It should be emphasized that we have shown that an extra molecular entity is present only in the crystal data FBT's data arrived at the same conclusion as we (that there is present a molecular entity). In addition, their results (on crystals prepared by the method of FCC; Tomlinson, Hathaway, Billing & Nichols, 1969) are supported by polarized single-crystal electronic spectra and electron spin resonance spectra.

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Refinement of crystal structure of $CoMo_2S_4$

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In continuation of a structure analysis of $CoMo_2S_4$ based on powder diffraction data, the authors have refined the structure from single-crystal data. The space group was determined as $C2/m$; the final R index was 8·7%. The distorted S-octahedra about the Co and Mo atoms are discussed in detail.

A structure analysis of $CoMo_2S_4$ based on powder data (van den Berg, 1968) revealed that the compound crystallizes in the monoclinic system with the space group assumed to be $C2/m$. Fig. 1 shows a projection of the structure along the b axis with the unshaded atoms at $y=0$ and the shaded atoms at $y=\frac{1}{2}$. In order to determine the space group, and to determine the positional parameters and the individual anisotropic temperature parameters accurately, we have carried out a complete refinement of the structure by use of single-crystal data.

Single crystals were prepared (by J. N. Helle of this laboratory) in a gas transport reaction with iodine as the carrier gas. The cell constants obtained from diffractometer measurements were:

$$a = 13{\cdot}091 \pm 0{\cdot}002 \text{ Å}$$
$$b = 3{\cdot}277 \pm 0{\cdot}001$$
$$c = 5{\cdot}897 \pm 0{\cdot}001$$
$$\beta = 118{\cdot}91 \pm 0{\cdot}02°.$$

There are two structure units in a cell. The integrated intensities were measured on a Nonius automatic three-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation and the θ–2θ scan method. The measurements were extended to $d_{max} = 1{\cdot}6$ Å^{-1}. A total of 594 reflexions proved to be of significant intensity.

The crystal used for diffractometry was plate-like with dimensions of 0·2 × 0·15 × 0·07 mm; it was rotated about the b axis, pointing in the direction of the 0·2 mm edge. An azimuthal scan of the 020 and 040 reflexion was carried

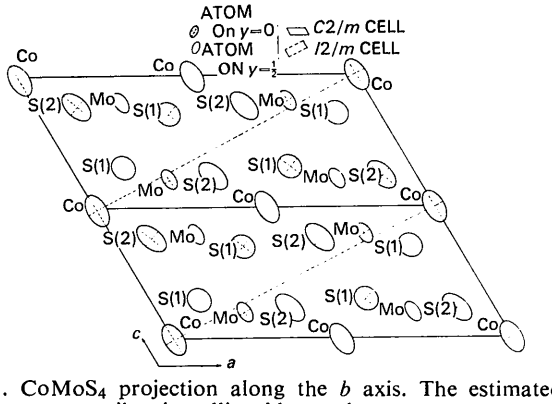
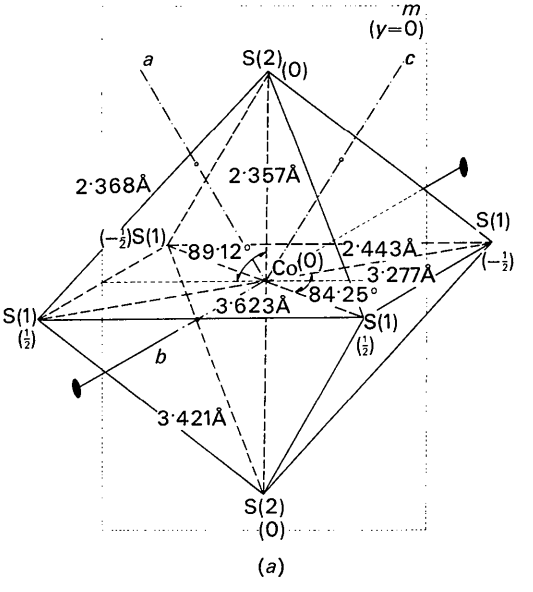
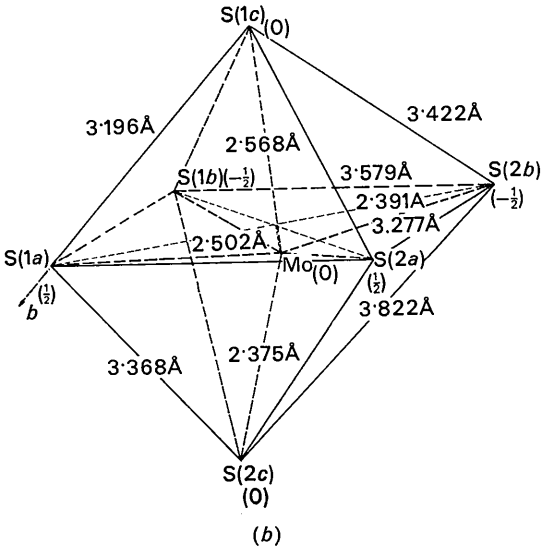


Fig. 1. $CoMoS_4$ projection along the b axis. The estimated vibration ellipsoids are shown.



