ACTA CHEMICA SCANDINAVICA 18 (1964) 619–626

The Crystal Structure of Sodium Methanethiosulphonate Monohydrate

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Sodium methanethiosulphonate monohydrate, $CH_3SO_2SNa \cdot H_2O$, crystallizes in the space group D_{2h}^{16} – *Pnma* with four formula units per unit cell, of dimensions $a = 6.49$ Å, $b = 5.55$ Å, $c = 16.23$ Å. The structure has been determined by X-ray methods, through projections along the a and b axes.

The methanethiosulphonate ion has mirror plane symmetry in the crystals. The bond lengths and angles found are. S–S = 1.98 ± 0.01 Å, S–O = 1.45 Å, S–C = 1.77 Å, ∠S–S–O = 110.8°, ∠O–S–O = 115.4°, ∠S–S–C = 108.4°. The S–S bond is shorter than bonds between two divalent sulphur atoms, and probably has some double-bond character.

The sodium ion and the water oxygen atom also lie in mirror planes. The sodium ion is surrounded by six nearest oxygen atoms at distances from 2.39 Å to 2.46 Å, in a distorted octahedral arrangement. Columns of such sodium-oxygen octahedra, joined through shared opposite faces, run through the crystal in the direction of the a axis.

Sulphur-sulphur bonds, where one of the sulphur atoms forms bond to its sulphur bonding partner only and to no other atom, are comparatively rare. They occur in the disulphide ion, as terminal bonds in the polysulphide ions, and in the thiosulphate and thiosulphonate ions. A sulphur atom, as acceptor, can be expected to add to another sulphur atom, as donor, to give a coordinate bond only if the donor is less electronegative than the acceptor, for example if the donor carries a negative charge as in the sulphide, disulphide and polysulphide ions. Since in sulphite and sulphinate ions the sulphur atom has, presumably, some positive charge and therefore is more electronegative than electroneutral sulphur, the sulphur-sulphur bonds in thiosulphate and thiosulphonate ions cannot be pure coordinate bonds, but should possess some π-bond character.[1]

The present work was carried out in order to determine the length of the sulphur-sulphur bond in a thiosulphonate ion. A survey of unit cells and space groups of some sodium and potassium thiosulphonates[2] indicated that sodium methanethiosulphonate monohydrate would be suitable for a crystal structure analysis. A discussion of some aspects of the results has been published.[3]

THE STRUCTURE ANALYSIS

Sodium methanethiosulphonate monohydrate, $CH_3SO_2SNa{\cdot}H_2O$, crystallizes from water as orthorhombic plates {001} bounded by {012} and {102}. There is perfect cleavage along the plate face. The axial lengths are,[2] $a = 6.49$ Å, $b = 5.55$ Å, $c = 16.23$ Å, and there are four formula units per unit cell. On the basis of systematic absences, the space group D_{2h}^{16}- *Pnma* was assumed, and proved correct through the structure analysis. This space group requires that the methanethiosulphonate ion, and also the water molecule and sodium ion, occupy special, fourfold positions; for the two former species these must be the mirror planes while the sodium ion could lie in mirror plane or symmetry centre.

The structure analysis is based on 53 observed $0kl$ reflections and 115 observed $h0l$ reflections, out of 61 and 133 attainable with Cu$K\alpha$ radiation. Intensities were estimated visually from zero-level Weissenberg photographs. Small crystals were used in order to minimize absorption (μ for Cu$K\alpha = 82$ cm^{-1}). The intensities were converted to relative structure amplitudes, and eventually brought to an approximately absolute scale by comparison with the calculated values. Viervoll and Ögrim's[4] atomic scattering curves for sulphur and hydrogen were used in the calculation of structure factors, and the curves of Berghuis *et al.*[5] for oxygen and carbon. For the sodium ion, a curve was constructed based on the neon curve of Berghuis *et al.*[5] at small scattering angles and the electroneutral sodium curve at intermediate and larger scattering angles. Summations were made by means of Beevers-Lipson strips, at 12° intervals along the *a* and *b* axes and at 6° intervals along the axis.

The projection along the *b* axis, normal to the mirror plane in which the S—S bond must lie if the assumed space group was correct, was worked out first. The $h0l$ Patterson map could be interpreted to give approximate coordinates for the two sulphur atoms and the sodium ion. These coordinates gave signs for 25 strong $h0l$ reflections, of which no signs changed later. The Fourier map based on these reflections indicated the positions of the lighter atoms, and a new Fourier summation including 55 additional reflections was carried out. The *a*-axis projection was then solved by means of the known *z* coordinates and the $0kl$ Patterson map.

