Compounds with Intermediate Spin.
3.* Structure of Tris[*N,N*-bis(2-hydroxyethyl)dithiocarbamato]iron(III) at 150 and 295 K

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Abstract. $Fe[S_2CN(C_2H_4OH)_2]_3$, $C_{15}H_{30}FeN_3O_6S_6$, $M_r = 596.7$, triclinic, $P\bar{1}$, $Z = 2$; $a = 8.623$ (3), $b = 11.657$ (3), $c = 14.465$ (4) Å, $\alpha = 109.39$ (2), $\beta = 103.74$ (3), $\gamma = 93.59$ (3)°, $V = 1316.3$ Å^3, $D_x = 1.506$ Mg m^{-3} at 150 K; and $a = 8.7193$ (7), $b = 11.7173$ (6), $c = 14.5053$ (10) Å, $\alpha = 109.299$ (6), $\beta = 103.555$ (8), $\gamma = 93.581$ (8)°, $V = 1343.8$ Å^3, $D_x = 1.475$ Mg m^{-3} at 295 K. At both temperatures mononuclear tris[*N,N*-bis(2-hydroxyethyl)dithiocarbamato]iron(III) complexes of pseudosymmetry D_3 are held together by O—H$\cdots$O hydrogen bonds and van der Waals forces. The main structural difference at the two temperatures is a decrease of the average Fe—S distance from 2.390 (3) Å at 295 K to 2.331 (3) Å at 150 K. This is accompanied by a decrease in the magnetic moment from $\mu_{eff} = 4.20$ to $\mu_{eff} = 2.40$.

Introduction. Most solid Fe^{III} dithiocarbamates exhibit strongly temperature-dependent magnetic moments (White, Roper, Kokot, Waterman & Martin, 1964; Ewald, Martin, Sinn & White, 1969). The crystal structures of several such compounds are known and
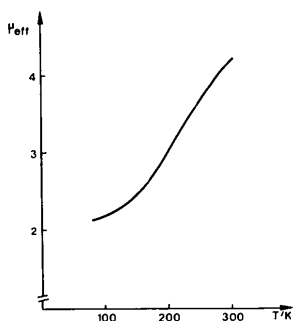
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they all comprise mononuclear tris complexes with or without solvate molecules in the structure. All crystal structure determinations except two (Albertsson & Oskarsson, 1977; Leipoldt & Coppens, 1973) were made at room temperature. The present series of investigations aims at correlating the temperature-dependent magnetic behaviour of some solid dithiocarbamates with their geometrical features (Albertsson & Oskarsson, 1977). Solvent molecules included in the crystal structure have significant effects on the magnetic behaviour. Molecules like CH_2Cl_2 and $CHCl_3$, which might interact with the S atoms in the complexes, increase the magnetic moments, while molecules like benzene and nitrobenzene have the opposite effect (Cukauskas, Deaver & Sinn, 1977; Butcher & Sinn, 1976). In a compound like $Fe[S_2CN(C_2H_4OH)_2]_3$ there

Fig. 1. μ_{eff} (the number of Bohr magnetons) as a function of temperature. $Fe(C_5H_{10}NO_2S_2)_3$ decomposes above 300 K.

Table 1. *Collection and reduction of intensities and the least-squares refinement*

Crystal size (mm)	0.13 × 0.09 × 0.05	
Radiation (Nb-filtered)	Mo $K\alpha$	
Take-off angle (°)	3	
ω interval (°) (ω–2θ scan)	$0.8 + 0.5 \tan \theta$	
θ interval (°)	3–25	
Minimum number of counts in a scan	3000	
Maximum recording time (s)	180	

	150 K	295 K
μ(Mo $K\alpha$) (mm^{-1})	1.10	1.08
Range of transmission factor	0.89–0.95	0.89–0.95
Number of measured reflexions	4775	4945
Number of reflexions given zero weight, $I < 3\sigma_c(I)$	2031	2189
Number of reflexions in the final refinements, m	2744	2756
Number of parameters refined, n	281	281
$R = \Sigma|\Delta F|/\Sigma|F_o|$*	0.078	0.067
$R_w = [\Sigma\, w(\Delta F)^2/\Sigma w|F_o|^2]^{1/2}$	0.112	0.095
$S = [\Sigma\, w(\Delta F)^2/(m - n)]^{1/2}$	1.86	1.76
C (weighting function)	0.05	0.04

* $\Delta F = |F_o| - |F_c|$.

