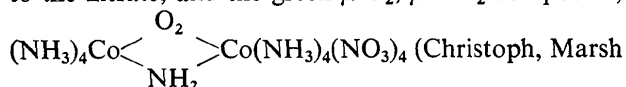
& Schaefer, 1969), was removed by washing. The red nitrate which remained was used for the recrystallizations. The 'mixed' NH$_2$, (OH, Cl) bridged cation formed when 0·5 M HCl was used once in recrystallizing the powder; the pure μ-NH$_2$, μ-OH compound was obtained by recrystallizing the starting material from 0·1 M H$_2$SO$_4$.
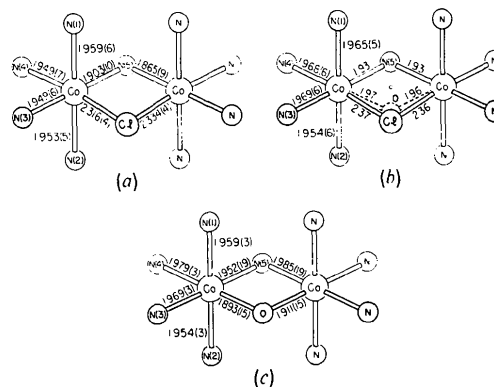

Fig. 1. Representations of three dicobalt cations: (*a*) the Cl, NH$_2$ bridged complex, (*b*) the 'mixed' complex, and (*c*) the OH, NH$_2$ bridged complex. For the 'mixed' crystal (*b*), we were unable to determine realistic standard deviations for the bridging atoms. These occur so close together that simultaneous refinement was not possible. We have therefore reported these lengths to a hundredth of an ångström, and we believe the e.s.d.'s should be at least ±0·04 Å for each of these distances.

The 'mixed' compound

Preliminary Weissenberg photographs indicated a triclinic cell. A sphere of average radius 0·075 (6) mm was ground from a larger chunk and carefully centered in a random orientation on the diffractometer. Unit-cell dimensions were obtained from a least-squares fit of the 2θ values of 27 reflections; these and other crystal data are given in Table 1. A Delaunay (1933) reduction revealed no higher symmetry; the reduced cell had two angles greater than 120°, so the original cell was used for all further work. Data were collected on a Datex-automated GE diffractometer using cobalt $K\alpha$ radiation. All reflections within the 2θ range of 4 to 140° were surveyed using a θ–2θ scan technique. The scan range varied from 2·5° at $2\theta = 12\cdot5°$ to 3·75° at $2\theta = 120°$

Table 1. *Crystal data for the two compounds*

Space group No. 2, $P\bar{1}$ $Z = 1$

$$(NH_3)_4Co\overset{NH_2}{\underset{\begin{pmatrix}OH\\Cl\end{pmatrix}}{\diagup\!\!\!\diagdown}}Co(NH_3)_4(SO_4)_2\cdot 2H_2O$$

$$(NH_3)_4Co\overset{NH_2}{\underset{OH}{\diagup\!\!\!\diagdown}}Co(NH_3)_4(SO_4)_2\cdot 2H_2O$$

	$\begin{pmatrix}OH\\Cl\end{pmatrix}\begin{matrix}0\cdot786\\0\cdot214\end{matrix}$	
a	9·151 (6) Å	9·066 (4) Å
b	8·633 (6)	8·601 (4)
c	6·910 (3)	6·977 (3)
α	106·66 (7)°	106·92 (3)°
β	111·94 (4)	111·72 (4)
γ	68·95 (9)	68·62 (4)
V	465·2 (7) Å³	462·9 (5) Å³
Formula	Co$_2$Cl$_{0\cdot214}$S$_2$O$_{10\cdot786}$N$_9$H$_{30\cdot786}$	Co$_2$S$_2$O$_{11}$N$_9$H$_{31}$
M.W.	519·24	515·30
ϱ_{obs}	1·88 (2) g.cm⁻³	1·86 (2) g.cm⁻³
ϱ_{calc}	1·853 (2) g.cm⁻³	1·848 (2) g.cm⁻³
$F(000)$	269·71 e.	268 e.

λCo $K\alpha_1$	1·78892 Å	
λCo $K\alpha_2$	1·79278	
λCo $K\alpha$		1·79021 Å
λCo $K\beta$		1·62075

and included both the α_1 and α_2 peaks. Background was counted for 60 seconds at both ends of the scan. Of the 1115 reflections scanned, 1106 were observed greater than background and were used in the solution and refinement of the structure. The data were corrected for background and for Lorentz and polarization factors; no correction for absorption was made because of the small value of μR (0·31). Standard deviations were assigned the measured intensities according to:

$$I = S - (B_1 + B_2) \frac{t}{120}$$

$$\sigma(I) = [S + (B_1 + B_2) \left(\frac{t}{120}\right)^2 + (0 \cdot 02S)^2]^{1/2},$$

where S is the scan count, B_1 and B_2 are background counts and t is scan time. The additional term in $\sigma(I)$, $(0 \cdot 02S)^2$, is included to take account of errors other than those due to counting statistics (Busing & Levy, 1957). During the initial data processing, the values of $\langle|E|\rangle$, $\langle|E^2|\rangle$, and $\langle|E^2 - 1|\rangle$ were calculated; these were, seriatim, 0·818, 0·999, and 0·917, indicating that the space group has a center of symmetry and is thus No. 2, $P\bar{1}$.

A three-dimensional Patterson map was calculated from which the coordinates of the cobalt atom, one sulfur atom, and one bridging atom were obtained. There is one molecule of
$(NH_3)_4Co(OH)$ $(NH_2)Co(NH_3)_4(SO_4)_2.2H_2O$ in the unit cell, or half a molecule in the asymmetric unit; therefore the bridging groups have to be disordered if the space group is to be $P\bar{1}$. Successive electron density maps and structure factor calculations located the rest of the nonhydrogen atoms in the structure. Full-matrix least-squares refinement converged with an R index of 0·081; at this stage, the bridging atoms were considered to be an oxygen atom and a nitrogen atom. The hydrogen atoms of the ammine groups were then added, their coordinates being taken from difference maps calculated in the planes where they were expected. Four cycles of least-squares calculations, varying the positional and thermal parameters of all the atoms (hydrogen atoms isotropic, others anisotropic), a scale factor, and a secondary extinction factor (Larson, 1967), gave an R index of 0·043. However, one of the bridging atoms, assumed to be an oxygen atom, was 2·23 Å from the cobalt atom. This distance is much too long to be a Co–O bond. Since such a distance is appropriate for a Co–Cl bond, and since there were positive regions of electron density remaining around this atom, we began to try various combinations of Cl and

