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A Tetranuclear Cobalt Complex*

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$[Co_4(OH)_6(C_2N_2H_8)_6]^{6+} \cdot 4SCN^- \cdot 2NO_3^- \cdot 2H_2O$; monoclinic, space group $P2_1/n$, $a = 13.489$ (6), $b = 11.713$ (2), $c = 27.102$ (5) Å, $\beta = 100.02$ (8)°, $Z = 4$. The cation comprises a central Co atom, bridged through pairs of OH groups to three peripheral Co atoms. The configurations of the Co atoms in the two enantiomeric forms of the cation are $\Lambda(\Delta\Delta\Delta)$ and $\Delta(\Lambda\Lambda\Lambda)$.

Introduction

The tetranuclear cobalt cations (I) and (II) were first prepared by Jörgensen (1898) and Werner (1907), and were used by Werner to prove his theories of optical activity. Cation (I) was the first completely inorganic complex to be resolved into its optical isomers (Werner, 1914).

(I)   (II)
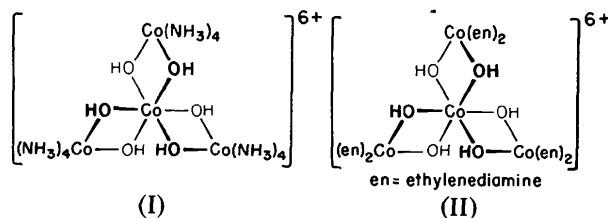
Thewalt (1971) has reported on the structure of the trisdithionate octahydrate salt of (II), which confirmed Werner's description of the cation as a tetranuclear species with six bridging OH groups; later, Thewalt &

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Ernst (1975) also reported on the structure of the monobromide pentathiocyanate trihydrate salt of the same cation. We report here the structure of another mixed salt of cation (II), containing two nitrate groups, four thiocyanate groups, and two water molecules per cation.

The compound was prepared by U. Thewalt in these laboratories as follows: 150 g of cobaltous nitrate were added to 150 g of water, and 300 ml of ethylenediamine were added to the solution. Soft, brown, powderish crystals were filtered out and were recrystallized from KSCN solution and further recrystallized from water; well-formed black crystals resulted. Subsequent attempts to repeat the preparation have resulted, instead, in small, grayish crystals of irregular habit, which we have not characterized.

Preliminary crystal data (Table 1) were obtained from Straumanis-type Weissenberg photographs. Intensities were collected from a cube-shaped crystal approximately 0.15 mm on an edge, with a Datex-automated General Electric diffractometer, Co $K\alpha$ radiation ($\lambda = 1.7902$ Å), a θ–2θ scan mode at a scanning rate of 4° min^{-1}, and 15 s background counts at each end of the scans. Observational variances $\sigma^2(I)$ were calculated on the basis of normal counting

statistics plus an additional term $(0.02S)^2$, where S is the scan count. Intensities and their standard deviations were corrected for Lorentz and polarization effects but not for absorption. Of the 2682 independent reflections with 2θ less than $100°$, 111 had negative net intensities and were assigned weights of zero; all others were retained.

Positions of the Co atoms were obtained from a three-dimensional Patterson map, and electron density maps then yielded the positions of the N, C and O atoms of the cation. The nature of the anions was determined by the crystallographic analysis and was later confirmed by elemental analysis. [Measured: C 17·65, H 5·21, N 22·53, S 10·90, Co 23·81%. Calculated for $Co_4(OH)_6(C_2N_2H_8)_6(SCN)_4(NO_3)_2(H_2O)_2$: C 17·62, H 5·36, N 23·11, S 11·76, Co 21·61%. The analysis for cobalt was undeniably high, for which we can offer no

explanation. The ratios of C:H:N:S, however, agree well with our formulation and rule out formulas containing $(SCN)_3(NO_3)_3$ or $(SCN)_5(NO_3)$. The ultimate confirmation of our formulation lies in the successful refinement of the structure and in the chemically reasonable anions which were found]. Three thiocyanate and two nitrate anions were seen on early difference maps, and a later map suggested the presence of a fourth, disordered thiocyanate group and two water molecules of crystallization. The disordered thiocyanate group was represented as a C atom approximately centered between two composite atoms; eventually, difference maps led to the assignment of one of these composite atoms as $\frac{3}{4}S$ and $\frac{1}{4}N$ and the other as $\frac{1}{4}S$ and $\frac{3}{4}N$.

