

Structure Determination of a Complex Pentamolybdodisulfate from Synchrotron Radiation Laue Diffraction Photographs: Derivation and Application of a Wavelength-Dependent Absorption Correction

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Abstract

Laue diffraction photographs were recorded with the SRS wiggler beam at the SERC Daresbury Laboratory for small electrochemically grown crystals of uncertain composition. Diffraction intensities were obtained from these photographs and the structure successfully solved using direct methods, the cell dimensions and space group having been previously determined from weak diffractometer measurements and Weissenberg photography. The formula of the compound was found to be $[\text{Mo}_5\text{S}_2\text{O}_{23}] \cdot [\text{N}(\text{C}_2\text{H}_5)_4]_4 \cdot \text{C}_6\text{H}_5\text{CN}$, containing a sulfate analogue of a previously determined pentamolybdodiphosphate ion. Refinement converged initially at $R = 0.131$ for 2858 unique reflections, but subsequent application of a new Laue absorption correction procedure improved the data, allowing convergence at $R = 0.107$. Tetrakis(tetraethylammonium) pentamolybdodisulfate benzonitrile solvate, $\text{C}_{39}\text{H}_{85}\text{Mo}_5\text{N}_5\text{O}_{23}\text{S}_2$, $M_r = 1535.9$, monoclinic, $P2_1/n$, $a = 12.712(5)$, $b = 30.83(2)$, $c = 14.745(6)$ Å, $\beta = 88.02(1)^\circ$, $V = 5775.3$ Å³, $Z = 4$, $D_x = 1.766$ g cm⁻³, $\mu = 27.22$ cm⁻¹ at $\lambda = 0.5$ Å, 42.89 cm⁻¹ at $\lambda = 0.6$ Å, 9.09 cm⁻¹ at $\lambda = 0.65$ Å and 22.83 cm⁻¹ at $\lambda = 0.9$ Å, $F(000) = 3120$, $T = 298$ K.

Introduction

It is now well known that crystal structures may be solved *ab initio* from data collected by Laue photography (Harding, Maginn, Campbell, Clifton & Machin, 1988; Clucas, Harding & Maginn, 1988; Gomez de Anderez, Helliwell, Habash, Dodson, Helliwell, Bailey & Gammon, 1989; Helliwell, Gomez de Anderez, Habash, Helliwell & Vernon, 1989). In each case, however, the composition of the crystal has been that expected on chemical grounds. Furthermore, the final converging R factor of the refinements has been consistently lower for organic than for organometallic compounds [previous refer-

ences and Maginn (1989)]. The quality of data collected by Laue photography can now approach that of conventionally collected monochromatic data for compounds which do not contain a significant anomalous scatterer or absorber, as shown by the structure determination of $\text{C}_{25}\text{H}_{20}\text{N}_2\text{O}_2$ (Helliwell, Gomez de Anderez *et al.*, 1989); the Laue intensity measurements allowed refinement to $R = 0.0529$ for 1914 reflections, compared with conventional Mo $K\alpha$ data which gave $R = 0.0460$ for 3487 reflections.

In the suite of computer programs hitherto used for processing Laue film images for structure solution (Helliwell, Habash, Cruickshank, Harding, Greenhough, Campbell, Clifton, Elder, Machin, Papiz & Zurek, 1989), there were no deliberate corrections for crystal absorption, although the wavelength-dependent part of this is to some extent compensated for in the *LAUENORM* wavelength-normalization procedure. The sample whose analysis is described here presented a significant challenge because of its uncertain composition, and because of the significant absorption and anomalous scattering. The crystals were grown electrochemically from a solution in benzonitrile containing tetrathiafulvalene, MoS_4^- and $\text{N}(\text{C}_2\text{H}_5)_4^+$ ions. It was expected that these crystals, which took some weeks to form on an electrode, would contain stacks of charged tetrathiafulvalene units interspersed with MoS_4^- ions (Bucket & Iggo, 1988).

