Table 3. *Bond distances (Å) in thiosulfates, including libration corrections*

	S—S	S—O(1)	S—O(2)	S—O(3)	⟨S—O⟩	Reference
$BaS_2O_3.H_2O$	1·987 (3)	1·493 (3)	1·482 (3)	1·483 (3)	1·486 (3)	(*a*)
$Na_2S_2O_3.5H_2O$	2·031 (4)	1·465 (3)	1·468 (3)	1·487 (3)	1·473 (3)	(*a*)
$(NH_4)_2S_2O_3$	1·997 (2)	1·492 (3)	1·488 (4)	1·487 (3)	1·489 (3)	(*a*)
$Na_2S_2O_3$	2·007 (1)	1·479 (1)	1·474 (1)	1·483 (1)	1·479 (1)	(*b*)
$MgS_2O_3.6H_2O$	2·024 (2)	1·474 (1)	1·474 (1)	1·481 (2)	1·476 (1)	(*c*)

References: (*a*) Armağan (1983). (*b*) This work. (*c*) Elerman *et al.* (1983).

found in combined X-ray and neutron studies and have been attributed to diffuse scattering (Bats & Fuess, 1982; Elerman *et al.*, 1983).

A rigid-body analysis of the thermal parameters of the thiosulfate group with the method of Schomaker & Trueblood (1968) gave no significant differences in thermal parameters from the neutron refinement and the rigid-body model.* Thus the $S_2O_3^{2-}$ group appears rigid in agreement with the observation by Armağan (1983) for other thiosulfates. Bond lengths corrected for libration are compared in Table 3 with similar values in other thiosulfates. From these data it is seen that there is some spread in bond distances among the various thiosulfates, resulting from the crystalline environment. The shortest S—S bond lengths correspond to the longer S—O lengths. The data for $Na_2S_2O_3$ coincide with the mean values of Table 3.

* See deposition footnote.

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$Pb_3Mn_7O_{15}$: a Further Change in the Space Group of a Published Crystal Structure

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Abstract. It was recently pointed out that the structure of $Pb_3Mn_7O_{15}$ which had been previously described in space group $Cmc2_1$ is better described in *Cmcm* using the original diffractometer data. It is shown here that a description in $P6_3/mcm$ with the metrically hexagonal cell (**a**—**b**)/2, **b**, **c** discloses a new class of systematic absences. It gives a residual of 3·1% when refined with 29 parameters on 274 unique reflections averaged from the same data. The σ's are improved, the distances, angles and thermal parameters are more regular and there is no indication of disorder. It is noted that quite accurate orientation is required to establish symmetry from Laue patterns and, in view of the hexagonal symmetry observed on Weissenberg photographs of $Pb_3Mn_7O_{15}$, it is argued that the orthorhombic symmetry of this compound is not beyond question.

Introduction. The lattice of $Pb_3Mn_7O_{15}$, described with the orthorhombic cell $a_o = 17{\cdot}28$ (1), $b_o = 9{\cdot}98$ (1), $c_o = 13{\cdot}55$ (1) Å by Marsh & Herbstein (1983) (MH) and Darriet, Devalette & Latourrette (1978) (DDL), is metrically hexagonal within the standard deviations with transformation matrix $\mathbf{a}_h = [\frac{1}{2}, -\frac{1}{2}, 0/010/001]\mathbf{a}_o$. The atomic coordinates in MH, transformed to this cell with the same origin, match within a few hundredths of an Å special positions in space group $P6_3/mcm$ except for one O atom which occupies a general position. The structure factor data from DDL transformed to intensities and averaged in this space group gave $R_{sym} = \sum(I_{obs}-\bar{I})/\sum I_{obs} = 12{\cdot}9\%$, the summations extending over the reflections for which multiple measurements could be found in the reported data. The 85 orthorhombic reflections hhl, $h \neq 0$, $l \neq 2n$ with Bragg

Table 1. *Cell data and atomic parameters for* $Pb_3Mn_7O_{15}$

Space group: $P6_3/mcm$, $a = 9{\cdot}98$ (1), $c = 13{\cdot}55$ (1) Å, $Z = 4$.

	Wyckoff position	x	y	z	B(Å^2)
Pb(1,4)†	6(g)	0·61181 (20)	0·61181	$\frac{1}{4}$	1·19 (8)‡
Pb(2,3)	6(g)	0·26524 (19)	0·26524	$\frac{1}{4}$	1·76 (9)‡
Mn(1,2,7)	12(i)	0·8317 (3)	0·1683	$\frac{1}{2}$	0·73 (7)
Mn(3,8)	8(h)	$\frac{1}{3}$	$\frac{2}{3}$	0·1480 (4)	0·39 (8)
Mn(4,6)	6(f)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0·63 (10)
Mn(5)	2(b)	0	0	0	0·73 (19)
O(1,3,4,9,12,14)	24(l)	0·4918 (19)	0·3346 (19)	0·0794 (11)	1·0 (3)
O(2,13,15)	12(j)	0·519 (3)	0·172 (3)	$\frac{1}{4}$	1·8 (4)
O(5,7,10,11)	12(k)	0·8355 (21)	0·8355	0·9257 (17)	0·8 (4)
O(6,8,16,17)*	12(k)	0·666 (3)	0·666	0·0659 (19)	1·5 (5)

† Numbers in parentheses correspond to the DDL nomenclature.