Table 2. *The cell dimensions of* $Fe(C_5H_{10}NO_2S_2)_3$ *in the interval 125–295 K*

T (K)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å³)
125	8·604 (2)	11·650 (2)	14·455 (2)	109·31 (1)	103·76 (2)	93·62 (2)	1312·2
150	8·623 (3)	11·657 (3)	14·465 (4)	109·39 (2)	103·74 (3)	93·59 (3)	1316·3
175	8·627 (2)	11·664 (2)	14·478 (3)	109·39 (2)	103·76 (2)	93·56 (2)	1318·9
200	8·645 (2)	11·680 (2)	14·486 (3)	109·42 (2)	103·71 (2)	93·56 (2)	1324·1
225	8·665 (2)	11·692 (2)	14·491 (2)	109·40 (1)	103·64 (2)	93·60 (2)	1329·6
250	8·681 (2)	11·708 (2)	14·499 (3)	109·38 (1)	103·38 (2)	93·59 (2)	1335·2
295	8·7193 (7)	11·7173 (6)	14·5053 (10)	109·299 (6)	103·555 (8)	93·581 (8)	1343·8

is a possibility of hydrogen bonding without including any solvate molecules. We report here the crystal structure of the title compound, (I), at 150 and 295 K and its magnetic moments in the range 80–300 K.

(I) was prepared in a nitrogen atmosphere by mixing ethanol solutions of $Na(C_5H_{10}NO_2S_2)$ and anhydrous $FeCl_3$. Single crystals were grown from chloroform by slow addition of water-free ethanol. The magnetic-susceptibility measurements (Fig. 1) were made by the Faraday method (Blom & Hörlin, 1977). Table 1 gives information concerning the collection and reduction of the intensities and the refinements based on them. Weissenberg photographs revealed Laue class $\bar{1}$ and the space group $P\bar{1}$ was chosen. A four-circle diffractometer was used for intensity collection. The cell dimensions given in Table 2 were obtained from 50 θ values measured on the diffractometer at seven temperatures in the interval 125–295 K (Danielsson, Grenthe & Oskarsson, 1976). During the intensity-data collection three standard reflexions were checked at regular intervals and no systematic variation in their intensities was observed. The values of I and $\sigma_c(I)$ were corrected for Lorentz, polarization and absorption effects, the latter by numerical integration [$\sigma_c(I)$ is based on counting statistics].

The position of Fe was deduced from a vector map. Subsequent difference syntheses revealed all the non-H atoms. The parameters were refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$ with weights $w = [\sigma_c^2(|F_o|^2)/4|F_o|^2 + C^2|F_o|^2]^{-1}$. The parameter C was adjusted so that constant values of $\langle w(|F_o| - |F_c|)^2 \rangle$ were obtained in different $|F_o|$ and $\sin \theta$ intervals. Before the last cycles the positions of the methylene H atoms were calculated from geometrical considerations

and included with fixed coordinates ($B = 5·0$ Å²). The final difference synthesis indicates that the terminal —C—OH groups are disordered resulting in large thermal ellipsoids (Fig. 2). The data set obtained at 150 K also gave a slightly negative temperature factor for C(4).

Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Table 3 gives the positional parameters and Table 4 selected bond distances and angles.*

Discussion. Fig. 2 shows the structure of the mononuclear complex (I) and Fig. 3 the crystal packing. The complexes are connected through hydrogen bonds formed by the hydroxyl groups. The closest contacts between the coordination polyhedra are across the centres of symmetry with S(3)—S(3^{vi}) 3·67 Å at 150 K and 3·66 Å at 295 K. These are typical van der Waals distances (Bondi, 1964). The corresponding Fe—Fe^{vi} distances are 6·68 and 6·69 Å.