Table 2. *Positional, thermal, and population parameters of the heavy atoms*

All positional and anisotropic thermal parameters have been multiplied by 10^4. Anisotropic temperature factors are of the form:
$$\exp[-(h^2 b_{11} + k^2 b_{22} + l^2 b_{33} + hk b_{12} + hl b_{13} + kl b_{23})].$$

	x	y	z	B or b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}	Population*
(a) The 'mixed' compound										
Co	6727 (0·9)	3808 (0·9)	5374 (1)	51 (2)	65 (2)	128 (3)	−40 (2)	37 (3)	26 (3)	
N(1)	5889 (6)	1824 (6)	4232 (8)	55 (7)	61 (8)	170 (15)	−26 (13)	51 (18)	16 (16)	
N(2)	7739 (6)	5656 (6)	6514 (8)	47 (8)	82 (8)	150 (14)	−40 (13)	35 (16)	16 (18)	
N(3)	8317 (6)	2754 (8)	7811 (8)	90 (9)	108 (9)	151 (14)	−88 (15)	33 (17)	92 (21)	
N(4)	8206 (6)	2839 (7)	3599 (8)	68 (8)	109 (9)	155 (13)	−37 (14)	63 (17)	35 (19)	
N(5)	4957 (9)	4998 (9)	3250 (13)	2·21 (14)						0·5
Cl	4937 (23)	5049 (20)	2365 (16)	598 (54)	405 (42)	−11 (22)	−915 (88)	163 (52)	−96 (44)	0·107
O(1)	4955 (8)	5015 (8)	3179 (11)	2·28 (20)						0·393
S	2439 (1)	2531 (2)	7844 (2)	54 (2)	70 (2)	135 (4)	−16 (3)	44 (4)	51 (4)	
O(2)	3283 (5)	2091 (5)	9955 (6)	144 (7)	132 (8)	128 (10)	−29 (12)	30 (14)	93 (14)	
O(3)	1402 (4)	4295 (5)	7991 (6)	78 (6)	72 (6)	271 (12)	8 (10)	80 (14)	75 (14)	
O(4)	1425 (5)	1392 (5)	6564 (7)	75 (6)	105 (8)	345 (14)	−50 (11)	24 (15)	−17 (16)	
O(5)	3689 (5)	2305 (5)	6863 (7)	106 (7)	171 (8)	285 (13)	16 (12)	210 (16)	191 (17)	
O(6)	6923 (5)	838 (5)	9296 (6)	99 (7)	134 (8)	243 (12)	−87 (12)	47 (14)	143 (15)	
(b) The 'pure' compound										
Co	6692 (0·5)	3834 (0·5)	5354 (0·6)	55 (1)	60 (1)	112 (1)	−26 (1)	52 (2)	28 (1)	
N(1)	5870 (3)	1837 (3)	4192 (4)	68 (4)	64 (4)	159 (7)	−31 (7)	62 (9)	25 (8)	
N(2)	7730 (3)	5672 (3)	6525 (4)	68 (5)	73 (4)	116 (6)	−41 (7)	58 (8)	22 (9)	
N(3)	8293 (3)	2760 (4)	7769 (4)	73 (4)	96 (4)	158 (7)	−42 (7)	37 (9)	104 (10)	
N(4)	8208 (3)	2845 (4)	3610 (4)	64 (4)	90 (4)	136 (7)	−37 (7)	59 (8)	9 (10)	
N(5)	4944 (20)	5034 (21)	3111 (27)	1·78 (48)						0·5
O(1)	4971 (16)	4976 (17)	3250 (20)	1·38 (42)						0·5
S	2456 (0·8)	2564 (0·8)	7865 (1)	64 (1)	70 (1)	128 (2)	−24 (2)	57 (2)	47 (2)	
O(2)	3252 (3)	2092 (3)	9955 (3)	159 (4)	123 (4)	131 (5)	−67 (7)	49 (8)	78 (7)	
O(3)	1410 (3)	4339 (3)	8028 (4)	105 (4)	75 (3)	279 (7)	5 (6)	108 (8)	74 (8)	
O(4)	1454 (3)	1422 (3)	6524 (4)	75 (3)	104 (4)	242 (6)	−56 (6)	22 (8)	−8 (8)	
O(5)	3764 (3)	2350 (3)	6966 (4)	110 (4)	156 (4)	288 (7)	−29 (7)	206 (9)	176 (9)	
O(6)	6993 (3)	823 (3)	9341 (4)	98 (4)	135 (5)	317 (8)	−82 (7)	40 (9)	195 (10)	

* Unless a number is given here, the population was 1·0.

Table 3. Positional, thermal, and population parameters of the hydrogen atoms

All positional parameters have been multiplied by 10^3.

	x	y	z	B(Å²)	Population
(a) The 'mixed' compound					
H(1)	530 (7)	183 (7)	291 (10)	3·0 (13)	
H(2)	518 (8)	172 (7)	480 (9)	3·0 (13)	
H(3)	677 (9)	88 (8)	413 (9)	4·5 (14)	
H(4)	751 (8)	621 (8)	762 (10)	3·1 (15)	
H(5)	864 (8)	517 (8)	673 (9)	0·4 (15)	
H(6)	728 (8)	642 (8)	535 (11)	3·9 (14)	
H(7)	827 (8)	352 (9)	887 (10)	4·2 (17)	
H(8)	803 (7)	205 (8)	797 (9)	2·9 (15)	
H(9)	933 (8)	208 (8)	732 (9)	2·8 (13)	
H(10)	903 (8)	224 (7)	422 (9)	2·0 (13)	
H(11)	827 (8)	378 (9)	292 (10)	5·4 (16)	
H(12)	785 (10)	207 (11)	211 (13)	6·3 (21)	
H(13)	539 (−)	599 (−)	317 (−)	4·0 (−)	0·683
H(14)	452 (−)	409 (−)	211 (−)	4·0 (−)	0·683

[H(15) and H(16), attached to the water oxygen atom, were not assigned.]