‡ The Pb(1,4) and Pb(2,3) atoms were refined anisotropically. The U_{ij} coefficients (×100) for $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12})]$ and $U_{11} = U_{22}$, are

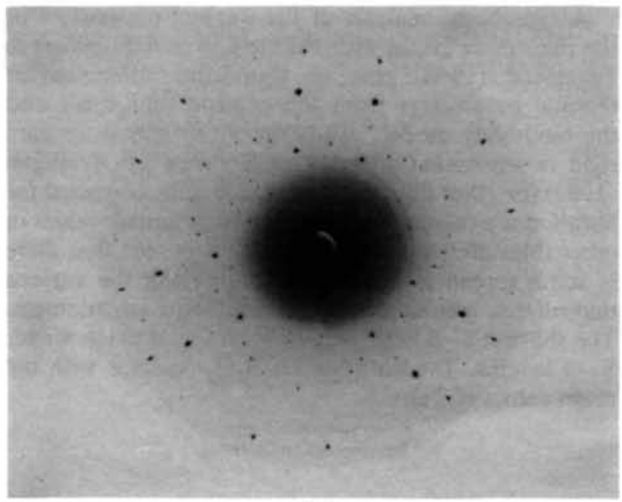
	U_{11}	U_{33}	U_{12}
Pb(1,4)	0·87 (6)	2·73 (12)	0·40 (8)
Pb(2,3)	0·78 (7)	4·93 (17)	0·25 (7).

angles below 60°, which are not systematic absences in $Cmcm$, but which transform to $0kl$, $l \neq 2n$ systematic absences in $P6_3/mcm$ are represented by seven measurements above $1{\cdot}5\sigma(I)$, all of them among the weakest intensities in the data set. Refinement gave $R_F = 3{\cdot}1\%$ with 29 parameters on 274 unique reflections with unit weights. Measurements for which one or more of the hexagonal equivalents in the orthorhombic unique set had not been reported were omitted before averaging. The results of this are shown in Table 1. The distances and angles are more regular than with orthorhombic symmetry, their σ's are reduced and the anomalies in thermal motion attributed to disorder by MH vanish.

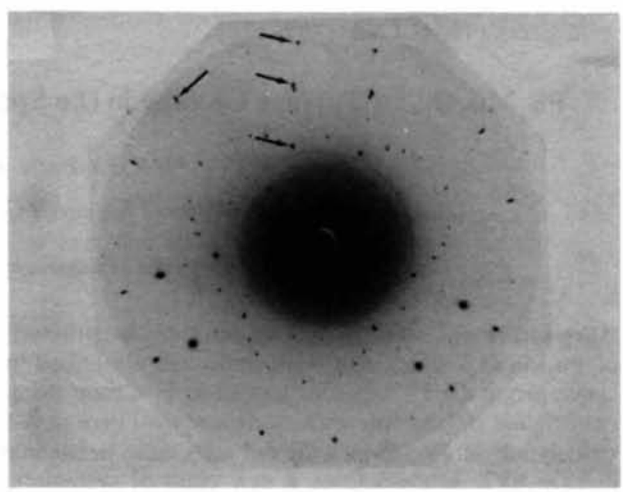
Although they were not included in the present refinement, none of the 243 unique hexagonal reflections for which no measurement at all was to be found in the DDL data was calculated larger than the lowest reported intensity. It is therefore consistent with the hexagonal model that they were not observed.

Discussion. In their assessment of the symmetry, DDL report conflicting results from their Weissenberg and Laue patterns indicating respectively hexagonal and orthorhombic symmetry. They accept the lower symmetry from Laue patterns and reject the higher one. It is well known that the intensities of some symmetry-related reflections on Laue patterns can be very much affected by tiny crystal-orientation errors, thus mimicking lower symmetry, if characteristic radiation is present in the incident spectrum (see Figs. 1a and 1b; see also Friedel, 1916). As there is no indication from their report that special precautions were taken to avoid characteristic radiation or to use an extremely well set crystal, the symmetry from their Laue patterns could be considered unreliable. The hexagonal symmetry from their Weissenberg patterns, which seems to be supported by their diffractometer data, should be accepted.