Experimental

Although the crystals were too thin to obtain diffraction data of sufficient intensity using a conventional source, it was possible to obtain a , c and β using a Stoe Stadi-2 diffractometer, measuring the positions of 15 reflections with $2\theta < 30^\circ$, and make a provisional space-group assignment from weak long-exposure Weissenberg photographs. The unique b

axis was determined less accurately firstly from photography and later by positioning of the 040, 060 and 080 reflections during crystal alignment on the diffractometer.

The crystals were thin irregularly shaped plates of a rich deep-blue colour. One, of size $100 \times 140 \times 15 \mu\text{m}$, was used for Laue photographic data collection on station 9.7 of the SRS at the SERC Daresbury Laboratory. During data collection, the SRS conditions were: ring current = 163 mA, 2 GeV, wiggler at 5 T. The data set consisted of nine film packs, each consisting of six films interspersed with spacer films in the arrangement *FFsFsFsFsF*, exposed for 2 s each, at intervals of 20° rotation about the spindle (crystal in random orientation, *i.e.* not aligned along any axis), using a 0.2 mm collimator. The crystal-to-film distance was 48 mm. A 0.2 mm-thick aluminium attenuator was placed in the incident beam, to cut down the unused (but damaging) longer wavelengths present (Maginn, 1989).

A typical Laue photograph from this set is shown in Fig. 1. The spots are clear and sharp, indicating a high degree of order and low mosaic spread within the crystal.

This spot sharpness, together with the foreknowledge of cell dimensions, speeded processing through the suite of programs (Helliwell, Habash *et al.*, 1989); *NEWLAUE* (formerly *LGEM*) for crystal orientation determination, *GENLAUE* for orientation refinement and reflection position prediction, *INTLAUE* for reflection integration, *AFSCALE* for scaling within film packs and *LAUENORM* for wavelength normalization. Soft limits were set at

$\lambda_{\text{min}} = 0.25$, $\lambda_{\text{max}} = 2.5 \text{ \AA}$ and resolution limit $d_{\text{min}} = 1.05 \text{ \AA}$. The final data set was formed from seven of the nine film packs recorded (two performed poorly during processing, and were thus omitted from the final data set as their inclusion would have degraded data quality), and contained reflections measured in two wavelength ranges, 0.49–0.61 and 0.625–0.91 \AA . These ranges represent the regions between the Ag and Mo, and Mo and Br absorption edges, respectively, Ag and Br being present in the film and Mo present in the sample crystal. This data set, created from 5580 unmerged reflections, contained 2878 unique reflections with a merging *R* in *LAUENORM* of 0.132. The inclusion of data from lower and higher wavelength ranges would have given substantially poorer merging *R* factors of greater than 0.15.

Structure solution and refinement

Attempts at structure solution using the automatic Patterson-search routine of *SHELXS* (Sheldrick, 1986) failed, but application of the direct-methods option revealed a pentagonal arrangement of heavy atoms. These were assigned as molybdenum, and a Fourier synthesis phased on these atoms (*SHELX*; Sheldrick, 1976) revealed them to be linked into a larger cluster of lighter atoms, which were initially assigned as sulfur. On the basis of interatomic distances and apparent vibration parameters on refinement, all but two of these were eventually recognized to be oxygen. In subsequent Fourier syntheses, four tetraethylammonium ions and one benzonitrile solvent molecule were also located in the structure, giving the final formula of $[\text{Mo}_5\text{S}_2\text{O}_{23}]\text{[N}(\text{C}_2\text{H}_5)_4\text{]}_4\text{.C}_6\text{H}_5\text{CN}$. This agrees with CHN microanalysis results; calculated C = 30.47, H = 5.53, N = 4.56%, found C = 30.05, H = 5.59, N = 4.46%, and is a chemically understandable product of the reaction mixture.

Refinement converged at $R = 0.1307$ for 2858 reflections with $|F_o| > 4\sigma(|F_o|)$. Only the five molybdenum atoms were allowed to refine anisotropically; all atoms took up physically reasonable temperature factors, although those for some carbons in the tetraethylammonium groups were quite large, perhaps due to conformational disorder. No constraints or restraints of any sort were applied, except for constraining the phenyl ring of the solvent molecule as a regular hexagon.