(b) The 'pure' compound					
H(1)	520 (4)	185 (4)	278 (5)	2·5 (6)	
H(2)	532 (4)	168 (4)	479 (5)	2·6 (7)	
H(3)	666 (5)	85 (5)	427 (5)	3·6 (8)	
H(4)	755 (4)	626 (4)	758 (5)	2·1 (7)	
H(5)	879 (5)	520 (4)	688 (5)	2·6 (7)	
H(6)	746 (4)	629 (5)	571 (6)	3·3 (8)	
H(7)	837 (5)	351 (5)	885 (6)	4·2 (9)	
H(8)	800 (4)	206 (4)	806 (5)	3·0 (8)	
H(9)	936 (5)	220 (5)	760 (6)	4·5 (8)	
H(10)	925 (5)	233 (4)	429 (5)	3·2 (7)	
H(11)	836 (4)	365 (5)	324 (5)	4·0 (9)	
H(12)	787 (4)	221 (4)	264 (6)	2·4 (8)	
H(13)	524 (6)	568 (6)	279 (7)	3·1	0·750
H(14)	471 (5)	440 (6)	211 (7)	3·1	0·750
H(15)	703 (4)	995 (4)	949 (5)	3·1	
H(16)	615 (4)	120 (5)	891 (6)	3·1	

Table 4. Supplementary bond distances and bond angles

	'Mixed'	'Pure'
N(1)–H(1)	0·87 Å	0·95 Å
N(1)–H(2)	0·92	0·83
N(1)–H(3)	0·93	0·89
N(2)–H(4)	0·83	0·80
N(2)–H(5)	0·76	0·87
N(2)–H(6)	1·06	0·80
N(3)–H(7)	0·84	0·84
N(3)–H(8)	0·80	0·84
N(3)–H(9)	1·02	0·95
N(4)–H(10)	0·79	0·90
N(4)–H(11)	1·08	0·87
N(4)–H(12)	1·06	0·78
N(5)–H(13)	1·09	0·81
N(5)–H(14)	1·01	0·77
O(6)–H(15)	−	0·77
O(6)–H(16)	−	0·69
S–O(2)	1·460 (4)	1·472 (2)
S–O(3)	1·475 (4)	1·472 (2)
S–O(4)	1·467 (5)	1·467 (3)
S–O(5)	1·466 (5)	1·468 (3)
Co–Co'	3·035 (1)	2·941 (1)

	'Mixed'	'Pure'
N(1)–Co–N(2)	175·4 (2)°	174·4 (1)°
N(1)–Co–N(3)	90·0 (2)	89·9 (1)
N(1)–Co–N(4)	89·8 (2)	89·1 (1)
N(1)–Co–N(5)	90·5 (4)	92·3 (6)
N(1)–Co–O(1)	90·8 (5)	90·0 (5)
N(1)–Co–Cl	91·0 (5)	−
N(2)–Co–N(3)	87·4 (2)	86·7 (1)
N(2)–Co–N(4)	86·7 (2)	86·6 (1)
N(2)–Co–N(5)	92·7 (4)	92·3 (6)
N(2)–Co–O(1)	92·3 (3)	93·9 (5)
N(2)–Co–Cl	91·4 (5)	−
N(3)–Co–N(4)	94·7 (2)	94·4 (1)
N(3)–Co–N(5)	171·4 (5)	174·4 (5)
N(3)–Co–O(1)	172·5 (3)	172·7 (5)
N(3)–Co–Cl	176·8 (5)	−
N(4)–Co–N(5)	93·9 (5)	91·2 (5)
N(4)–Co–O(1)	92·8 (3)	92·9 (5)
N(4)–Co–Cl	82·3 (5)	−
N(5')–Co—O(1)	77·7 (5)	81·2 (7)
N(5')–Co—Cl	88·0 (6)	−
O(1)–Co—Cl	10·5 (5)	−
Co—N(5)–Co'	103·6 (6)	96·6 (8)
Co—O(1)–Co'	101·2 (3)	101·2 (6)
Co—Cl—Co'	79·9 (4)	−
O(2)–S–O(3)	110·3 (2)	110·3 (1)
O(2)–S–O(4)	109·2 (3)	108·8 (1)
O(2)–S–O(5)	108·0 (3)	108·2 (2)
O(3)–S–O(4)	110·1 (3)	110·4 (1)
O(3)–S–O(5)	110·0 (3)	110·0 (1)
O(4)–S–O(5)	109·2 (3)	109·0 (1)
Co—N(1)–H(1)	110	111
Co—N(1)–H(2)	119	118
Co—N(1)–H(3)	108	114
H(1)—N(1)–H(2)	101	106
H(1)—N(1)–H(3)	102	109
H(2)—N(1)–H(3)	115	98
Co—N(2)–H(4)	110	115
Co—N(2)–H(5)	101	108
Co—N(2)–H(6)	108	112
H(4)—N(2)–H(5)	112	105
H(4)—N(2)–H(6)	111	107
H(5)—N(2)–H(6)	115	111
Co—N(3)–H(7)	105	109
Co—N(3)–H(8)	111	115
Co—N(3)–H(9)	104	113
H(7)—N(3)–H(8)	106	104
H(7)—N(3)–H(9)	127	109
H(8)—N(3)–H(9)	103	107
Co—N(4)–H(10)	108	115
Co—N(4)–H(11)	112	110
Co—N(4)–H(12)	120	110
H(10)–N(4)–H(11)	119	101
H(10)–N(4)–H(12)	103	109
H(11)–N(4)–H(12)	93	112
Co—N(5)–H(13)	105	114
Co—N(5)–H(14)	105	117
Co'—N(5)–H(13)	104	113
Co'—N(5)–H(14)	105	111
H(13)–N(5)–H(14)	131	106
H(15)–O(6)–H(16)	−	104

An approximate e.s.d. of an N–H bond length would be 0·1 Å; for a bond angle involving H: 2–3°.

O atoms to explain the electron density in this region. We represented the bridging groups as a nitrogen atom with population one, and a combination of a chlorine atom and an oxygen atom whose populations summed to one. Refinement of our final model by the least-

squares method led to an R index of 0·036. The ratio of chlorine to oxygen atoms in the bridge turned out to be 21:79. The parameters obtained from the refinement are given in Tables 2 and 3; the estimated standard deviations listed there are underestimated, because the final cycles were block diagonal rather than full matrix. A drawing of the cation is given in Fig. 1(b), and supplementary bond distances and angles are listed in Table 4.

Some of the thermal parameters in Tables 2 and 3 deserve comment. The B's of the hydrogen atoms range from 0·39 to 6·29 Å, but do not differ significantly from an average value of about 3·5 Å². The thermal parameters of the bridging Cl atom are very large and are nonpositive definite, i.e. physically unreal. The problem is caused by the nearness of the bridging N and O atoms and by the very strong coupling between the thermal and population parameters of these atoms.

Because this crystal obviously contained some chloride in the bridging groups, we decided to discontinue further work and to prepare the pure material. However, since the data were of high quality, it seemed appropriate to report these results in the present abbreviated form.

