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The Structure of Δ-(R)-μ-Cystinato-tetrakis(ethylenediamine)dicobalt(III) Tetraperchlorate Hexahydrate

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Abstract

$[C_{14}H_{42}Co_2N_{10}O_4S_2]^{4+}[ClO_4^-]_4.6H_2O$, $M_r = 1103$, orthorhombic, space group $P2_12_12$, $a = 35{\cdot}708\ (4)$, $b = 8{\cdot}869\ (1)$, $c = 6{\cdot}847\ (1)$ Å, $U = 2168{\cdot}4$ Å^3, $D_m = 1{\cdot}74\ (2)$ (by flotation), $Z = 2$, $D_c = 1{\cdot}69$ Mg m^{-3}. $R = 0{\cdot}072$ for 1996 reflections. The absolute configurations at Co and the asymmetric C atom are Δ and R respectively. Results of strain-energy-minimization calculations on the cation suggest that differences in energy between λ and δ conformers for the ethylenediamine rings are small and that their observed conformations are probably controlled by interionic interactions.

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Introduction and experimental

Jackson, Sargeson & Tucker (1977) reported that oxidation of the N,S-bound Δ-(R)-cysteinatobis(ethylenediamine)cobalt(III) cation in DMSO/Ac_2O mixture yields an N,O-bound sulphenamide complex in which the cysteinato S is bound to a N atom of one of the ethylenediamine ligands. The sulphenamide complex reacts with N,O-bound cysteinatobis(ethylenediamine)cobalt(III), obtained by borohydride reduction of the sulphenamide, to give the cation of the title complex, the structure of which was briefly reported (Jackson *et al.*, 1977). In this paper the structure of the tetraperchlorate salt is described in detail.

Deep-red crystals of the complex, commonly parallelepipeds, were efflorescent and were thinly coated with hair lacquer (after mounting on quartz fibres) to prevent crystal decay. The space group was uniquely determined as $P2_12_12$ by the systematic absences $h00$, $h = 2n + 1$ and $0k0$, $k = 2n + 1$. The cell dimensions and orientation matrix were derived by least-squares refinement, from the optimized 2θ, ω and χ angles for 12 reflections (Cu $K\alpha_1$ radiation, $2\theta > 62°$) on a Picker FACS-I four-circle diffractometer. Intensities for the 4357 reflections in quadrants hkl and $\bar{h}kl$ with $3 \leq 2\theta \leq 120°$ were measured with monochromated (graphite crystal, $\theta_m = 13{\cdot}25°$) Cu $K\alpha$ radiation. A $\theta/2\theta$ scan from 1·0° below the $K\alpha_1$ to 1·0° above the $K\alpha_2$ maximum at 2° min^{-1} in 2θ, with stationary background counts of 10 s at the scan limits, was used. The measurement, every 97 reflections, of three standards indicated a linear but anisotropic intensity loss (<12%) over the period of data collection. Correction for this decay (Churchill & Kalra, 1974), and for absorption [μ(Cu $K\alpha$) = 10·36 mm^{-1}] was made. The crystal was bounded by forms {001}, {100} and {110} with perpendicular distances between pairs of faces of 0·212, 0·112 and 0·538 mm respectively. The intensities were reduced to $|F_o|$ (Bennett, Matheson, Robertson, Smith & Tucker, 1978), the data sorted and equivalent reflections ($h0l$, $hk0$ and standards only) averaged. The statistical R factor $\sum \sigma_s(F_o)/\sum |F_o|$ was 0·030 for the 1996 unique reflections ($\pm h,k,l$) with $I > 3\sigma(I)$.

