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trans-Dichlorotetraamminecobalt(III) Bisulfate*

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Abstract. *trans*-[$CoCl_2(NH_3)_4$]HSO_4, F.W. 295·03, $P2_12_12_1$, $a=8{\cdot}815$ (1), $b=18{\cdot}639$ (1), $c=5{\cdot}934$ (1) Å, $D_m=2{\cdot}01$, $D_x=2{\cdot}009$ g cm^{-3}; $\mu=25{\cdot}6$ cm^{-1}, λ(Mo $K\alpha$) = 0·70926 Å. Final $R=0{\cdot}039$ for 779 reflections. The coordination about the cobalt atom is closely octahedral with average Co–Cl and Co–N distances of 2·255 (2) and 1·987 (3) Å respectively.

Introduction. In the course of preparing the family of compounds known as 'melanochlorides' (Werner, 1910), several different crystalline materials are formed. The aqueous filtrate from the synthesis was left to evaporate, and the resulting crystals were dissolved in dilute sulfuric acid and recrystallized by solvent evaporation. Mainly red-colored crystals formed first, and were periodically removed; these crystals are thought to be the *cis* isomer of the title compound. When only 2–3 mls of solution were left, bright-green crystals began to appear from the red solution. These crystals dissolved in water to give a pink solution, probably due to hydrolysis replacement of one Cl atom, and this behavior led us to investigate their structure. They have been identified as *trans*-dichlorotetraamminecobalt(III) bisulfate, [$CoCl_2(NH_3)_4$]HSO_4.

A truncated pyramid with rectangular base 0·4 × 0·2 mm and a height of 0·25 mm was used for both preliminary photographic studies and diffractometer data collection. Systematic absences coupled with orthorhombic diffraction symmetry uniquely determined the space group as $P2_12_12_1$; The density was measured by flotation in a bromoform/carbon tetrachloride solution. The lattice constants and diffractometer orientation matrix were obtained from a least-squares refinement based on the diffractometer angles for 15 reflections with 2θ values greater than 25°, measured on a General Electric Datex-automated quarter-circle diffractometer using graphite-monochromatized Mo $K\alpha$ radiation at room temperature. Data were collected to a maximum $2\theta=40°$, with a scan speed of 2° min^{-1}, 20 s background counts collected on both sides of the scan, and a scan range varying linearly from 2·5° at $2\theta=5°$ to 3·5° at $2\theta=40°$. Three check reflections collected at 30 reflection intervals showed a 15% total drop in intensity. The intensities and their variances were corrected for the decay as well as for Lorentz and polarization effects. Observational variances, $\sigma^2(I)$, included counting statistics plus an additional empirical term ($0{\cdot}02S^2$), where S is the scan count. Of the 779 total reflections, eleven were given zero weight owing to presumed counting errors, and 26 had negative net intensities.†

The structure was solved by the heavy-atom technique with preliminary coordinates for the Co and one Cl atom obtained from a three-dimensional, origin-removed, sharpened Patterson map. Electron density maps yielded coordinates for all remaining non-hydrogen atoms in the structure. Several cycles of isotropic full-matrix refinement followed. Coordinates for the 12 ammine H atoms were then generated by fitting tetrahedral $-NH_3$ groups to difference maps calculated in planes perpendicular to the Co–N bonds at positions corresponding to N–H bond lengths of 0·95 Å. For N(1), N(2), and N(3) the most probable orientation indicated by the difference maps agreed with the expected hydrogen-bonding scheme, while the difference map about N(4) suggested disorder that was represented by six half-hydrogen atoms. The bisulfate H atom was clearly indicated in a three-dimensional difference map. The H coordinates were not adjusted further (Table 1). Additional full-matrix least-squares calculations varying a scale factor and the positional and anisotropic temperature parameters for the 12 non-hydrogen atoms led to a final R of 0·039, and a goodness-of-fit $(=[\sum_w(|F_o|^2-|F_c|^2)^2/(m-s)]^{1/2}$ for $m=742$ observations and $s=109$ parameters) of 2·49. Scattering factors were those in *International Tables for X-ray Crystallography* (1962), except for H (Stewart, Davidson & Simpson, 1965) and Co (Cromer & Waber 1965). Anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$ were applied to the Co, Cl, and S scattering-factor tables using the values of Cromer & Waber (1965). The chirality of the crystal was checked and the enantiomorph we report here showed an R index and a goodness-of-fit about 11% smaller than the other enantiomorph. Final positional and thermal parameters for the heavy atoms are given in Table 2.