The 'pure' compound

Well-formed red crystals were obtained from 0·1 M H_2SO_4. Weissenberg and rotation photographs showed about the same triclinic cell as found for the mixed compound. A nearly cubic crystal was found, with sides of 0·19 mm. This crystal was mounted (again in a random orientation), carefully centered on the diffractometer, and cell dimensions measured. These are given, along with the other crystal data, in Table 1. The cell dimensions are, of course, nearly the same as for the mixed compound; the shortening of a and b

Table 5. The 'pure' compound

The columns contain, in order, l, $10F_{obs}$, and $10F_{calc}$ on an absolute scale.

reflects the shorter Co–Co distance in the 'pure' compound. Data were collected using Fe foil-filtered cobalt radiation and a θ–2θ scan technique. The scan range varied from 2·2° at $2\theta=30°$ to 3·2° at $2\theta=110°$. Background was counted for 30 seconds at each end of the scan. Three standard reflections ($\bar{5}61$, 570, and $\bar{7}01$) were followed throughout the data collection. Their intensities showed no variations greater than those expected from counting statistics. The intensities and their standard deviations were obtained from the

Table 6. *The 'mixed' compound*

The columns contain, in order, h, $10F_{\rm obs}$, and $10F_{\rm calc}$ on an absolute scale.