At this point, a set of calculated structure factors for all 2878 reflections in the data set was produced from refined positional parameters and isotropic thermal parameters for all atoms, and they were used in an absorption correction procedure, as described below. This produced an absorption-corrected data set of 5580 reflections in seven unmerged batches, each corresponding to one of the contributing Laue

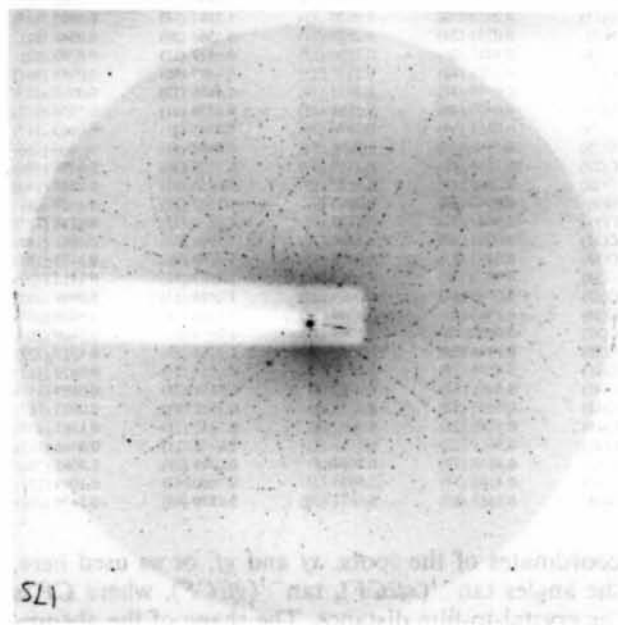


Fig. 1. A typical Laue photograph from this data set.

film packs, which was subsequently merged in *SHELX* to 2811 unique reflections with a merging R of 0.046, and used for final positional and thermal parameter refinement, with constraints as above. This time, again with only the five heavy atoms allowed to refine anisotropically and with unit weights, refinement converged at $R = 0.107$, number of parameters = 310, maximum shift/e.s.d. = 0.7 (except for one shift on U_{eq} of a carbon atom of 3.5), $S = 12.4$, maximum and minimum electron density in final difference map = 1.0 and $-1.0 e \text{ \AA}^{-3}$. H-atom contributions have not been included, and anomalous-scattering terms f' and f'' have not been included in the atomic scattering factors. Scattering factors for molybdenum were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic coordinates, thermal parameters, and selected bond lengths and angles are given in Tables 1 and 2.*

Absorption correction procedure

The Laue data used for structure solution and refinement was measured in the wavelength ranges 0.49–0.62 and 0.625–0.91 Å. The linear absorption coefficient of the compound rises from 27.22 cm^{-1} at 0.50 Å to 42.89 cm^{-1} at 0.60 Å, drops sharply at the molybdenum absorption edge (0.62 Å), and then rises slowly again from 9.09 cm^{-1} at 0.65 Å to 22.83 cm^{-1} at 0.90 Å. The variation of transmission through the crystal with wavelength is taken up in the wavelength-normalization procedure, *LAUENORM* (Helliwell, Habash *et al.*, 1989), whose primary purpose is to correct for the variation of incident intensity, scattering power and film response with wavelength. Allowance still needs to be made for angular variations in transmission of reflections measured at the same wavelength. For this, the process devised is a close analogue of *DIFABS* (Walker & Stuart, 1983) and has now been incorporated into the wavelength-normalization program *LAUESCALE* [previously described in Helliwell, Habash *et al.* (1989)].