Final refinement was by least-squares minimization of the quantity $\sum w(F_o^2 - F_c^2)^2$, with weights w equal to $1/\sigma^2(F_o^2)$. Coordinates were assigned to the H atoms of the ethylenediamine groups, based on C–H distances of 1·0 Å and N–H of 0·9 Å; for the H atoms of the bridging hydroxyl groups, the two allowed (tetrahedral) positions were calculated and the correct choice was made on the basis of difference maps. The H atoms of the water molecules were ignored. None of the H atoms was further adjusted. In the final two least-squares cycles, the coordinates of the Co, O, N, S and C atoms were included in one matrix and their

Table 1. *Crystal data*

$Co_4C_{12}H_{54}N_{12}O_6.2NO_3.4SCN.2H_2O$	FW 1090·74
Monoclinic	$P2_1/n$
$a = 13.489\ (6)$ Å	$Z = 4$
$b = 11.713\ (2)$	$F(000) = 2256$
$c = 27.102\ (5)$	$D_m = 1.721\ \text{g cm}^{-3}$
$\beta = 100.02\ (8)°$	$D_x = 1.718$
$\lambda(\text{Cu } K\alpha) = 1.5418$ Å	$\mu r\ (\text{mean}) = 0.47$

Table 2. *Final least-squares parameters, with their e.s.d.'s in parentheses*

Coordinates have been multiplied by 10^5 for Co(1)–Co(4) and S(1)–S(3), by 10^4 for the other atoms. Thermal parameters for Co(1) to W(2) are anisotropic, see text.