(*a*)

Fig. 2. (*a*) Octahedral environment of the Co atom at (0,0,0). Local symmetry 2/*m*, *y* coordinates are given in brackets. Mirror planes at $y=0$ (drawn) and at $y=+\frac{1}{2}$, $y=-\frac{1}{2}$. (*b*) Octahedral environment of the Mo atom at (0·2569, 0, 0·2043). Mirror plane through the Mo, S(1*c*) and S(2*c*) atoms ($y=0$) and parallel to it at $y=+\frac{1}{2}$, $y=-\frac{1}{2}$. Local symmetry *m*, *y* coordinates are given in brackets.



(*b*)

Fig. 2 (*cont.*)

out to provide an estimate of the absorption correction. The ratio (maximum intensity/minimum intensity) was expected to be about 1·3 ($\mu_{Mo\ K\alpha}=57$ cm^{-1}). Instead, we observed for 020, $I_{max}/I_{min}=2{\cdot}56$, and for 040, $I_{max}/_{min}=2{\cdot}16$. This deviation from the expected value, together with the clearly visible splitting of the reflexions into $K\alpha_1$–$K\alpha_2$-peaks at a θ as low as 20°, suggested that the crystal was almost perfect, and that the intensities were affected by primary extinction. The same was also observed in the structure analyses of the MNb_3S_6 series (M = Mn, Fe, Co, Ni; Anzenhofer, van den Berg & Helle, 1968) and in this case a correction procedure was applied which led to very good results. This therefore encouraged us to use the same correction procedure for the $CoMo_2S_4$ intensity data. Essentially this meant an extrapolation of the intensities, I, to values which would have been measured at the azimuth angle, where $I=I_{max}$. The correction factor was derived from the azimuthal scans.

The refinement was started in $C2/m$ with the structure model derived by van den Berg (1968). After a few cycles, the conventional R index had dropped to 16·2%. From this point onwards 14 poorly determined structure factors were omitted; also individual anisotropic temperature factors were introduced into the subsequent refinement cycles, which finally brought R down to 8·7%.

The next problem was to verify the space group $C2/m$. We modified the structure parameters to meet the specific symmetry requirements of Cm and $C2$, respectively, and refined both models. Both models clearly moved towards the $C2/m$ model, finally terminating with a singularity in the matrix when the two models approached values of structure parameters which are fixed in $C2/m$. So the space group was verified as $C2/m$. The final structure parameters are presented in Table 1 together with the estimated standard deviations. Fig. 2(*a*) and (*b*) shows the distorted sulphur octahedra about the Co and Mo atoms respectively. Bond lengths and angles are included to give the shape and distortion of the octahedra. A discussion of the $CoMo_2S_4$ structure and its relation to the magnetic properties has been presented by van den Berg (1968).

A list of the structure factors involved in the refinement calculations may be obtained on request.

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Table 1. *Final structure parameters of* $CoMo_2S_4$

If parameters are not fixed by space group symmetry, their standard deviation in the last decimal figure is given between brackets. Space group symmetry requires $\beta_{12}=\beta_{23}=0$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{13}
Co	0	0	0	0·0010 (3)	0·037 (4)	0·012 (2)	0·0009 (4)
Mo	0·2569 (1)	0	0·2043 (3)	0·0003 (2)	0·052 (3)	0·005 (1)	0·0002 (2)
S(1)	0·3622 (3)	0	0·7016 (8)	0·0010 (3)	0·027 (4)	0·006 (2)	0·0005 (5)
S(2)	0·1045 (3)	0	0·7679 (8)	0·0010 (3)	0·026 (4)	0·007 (2)	0·0030 (5)

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Further refinement of the structure of WO_3.

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The structure of WO_3, previously determined from neutron diffraction data, has been further refined with the use of improved experimental and computational techniques. Standard deviations of position parameters were reduced by an average factor of 4·8.

Recently the structure of WO_3 was determined from neutron powder diffraction data (Loopstra & Boldrini, 1966). Since this determination was completed the neutron powder diffraction technique has been improved by the use of a wavelength of about 2·6 Å (Loopstra, 1966). Moreover, the least-squares refinement method based on peak profiles was