The Fe^{III} ion is coordinated by six S atoms forming a twisted trigonal prism with approximate D_3 symmetry (Table 5). The main structural difference at the two temperatures is the mean Fe—S distance, 2·331 (3) Å at 150 K and 2·390 (3) Å at 295 K. Bond distances

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* Lists of structure factors and anisotropic thermal parameters obtained at 150 and 295 K have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34245 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
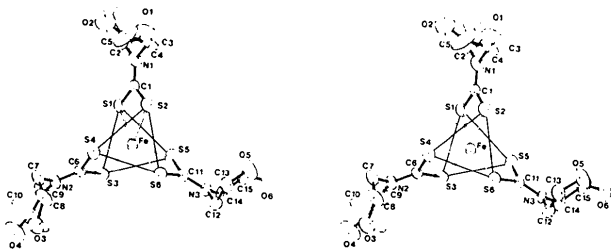

Fig. 2. A stereoscopic drawing of $Fe(C_5H_{10}NO_2S_2)_3$ viewed along the pseudo threefold axis. The thermal ellipsoids are scaled to include 50% probability.
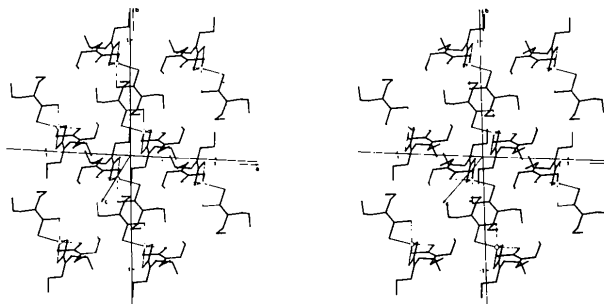

Fig. 3. The crystal packing of $Fe(C_5H_{10}NO_2S_2)_3$. **a** is to the right, **b** is vertical and **c** is out of the paper.

Table 3. *Positional parameters* (×10⁴) *of the non-H atoms, with e.s.d.'s*

	150 K x	150 K y	150 K z	295 K x	295 K y	295 K z
Fe	2117 (2)	2745 (1)	1538 (1)	2121 (2)	2727 (1)	1523 (1)
S(1)	2047 (3)	1203 (2)	2227 (2)	2047 (3)	1190 (2)	2266 (2)
S(2)	3583 (4)	3690 (2)	3236 (2)	3633 (4)	3669 (2)	3252 (2)
N(1)	3666 (14)	2066 (8)	4215 (7)	3679 (11)	2058 (6)	4217 (6)
C(1)	3191 (13)	2287 (9)	3359 (8)	3198 (11)	2279 (8)	3371 (7)
C(2)	3287 (18)	881 (10)	4286 (9)	3302 (16)	899 (9)	4327 (8)
C(3)	1929 (23)	850 (12)	4778 (10)	1831 (24)	903 (12)	4767 (12)
C(4)	4694 (24)	3099 (11)	5186 (8)	4734 (17)	3088 (10)	5200 (8)
C(5)	6717 (22)	3050 (13)	5146 (14)	6631 (19)	3062 (11)	5203 (14)
O(1)	1795 (30)	−479 (16)	4655 (15)	1746 (27)	−349 (19)	4715 (15)
O(2)	7277 (18)	2120 (18)	5179 (13)	7199 (14)	2091 (12)	5227 (8)
S(3)	1167 (3)	1294 (3)	−115 (3)	1220 (3)	1223 (2)	−153 (2)
S(4)	4384 (3)	2479 (2)	930 (2)	4414 (3)	2461 (2)	887 (2)
N(2)	3651 (13)	725 (8)	−931 (7)	3710 (10)	705 (7)	−953 (6)
C(6)	3157 (13)	1382 (9)	−174 (8)	3170 (11)	1370 (8)	−199 (7)
C(7)	5381 (15)	906 (11)	−892 (9)	5404 (13)	908 (10)	−909 (8)
C(8)	5840 (16)	1974 (11)	−1227 (10)	5864 (16)	1948 (11)	−1221 (9)
C(9)	2541 (20)	−327 (17)	−1789 (12)	2622 (18)	−397 (13)	−1780 (10)
C(10)	2561 (50)	−700 (36)	−2684 (17)	2438 (31)	−669 (26)	−2709 (14)
O(3)	5206 (13)	1669 (8)	−2293 (7)	5202 (10)	1700 (7)	−2297 (6)
O(4)	3404 (16)	−567 (11)	−3309 (8)	3336 (13)	−496 (9)	−3314 (6)
S(5)	−462 (4)	3173 (2)	1606 (2)	−488 (3)	3186 (2)	1569 (2)
S(6)	2028 (3)	4663 (2)	1354 (2)	2031 (3)	4697 (2)	1360 (2)
N(3)	−888 (11)	5382 (7)	1416 (7)	−851 (9)	5385 (6)	1404 (5)
C(11)	91 (13)	4547 (9)	1479 (8)	94 (11)	4556 (8)	1452 (7)
C(12)	−338 (15)	6568 (11)	1325 (9)	−281 (14)	6562 (9)	1358 (8)
C(13)	850 (17)	7489 (10)	2336 (10)	818 (14)	7454 (9)	2341 (8)
C(14)	−2624 (14)	5077 (10)	1334 (9)	−2614 (12)	5089 (9)	1286 (9)
C(15)	−3099 (16)	5555 (11)	2301 (11)	−3103 (14)	5520 (10)	2228 (10)
O(5)	51 (13)	7772 (9)	3133 (8)	36 (11)	7719 (8)	3129 (6)
O(6)	−3069 (12)	6862 (8)	2685 (7)	−3051 (11)	6834 (7)	2640 (7)