Scattering factors other than for H were taken from Cromer & Mann (1968), that for H and the anomalous dispersion corrections for Co, Cl and S from *International Tables for X-ray Crystallography* (1974). Computer programs are described elsewhere (Bennett *et al.*, 1978). The positions of the non-hydrogen atoms were found by the heavy-atom method. A crystallographic diad at $x = \frac{1}{2}$, $y = \frac{1}{2}$ intersects the S–S bond of the cation. Positional and anisotropic thermal parameters were refined initially by a block-diagonal least-squares procedure with unit weights. A difference synthesis calculated at this stage showed evidence of H atoms attached to C(2), C(3) and N(1) through N(5) and these were included with isotropic thermal parameters equal to those of the atoms to which they were bound, but were not refined. The coordinates of these H atoms were calculated assuming N–H and C–H = 0·95 Å. Probably because of the high thermal motion of C(4) through C(7), H atoms attached thereto could not be located with certainty and were omitted from the calculations. Likewise the H atoms attached to the atoms O(5) through O(7) were omitted. Full-matrix least-squares refinement, mimimizing $\sum w(|F_o| - |F_c|)^2$, with $w = [\sigma^2(F_o) + 0{\cdot}002F_o^4]^{-1}$ converged with $R = 0{\cdot}129$. Refinement on the enantiomorphic model, however, converged with a final R of 0·072 $\{R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0{\cdot}105\}$ establishing the absolute configuration at Co as $\varDelta$ and at C(3) as R. The perchlorate anions and the water molecules lie in general positions in the cell and are poorly determined.

In the final cycle no parameter shift exceeded 0·1 σ. A final difference synthesis showed no features $>|0{\cdot}9|$ e Å^{-3} with the most prominent positive features on diads at $x = \frac{1}{2}$, $y = 0$. The poor agreement between observed and calculated densities is possibly due to an additional two water molecules per Co atom. There is no clear-cut evidence of these in the final difference map but the possibility exists that they are extensively disordered along the diad at $x = \frac{1}{2}$, $y = 0$. The standard deviation of an observation of unit weight, $[\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2}$, was 2·1. The minimized function

Table 1. *Final atomic coordinates with e.s.d.'s in parentheses*

	x	y	z	B (Å^2)
Co	−0·3550 (1)	0·3770 (2)	0·0651 (3)	
S	−0·4971 (1)	0·3861 (5)	0·0391 (6)	
O(1)	−0·3663 (2)	0·3769 (9)	0·3355 (10)	
O(2)	−0·4126 (2)	0·3933 (11)	0·5492 (14)	
C(1)	−0·4015 (3)	0·3951 (14)	0·3837 (19)	
C(2)	−0·4266 (3)	0·4352 (12)	0·2268 (20)	
C(3)	−0·4638 (3)	0·3533 (16)	0·2299 (20)	
C(4)	−0·3297 (4)	0·0910 (14)	0·1714 (32)	
C(5)	−0·2957 (3)	0·1675 (13)	0·1340 (24)	
C(6)	−0·3337 (4)	0·5438 (15)	−0·2743 (21)	
C(7)	−0·3242 (7)	0·6302 (21)	−0·1193 (25)	
N(1)	−0·4080 (2)	0·4074 (10)	0·0212 (13)	
N(2)	−0·3028 (2)	0·3350 (9)	0·1378 (13)	
N(3)	−0·3607 (2)	0·1586 (9)	0·0607 (15)	
N(4)	−0·3436 (2)	0·3894 (11)	−0·2104 (14)	
N(5)	−0·3459 (2)	0·5949 (9)	0·0616 (16)	
Cl(1)	−0·2400 (1)	0·2623 (4)	0·6478 (5)	
O(11)	−0·2773 (3)	0·2466 (18)	0·5762 (20)	
O(12)	−0·2288 (3)	0·1162 (12)	0·6979 (17)	
O(13)	−0·2436 (3)	0·3529 (12)	0·8153 (16)	
O(14)	−0·2166 (5)	0·3175 (16)	0·5156 (27)	
Cl(2)	−0·0814 (2)	0·3820 (6)	−0·3584 (9)	
O(21)	−0·0880 (4)	0·5271 (13)	−0·3851 (22)	
O(22)	−0·1086 (6)	0·2944 (25)	−0·4213 (42)	
O(23)	−0·0498 (5)	0·3218 (22)	−0·4283 (37)	
O(24)	−0·0846 (11)	0·3511 (32)	−0·1454 (32)	
O(5)	−0·4322 (3)	0·1306 (14)	0·8190 (17)	
O(6)	−0·0839 (5)	0·2278 (22)	0·1401 (28)	
O(7)	−0·3390 (3)	0·0153 (14)	−0·3113 (17)	
H(2)	−0·432	0·540	0·230	4·6
H(31)	−0·458	0·244	0·231	5·1
H(32)	−0·475	0·375	0·354	5·1
HN(11)	−0·413	0·489	−0·059	3·6
HN(12)	−0·419	0·317	−0·031	3·6
HN(21)	−0·287	0·383	0·047	3·5
HN(22)	−0·298	0·371	0·265	3·5
HN(31)	−0·383	0·131	0·125	4·3
HN(32)	−0·361	0·124	−0·069	4·3
HN(41)	−0·324	0·323	−0·237	4·2
HN(42)	−0·365	0·359	−0·281	4·2
HN(51)	−0·369	0·648	0·072	3·8
HN(52)	−0·331	0·622	0·173	3·8