H	1	-7
2	102	105
3	160	-172
4	28	-26
H	2	-7
2	143	-147
3	63	69
4	22	8
5	61	-56
H	3	-7
2	32	33
3	15	-11
4	91	96
5	145	-150
H	4	-7
3	65	74
4	183	-185
5	62	63
H	0	-6
1	215	-210
2	48	50
3	111	109
4	143	-148
5	0	0*
6	132	134
H	1	-6
1	34	32
2	24	22
3	63	66
4	43	-51
5	94	-85
6	103	101
7	72	67
H	2	-6
1	116	116
2	171	150
3	383	-397
4	39	34
5	300	299
6	148	-143
7	76	-70
H	3	-6
1	167	-164
2	118	-116
3	194	156
4	55	50
5	43	-29
6	38	-33
7	71	-69
H	4	-6
1	82	73
2	62	-65
3	98	96
4	51	54
5	227	-227
6	25	26
7	187	175
H	5	-6
1	101	-104
2	172	171
3	34	37
4	228	-231
5	164	170
6	57	55
7	165	-171
H	6	-6
2	56	-49
3	9	9
4	24	-19
5	65	-66
6	116	109
7	55	-55
H	0	-5
1	239	236
2	221	-225
3	61	-60
4	244	242
5	174	-162
6	195	-207
7	267	275
H	1	-5
1	261	-259
2	377	362
3	123	117
4	252	-257
5	40	41
6	15	10
7	75	-81
8	147	155
H	2	-5
1	43	38
2	55	-85
3	138	141
4	152	-154
5	14	-17
6	156	144
7	71	-69
8	118	-117
H	3	-5
1	253	253
2	17	2
3	491	-456
4	183	180
5	294	286
6	115	-113
7	17	-15
8	63	[illegible]
H	4	-5
1	151	-143
2	24	-17
3	162	157
4	65	-67
5	67	[illegible]
6	0	10*
7	65	-69
8	57	91
H	5	-5
1	91	-104
2	64	-67
3	218	214
4	114	100
5	338	-325
6	88	84
7	205	197
8	162	-158
H	6	-5
1	50	-45
2	213	213
3	54	-57
4	161	-163
5	311	315
6	20	-16
7	191	-188
8	15	-17
H	7	-5
1	9	-2
2	80	-70
3	27	25
4	105	-101
5	9	1
6	124	116
7	75	-71
H	8	-5
4	194	155
5	164	-160
H	0	-4
1	159	-150
2	23	0
3	107	107
4	149	-140
5	174	173
6	51	51
7	258	-260
8	51	54
H	1	-4
1	163	153
2	475	-450
3	68	-59
4	490	484
5	170	-166
6	109	-109
7	159	154
8	34	-31
H	2	-4
1	17	-23
2	612	608
3	87	-79
4	140	[illegible]
5	21	-4
6	126	-127
7	55	43
8	126	129
9	104	-106
H	3	-4
1	3	13
2	8	-1
3	65	75
4	257	-254
5	0	-3*
6	253	253
7	134	-130
8	140	-142
9	194	199
H	4	-4
1	184	196
2	88	-84
3	243	-242
4	253	250
5	175	172
6	310	-308
7	54	47
8	60	61
9	59	-62
H	5	-4
1	216	-204
2	93	99
3	27	22
4	272	-272
5	124	125
6	53	57
7	102	-98
8	197	155
9	6	-2
H	6	-4
1	92	-99
2	123	-118
3	243	252
4	32	32
5	310	-305
6	209	207
7	121	116
8	154	-176
H	7	-4
1	120	118
2	137	190
3	208	-210
4	50	-48
5	157	160
6	4	-12
7	63	-74
8	5	-3
H	8	-4
1	58	-91
2	128	-118
3	30	24
4	9	-5
5	55	89
6	67	77
H	0	-3
1	335	326
2	57	-36
3	426	-432
4	255	258
5	74	74
6	43	-40
7	13	-25
8	77	-77
H	1	-3
1	201	-253
2	137	[illegible]
3	231	-206
4	421	-411
5	474	477
6	34	-43
7	127	-117
8	103	103
9	49	42
H	2	-3
1	22	-20
2	236	-235
3	73	73
4	443	435
5	246	-240
6	126	-118
7	101	100
8	44	-47
9	84	-87
H	3	-3
1	170	160
2	244	245
3	44	-33
4	83	70
5	75	77
6	275	-270
7	110	103
8	127	121
9	172	-164
H	4	-3
1	102	-96
2	37	-25
3	76	75
4	229	-232
5	112	105
6	469	457
7	394	-356
8	176	-171
9	173	171
H	5	-3
1	325	332
2	153	-150
3	97	-100
4	176	175
5	68	-68
6	243	-242
7	114	100
8	43	51
9	73	71
H	6	-3
1	341	-338
2	309	309
3	52	-59
4	148	-145
5	76	87
6	100	-110
7	28	-24
8	240	246
9	62	-63
H	7	-3
1	92	-90
2	69	-66
3	254	254
4	75	-71
5	138	-136
6	134	134
7	51	55
8	229	-233
H	8	-3
1	195	194
2	27	23
3	242	-245
4	0	-6*
5	83	63
6	45	45
7	44	56
H	0	-2
1	300	-314
2	16	17
3	534	531
4	370	-362
5	376	-374
6	208	207
7	21	20
8	142	-144
H	1	-2
1	724	714
2	64	-76
3	220	-213
4	179	168
5	156	-146
6	41	-37
7	12	-16
8	44	-37
9	25	28
H	2	-2
1	50	-55
2	254	-223
3	474	-480
4	[illegible]	-17
5	588	604
6	182	-185
7	242	-236
8	311	302
9	13	-17
H	3	-2
1	124	100
2	63	36
3	41	-5
4	148	136
5	480	-483
6	89	90
7	266	287
8	92	-87
9	34	-31
H	4	-2
1	190	175
2	94	100
3	319	-313
4	179	177
5	101	94
6	217	-216
7	208	204
8	26	-23
9	174	-164
H	5	-2
1	373	-360
2	215	209
3	169	177
4	256	-271
5	275	277
6	242	246
7	417	-430
8	59	-56
9	168	165
H	6	-2
1	242	243
2	350	-374
3	32	-34
4	83	86
5	56	55
6	57	-55
7	15	15
8	23	-20
H	7	-2
1	183	-180
2	272	285
3	19	6
4	15	14
5	0	4*
6	172	-178
7	10	-9
8	255	263
H	8	-2
1	53	-48
2	73	69
3	198	200
4	171	-170
5	172	-170
6	167	160
7	12	-7
H	9	-2
3	184	-191
4	142	139
H	0	-1
1	104	-83
2	125	-99
3	156	-153
4	334	333
5	22	1
6	207	-205
7	268	263
8	34	37
H	1	-1
1	741	-732
2	446	462
3	374	359
4	74	-80
5	96	-87
6	188	155
7	220	-210
8	115	-116
9	124	128
H	2	-1
1	723	712
2	260	-227
3	255	-261
4	138	123
5	55	-67
6	14	3
7	178	178
8	227	-224
9	34	24
H	3	-1
1	168	151
2	157	162
3	305	-323
4	157	152
5	374	354
6	440	-440
7	155	-153
8	364	373
9	72	-65
H	4	-1
1	144	-145
2	172	-172
3	539	553
4	225	-222
5	308	-354
6	81	82
7	157	147
8	39	41
9	37	34
H	5	-1
1	270	278
2	21	14
3	361	-350
4	108	170
5	15	8
6	82	67
7	130	130
8	122	-118
H	6	-1
1	57	-54
2	258	264
3	143	-150
4	266	-275
5	270	269
6	90	88
7	247	-242
8	78	82
H	7	-1
1	16	-18
2	247	-254
3	15	0
4	160	161
5	62	-58
6	46	45
7	21	26
H	8	-1
1	103	-100
2	96	105
3	28	27
4	90	[illegible]
5	67	61
6	255	-255
H	-7	0
1	181	176
2	103	-97
3	132	-136
H	-6	0
1	209	-215
2	330	334
3	40	-33
4	154	-157
H	-5	0
1	173	166
2	264	-256
3	127	126
4	56	-52
5	21	18
H	-4	0
1	226	-205
2	111	-100
3	186	-201
4	237	229
5	238	247
6	177	-176
H	-3	0
1	230	-244
2	380	365
3	379	367
4	360	-365
5	64	-57
6	76	76
7	35	-38
H	-2	0
1	213	218
2	127	135
3	53	-50
4	251	252
5	433	-430
6	84	79
7	267	267
H	-1	0
1	141	140
2	205	214
3	103	-110
4	97	-100
5	293	303
6	110	-109
7	182	-189
8	0	1*
H	0	0
1	358	-364
2	759	-772
3	72	61
4	139	-125
5	142	-150
6	258	263
7	62	-47
8	0	3*
H	1	0
0	494	-489
1	80	64
2	55	5
3	280	256
4	12	15
5	115	-115
6	232	-239
7	421	410
8	35	40
H	2	0
0	448	-457
1	322	-301
2	543	543
3	84	-73
4	206	-221
5	119	130
6	168	161
7	233	-222
6	56	51
H	3	0
0	164	-136
1	453	435
2	973	-938
3	47	19
4	458	503
5	37	-34
6	58	101
7	26	18
8	291	-295
H	4	0
0	12	-9
1	323	323
2	238	217
3	446	-448
4	247	275
5	61	71
6	292	-286
7	21	-22
8	219	216
H	5	0
0	224	216
1	435	-443
2	87	90
3	467	475
4	274	-271
5	123	-120
6	14	-8
7	53	41
8	52	51
H	6	0
0	250	-244
1	122	131
2	197	198
3	90	-88
4	100	98
5	112	-103
6	12	-21
7	88	85
H	7	0
0	40	-41
1	145	151
2	65	62
3	209	-276
4	215	-208
5	380	377
6	20	-25
7	164	-159
H	8	0
0	184	181
1	29	-24
2	179	-179
3	114	112
4	65	66
5	175	-180
H	-8	1
0	144	-143
1	135	130
H	-7	1
0	234	231
1	137	-129
2	19	-6
H	-6	1
0	77	-74
1	171	171
2	180	-180
3	35	30
4	117	119
H	-5	1
0	377	-381
1	40	33
2	356	362
3	110	-109
4	141	-136
5	51	45
H	-4	1
0	349	334
1	71	71
2	192	-176
3	25	-23
4	164	-164