The projections were refined through Fourier and Fourier difference syntheses. In the last structure-factor calculations, hydrogen contributions were included, with hydrogen positions in or close to peaks in the difference maps, particularly in the $h0l$ map where two carbon hydrogen atoms overlap exactly and the two water hydrogen atoms also do so if, as the difference maps indicated, they lie on each side of the mirror plane and not in the plane. The *R* indexes showed little change on inclusion of the hydrogen contributions, but the difference maps improved. The hydrogen coordinates used were, $x = 0.480$, $y = -0.114$, $z = 0.108$ for water hydrogen, $x = -0.170$,

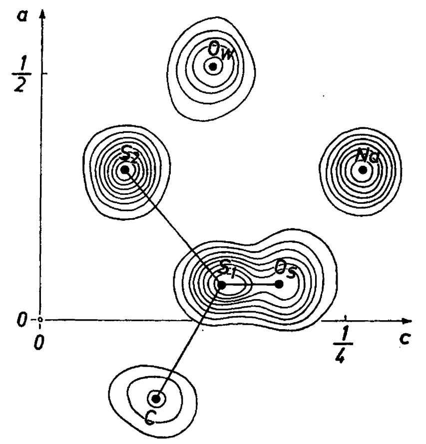

Fig. 1. Electron density projection of sodium methanethiosulphonate monohydrate along the *b* axis, showing one asymmetric unit. Contours at 3, 6, 9, ...e.Å^{-2} for sulphur and sulphonate oxygen, and at 3, 5, 7, ... e.Å^{-2} for carbon, sodium and water oxygen.

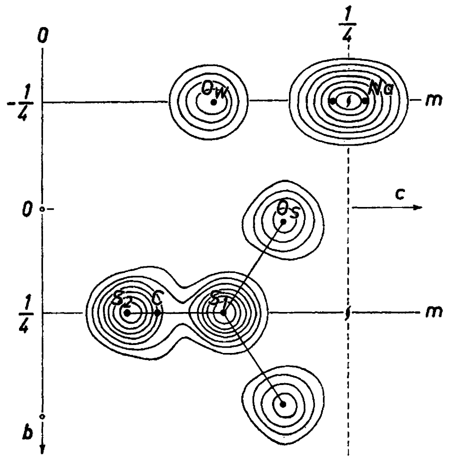

Fig. 2. Electron density projection of sodium methanethiosulphonate monohydrate along the *a* axis. Contours at 4, 6, 8, ...e.Å^{-2} for oxygen, and at 4, 8, 12, ... e.Å^{-2} for the other atoms.

$y = 0.088$, $z = 0.058$ for methyl hydrogen off the mirror plane, and $x = -0.302$, $y = 0.250$, $z = 0.132$ for the methyl hydrogen in the plane.

The $h0l$ and $0kl$ Fourier maps are shown in Figs. 1 and 2, and the final atomic coordinates are listed in Table 1. The following coordinates, used for the last structure-factor calculations, differ from those of Table 1: $x(S_1) = 0.0750$, $x(O_S) = 0.075$, $x(C) = -0.163$, $x(O_W) = 0.510$; $z(S_1) = 0.1495$ and 0.1490, $z(C) = 0.094$ and 0.093, in the $h0l$ and $0kl$ zone, respectively, $z(O_S) = 0.198$ in both zones. They were changed on the basis of gradients still present at the atomic positions in the difference maps, except for $z(S_1)$ which was taken as the weighted mean of the two values.

The observed and calculated $h0l$ and $0kl$ structure factors are listed in Table 2. The values of B in the temperature factor used in the calculation of structure factors were, in Å^2 units: $B = 2.5$ for S_1 and hydrogen, 2.8 for

Table 1. Atomic coordinates for sodium methanethiosulphonate monohydrate, in fractions of cell edges. Origin at a centre of symmetry.

	x	y	z
S_1	0.0756	0.250	0.1492
S_2	0.3030	0.250	0.0680
O_S	0.076	0.029	0.197
C	−0.161	0.250	0.095
Na	0.305	−0.250	0.263
O_W	0.512	−0.250	0.141

Table 2. Observed and calculated *h*0*l* and 0*kl* structure factors for sodium methanethiosulphonate monohydrate. The signs of the 0*kl* reflections correspond to an origin located at $y=\frac{1}{4}$, $z=\frac{1}{4}$, relative to the origin of Table 1.