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† The structure factor table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31104 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Hydrogen atom positions* ($\times 10^3$)

For structure factor calculations an isotropic temperature factor of 3·0 Å^2 was assumed, and the six H atoms attached to N(4) were assigned population factors of $\frac{1}{2}$.

	x	y	z
H(1)N(1)	460	398	123
H(2)	361	437	−59
H(3)	421	360	−105
H(1)N(2)	140	454	−94
H(2)	8	441	67
H(3)	24	392	−145
H(1)N(3)	38	261	315
H(2)	−62	314	179
H(3)	−4	336	412
H(1)N(4)	403	268	232
H(2)	261	247	371
H(3)	362	310	448
H(4)	427	302	318
H(5)	290	288	473
H(6)	312	239	264
H(1)O(4)	250	35	700

Discussion. Bond distances and angles are given in Table 3. Bonding about the Co atom is closely octahedral. The Co–N distances vary from 1·946 Å to 1·973 Å. The average Co–N distance, 1·958 (3) Å, is slightly below the average values of 1·973, 1·968, and 1·978 Å found in the pentaammines [CoCl$(NH_3)_5$]Cl_2 (Messmer & Amma, 1968), [Co$(NH_3)_5N_3$] $(N_3)_2$ (Palenik, 1964), [$(NH_3)_5CoNO_2$]Br_2 (Cotton & Edwards, 1968), and 1·972 and 1·968 Å in the hexaammines [Co$(NH_3)_6$]-[Co$(CN)_6$] (Iwata & Saito, 1973) and [Co$(NH_3)_6$]-[$ZnCl_4$]Cl (Meek & Ibers, 1970). In a recent survey of 11 pentaammine cobalt(III) structures, the weighted mean value for the Co–N distance was 1·969 Å (Fronczek, 1975). The two Co–Cl distances are effectively equal with an average value, 2·255 (2) Å, slightly shorter than 2·286 Å reported in [Co$(NH_3)_5$Cl]Cl_2 (Messmer & Amma, 1968). The S–O distances in the bisulfate ion are in good agreement with those reported in $K_{0.55}Rb_{0.45}HSO_4$ and $RbHSO_4$ (Mumme, 1973), and in $(NH_3)_5CoO_2Co(NH_3)_5(SO_4)(HSO_4)_3$ (Schaefer & Marsh, 1966). The S–O(4) distance is significantly longer than the other S–O distances owing to the presence of the proton on O(4). Within the bisulfate group the O–S–O angles involving the long S–O(4) bond are systematically smaller than tetrahedral, while the remaining angles are larger; the effect of this distortion is to equalize the non-bonded O···O distances (Donohue, 1965). The average of these O···O distances is 2·40 Å, with an average deviation of only 0·02 Å. The bisulfate ions form hydrogen bonds along the screw axes (Fig. 1) with an O(1)···O(4) distance of 2·617 Å. The cations form eight hydrogen bonds shor-

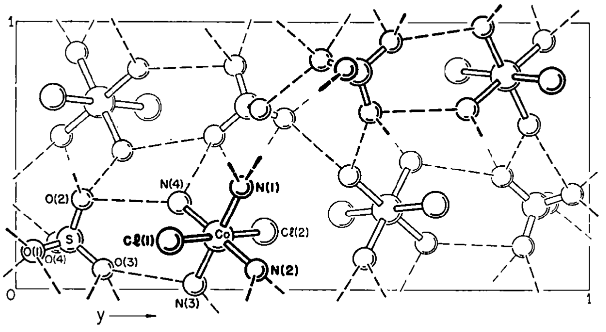

Fig. 1. View along [001] indicating proposed anion–anion and anion–cation hydrogen bonds. H-bonds between cations are excluded.

Table 3. *Interatomic distances and angles*

(The e.s.d.'s are 0·003 Å for Co–Cl and 0·006 Å for all other distances. For the angles the e.s.d.'s are approximately 0·2°.)

Co–Cl(1)	2·258 Å	Cl(1)–Co–Cl(2)	178·3°
Co–Cl(2)	2·251	Cl(1)–Co–N(1)	91·4
Co–N(1)	1·957	Cl(1)–Co–N(2)	90·8
Co–N(2)	1·955	Cl(1)–Co–N(3)	89·0
Co–N(3)	1·946	Cl(1)–Co–N(4)	89·8
Co–N(4)	1·973	Cl(2)–Co–N(1)	89·6
S—O(1)	1·443	Cl(2)–Co–N(2)	90·5
S—O(2)	1·438	Cl(2)–Co–N(3)	89·9
S—O(3)	1·438	Cl(2)–Co–N(4)	88·7
S—O(4)	1·569	N(1)–Co–N(2)	90·6
O(1)–S–O(2)	111·9°	N(1)–Co–N(3)	179·0
O(1)–S–O(3)	113·7	N(1)–Co–N(4)	90·3
O(1)–S–O(4)	106·4	N(2)–Co–N(3)	90·3
O(2)–S–O(3)	113·1	N(2)–Co–N(4)	178·8
O(2)–S–O(4)	107·3	N(3)–Co–N(4)	88·8
O(3)–S–O(4)	103·7		