Table 4. *The geometry of the complex*

Distances are in Å and angles in degrees.

(a) The FeS₆ polyhedron

	150 K	295 K		150 K	295 K		150 K	295 K
Fe—S(1)	2·331 (3)	2·390 (3)	S(1)—S(2)	2·844 (4)	2·867 (3)	S(2)—S(4)	3·418 (4)	3·500 (4)
Fe—S(2)	2·323 (3)	2·385 (3)	S(3)—S(4)	2·833 (4)	2·866 (4)	S(2)—S(5)	3·602 (5)	3·730 (4)
Fe—S(3)	2·337 (3)	2·393 (3)	S(5)—S(6)	2·844 (4)	2·870 (4)	S(4)—S(5)	4·686 (4)	4·792 (4)
Fe—S(4)	2·324 (3)	2·387 (3)	S(1)—S(3)	3·330 (4)	3·427 (3)	S(1)—S(4)	3·615 (4)	3·742 (3)
Fe—S(5)	2·327 (3)	2·382 (3)	S(1)—S(6)	4·611 (4)	4·712 (4)	S(3)—S(5)	3·375 (4)	3·482 (4)
Fe—S(6)	2·341 (3)	2·401 (3)	S(3)—S(6)	3·720 (4)	3·859 (3)	S(6)—S(2)	3·316 (4)	3·396 (4)

(b) Ligand 1

	150 K	295 K		150 K	295 K		150 K	295 K
S(1)—C(1)	1·72 (1)	1·71 (1)	N(1)—C(2)	1·44 (1)	1·44 (1)	N(1)—C(4)	1·54 (2)	1·56 (1)
S(2)—C(1)	1·73 (1)	1·72 (1)	C(2)—C(3)	1·51 (2)	1·56 (2)	C(4)—C(5)	1·76 (3)	1·66 (2)
C(1)—N(1)	1·32 (1)	1·32 (1)	C(3)—O(1)	1·49 (2)	1·44 (3)	C(5)—O(2)	1·23 (2)	1·28 (2)
S(1)—C(1)—S(2)	111·4 (6)	113·1 (5)	C(1)—N(1)—C(2)	123·1 (9)	124·6 (8)	N(1)—C(2)—C(3)	119·9 (10)	110·4 (10)
S(1)—C(1)—N(1)	123·7 (8)	122·5 (7)	C(1)—N(1)—C(4)	119·6 (9)	120·1 (7)	C(2)—C(3)—O(1)	97·3 (13)	95·6 (14)
S(2)—C(1)—N(1)	125·0 (8)	124·3 (7)	C(2)—N(1)—C(4)	117·4 (9)	115·3 (8)	N(1)—C(4)—C(5)	106·1 (11)	108·8 (9)
						C(4)—C(5)—O(2)	117·3 (14)	117·1 (11)

(c) Ligand 2

	150 K	295 K		150 K	295 K		150 K	295 K
S(3)—C(6)	1·74 (1)	1·72 (1)	N(2)—C(7)	1·48 (2)	1·46 (1)	N(2)—C(9)	1·50 (2)	1·52 (2)
S(4)—C(6)	1·73 (1)	1·73 (1)	C(7)—C(8)	1·54 (2)	1·50 (2)	C(9)—C(10)	1·23 (3)	1·25 (2)
C(6)—N(2)	1·29 (1)	1·32 (1)	C(8)—O(3)	1·42 (2)	1·45 (1)	C(10)—O(4)	1·33 (4)	1·36 (3)
S(3)—C(6)—S(4)	109·6 (6)	112·6 (5)	C(6)—N(2)—C(7)	119·8 (10)	120·4 (8)	N(2)—C(7)—C(8)	112·8 (10)	114·1 (9)
S(3)—C(6)—N(2)	125·3 (9)	125·1 (7)	C(6)—N(2)—C(9)	120·8 (11)	119·2 (9)	C(7)—C(8)—O(3)	111·5 (10)	112·8 (10)
S(4)—C(6)—N(2)	124·9 (9)	122·3 (7)	C(7)—N(2)—C(9)	118·9 (10)	119·7 (9)	N(2)—C(9)—C(10)	126·9 (24)	125·8 (17)
						C(9)—C(10)—O(4)	143·0 (35)	136·2 (23)