was essentially independent of sin θ/λ or $|F_o|$ and a comparison of $|F_o|$ with $|F_c|$ shows extinction to be unimportant. The final atomic parameters are listed in Table 1.* The geometry and atom numbering of the cation are illustrated in Fig. 1, the packing is shown in Fig. 2. Bond lengths and angles with standard deviations estimated from the full variance/covariance matrix are listed in Table 2.

Discussion

The cation has crystallographic twofold symmetry through the disulphide linkage of the cystinato ligand, the amino acids ends of which each act as a bidentate (N,O)-chelate to Co. Co, O(1), N(1) and C(1) are approximately coplanar and C(2) lies 0·21 Å from that plane. The bond lengths and angles in the central part of the cystinato ligand are similar to the corresponding values in (*R*)-cystine and its derivatives (Chaney & Steinrauf, 1974). C(2)–N(1) and C(1)–O(1) are slightly longer, and C(1)–O(2) is slightly shorter than in (*R*)-cystine. C(1)–O(1) and C(1)--O(2) are similar to the usual values for, respectively, the longer (1·312 Å) and shorter (1·233 Å) bonds in carboxylic acids and esters (*Interatomic Distances and Configuration in Molecules and Ions*, 1965). The disulphide linkage has a left-handed chirality (Chaney & Steinrauf, 1974) similar to that in several (*R*)-cystine derivatives but different from the right-handed chirality in tetragonal or hexagonal (*R*)-cystine. The C–S–S–C torsion angle is 98·1°.

The Co–O(1) length is similar to that in other carboxylate linkages to Co^{III} and, although the spread in Co–N distances is large, they fall well within the range common for Co–N(amine) bonds (*Molecular Structure by Diffraction Methods*, 1975). Individual differences in Co–N lengths are almost certainly related to differences in hydrogen-bonding interactions, Table 3. The apparent trend is that the shorter Co–N bonds are to those N atoms involved in the stronger N–H···O interactions.

The ethylenediamine (en) rings I and II (Fig. 3) adopt δ and λ conformations respectively. The C–N lengths are unexceptional but C(4)–C(5) and C(6)–C(7) are much shorter than expected for a C–C single bond. C(4) through C(7) have large and anisotropic thermal parameters with the major axes of vibration approximately perpendicular to the local N–C–C plane (Fig. 1). Similar observations have been