l	F_o	F_c
	*h*0*l* zone	
	00*l*	
2	46.0	−56.3
4	39.6	−44.9
6	15.9	−16.7
8	14.8	−15.9
10	34.9	−32.5
12	12.4	+14.4
14	33.8	+33.6
16	3.6	+2.6
18	10.5	−12.0
20	10.5	+10.0
	10*l*	
1	21.0	+18.1
2	45.6	−46.8
3	57.6	−62.1
4	9.3	−5.9
5	48.2	+52.0
6	17.3	−16.2
7	9.6	−8.8
8	17.3	−19.2
9	<2.3	+3.2
10	34.7	+33.9
11	<2.6	+0.9
12	14.2	+14.0
13	3.0	+3.7
14	15.1	+16.0
15	3.0	−4.3
16	20.1	−20.9
17	11.7	−14.0
18	2.5	−1.3
19	4.8	+5.8
20	6.6	−10.0
	20*l*	
0	8.9	+9.7
1	29.8	−26.0
2	34.2	−33.9
3	28.5	+27.9
4	43.0	−45.0
5	69.8	+71.8
6	70.4	+73.2
7	38.5	−38.1
8	10.7	+10.8
9	13.8	−8.8
10	5.9	+4.3
11	15.4	−15.5
12	16.7	−17.9
13	10.3	+10.2
14	6.0	+5.8
15	11.5	−10.6
16	13.0	−13.0
17	3.7	+3.8
18	7.4	−8.0
19	10.6	+13.0
	30*l*	
1	7.1	+5.3
2	37.4	−37.7
3	18.6	+18.3
4	64.2	+64.4
5	5.7	−2.8
6	5.0	−3.3
7	18.3	−16.6
8	10.5	−10.7
9	27.8	−27.1
10	15.3	−13.8
11	12.3	+8.2
12	5.2	+4.9
13	<3.0	+1.0
14	8.7	−6.3
15	15.3	+17.7
16	4.3	−6.2
17	<2.4	+2.4
18	10.8	+13.3
19	<1.5	+2.3
	40*l*	
0	2.4	+4.0
1	81.3	−76.0
2	4.5	+4.4
3	10.0	−9.6
4	3.9	−0.1
5	8.3	−10.5
6	6.6	−7.2
7	2.8	−4.1
8	3.5	+4.5
9	<3.0	+1.1
10	7.4	−8.0
11	27.0	+25.8
12	<3.0	−0.1
13	11.1	+11.4
14	<2.8	+2.4
15	12.0	−17.3
16	6.2	+5.4
17	6.4	−7.4
	50*l*	
1	33.8	−33.4
2	20.4	−21.5
3	20.9	+19.4
4	14.9	+15.3
5	6.6	+6.5
6	<3.0	+0.5
7	3.0	−1.3
8	3.0	−2.5
9	25.4	+24.0
10	2.2	+0.1
11	2.0	+3.2
12	2.7	+2.6
13	9.7	−9.0
14	<2.4	−4.0
15	16.1	−18.3
16	<1.5	−4.7
	60*l*	
0	10.1	−5.5
1	6.0	+5.5
2	12.3	+12.3
3	<3.0	+4.5
4	9.2	+6.9
5	23.6	+23.9
6	24.4	−23.1
7	6.8	−5.7
8	<2.8	+0.1
9	2.7	−5.2
10	4.3	+2.7
11	10.0	−10.4
12	5.9	+3.9
13	<1.8	−1.6
14	3.4	−4.1
	70*l*	
1	2.7	−2.2
2	<2.7	+0.5
3	21.2	+21.5
4	10.4	−9.7
5	10.9	−11.5
6	3.8	−4.0
7	13.0	−14.9
8	1.8	−0.2
9	<1.9	−0.6
10	8.3	+6.8
	80*l*	
0	17.1	−20.6
1	3.8	+4.0
2	4.4	+3.2
3	<1.6	−0.3
4	<1.5	+1.9
	0*kl* zone	
	00*l*	
2	47.7	+55.3
4	40.9	−45.8
6	18.2	+16.9
8	16.3	−17.0
10	36.2	+32.7
12	13.6	+11.1