(d) Ligand 3

	150 K	295 K		150 K	295 K		150 K	295 K
S(5)—C(11)	1·72 (1)	1·73 (1)	N(3)—C(12)	1·49 (2)	1·46 (1)	N(3)—C(14)	1·48 (2)	1·51 (1)
S(6)—C(11)	1·72 (1)	1·73 (1)	C(12)—C(13)	1·57 (2)	1·51 (2)	C(14)—C(15)	1·49 (2)	1·47 (2)
C(11)—N(3)	1·34 (1)	1·32 (1)	C(13)—O(5)	1·44 (2)	1·42 (1)	C(15)—O(6)	1·43 (2)	1·45 (1)
S(5)—C(11)—S(6)	111·2 (6)	112·4 (5)	C(11)—N(3)—C(12)	122·4 (9)	122·0 (8)	N(3)—C(12)—C(13)	112·7 (9)	114·8 (8)
S(5)—C(11)—N(3)	124·6 (8)	123·9 (7)	C(11)—N(3)—C(14)	119·3 (8)	120·3 (7)	C(12)—C(13)—O(5)	109·4 (11)	110·6 (9)
S(6)—C(11)—N(3)	124·1 (8)	123·7 (7)	C(12)—N(3)—C(14)	118·1 (9)	117·5 (8)	N(3)—C(14)—C(15)	115·9 (10)	115·3 (9)
						C(14)—C(15)—O(6)	114·5 (10)	114·0 (10)

and angles within the S_2CNC_2 groups of the three ligands are the same within experimental error and agree with corresponding distances and angles in other dithiocarbamatoiron(III) compounds (Albertsson & Oskarsson, 1977; Leipoldt & Coppens, 1973). Table 6 gives the deviations from least-squares planes through the S_2CN groups. The three $Fe{<}^S_S{>}C{-}N{<}^C_C$ groups are planar within 0·27 Å.

Since the hydroxy H atoms have not been located, the hydrogen bonds are inferred from the geometrical criterion $O\cdots O < 3.2$ Å. There are eight possible hydrogen-bond distances (Table 7), but only six H atoms are available for bonding so the hydrogen-bond system is probably disordered. This disorder is transmitted to the terminal $-C-OH$ groups, explaining their large thermal parameters and some odd bond distances.

Table 5. *The geometry of the coordination polyhedron compared with those of an O_h octahedron and a D_3 trigonal prism*

The torsion angles are calculated by method 1 of Dymock & Palenik (1975).

	150 K	295 K	O_h	D_3
Edge of triangular face (Å)	3·36 (2)	3·46 (3)	a	a
Height of prism (Å)	2·582 (4) (0·77a)	2·622 (4) (0·76a)	0·816a	–
Torsion angle (°)	37 (5)	34 (2)	60	–
Tilt angle (between the triangular faces) (°)	2·1 (1·0)	2·2 (1·0)	0	0
Fe^{3+}–centre of prism (Å)	0·0800 (3)	0·0702 (2)	0	0
Ligand bite (Å)	2·840 (4) (0·84a)	2·868 (1) (0·83a)	a	–

Table 6. *Deviations (δ_i in Å $\times 10^3$) from the least-squares planes through the S_2CN groups*

Atoms marked with asterisks are not included in the least-squares calculations. The mean deviation $\sigma = (\sum w_i \delta_i^2 / \sum w_i)^{1/2}$ (one degree of freedom) is also given; w_i is the inverted mean variance for the atomic coordinates.