	x	y	z	B (Å²)		x	y	z	B (Å²)
Co(1)	54898 (16)	24369 (21)	64511 (8)		N(5)	4204 (9)	5618 (10)	7169 (4)	2·57 (0·29)
Co(2)	18317 (16)	23562 (20)	56804 (8)		N(6)	4003 (8)	7284 (10)	6485 (4)	2·53 (0·28)
Co(3)	32751 (16)	58646 (19)	65491 (8)		N(7)	2280 (8)	6642 (10)	6871 (4)	2·43 (0·28)
Co(4)	35503 (16)	35375 (19)	62467 (8)		N(8)	2319 (7)	6107 (9)	5920 (4)	1·84 (0·24)
S(1)	20037 (34)	36559 (40)	96816 (17)		N(9)	943 (8)	2654 (10)	5053 (4)	2·40 (0·28)
S(2)	90987 (32)	44930 (41)	52940 (16)		N(10)	2701 (8)	1565 (9)	5278 (4)	2·16 (0·25)
S(3)	56486 (37)	37536 (48)	81718 (17)		N(11)	972 (8)	3133 (9)	6070 (4)	2·18 (0·28)
SN(1)	5466 (6)	−272 (7)	8035 (4)		N(12)	1088 (8)	982 (10)	5815 (4)	2·75 (0·29)
C(16)	4893 (16)	354 (21)	7713 (8)		N(13)	4093 (11)	3831 (13)	9824 (5)	5·69 (0·38)
NS(1)	4411 (10)	1211 (12)	7497 (5)		N(14)	7922 (13)	3576 (16)	5938 (7)	8·64 (0·50)
W(1)	2330 (17)	3324 (15)	3513 (8)		N(15)	7124 (12)	5360 (14)	8272 (6)	7·16 (0·42)
W(2)	4274 (15)	2810 (16)	4103 (9)		N(16)	7550 (10)	273 (13)	2991 (5)	3·97 (0·33)
O(1)	4473 (6)	2825 (7)	5889 (3)	1·92 (0·21)	N(17)	6127 (15)	4688 (9)	5091 (8)	9·86 (0·54)
O(2)	4552 (6)	3150 (7)	6817 (3)	1·82 (0·20)	C(1)	5343 (12)	100 (14)	6165 (6)	4·31 (0·42)
O(3)	2867 (6)	2115 (7)	6257 (3)	1·25 (0·19)	C(2)	5783 (12)	721 (15)	5775 (6)	3·62 (0·43)
O(4)	2549 (6)	3771 (7)	5654 (3)	1·58 (0·20)	C(3)	7256 (12)	2957 (14)	7152 (6)	3·96 (0·41)
O(5)	2684 (6)	4377 (7)	6611 (3)	1·62 (0·20)	C(4)	6778 (11)	4111 (13)	6988 (5)	3·37 (0·35)
O(6)	4171 (6)	5003 (7)	6216 (3)	1·51 (0·20)	C(5)	5035 (12)	6477 (15)	7213 (6)	4·53 (0·41)
O(7)	7917 (7)	−670 (10)	2956 (4)	3·79 (0·26)	C(6)	4663 (13)	7526 (16)	6957 (7)	5·33 (0·44)
O(8)	7200 (8)	515 (9)	3375 (4)	4·62 (0·29)	C(7)	1456 (12)	7069 (14)	6501 (6)	5·05 (0·44)
O(9)	7520 (7)	991 (9)	2649 (4)	3·96 (0·25)	C(8)	1340 (12)	6451 (15)	6042 (6)	4·24 (0·43)
O(10)	6034 (11)	4057 (13)	4724 (6)	9·71 (0·42)	C(9)	1363 (18)	2226 (21)	4644 (9)	9·45 (0·71)
O(11)	5697 (11)	4284 (13)	5435 (6)	9·94 (0·44)	C(10)	2261 (13)	1614 (15)	4749 (6)	5·25 (0·44)
O(12)	6443 (10)	5723 (13)	5123 (5)	8·13 (0·38)	C(11)	459 (10)	2351 (13)	6359 (5)	2·78 (0·35)
N(1)	4821 (8)	982 (10)	6442 (4)	2·56 (0·27)	C(12)	222 (12)	1301 (14)	6047 (6)	3·66 (0·39)
N(2)	6322 (8)	1720 (10)	6023 (4)	2·80 (0·29)	C(13)	3219 (13)	3733 (15)	9785 (6)	4·19 (0·42)
N(3)	6437 (8)	2083 (10)	7066 (4)	2·68 (0·29)	C(14)	8378 (14)	4011 (17)	5639 (7)	5·64 (0·52)
N(4)	6199 (8)	3911 (10)	6471 (4)	2·77 (0·29)	C(15)	6505 (13)	4699 (15)	8254 (6)	4·79 (0·43)

temperature parameters, plus a scale factor, in a second. Anisotropic temperature parameters were assigned to the Co atoms, the S atoms of the ordered thiocyanate groups, all three atoms of the disordered thiocyanate group and the two O atoms of the waters

Table 3. Coordinates assigned to the hydrogen atoms $(\times 10^4)$

The isotropic temperature factor was set at $B = 5 \cdot 0$ Å^2. The H atoms of the water molecules [$W(1)$ and $W(2)$, Table 2] were not included.

Parent atom	x	y	z	Parent atom	x	y	z
O(1)	4714	3325	5672	O(4)	2831	3822	5368
O(2)	4816	3784	6990	O(5)	2720	4123	6931
O(3)	2597	2036	6545	O(6)	4159	5228	5884
N(1) {	4164	1058	6298	C(1) {	4834	−505	6027
	4882	752	6769		5887	−280	6411
N(2) {	6910	1474	6197	C(2) {	5186	967	5495
	6455	2211	5782		6200	188	5611
N(3) {	6700	1386	7057	C(3) {	7780	2774	6944
	6103	2098	7340		7585	3004	7512
N(4) {	5754	4497	6392	C(4) {	6338	4379	7222
	6627	3924	6248		7327	4712	6983
N(5) {	4476	4947	7196	C(5) {	5613	6157	7043
	3910	5777	7442		5354	6659	7566
N(6) {	3568	7883	6425	C(6) {	5265	7993	6876
	4363	7245	6240		4321	7984	7177
N(7) {	2565	7268	7044	C(7) {	1553	7905	6429
	2032	6188	7078		801	7022	6646
N(8) {	2543	6665	5737	C(8) {	953	6905	5776
	2250	5460	5737		946	5731	6097
N(9) {	842	3427	5021	C(9) {	1486	2910	4423
	339	2330	5058		838	1739	4429
N(10) {	2793	840	5382	C(10) {	2141	791	4650
	3314	1918	5326		2789	1934	4578
N(11) {	495	3537	5870	C(11) {	−189	2698	6437
	1334	3614	6292		890	2146	6688
N(12) {	1494	514	6028	C(12) {	46	648	6287
	860	608	5533		−414	1418	5801