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Co–O(1)	1·895 (7)	O(1)–C(1)–O(2)	123·6 (10)
		O(1)–C(1)–C(2)	116·0 (11)
Co–N(1)	1·934 (8)	O(2)–C(1)–C(2)	120·0 (10)
Co–N(2)	1·968 (7)		
Co–N(3)	1·948 (8)	C(1)–C(2)–C(3)	114·6 (11)
Co–N(4)	1·933 (10)	C(1)–C(2)–N(1)	111·3 (8)
Co–N(5)	1·960 (8)	C(3)–C(2)–N(1)	107·9 (8)
C(3)–S	1·790 (13)	C(2)–C(3)–S	119·6 (10)
		C(3)–S–S	103·3 (5)
S–S	2·032 (8)		
		Co–N(1)–C(2)	107·2 (6)
C(4)–C(5)	1·41 (2)	Co–N(2)–C(5)	109·9 (6)
C(6)–C(7)	1·35 (2)	Co–N(3)–C(4)	108·6 (7)
		Co–N(4)–C(6)	113·0 (8)
C(1)–O(1)	1·31 (1)	Co–N(5)–C(7)	107·6 (9)
C(1)–O(2)	1·20 (1)	Co–O(1)–C(1)	116·8 (7)
C(1)–C(2)	1·44 (2)		
C(2)–C(3)	1·51 (1)	N(3)–C(4)–C(5)	110·9 (12)
		N(2)–C(5)–C(4)	109·0 (10)
N(1)–C(2)	1·58 (2)	N(4)–C(6)–C(7)	110·6 (12)
N(3)–C(4)	1·47 (2)	N(5)–C(7)–C(6)	113·7 (14)
N(2)–C(5)	1·51 (1)		
N(4)–C(6)	1·48 (1)	O(1)–Co–N(1)	86·8 (3)
N(5)–C(7)	1·49 (2)	N(2)–Co–N(3)	85·1 (3)
		N(4)–Co–N(5)	84·1 (4)
Cl(1)–O(11)	1·43 (1)	O(1)–Co–N(3)	89·6 (4)
Cl(1)–O(12)	1·40 (1)	O(1)–Co–N(5)	92·7 (4)
Cl(1)–O(13)	1·41 (1)	O(1)–Co–N(2)	87·4 (3)
Cl(1)–O(14)	1·33 (1)	N(4)–Co–N(3)	93·6 (4)
Cl(2)–O(21)	1·32 (1)	N(4)–Co–N(2)	93·3 (3)
Cl(2)–O(22)	1·31 (2)	N(4)–Co–N(1)	92·7 (3)
Cl(2)–O(23)	1·34 (1)	N(1)–Co–N(3)	92·0 (3)
Cl(2)–O(24)	1·49 (2)	N(1)–Co–N(5)	91·4 (3)
		N(2)–Co–N(5)	91·8 (3)

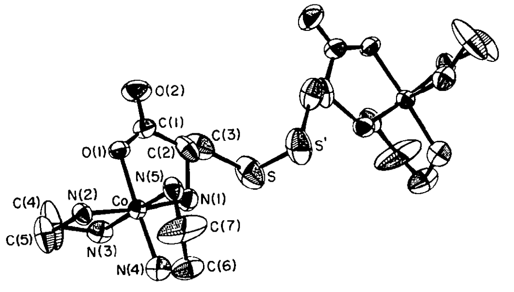

Fig. 1. Geometry of and atom numbering for the cation. The thermal ellipsoids are scaled to include 50% probability. H atoms are omitted for clarity.

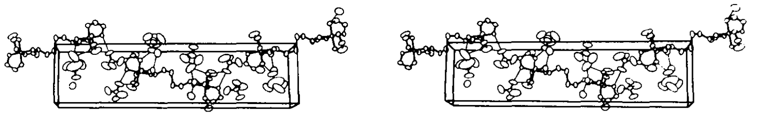

Fig. 2. Stereoscopic view of the cell contents viewed approximately along *c*. The thinner lines indicate possible hydrogen bonds.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33890 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Possible hydrogen-bonding contacts and selected non-bonding contacts*

Superscripts refer to atoms related to those in Table 1 by the operations:

(i) $x, y, 1+z$
(ii) $-\frac{1}{2}-x, y-\frac{1}{2}, -z$
(iii) $-\frac{1}{2}-x, y-\frac{1}{2}, 1-z$
(iv) $-\frac{1}{2}-x, \frac{1}{2}+y, -z$
(v) $x, y, z-1$
(vi) $-\frac{1}{2}-x, \frac{1}{2}+y, 1\quad z$.