l	F_o	F_c
14	35.6	−37.7
16	<4.9	+ 0.9
18	14.6	+17.6
20	12.4	+16.1
	01*l*	
1	32.7	+29.6
3	87.8	−97.3
5	11.2	−12.2
7	32.4	−34.8
9	31.4	−31.9
11	26.7	+26.3
13	20.4	−18.8
15	21.8	−24.2
17	< 4.6	+ 2.2
19	< 3.5	+ 5.2
	02*l*	
0	109.4	+105.9
2	18.8	−15.0
4	47.2	−45.2
6	32.6	+32.8
8	31.2	+30.5
10	61.6	+67.2
12	30.8	+32.3
14	30.4	−29.4
16	< 4.6	− 6.9
18	< 3.8	+ 3.1
	03*l*	
1	7.3	− 4.4
3	69.2	−69.6
5	20.8	−13.7
7	16.2	−11.6
9	9.3	− 6.8
11	30.5	+31.6
13	10.4	−10.4
15	18.7	−21.4
17	< 3.7	− 1.7
	04*l*	
0	90.2	+94.3
2	24.6	+20.4
4	21.0	−17.6
6	4.8	+ 5.1
8	4.9	− 5.6
10	26.5	+24.6
12	11.1	+10.0
14	23.1	−24.7
16	< 3.3	− 1.7
	05*l*	
1	23.0	+21.1
3	31.1	−28.6
5	12.6	−10.7
7	16.8	−16.5
9	12.6	−12.6
11	10.5	+12.1
13	12.6	−11.1
	06*l*	
0	38.2	+38.1
2	< 4.4	− 0.4
4	13.9	−15.4
6	5.2	+ 4.2
8	5.4	+ 4.4
10	24.4	+21.5

S_2 and carbon, 3.5 for oxygen and 3.3 for sodium in the *h*0*l* zone; $B = 1.6$ for S_1, 2.8 for S_2, 2.4 for O_S, 3.0 for O_W, 2.0 for carbon, 3.0 for sodium and 2.7 for hydrogen in the 0*kl* zone. The reliability index *R*, with unobserved reflections included when $|F_c|$ exceeds the observable limit, is 0.010 for the *h*0*l* zone and 0.087 for the 0*kl* zone.

Standard deviations of atomic coordinates, estimated from the root-mean-square gradients in the difference maps and the curvatures of peaks in the electron density maps, are 0.004—0.005 Å for sulphur, 0.007—0.009 Å for sodium, 0.01—0.015 Å for oxygen and 0.02—0.025 Å for carbon. The *y* coordinates of all atoms except the two sulphonate oxygen atoms (and four hydrogen atoms) are fixed by symmetry relations. This gives standard deviations of 0.006 Å, 0.013 Å, and 0.023 Å, respectively, in S—S, S—O, and S—C bond lengths, about 0.015 Å in sodium-oxygen distances, and about 0.5°, 0.8°, and 1.5°, respectively, in S—S—O, S—S—C, and O—S—O bond angles.

THE METHANETHIOSULPHONATE ION

The ion has mirror plane symmetry in the crystals. Unit cell and space group data indicate that also the *p*-toluenethiosulphonate ion, in the potassium monohydrate salt and the anhydrous sodium salt, lies in a crystallographic

Table 3. Dimensions of the methanethiosulphonate ion

S−S = 1.979 Å
S−O = 1.45
S−C = 1.77

∠S−S−O = 110.8°
∠S−S−C = 108.4
∠O−S−O = 115.4

mirror plane.[2] Bond lengths and angles, from the atomic coordinates of Table 1, are given in Table 3.

The S—C bond, 1.77 Å, has the same length as in potassium methylenedisulphonate,[6] $K_2CH_2(SO_3)_2$. The S—O bond length, 1.45 Å, lies in the range, 1.44—1.46 Å, reported for sulphonates.[6,7]

The S—S bond, of length 1.98 ± 0.01 Å, is relatively short. The single covalent S—S bond length is usually taken [8,9] as 2.08 Å, and the double bond length as in the S_2 molecule in the ground state, 1.887 Å. In orthorhombic S_8 and rhombohedral S_6, the S—S bonds are 2.059 ± 0.002 Å and 2.057 ± 0.018 Å, respectively.[10] The shortest disulphide bonds reported are 2.02 ± 0.01 Å in sodium tetrathionate dihydrate,[11,12] 2.024 ± 0.014 Å in L-cystine dihydrobromide,[13] and 2.032 ± 0.004 Å in hexagonal L-cystine.[14] In disulphur monoxide, which has a bent structure like ozone, S—S = 1.884 ± 0.010 Å and is essentially a double bond.[15] It would appear from the length that the S—S bond in the methanethiosulphonate ion has some π-bond character; this agrees with the observed high stretching frequency of the bond.[16]