Table 4. Average bond distances (Å) and angles (°) in the tetranuclear cation, as found in crystal structure determinations of three different salts

Values in parentheses are standard deviations as evaluated from the spread among chemically equivalent values.

	Br⁻.5SCN⁻ .3H₂Oᵃ	3S₂O₆²⁻ .8H₂Oᵇ	4SCN⁻.2NO₃⁻ .2H₂Oᶜ
Co—O	1·918 (13)	1·922 (18)	1·921 (10)
Co—N	1·949 (15)	1·956 (18)	1·950 (17)
C—N		1·505 (33)	1·473 (26)
C—C		1·515 (39)	1·479 (40)*
Co···Co	2·885 (9)	2·885 (3)	2·890 (9)
O—Co—O	82·4 (6)	82·7 (10)	82·4 (4)
N—Co—N	87·2 (9)	86·3 (13)	85·8 (7)
Co—O—Co	97·6 (9)	97·2 (7)	97·6 (6)
Co—N—C	109·3 (20)	110·2 (21)	110·1 (11)

References: (a) Thewalt & Ernst (1975). (b) Thewalt (1971). (c) This investigation.
* Excludes disordered en group.

of crystallization; the remaining atoms were given isotropic parameters. The final R value was $0 \cdot 088$ and the goodness-of-fit, $[\Sigma\, w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, for $n = 2571$ observations and $p = 285$ parameters, was $3 \cdot 09$.

Initial calculations were carried out with the *CRYRM* system on an IBM 7094 computer and final calculations with the *CRYM* system on an IBM 360-75. Atomic form factors were taken from *International Tables for X-ray Crystallography* (1962) with the values for Co reduced by $2 \cdot 19$ e and for S by $0 \cdot 34$ e to account for anomalous dispersion; the $\Delta f''$ component was ignored for this centrosymmetric space group.