In the Laue method, the crystal is stationary and, for any one film pack, it is only necessary to consider different path lengths for different diffracted beams; these should vary smoothly as a function of θ and azimuth, φ , and therefore as a function of position of the spot measured on the film. A two-dimensional polynomial surface is fitted in terms of the variables Q and R . Currently these may either be the film

* Lists of observed and calculated structure factors, anisotropic thermal parameters for heavy atoms, and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55729 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0303]

Table 1. Fractional coordinates of all located atoms with e.s.d.'s in parentheses

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U_{eq}
Mo(1)	-0.01454 (18)	0.13125 (9)	0.65717 (16)	0.0234 (16)
Mo(2)	0.36074 (19)	0.09955 (9)	0.84126 (16)	0.0261 (16)
Mo(3)	0.24518 (18)	0.11125 (9)	0.61877 (15)	0.0230 (15)
Mo(4)	-0.04840 (19)	0.16154 (10)	0.87916 (17)	0.0312 (17)
Mo(5)	0.17854 (21)	0.14366 (10)	0.98981 (16)	0.0329 (17)
S(1)	0.1042 (5)	0.0700 (2)	0.8267 (5)	0.0243 (18)
S(2)	0.1933 (5)	0.1895 (3)	0.7747 (5)	0.0244 (18)
O(3)	0.3345 (13)	0.1006 (6)	0.7168 (11)	0.0201 (43)
O(4)	-0.0831 (16)	0.1330 (7)	0.7755 (14)	0.0373 (52)
O(5)	0.0618 (15)	0.1792 (7)	0.9542 (12)	0.0309 (49)
O(6)	0.1097 (14)	0.1329 (6)	0.5882 (12)	0.0255 (46)
O(7)	0.0741 (14)	0.1013 (7)	0.8867 (12)	0.0270 (46)
O(8)	0.1108 (14)	0.0948 (6)	0.7299 (12)	0.0238 (44)
O(9)	0.0804 (14)	0.1804 (6)	0.7653 (11)	0.0225 (43)
O(10)	0.2303 (16)	0.0617 (7)	0.5803 (14)	0.0416 (53)
O(11)	0.4573 (21)	0.1392 (10)	0.8386 (18)	0.0626 (71)
O(12)	-0.0727 (15)	0.1738 (7)	0.6103 (13)	0.0347 (51)
O(13)	-0.0716 (15)	0.0897 (7)	0.6095 (13)	0.0334 (50)
O(14)	0.0288 (15)	0.0368 (7)	0.8144 (13)	0.0347 (50)
O(15)	0.2122 (16)	0.0531 (7)	0.8324 (13)	0.0359 (51)
O(16)	0.2918 (15)	0.1080 (7)	0.9543 (13)	0.0331 (49)
O(17)	0.2350 (16)	0.1596 (7)	0.8431 (14)	0.0373 (52)
O(18)	-0.1030 (21)	0.2098 (10)	0.8607 (18)	0.0650 (72)
O(19)	0.2069 (17)	0.2341 (8)	0.7975 (15)	0.0458 (56)
O(20)	0.4284 (18)	0.0536 (8)	0.8532 (15)	0.0497 (60)
O(21)	0.3252 (18)	0.1321 (8)	0.5436 (15)	0.0490 (60)
O(22)	0.2455 (16)	0.1791 (7)	0.6918 (14)	0.0406 (55)
O(23)	0.1253 (19)	0.1154 (9)	0.1718 (16)	0.0556 (66)
O(24)	0.2405 (19)	0.1838 (9)	1.0453 (16)	0.0544 (63)
O(25)	-0.1333 (20)	0.1403 (9)	0.9549 (17)	0.0597 (67)
N(1)	0.5932 (21)	0.1956 (10)	0.5868 (18)	0.0422 (69)
C(1)	0.4870 (36)	0.2068 (16)	0.6402 (31)	0.0699 (120)
C(2)	0.4767 (56)	0.2532 (23)	0.6625 (49)	0.1117 (194)