For the S—S bond in the analog, the thiosulphate ion, the following lengths have been reported: 1.97 ± 0.02 Å in sodium thiosulphate pentahydrate,[17] 2.01 ± 0.02 Å in anhydrous sodium thiosulphate,[18] 2.02 ± 0.01 Å in magnesium thiosulphate hexahydrate,[19] and 1.96 ± 0.01 Å in barium thiosulphate monohydrate;[20] the weighted mean is 1.99 Å. The S—S stretching frequency is higher than for the presumably single S—S bond in S-alkyl thiosulphate ions.[21]

According to Craig *et al.* [22,23] the sulphur 3*d* orbitals, which in the free atom are too diffuse to be likely to form useful bonds, become contracted and more suitable for π-bonding when sulphur is σ-bonded to electronegative atoms like oxygen. Cruickshank [7] has shown that two of the *3d* orbitals of sulphur are suitably oriented for overlapping with $p\pi$ orbitals of tetrahedral ligand atoms.

In covalent derivatives, the thiosulphonate and thiosulphate S—S bonds are markedly longer than in the ions. For example, in the oxidative dimerization products of the methanethiosulphonate and thiosulphate ions, dimethanesulphonyl disulphide [24,25] and the tetrathionate ion, [11,12] these bonds, the terminal ones, are 2.10—2.12 Å. This would be analogous to other cases where double-bond character is reduced or lost upon covalent bonding of coordinated sulphur or oxygen to a second centre, for example, to the increase in length of a S—O bond from 1.49 Å in the sulphate ion [7] to 1.603 ± 0.007 Å in potassium ethylsulphate [26-28] and 1.645 ± 0.005 Å in potassium pyrosulphate.[28]

THE IONIC ENVIRONMENT

The sodium ion lies in the mirror plane, 0.21 Å from the glide plane a which intersects the mirror plane at $z = \frac{1}{4}$, and is thus repeated every $a/2$ = 3.25 Å in an only slightly zigzagging line. The ion is surrounded by six oxygen atoms in a distorted octahedral arrangement: Two sulphonate oxygen atoms, O_S, at 2.40 Å and two O_S' atoms at 2.43 Å, one of each on each side of the mirror plane, one water oxygen atom, O_W, at 2.39 Å and one O_W' atom at 2.46 Å, both in the mirror plane, the primed and unprimed atoms being related

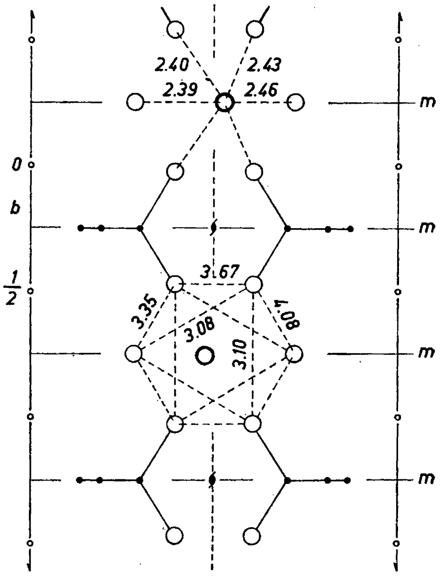

Fig. 3. The sodium-oxygen octahedra as seen along the *a* axis, with Na — O distances and O — O octahedral edges (Å). Heavy circles: sodium; light circles: oxygen. The screw axes parallel to the *a* axis close to the sodium positions (*cf.* Fig. 2) and the sodium ions on the other side of these screw axes, are not drawn.

through the operation of the glide plane. The lengths of the O — O edges of the octahedra range from 3.08 to 4.08 Å. Similar octahedral coordination of sodium ion, with comparable Na — O distances, occurs for example in sodium thiosulphate pentahydrate,[17] sodium dithionate dihydrate,[29] sodium tetrathionate dihydrate,[12] and rongalite.[30]

The top and bottom octahedral faces as seen down the *a* axis, with edges 3.10 Å and twice 3.08 Å, are shared between two and two adjacent octahedra and thus join the octahedra into an infinite chain in the *a*-axis direction, successive octahedra being symmetry related through the glide plane.

In the *b*-axis direction, parallel chains of octahedra $b = 5.55$ Å apart, are held together through sulphonate groups of thiosulphonate ions. Two O — S — O bridges per octahedron occur on each side of the mirror plane. Across the *c* plane at $z = 0$ and $\frac{1}{2}$ there are only loose non-bonded contacts between such layers of interconnected chains; this accounts for the observed perfect cleavage along the *c* plane.