Discussion

The atomic coordinates and isotropic temperature parameters for C, N, O and H are given in Tables 2 and 3, and average values of the bond distances are given in Table 4.* The cation is shown in Fig. 1 and, in stereoscopic projection, in Fig. 2. The crystal is racemic with configurations about the Co atoms of $\Lambda(\Lambda\Lambda\Lambda)$ and $\Delta(\Delta\Delta\Delta)$ (Thewalt, Jensen & Schäffer, 1972) as shown in Fig. 1. The Co, N and O atoms of the cation are related by an approximate twofold axis passing through Co(2) and Co(4), but the arrangement of C atoms in the en rings destroys the symmetry. In contrast, in the trisdithionate octahydrate salt studied by Thewalt (1971), where the configurations of the Co atoms are also $\Lambda(\Lambda\Lambda\Lambda)$ and $\Delta(\Delta\Delta\Delta)$, the puckering of the en rings is such as to maintain the C_2 symmetry. The mono-bromide pentathiocyanate trihydrate salt (Thewalt & Ernst, 1975) shows configurations $\Lambda(\Lambda\Lambda\Lambda)$ and
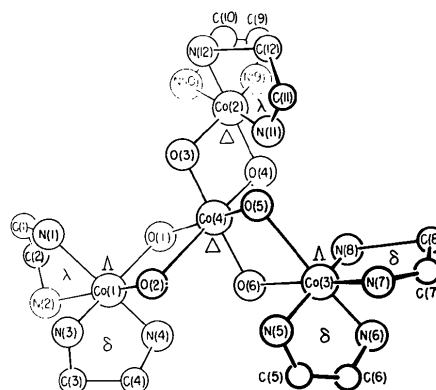
Fig. 1. The cation, and the numbering system we have used. The conformational notations Λ and Δ for the Co atoms and λ and δ for the en rings are as described by Thewalt et al. (1972). The en ring involving N(9) and N(10) is disordered.
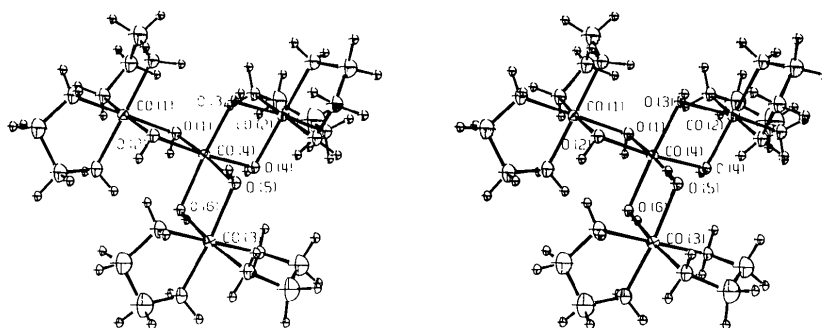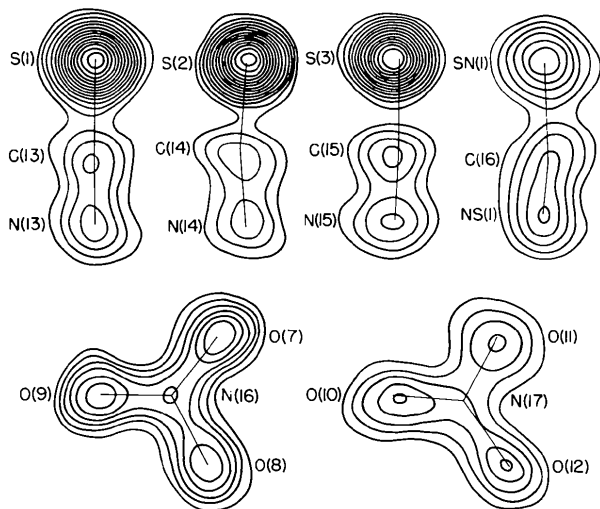
Fig. 2. A sterodrawing of the cation (Johnson, 1965).

Fig. 3. Electron-density maps through the planes of the anions. Contours are at 2, 3, 4 ... e Å⁻³.

$\Delta(\Lambda\Lambda\Lambda)$, and the approximate symmetry of the cation is C_3.

In the present compound, the en group N(9)—C(9)—C(10)—N(10) is disordered, as evidenced by large temperature factors for C(9) and C(10), a short apparent C(9)—C(10) distance of 1·39 Å, and most convincingly by the closely coplanar arrangement of the five atoms of this Co(en) ring. The two conformers (δ and λ, see Thewalt et al., 1972) probably occur in an approximate 1:1 ratio. The C—C distances in the other five en rings also tend to be shorter than usual (Table 4); however, each of these rings shows a normal pucker and there is no evidence of disorder.

Electron-density maps in the planes of the anions are shown in Fig. 3. The three ordered thiocyanate groups are approximately linear (average C—N—S angle 174°) with average S—C and C—N bond lengths of 1·59 and 1·17 Å. The dimensions of the disordered thiocyanate group are less satisfactory, with apparent distances C(16)—SN(1) = 1·29 (4), C(16)—NS(1) = 1·28 (4) Å,

and a central bond angle of 162 (2)°. However, the disorder and the high temperature parameters associated with this anion preclude any meaningful discussion. The nitrate group centered at N(16) is plane trigonal within 0·01 Å, with an average N—O distance of 1·25 Å. On the other hand, the other nitrate group appears distorted, with N(17) lying about 0·08 Å from the plane of the O atoms and with O—N—O angles of 112, 119, and 128°. The large temperature factors and diffuse electron density associated with this group again suggest disorder. The water molecules also show very large thermal parameters, with implied mean-square displacements ranging up to 0·4 Å² for $W(1)$ and to 0·74 Å² for $W(2)$; this latter value is obviously too large to be meaningful in terms of dynamic displacement. It is possible that these high thermal parameters reflect partial occupancies of the water sites.