Table 2. *Final positional and thermal parameters with e.s.d.'s in parentheses*

Positional parameters and U_{ij}'s have been multiplied by 10^4. The anisotropic temperature factor has the form

$$\exp\left[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)\right].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	2000 (1)	3523 (1)	1440 (2)	190 (4)	196 (5)	112 (7)	−8 (4)	9 (6)	−14 (5)
Cl(1)	1824 (2)	2689 (3)	−1308 (4)	330 (10)	299 (11)	164 (13)	−14 (8)	−1 (15)	−92 (11)
Cl(2)	2171 (2)	4329 (1)	4255 (4)	345 (10)	231 (10)	133 (12)	−21 (8)	13 (13)	−64 (10)
S	1840 (2)	944 (1)	4145 (4)	194 (9)	209 (10)	164 (15)	25 (8)	2 (13)	−20 (11)
N(1)	3837 (7)	3926 (3)	88 (11)	280 (31)	269 (36)	61 (44)	−26 (27)	69 (36)	−8 (34)
N(2)	741 (7)	4186 (3)	−300 (13)	275 (32)	260 (37)	212 (47)	13 (27)	−12 (39)	10 (38)
N(3)	194 (7)	3118 (3)	2833 (13)	261 (32)	285 (34)	118 (44)	−71 (27)	69 (38)	−44 (38)
N(4)	3243 (7)	2857 (3)	3248 (12)	337 (36)	243 (34)	194 (44)	74 (27)	−95 (47)	32 (37)
O(1)	1416 (6)	308 (3)	2905 (11)	370 (31)	265 (29)	461 (44)	−2 (25)	13 (36)	−140 (34)
O(2)	3371 (5)	1161 (3)	3661 (12)	241 (27)	543 (38)	443 (43)	−111 (25)	54 (41)	−119 (40)
O(3)	763 (5)	1520 (3)	3951 (10)	343 (10)	232 (28)	292 (41)	85 (23)	−14 (37)	26 (36)
O(4)	1773 (8)	737 (3)	6706 (10)	680 (44)	538 (42)	123 (38)	251 (37)	34 (44)	53 (32)

ter than 3·25 Å to the anions; these are indicated in Fig. 1. There are six N–H···Cl hydrogen bonds shorter than 3·52 Å formed between the cations.

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2-Methoxyphenothiazine

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Abstract. $C_{13}H_{11}ONS$, orthorhombic, $P2_12_12_1$, $a=11·585$ (7), $b=5·720$ (2), $c=16·459$ (8) Å, $Z=4$, $D_c=1·40$, $D_m=1·40$ (2) g cm^{-3} (by suspension). The C–S and C–N bond distances average 1·779 (5) and 1·39 (1) Å, the CSC angle is 99·4 (4)°, the CNC angle is 121·0 (8)°, and the dihedral angle of the heterocyclic system is 146·4 (2)°.

Introduction. Crystals of the title compound were obtained by slow evaporation of a mixed solvent of methylene chloride, hexane, and 2-propanol in approximate ratios of 5:2:1. Data were collected with a parallelepiped crystal of dimensions 0·81 × 0·31 × 0·43 mm (all ±0·01 mm) in the [010], [001], and [101] directions, mounted with **b** approximately parallel to the φ axis of the G.E. XRD-5 manually operated quarter-circle diffractometer. Zr-filtered Mo $K\alpha$ ($\lambda=0·71069$ Å) radiation was used for unit-cell parameter measurements and intensity-data collection. Systematic absences of $h00$ with h odd, $0k0$ with k odd, and $00l$ with l odd indicated space group $P2_12_12_1$. The linear absorption coefficient is 2·70 cm^{-1}; no absorption corrections were made. All 1166 reflections with $0° < 2\theta < 50°$ were scanned (θ–2θ scans) 2° in 2θ at 2° min^{-1}, with 20s stationary backgrounds at each end of the scan. Only the 430 reflections with $I > 2\sigma(I)$ were used for the structure determination; seven of the most intense low-angle reflections were omitted from the refinement because of extinction. The intensities of four reflections measured periodically during the five-day data collection varied less than 1σ and thereby indicated crystal and electronic stability.

The standard deviations for I were calculated by $\sigma(I)=(S+2·25B+0·0016I^2)^{1/2}$ (where S = scan count, B = sum of the background counts, and $I=S-1·5\,B$), except for a number of reflections for which the two background readings differed by more than twice the calculated σ owing to the tailing of the reflection peak. For the latter reflections the standard deviations were set equal to the deviation of the background readings from the mean background value. Neutral atom scattering factors were used (*International Tables for X-ray Crystallography*, 1975) for all atoms.

The trial structure was initiated by analysis of a Patterson map, which revealed the location of the sulfur atom. Hydrogen atoms bonded to the N and methyl C atoms were located on a difference map; phenyl hydrogen atoms were placed at calculated positions (C–H = 0·95 Å). Neither the positional nor the assigned thermal factors of the hydrogen atoms were refined. Successive full-matrix least-squares refinements allowing first the S, then the O and C of the methoxy group, and finally the N, anisotropic thermal motion gave significant changes in R values (Hamilton, 1965). The final refinement consisted of 85 parameters and 423 reflections, and gave an R of 0·048 and R_w of