Although the $R_{\rm sym}$ of 13% is not impressive, it is not unexpected. From the numbers in the absorption-factor tables for spheres by Weber (1969), a properly oriented out-of-round of ±20% for a ground sample with $\mu\bar{d} = 3{\cdot}0$ could produce an $R_{\rm sym}$ in that neighbourhood, as one of us experienced with an EuAs 'sphere' which



(a)



(b)

Fig. 1. Laue patterns along [001] for a 0·3 mm diameter sphere of Al_2O_3 with space group $R\bar{3}c$ exposed with Mo K excited at 50 kV. (a) The crystal is set to better than 0·05°. The pattern displays the two-dimensional symmetry $3m$ as expected. (b) The crystal has been turned by 0·3°. The intensities of some reflections symmetry-related to the unique reflections indicated by arrows are now very different and the pattern displays only m symmetry.

gave data which were at first interpreted as monoclinic.† It was only after full refinement that this structure turned out to be hexagonal (Wang, Gabe, Calvert & Taylor, 1977). It seems from the DDL report that their 'bloc sphérique' was not ground and furthermore no absorption correction was applied. In this case, the expected variations in absorption would be even larger and an orthorhombic distribution of intensities is possible.

The structure description and the chemical conclusions in DDL remain valid because they recognize the chemical similarity of the now symmetry-related Pb(1) and Pb(4) as well as Pb(2) and Pb(3). In fact, no deviations from the hexagonal structure were discussed by DDL: even the distortions shown in their Fig. 3 are hexagonal in nature and are confirmed by the present refinement.

Dr R. E. Marsh (private communication) raises the point that, in view of the non-singularity of the refinement in the *Cmcm* subgroup, it is disturbing that some Pb atoms in the orthorhombic refinement differ from their refined hexagonal positions by a number of σ's which is statistically highly significant, especially for the Pb(2) and Pb(3) atoms. To this valid statistical argument, we offer the following comments:

(*a*) All the atomic deviations between the MH refinement and the hexagonal model, except two, correspond to less than half the r.m.s. thermal-motion amplitude. The exceptions, atoms O(15) and O(16), deviate by about 0·1 Å, *i.e.* 0·8 r.m.s. amplitude or 4 positional σ's. If the orthorhombic distortion in MH is assumed to be correct, the room-temperature thermal motion would suffice to establish locally the hexagonal symmetry of the structure and consequently to produce alternate orientations of the orthorhombic structure in the metrically hexagonal lattice, leading to atomic disorder or twinning. The resulting diffraction intensities of a macroscopic sample would therefore mimic hexagonal symmetry.

(*b*) In the MH refinement, Pb(3) behaves abnormally, and they suggest some disorder. In the hexagonal refinement, Pb(2) and Pb(3) occupy the same site which refines normally.

The normal distribution indicates that 11 out of 85 measurements of systematically absent intensities are expected to be larger than $1{\cdot}5\sigma$. This is consistent with the seven reported new systematic absences.

The metrically hexagonal lattice, the new class of systematic absences found in the DDL data, the satisfactory refinement in $P6_3/mcm$ and the disappearance of the anomaly at the Pb(3) position raise doubts about the space-group symmetries $Cmc2_1$ and *Cmcm* proposed for $Pb_3Mn_7O_{15}$ by DDL and MH respectively. We feel that this compound should be re-examined and the possibility that it is truly hexagonal or twinned should be considered by future investigators. If its orthorhombic character were to be confirmed, its structure should be described in terms of a very slight distortion of the above hexagonal structure. Unfortunately, no single crystal from the original preparation could be found by DDL and we were unable to attempt to synthesize it due to experimental difficulties.

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† In this case, A^* varied by 30% (at $\theta = 15°$) for $r_1 = 0{\cdot}0063$ and $r_2 = 0{\cdot}0073$ cm respectively ($\mu\bar{r} = 2{\cdot}78$).

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trans-Aquachloro[(1*S*,4*S*,7*S*,8*R*,11*R*,14*R*)-5,5,7*e*,12,12,14*e*-hexamethyl-1,4,8,11-tetra-azacyclotetradecane]chromium(III) Nitrate, $[CrCl(H_2O)(C_{16}H_{36}N_4)](NO_3)_2$

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Abstract. $M_r = 513{\cdot}96$, monoclinic, *Cc*, $a = 14{\cdot}560\ (5)$, $b = 11{\cdot}740\ (5)$, $c = 14{\cdot}772\ (7)$ Å, $\beta = 110{\cdot}83\ (3)°$, $Z = 4$, $V = 2360{\cdot}0$ Å^3, $D_x = 1{\cdot}447$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}632$ mm^{-1}, $F(000) = 1092$, $T = 293$ K, final $R = 0{\cdot}0614$ for 1894 observed reflections. The macrocyclic ligand, teta, forms a CrN_4

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