	150 K	295 K		150 K	295 K		150 K	295 K
S(1)	0	0	S(3)	0	0	S(5)	1	0
S(2)	0	0	S(4)	0	0	S(6)	1	0
N(1)	−4	−1	N(2)	0	−6	N(3)	11	−4
C(1)	9	4	C(6)	0	17	C(11)	−25	15
*C(2)	−15	−13	*C(7)	23	8	*C(12)	−44	−80
*C(4)	15	12	*C(9)	−200	−266	*C(14)	243	259
*Fe	−11	−3	*Fe	−136	−128	*Fe	−3	−7
σ	4	2	σ	1	9	σ	12	8

Table 7. *Possible hydrogen bonds*

The superscripts give the transformation applied to the x,y,z values given in Table 3: (i) $1 - x, -y, 1 - z$; (ii) $x, y, 1 + z$; (iii) $x, -1 + y, z$; (iv) $1 - x, -y, -z$; (v) $-x, 1 - y, -z$; (vi) $-x,-y,-z$.

	150 K	295 K		150 K	295 K
O(1)$\cdots$O(2^i)	2·18 (3)	2·31 (3)	O(2)$\cdots$O(5^i)	2·89 (2)	2·90 (1)
O(1)$\cdots$O(4^{ii})	2·98 (2)	2·94 (2)	O(3)$\cdots$O(4)	2·69 (2)	2·70 (1)
O(1)$\cdots$O(5^{iii})	2·52 (2)	2·68 (2)	O(3)$\cdots$O(6^v)	2·69 (1)	2·69 (1)
O(2)$\cdots$O(4^{iv})	2·61 (2)	2·70 (1)	O(5)$\cdots$O(6)	2·67 (1)	2·66 (1)

Fig. 4. μ_{eff} as a function of mean observed Fe–S distances, d, for some structures with FeS_6 cores. Points (1)–(7) are from Leipoldt & Coppens (1973) and references therein; (8) this paper; (9) Albertsson & Oskarsson (1977); (10) Mitra, White & Raston (1976); (11) Healy & Sinn (1975); (12) Butcher & Sinn (1976); (13) Sinn (1976).

In spite of the hydrogen bonds in (I), its magnetic moments and those of $Fe[S_2CN(CH_3)_2]_3$ are almost the same over the whole range 80–300 K (the methyl complexes are only van der Waals bonded).

Fig. 4 shows the variation of μ_{eff} with the mean observed Fe–S distance (d) for some structures containing the FeS_6 core. It is an extension of Fig. 2 in Leipoldt & Coppens (1973). They reported a curvilinear relationship between μ_{eff} and d but the additional points indicate that μ_{eff} is also a function of other variables besides d, e.g. the substituent R in S_2CNR_2 and the number of solvate molecules in the structure. The outlier in the plot made by Leipoldt & Coppens (point No. 7) is now well within the set representing the high-spin compounds ($\mu_{eff} \geq 5$).

References

ALBERTSSON, J. & OSKARSSON, Å. (1977). *Acta Cryst.* B33, 1871–1877.

BLOM, B. & HÖRLIN, T. (1977). *Chem. Commun. Univ. Stockholm.* No. 5.

BONDI, A. (1964). *J. Phys. Chem.* 68, 441–451.

BUTCHER, R. J. & SINN, E. (1976). *J. Am. Chem. Soc.* 98, 2440–2449, 5159–5168.

CUKAUSKAS, E. J., DEAVER, B. S. & SINN, E. (1977). *J. Chem. Phys.* 67, 1257–1266.

DANIELSSON, S., GRENTHE, I. & OSKARSSON, Å. (1976). *J. Appl. Cryst.* 9, 14–17.

DYMOCK, K. R. & PALENIK, G. J. (1975). *Inorg. Chem.* 14, 1220–1222.

EWALD, A. H., MARTIN, R. L., SINN, E. & WHITE, A. H. (1969). *Inorg. Chem.* 8, 1837–1846.

HEALY, P. C. & SINN, E. (1975). *Inorg. Chem.* 14, 109–115.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

LEIPOLDT, J. G. & COPPENS, P. (1973). *Inorg. Chem.* 12, 2269–2274.

MITRA, S., WHITE, A. H. & RASTON, C. L. (1976). *Aust. J. Chem.* 29, 1899–1904.

SINN, E. (1976). *Inorg. Chem.* 15, 369–375.

WHITE, A. H., ROPER, R., KOKOT, E., WATERMAN, H. & MARTIN, R. L. (1964). *Aust. J. Chem.* 17, 294–313.