5	23	18
6	240	247
H	-3	1
0	25	35
1	136	-117
2	98	-100
3	223	-234
4	351	348
5	140	140
6	275	-278
H	-2	1
0	42	-44
1	776	-721
2	440	452
3	245	231
4	370	-369
5	64	76
6	28	25
7	12	11
H	-1	1
0	144	-128
1	188	156
2	330	-326
3	250	242
4	173	169
5	211	-203
6	192	198
7	45	45
H	0	1
0	494	-525
1	493	569
2	184	149
3	6	-66
4	15	-1
5	76	81
6	147	-143
7	115	-117
8	117	118
H	1	1
-8	0	6*
-7	12	7
-6	123	114
-5	324	-322
-4	193	200
-3	378	370
-2	757	-758
-1	68	62
0	909	879
1	447	-466
2	351	-330
3	310	312
4	150	-144
5	97	-91
6	202	201
7	172	-174
8	37	36
H	2	1
-7	255	-262
-6	137	141
-5	471	480
-4	344	-357
-3	207	-217
-2	16	22
-1	81	91
0	12	-19
1	120	115
2	12	7
3	26	30
4	202	205
5	330	-335
6	236	-232
7	381	367
8	46	-15
H	3	1
-7	234	221
-6	20	-8
-5	233	-233
-4	0	-8*
-3	165	-99
-2	140	175
-1	210	201
0	234	-244
1	36	-33
2	540	506
3	418	-426
4	347	-348
5	253	253
6	59	9
7	12	15
8	20	11
H	4	1
-6	29	22
-5	135	-134
-4	107	-107
-3	366	363
-2	81	70
-1	448	-449
0	253	293
1	152	152
2	504	-579
3	165	153
4	202	206
5	25	-21
6	95	90
7	68	-86
8	149	-140
H	5	1
-5	107	137
-4	60	49
-3	254	-261
-2	156	161
-1	19	24
0	49	-43
1	166	186
2	176	-174
3	157	-163
4	228	221
5	25	33
6	199	-199
7	75	79
H	6	1
-4	106	109
-3	39	33
-2	175	-169
-1	250	250
0	51	-49
1	337	-336
2	128	122
3	223	224
4	169	-163
5	51	53
6	43	67
7	131	-137
H	7	1
-2	145	143
-1	173	-170
0	140	-148
1	140	144
2	113	111
3	4	-11
4	59	54
5	170	-169
6	24	20
H	8	1
0	81	-81
1	96	96
2	100	94
3	249	-251
H	-8	2
0	18	-10
H	-7	2
0	228	-230
1	249	244
2	24	-24
H	-6	2
0	263	261
1	168	-160
2	53	-50
3	17	8
H	-5	2
0	5	9
1	79	-80
2	21	15
3	144	187
4	61	59
H	-4	2
0	523	-531
1	170	173
2	435	443
3	166	-164
4	149	-182
5	149	149
H	-3	2
0	275	274
1	148	-150
2	139	[illegible]
3	43	40
4	101	-97
5	107	107
6	167	171
H	-2	2
0	115	127
1	703	706
2	335	-363
3	[illegible]	-143
4	204	191
5	73	-67
6	126	-126
H	-1	2
0	104	-100
1	746	-722
2	455	469
3	56	41
4	211	-213
5	27	-20
6	64	65
7	38	44
H	0	2
0	113	-117
1	315	-262
2	65	-60
3	397	383
4	61	-58
5	110	-113
6	[illegible]	216
7	15	-17
H	1	2
-8	142	138
-7	173	174
-6	208	-203
-5	94	40
-4	178	180
-3	403	-397
-2	159	163
-1	84	87
0	205	220
1	105	117
2	123	-138
3	478	-440
4	235	240
5	256	260
6	150	-142
7	57	-54
H	2	2
-7	35	35
-6	128	-126
-5	50	-42
-4	420	427
-3	130	137
-2	488	-482
-1	37	-33
0	101	108
1	257	-262
2	7	2
3	469	461
4	242	-238
5	18	19
6	31	15
7	111	-109
H	3	2
-7	258	-258
-6	204	245
-5	224	222
-4	254	-250
-3	76	-70
-2	224	223
-1	373	-345
0	75	59
1	225	219
2	157	-163
3	269	262
4	214	222
5	431	-437
6	48	-49
7	199	196
H	4	2
-6	39	42
-5	121	-121
-4	76	-75
-3	21	-17
-2	148	138
-1	257	244
0	414	-410
1	71	70
2	210	223
3	[illegible]	-195
4	65	-60
5	141	151
6	34	-31
7	22	-15
H	5	2
-5	150	-146
-4	31	25
-3	225	219
-2	[illegible]	-305
-1	216	-218
0	420	416
1	92	96
2	122	-121
3	68	-92
4	23	-26
5	40	-34
6	161	179
H	6	2
-3	135	-132
-2	124	122
-1	40	42
0	17	-12
1	93	90
2	100	-105
3	72	-77
4	170	174
5	25	-21
H	7	2
-1	139	132
0	100	-97
1	252	-247
2	213	208
3	60	78
4	123	-119
H	-8	3
0	65	-62
H	-7	3
0	19	27
1	8	-7
H	-6	3
0	31	-33
1	331	335
2	134	-129
3	154	-154
H	-5	3
0	102	95
1	107	-107
2	146	-149
3	40	40
4	8	2
H	-4	3
0	118	113
1	215	-212
2	5	4
3	257	254
4	10	-1
H	-3	3
0	663	-700
1	263	204
2	374	383
3	354	-361
4	53	-49
5	175	179
H	-2	3
0	111	127
1	233	-242
2	134	120
3	17	8
4	12	11
5	112	113
H	-1	3
0	305	309
1	373	366
2	430	-432
3	110	108
4	111	110
5	178	-161
6	70	-72
H	0	3
0	31	-30
1	329	-321
2	311	318
3	64	36
4	199	-208
5	54	57
6	28	29
H	1	3
-8	194	-198
-7	153	151
-6	310	313
-5	420	-435
-4	141	-156
-3	503	505
-2	283	-266
-1	33	-27
0	28	25
1	111	-97
2	60	75
3	268	270
4	314	-321
5	105	-102
6	255	264
H	2	3
-7	20	14
-6	223	-219
-5	76	-74
-4	98	94
-3	85	-87
-2	242	243
-1	46	37
0	75	-79
1	213	217
2	241	-246
3	444	-440
4	400	394
5	127	135
6	101	-101
H	3	3
-6	104	-94
-5	102	100
-4	164	180
-3	97	-94
-2	305	-303
-1	295	291
0	81	78
1	252	-256
2	37	21
3	144	132
4	51	-33
5	50	43
6	74	-76
H	4	3
-5	81	82
-4	241	-243
-3	144	152
-2	179	177
-1	340	-343
0	180	181
1	15	-6
2	100	-111
3	200	198
4	17	23
5	253	-257
H	5	3
-4	10	-1
-3	12	7
-2	141	139
-1	16	-26
0	311	-309
1	83	60
2	159	164
3	57	-45
4	15	-8
5	140	135
H	6	3
-2	192	-190
-1	34	-32
0	213	211
1	1	-2
2	35	-32
3	28	-18
4	85	-90
H	-7	4
0	222	-228
H	-6	4
0	69	-62
1	3	0
2	125	120
H	-5	4
0	206	198
1	254	262
2	204	-268
3	138	-145
H	-4	4
0	16	-12
1	113	-121
2	101	105
3	41	-40
H	-3	4
0	143	139
1	269	-198
2	27	21
3	232	240
4	153	-156
H	-2	4
0	526	-537
1	213	214
2	64	72
3	235	-245
4	102	104
H	-1	4
0	72	64
1	36	30
2	37	34
3	114	-109
4	25	-24
5	153	155
H	0	4
0	240	237
1	71	-65
2	248	-252
3	242	234
4	127	133
5	263	-273
H	1	4
-7	18	16
-6	94	-98
-5	169	178
-4	64	68
-3	162	-196
-2	38	39
-1	164	162
0	294	-262
1	131	-129
2	369	370
3	12	2
4	165	-160
5	43	41
H	2	4
-7	158	158
-6	164	182
-5	259	-268
-4	100	-94
-3	162	161
-2	168	-171
-1	56	57
0	226	223
1	150	-181
2	91	92
3	61	55
4	253	-250
5	75	75
H	3	4
-6	105	-106
-5	47	41
-4	46	43
-3	16	9
-2	69	67
-1	258	-257
0	24	22
1	351	349
2	234	-231
3	153	-153
4	174	169
H	4	4
-5	30	31
-4	155	156
-3	196	-201
-2	111	-111
-1	260	259
0	25	20
1	125	-120
2	8	-4
3	38	34
4	4	13
H	5	4
-3	163	171
-2	93	90
-1	55	-54
0	40	34
1	123	-120
2	89	-91
3	197	203
H	-6	5
0	146	-151
H	-5	5
0	48	-41
1	34	-34
H	-4	5
0	158	141
1	143	148
2	286	-297
H	-3	5
0	134	-133
1	17	11
2	119	120
3	96	-103
H	-2	5
0	46	42
1	114	-102
2	168	163
3	100	95
H	-1	5
0	162	-164
1	153	144
2	11	14
3	116	-117
H	0	5
0	100	92
1	57	-61
2	16	-9
3	117	-111
H	1	5
-7	185	-189
-6	64	89
-5	72	73
-4	55	63
-3	30	-28
-2	93	-92
-1	26	-16
0	249	224
1	148	-148
2	196	-195
3	229	225
H	2	5
-6	64	-66
-5	137	140
-4	20	-26
-3	122	-121
-2	187	180
-1	39	33
0	300	-302
1	105	139
2	206	210
3	19	-20
H	3	5
-5	224	-232
-4	44	47
-3	161	157
-2	90	-89
-1	36	38
0	33	32
1	141	-133
2	67	85
H	4	5
-3	68	70
-2	56	-58
-1	156	-156
0	143	140
1	159	154
H	-5	6
0	105	-107
H	-4	6
0	28	-22
H	-3	6
0	155	148
1	55	53
H	-2	6
0	132	-133
1	50	54
H	-1	6
0	75	-72
1	103	-90
2	59	96
H	0	6
0	53	48
1	187	182
H	1	6
-5	60	-62
-4	184	181
-3	60	-58
-2	129	-130
-1	194	196
0	38	-39
1	39	-45
H	2	6
-4	29	36
-3	15	-14
-2	108	-106
-1	57	57
0	150	146