(*a*) Hydrogen-bonding contacts (Å). The H···O distances, computed from the calculated H atom positions, are given in square brackets where appropriate.

N(1)···O(5)^{i}	2·95 [2·00]	N(4)···O(2)^{i}	2·96 [2·08]
N(1)···O(6)^{ii}	3·06 [2·19]	N(4)···O(11)^{i}	3·06 [2·19]
N(2)···O(12)^{iii}	2·96 [2·40]	N(5)···O(6)^{ii}	3·10 [2·33]
N(2)···O(13)^{i}	3·06 [2·23]	N(5)···O(12)^{iii}	3·14 [2·30]
N(3)···O(7)	2·95 [2·07]	O(6)···O(24)	2·24
N(3)···O(21)^{iv}	3·11 [2·25]	O(7)···O(14)^{iv}	3·00
		O(5)···O(2)	3·06

(*b*) Non-bonded contacts (Å) shorter than 3·35 Å for C···O, 3·50 Å for C···N (and 4·00 Å for C···C)

C(1)···O(21)^{iv}	3·29	C(5)···O(13)^{i}	3·31
C(4)···O(21)^{iv}	3·33	C(6)···O(1)^{i}	3·27
C(5)···O(13)^{vi}	3·14	C(6)···O(2)	3·34
C(5)···O(11)	3·18	C(1)···N(4)^{v}	3·46

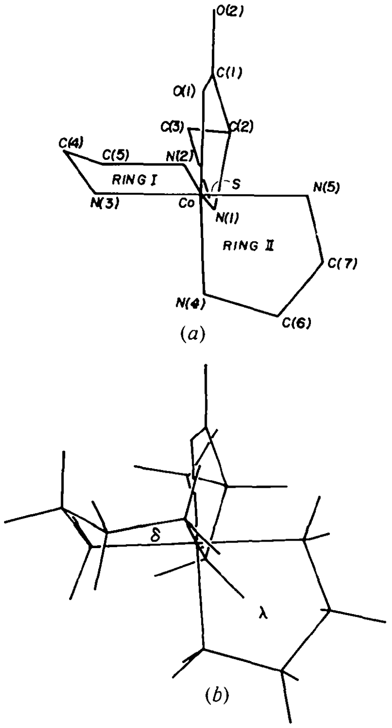

Fig. 3. (*a*) Observed configuration of the asymmetric half of the cation. H atoms, being poorly determined, are omitted. (*b*) Strain-energy-minimized configuration ($\delta\lambda$) of the asymmetric half of the cation.

made in other $Co^{III}(en)_2L_2$ complexes and it has been suggested that the large anisotropic vibration of the C atoms is responsible for a systematic shortening of the C–C bonds (Shintani, Sato & Saito, 1976). Because the temperature factors of both C atoms in each ring are large, a bond-length correction based on a riding motion of one C atom on the other seemed inappropriate. Bond lengths, corrected by assuming that the C atoms vibrate independently, are 1·56 and 1·53 Å for C(4)–C(5) and C(6)–C(7) respectively. The smaller vibrational amplitudes for C(5) and C(6) relative to C(4) and C(7) are probably related to the larger number of short non-bonded interactions in which they are involved (Table 3).