The hydrogen bonding is quite complex. Five of the six bridging hydroxyl groups form bonds to nitrate groups; surprisingly, the shortest three of these bonds, with O···O distances ranging from 2·75 to 2·81 Å, are to the disordered nitrate group at N(17). The ordered nitrate group at N(16) accepts two weaker O—H···O bonds, at 2·89 and 3·03 Å, but also accepts four N—H···O bonds from amino groups, with N···O distances from 2·98 to 3·12 Å. In all, the 12 amino N atoms appear to participate in 14 respectable hydrogen bonds.

Each of the four thiocyanate groups accepts two hydrogen bonds from amino groups of the cation, of lengths 2·97–3·12 Å. For the disordered thiocyanate group the acceptor site, in both cases, is NS(1), the site which was assigned as a N atom 75% of the time. One water molecule, $W(2)$, apparently participates in four hydrogen bonds, acting as a donor to two nitrate O atoms and as an acceptor from an amino group and from the other water molecule. The water molecule $W(1)$ has only one neighbor within 3·3 Å – $W(2)$, at 2·89 Å.

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The Crystal Structure and Absolute Configuration of Cinchoninium Tetrachlorocadmate(II) Dihydrate

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The crystal structure of the 1 : 1 complex of $CdCl_2$ with the hydrochloride of cinchonine, which crystallizes as $(C_{19}H_{24}N_2O)CdCl_4.2H_2O$, has been solved by the heavy-atom method and refined by full-matrix least-squares computations to $R = 0.056$ for 3871 independent reflexions measured on a diffractometer. The orthorhombic unit cell, space group $P2_12_12_1$, with $a = 8.918$ (2), $b = 32.891$ (6), $c = 8.292$ (2) Å contains four asymmetric units consisting of the tetrahedral $CdCl_4^{2-}$ anion, the cinchoninium^{2+} cation, and two water molecules. The units are linked spirally by hydrogen bonds between chlorine atoms, water molecules, and protonated nitrogen atoms. The absolute configuration and *erythro* configuration at C(9) have been confirmed.

Introduction

A series of cinchonine hydrochloride complexes with transition metals, formulated as $C_{19}H_{22}N_2O.MCl_2$. $2HCl.2H_2O$, where $M = Cd, Co, Zn, Hg, Cu$, was chosen as the promising object of an X-ray study aimed at determining the absolute configuration of the cinchonine molecule (II) and elucidating the metal coordination in complexes of this type.

(II)
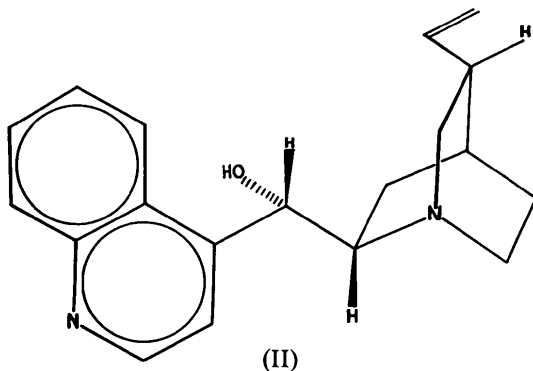
The results of preliminary crystallographic investigations of these compounds (Chojnacki, Oleksyn & Hodorowicz, 1975; Oleksyn, Stadnicka & Hodorowicz, 1976) revealed that the first four are isomorphous.

Crystals of the Cd complex were found to be the most suitable for structure determination by the heavy-atom method. The method of crystal preparation was described by Dyrek (1976), who kindly provided us with the samples.

A well-formed prism of dimensions: $0.10 \times 0.15 \times 0.17$ mm was mounted on a CAD-4 Enraf–Nonius automatic diffractometer.* The lattice parameters, determined together with other crystal data (Chojnacki *et al.*, 1975), were confirmed and refined in the auto-indexing procedure from the setting angles of 15 reflexions.

Crystal data

$C_{19}H_{22}N_2O.CdCl_2.2HCl.2H_2O$; FW 586.66; $a = 8.918$ (2), $b = 32.891$ (6), $c = 8.292$ (2) Å; $U = 2432.2$ Å^3, $Z = 4$; $D_m = 1.617$, $D_X = 1.602$ g cm^{-3};