Table 7. *The hydrogen bonding system ('pure' compound)*

From atom A	to atom B	at	Through hydrogen H	A–B	H···B	A–H···B
N(1)	O(2)	$x, y, z-1$	H(1)	3·04 Å	2·11 Å	166·7°
N(1)	O(5)	x, y, z	H(2)	3·03	2·26	157·2
N(1)	O(4)	$-x+1, -y, -z+1$	H(3)	3·02	2·17	160·8
N(2)	O(2)	$-x+1, -y+1, -z+2$	H(4)	2·85	2·06	172·0
N(2)	O(3)	$x+1, y, z$	H(5)	2·98	2·12	172·7
N(2)	O(5)	$-x+1, -y+1, -z+1$	H(6)	2·99	2·21	165·2
N(3)	—	—	H(7)	—	—	—
N(3)	O(6)	x, y, z	H(8)	2·97	2·15	165·3
N(3)	O(4)	$x+1, y, z$	H(9)	3·02	2·11	162·7
N(4)	O(4)	$x+1, y, z$	H(10)	2·95	2·07	165·2
N(4)	O(3)	$-x+1, -y+1, -z+1$	H(11)	3·13	2·26	174·4
N(4)	O(6)	$x, y, z-1$	H(12)	3·01	2·25	163·4
N(5)	O(5)	x, y, z	H(13)	2·91	2·13	161·0
		—	H(14)	—	—	—
O(6)	O(2)	$-x+1, -y, -z+2$	H(15)	2·79	2·03	169·1
O(6)	O(5)	x, y, z	H(16)	2·81	2·13	165·9

measured counts as described above. At the end of the data collection, all reflections which had given negative values for the intensity were remeasured, along with a number for which there were obvious errors in the data. In addition, all extremely strong reflections were remeasured with the tube current reduced sufficiently to ensure that the counting rate would never exceed the capacity of the system. All the reflections were put on a common scale by means of the check reflections and merged to give a data set of 1229 observed reflections (out of 1235 measured) which were used in the solution and refinement of the structure. Lorentz and polarization corrections were made, but no absorption corrections were considered necessary, as μ for this compound is $39 \cdot 84$ cm^{-1} and thus $\mu R_{avg} = 0 \cdot 52$. This neglect could have led to maximum errors of about 4% in the structure factors. The structure was solved independently of the first one; solution and refinement followed essentially the same course. After all heavy atoms had been located, their positional and anisotropic thermal parameters were refined by full-matrix least-squares methods to an R index of $0 \cdot 036$. Difference maps were calculated in the planes where the ammine hydrogen atoms were expected, and these were located; their positions and isotropic temperature factors were then refined. Several cycles of refinement, including a single scale factor, positional parameters for all atoms, isotropic thermal parameters for the disordered bridging nitrogen and oxygen atoms, and anisotropic thermal parameters for the rest of the heavy atoms (all arranged in several matrices) converged with an R index of $0 \cdot 029$; the goodness-of-fit was $2 \cdot 59$. The addition of a secondary extinction factor reduced R to $0 \cdot 027$ and lowered the goodness-of-fit to $2 \cdot 52$. In the final three cycles of refinement, 136 parameters were varied in a single matrix: positional and anisotropic thermal parameters for the cobalt and nonbridging ligand atoms, positional and isotropic thermal parameters for the bridging oxygen and nitrogen atoms and the hydrogen atoms, a single scale factor, and a secondary extinction factor (Larson, 1967). The final parameters are listed in Tables 2 and 3; the cation is depicted in Fig. 1(b), and supplementary bond distances are given in Table 4.