Strain-energy-minimization calculations on the cation have been performed in an attempt to rationalize the observed en ring conformations. The method, program and parameters have been described (Buckingham, Maxwell, Sargeson & Snow, 1970). Calculations were performed for both the entire cation, but omitting the unknown C–S–S–C torsional interaction, and for the asymmetric half of the cation. The results from both sets of calculations are compatible which is consistent with the observation that there are no important non-bonded contacts between symmetry-related halves of the cation. In the asymmetric half of the cation the relative energies for the configurations λ(ring I)λ(ring II), $\delta\delta$, $\delta\lambda$ and $\lambda\delta$ are computed as 0·00, 0·71, 0·88 and 1·17 kJ mol^{-1} respectively. The differences are small and, indeed, the configuration favoured according to the calculations (*i.e.* $\lambda\lambda$) is not that observed. It is concluded therefore that the observed configuration ($\delta\lambda$) is decided primarily by packing considerations, for example, the hydrogen-bonding network. These results are also consistent with the calculations of Gollogly & Hawkins (1970) on complexes of the general type $Co(en)_2X_2$ in that there

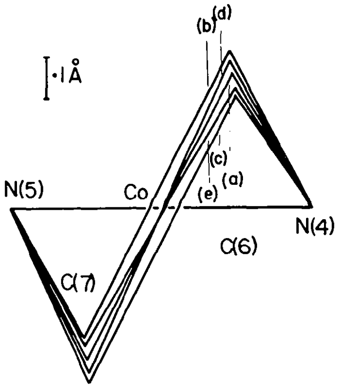

Fig. 4. Diagram of small distortions from the strain-energy-minimized conformation (λ) of ring II. For clarity the vertical scale is four times that of the horizontal. The relative energies for (*a*) the $\delta\lambda$ minimum, (*b*), (*c*), (*d*) and (*e*) are 0·88, 2·56, 2·34, 2·22 and 2·26 kJ mol^{-1} respectively.

is little energy difference between the possible configurations. The observed configuration is compared with the calculated $\delta\lambda$ minimum in Fig. 3. Configurations in which one en ring has an envelope conformation are approximately 21 kJ mol^{-1} higher in energy. The thermal parameters of the en C atoms are not large enough to be due either to interconversion between conformations or to a statistical distribution of different conformers in the crystal. The calculations do, however, indicate that for either λ or δ configurations of either ring the energy surface near the minimum is very shallow.

Fig. 4 shows, for en ring II (in the $\delta\lambda$ configuration), the energy for slightly differing conformations. This shallow energy minimum is believed to be responsible for the large libration of the en C atoms in the title compound and it seems likely that similar arguments apply to other Co^{III} (en)$_2L_2$ systems when L_2 is not too bulky.

The perchlorate ions are poorly determined, the O atoms exhibiting large anisotropic thermal parameters. In consequence the Cl—O lengths (Table 2), being uncorrected for thermal vibration, are shorter than expected. The perchlorate ions and the water molecules are involved in hydrogen-bonding interactions as listed in Table 3 and marked on Fig. 2.

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Ammine[1-(2-hydroxyphenyl)-3,5-diphenylformazanato]copper(II), $C_{19}H_{17}Cu^{II}N_5O$, and Ammine[1-(2-hydroxyphenyl)-3,5-diphenylformazanato]nickel(II), $C_{19}H_{17}N_5Ni^{II}O$

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Abstract

$C_{19}H_{17}Cu^{II}N_5O$ is monoclinic, $P2/n$, $a = 24{\cdot}231$ (4), $b = 6{\cdot}5223$ (5), $c = 11{\cdot}449$ (2) Å, $\beta = 90{\cdot}30$ (3)°, $Z = 4$. $C_{19}H_{17}N_5Ni^{II}O$ is triclinic, $P\bar{1}$, $a = 6{\cdot}096$ (3), $b = 12{\cdot}10$ (4), $c = 13{\cdot}60$ (5) Å, $\alpha = 115{\cdot}2$ (3), $\beta = 94{\cdot}3$ (2), $\gamma = 93{\cdot}4$ (3)°, $Z = 2$. The structures were refined to final R values of 4·8% for 2788 significant reflections and 4·7% for 2029 significant reflections respectively. Both structures have similar approximately square coordination of the metal atoms in which the two outer N atoms of the formazan part, the O atom of the phenyl group and the N atom of the NH_3 molecule are involved. The structures consist of columns of similarly stacked units which are packed in a slightly different manner in the two structures.

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