Analogous layers of sulphonate-bridged chains of sodium-oxygen octahedra occur in the crystals of sodium tetrathionate dihydrate.[12] There, adjacent layers are held together through S — S bonds between thiosulphate groups, and no cleavage results.

The water molecule, which lies across the mirror plane, has with the used hydrogen coordinates the dimensions, $O-H = 0.95$ Å and $\angle H-O-H = 105.4°$. The Na — O — Na angle at which its oxygen atom coordinates to two sodium ions, at 2.39 and 2.46 Å, is 84.8°. The hydrogen atoms are not in possible hydrogen-bonding contact with any other oxygen atoms, but are 2.41 Å from the outer sulphur atom S_2 of the thiosulphonate ion. This may indicate a $O-H \cdots S$ hydrogen bond ($\angle O-H \cdots S_2 = 157°$, $O \cdots S_2 = 3.21$ Å).

Water-sulphur distances of 3.25 and 3.20 Å, with in the former the water hydrogen directed towards sulphur, occur in magnesium thiosulphate hexahydrate.[19]

Each oxygen atom of the sulphonate group coordinates to two sodium ions at 2.40 and 2.43 Å, at a Na—O—Na angle of 85.3°. Each methanethiosulphonate ion through its two oxygen atoms thus coordinates to four sodium ions, two on each side of the mirror plane.

REFERENCES

1. Foss, O. *Acta Chem. Scand.* **4** (1950) 404.
2. Foss, O. *Acta Chem. Scand.* **10** (1956) 871.
3. Foss, O. and Hordvik, A. *Acta Chem. Scand.* **11** (1957) 1443.
4. Viervoll, H. and Ögrim, O. *Acta Cryst.* **2** (1949) 277.
5. Berghuis, J., Haanappel, I. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. and Veenendaal, A. L. *Acta Cryst.* **8** (1955) 478.
6. Truter, M. R. *J. Chem. Soc.* **1962** 3393.
7. Cruickshank, D. W. J. *J. Chem. Soc.* **1961** 5486.
8. Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, Ithaca, New York 1960.
9. Abrahams, S. C. *Quart. Rev. (London)* **10** (1956) 407.
10. Donohue, J., Caron, A. and Goldish, E. *J. Am. Chem. Soc.* **83** (1961) 3748.
11. Foss, O. and Hordvik, A. *Acta Chem. Scand.* **12** (1958) 1700.
12. Foss, O. and Hordvik, A. *Acta Chem. Scand.* **18** (1964) 662.
13. Peterson, J., Steinrauf, L. K. and Jensen, L. H. *Acta Cryst.* **13** (1960) 104.
14. Oughton, B. M. and Harrison, P. M. *Acta Cryst.* **12** (1959) 396.
15. Meschi, D. J. and Myers, R. J. *J. Mol Spectry.* **3** (1959) 405.
16. Simon, A. and Kunath, D. *Z. anorg. allgem. Chem.* **308** (1961) 321.
17. Taylor, P. G. and Beevers, C. A. *Acta Cryst.* **5** (1952) 341.
18. Sándor, E. and Csordás, L. *Acta Cryst.* **14** (1961) 237.
19. Nardelli, M., Fava, G. and Giraldi, G. *Acta Cryst.* **15** (1962) 227.
20. Nardelli, M. and Fava, G. *Acta Cryst.* **15** (1962) 477.
21. Simon, A. and Kunath, D. *Chem. Ber.* **94** (1961) 1980.
22. Crang, D. P., Maccoll, A., Nyholm, R. S., Orgel. L. E. and Sutton, L. E. *J. Chem. Soc.* **1954** 332.
23. Craing, D. P. and Magnusson, E. A. *J. Chem. Soc.* **1956** 4895.
24. Foss, O. *Acta Chem. Scand.* **3** (1949) 986.
25. Sörum, H. *Acta Chem. Scand.* **7** (1953) 1.
26. Jarvis, J. A. J. *Acta Cryst.* **6** (1956) 327.
27. Truter, M. R. *Acta Cryst.* **11** (1958) 680.
28. Lynton, H. and Truter, M. R. *J. Chem. Soc.* **1960** 5112.
29. Martínes, S., García-Blanco, S. and Rivoir, L. *Acta Cryst.* **9** (1956) 145.
30. Truter, M. R. *J. Chem. Soc.* **1955** 3064; **1962** 3400.

Received December 28, 1963.