We represented the disorder in the cation by giving the bridging atoms population factors of $0 \cdot 5$. A difference map in the plane where the hydrogen atoms of the bridging N and O atoms were expected clearly showed two areas of significant electron density ($\sim 0 \cdot 5 - 0 \cdot 6$ e.Å^{-3}). We assumed that the hydroxyl hydrogen atom was equally distributed between these two positions and that it coincided with the ammine hydrogen atoms. Therefore, each of these two positions was assigned a total H-atom population of $0 \cdot 75$.

The observed and calculated structure factors for both structure determinations are given in Tables 5 and 6. All calculations were done on an IBM 360/75 computer, using the programs of the CRYM X-ray computing system; form factors for hydrogen atoms were taken from Stewart, Davidson & Simpson (1965) and those for the heavy atoms from International Tables for X-ray Crystallography (1962). Anomalous dispersion corrections were made by subtracting $2 \cdot 19$ e, from the curve for cobalt and adding $0 \cdot 34$ e to the curve for sulfur (Cromer, 1965); $\Delta f''$ was ignored.

Description of the structure

The cation

Fig. 1(b) and (c) shows the cations of these compounds. The bond distances and angles are normal and are quite comparable to those found in the μ-Cl, NH$_2$-dicobalt cation (Barro et al., 1970), shown in Fig. 1(a). All three of these compounds have been refined to low values of the R index; the e.s.d.'s in the individual bond lengths are also all quite small. The out-of-plane cobalt–nitrogen distances average $1 \cdot 957$ Å, with an r.m.s. deviation from the mean of $0 \cdot 005$ Å. This agreement is as good as one could expect, and probably indicates that all six measurements are of chemically identical bonds. The in-plane cobalt–nitrogen bonds may, however, show the influence of the differing ligands (Cl, O, or N) trans to them. They average $1 \cdot 964$ Å, insignificantly different from the out-of-plane average, but the r.m.s. deviation from the mean is $0 \cdot 011$ Å, rather larger than the individual e.s.d.'s would predict. The two in-plane distances in the 'pure' μ-OH, μ-NH$_2$ compound differ by so much, however ($0 \cdot 010$ Å), that we are unable to offer any consistent explanation of these variations.

The situation with respect to the bridging groups is a bit less satisfactory. In all three compounds the cation crystallizes at a center of symmetry, requiring the bridging ligands to be disordered.* In the compounds with a chloro-bridge, the heavy chlorine atom obscures to some extent the lighter bridging atom; even for the μ-OH, μ-NH$_2$ compound, the data are not sufficiently precise to permit us to distinguish a half-nitrogen atom from a half-oxygen atom. In all cases, the chemical species were assigned so as to give chemically reasonable bond lengths. Thus, the region of electron density $1 \cdot 893$ and $1 \cdot 911$ Å from the cobalt atoms in the μ-OH, μ-NH$_2$ compound was called an oxygen atom; our identification of it as such is based on chemical reasoning and not on the X-ray evidence. Note that the

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* Even if the bridging groups are ordered, leading to the space group $P1$, the departures from a centric structure must be extremely small. The data, although of high quality, almost certainly cannot distinguish between the two cases. Structure factors calculated for an ordered structure would show phase angles slightly different from 0 or π, but their magnitudes would differ only trivially from those calculated for our disordered model. Least-squares refinement of the ordered structure would surely be catastrophic, because of near-singularities in many parameter matrices. Finally, there is no hint in the temperature factors of the nonbridging atoms of any molecular distortion that might suggest significant departure from the centric structure. All of these considerations lead us to conclude that the structure as determined here is appropriately described as disordered.

disordered half-atoms in the bridge of the μ-OH, μ-NH$_2$ compound are only 0·11 Å apart. During the early part of our work, we tried to include both of these atoms (positional parameters and isotropic temperature factors) in the refinement as part of a large matrix, but the refinement diverged. At the end of the refinement, when all other shifts were small ($R=0\cdot027$), we tried this again and found that the refinement converged. The same technique may work in other refinements with nearly singular matrices.

The sulfate groups

Each structure contains one independent sulfate group, and in each case the geometry is thoroughly satisfactory. The hydrogen-bonding to the sulfate groups does not distort either of the groups significantly, but both are held in the structure firmly enough so that their thermal motions are not extreme. The eight separate measurements of the S–O bond distance give 1·468 Å (standard deviation from the mean 0·004 Å). In a study of five different sulfates, Baur (1964) found 1·473 (1) Å for the S–O distance; thus, our results agree very well with those he considered. The average deviation of all the O–S–O angles from 109·5 is 0·8°, indicating the sulfate ions are almost regular tetrahedra.

The hydrogen bonding

The hydrogen-bonding scheme we propose for this compound is outlined in Table 7. All but one hydrogen atom of the coordinated ammine groups and both hydrogen atoms of the water molecule are involved in hydrogen bonds. Each oxygen atom of the sulfate group accepts at least one hydrogen bond and the water molecule accepts two, although none of these hydrogen bonds is very strong. Thus the entire crystal is held together by this extensive network of hydrogen bonds. Some of the N–H$\cdots$O distances are as long as 3·13 Å, indicating fairly weak interactions. Perhaps because of the disorder in the cation, or perhaps because of crowding, we are able to identify only one H-bonding contact involving the bridging atoms: this is a 2·91 Å distance between O(1) of the sulfate group and either the –OH or the –NH$_2$ bridging group.

The thermal motion

Overall, the thermal motion in this compound appears to be relatively small. Anisotropic motions are present but they correspond in general to physically reasonable models, with major axes of vibration gen-

erally perpendicular to chemical bonds. Table 8 lists the r.m.s. displacements along the three principal axes of the derived thermal ellipsoids for the heavy atoms. The bridging atoms show rather small temperature factors [1·78 and 1·38 Å^2 for N(5) and O(1)], and the isotropic temperature factors of the hydrogen atoms are not much larger (2·14 to 4·46 Å^2). The oxygen atom of the water molecule exhibits the largest motion of any in the structure, which is not surprising since it is the least strongly bonded atom.

Table 8. *R.m.s. displacements of atoms along the principal axes of their thermal ellipsoids ('pure' compound)*

Co	0·017, 0·020, 0·023 Å
N(1)	0·020, 0·024, 0·034
N(2)	0·021, 0·022, 0·025
N(3)	0·022, 0·026, 0·038
N(4)	0·021, 0·025, 0·035
S	0·020, 0·024, 0·027
O(2)	0·025, 0·039, 0·058
O(3)	0·020, 0·043, 0·059
O(4)	0·023, 0·031, 0·066
O(5)	0·021, 0·040, 0·071
O(6)	0·029, 0·033, 0·073

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