C(3)	0.6004 (36)	0.2167 (17)	0.4996 (30)	0.0698 (119)
C(4)	0.5151 (39)	0.2083 (18)	0.4386 (33)	0.0776 (133)
C(5)	0.6854 (30)	0.2145 (14)	0.6366 (25)	0.0521 (97)
C(6)	0.6873 (43)	0.1915 (21)	0.7367 (37)	0.0906 (150)
C(7)	0.5930 (37)	0.1497 (17)	0.5709 (31)	0.0715 (123)
C(8)	0.5141 (76)	0.1533 (38)	0.5120 (65)	0.1536 (303)
N(2)	0.2766 (19)	-0.0258 (9)	1.0648 (16)	0.0344 (63)
C(11)	0.3608 (32)	0.0085 (15)	1.0901 (28)	0.0579 (105)
C(12)	0.3226 (34)	0.0418 (16)	1.1434 (29)	0.0683 (116)
C(13)	0.1932 (49)	-0.0046 (20)	1.0036 (41)	0.0958 (172)
C(14)	0.1108 (39)	-0.0363 (18)	0.9723 (33)	0.0769 (129)
C(15)	0.3320 (41)	-0.0586 (19)	1.0218 (35)	0.0864 (142)
C(16)	0.3684 (52)	-0.0473 (25)	0.9188 (45)	0.1121 (190)
C(17)	0.2177 (31)	-0.0392 (14)	1.1497 (27)	0.0588 (105)
C(18)	0.2927 (39)	-0.0620 (18)	1.2197 (34)	0.0803 (135)
N(3)	0.0733 (24)	0.2809 (11)	0.5566 (20)	0.0546 (81)
C(21)	0.1317 (26)	0.2380 (12)	0.5427 (22)	0.0392 (82)
C(22)	0.1861 (46)	0.2337 (22)	0.4497 (40)	0.0989 (161)
C(23)	0.0146 (38)	0.2753 (18)	0.6406 (32)	0.0758 (129)
C(24)	-0.0403 (48)	0.3198 (23)	0.6779 (41)	0.1034 (172)
C(25)	0.0011 (34)	0.2870 (16)	0.4745 (31)	0.0669 (117)
C(26)	-0.0682 (54)	0.2586 (24)	0.4488 (45)	0.1064 (186)
C(27)	0.1514 (42)	0.3159 (20)	0.5575 (36)	0.0858 (146)
C(28)	0.2208 (41)	0.3122 (19)	0.6355 (35)	0.0858 (140)
N(4)	0.0043 (20)	0.0807 (9)	1.3382 (17)	0.0357 (64)
C(31)	-0.0607 (38)	0.1230 (17)	1.3950 (32)	0.0758 (127)
C(32)	-0.0954 (42)	0.1486 (20)	1.3198 (37)	0.0881 (148)
C(33)	0.0562 (53)	0.0610 (25)	1.4149 (46)	0.1152 (195)
C(34)	0.0920 (59)	0.1025 (28)	1.4669 (51)	0.1513 (209)
C(35)	-0.0713 (44)	0.0609 (20)	1.2894 (37)	0.0909 (155)
C(36)	-0.1563 (52)	0.0344 (24)	1.3393 (44)	0.1070 (183)
C(37)	0.0899 (70)	0.1003 (35)	1.2613 (61)	0.1469 (269)
C(38)	0.1696 (64)	0.1287 (30)	1.3358 (55)	0.1317 (227)
C(41)	0.4575 (22)	-0.0531 (8)	0.6684 (21)	0.0670 (113)
C(42)	0.5445 (22)	-0.0662 (8)	0.6151 (21)	0.0887 (147)
C(43)	0.6097 (22)	-0.0355 (8)	0.5729 (21)	0.0992 (167)
C(44)	0.5880 (22)	0.0082 (8)	0.5841 (21)	0.1365 (245)
C(45)	0.5011 (22)	0.0213 (8)	0.6375 (21)	0.0666 (113)
C(46)	0.4358 (22)	-0.0094 (8)	0.6796 (21)	0.0595 (106)
C(47)	0.4103 (54)	-0.0835 (25)	0.7000 (42)	0.1049 (171)
N(5)	0.3567 (62)	-0.1072 (29)	0.7179 (48)	0.1426 (206)

coordinates of the spots, xf and yf , or as used here, the angles $\tan^{-1}(xf/CF)$, $\tan^{-1}(yf/CF)$, where CF is the crystal-to-film distance. The shape of the absorption surface should be the same for all wavelengths.

Table 2. Selected bond lengths (Å) and bond angles (°)

Mo(1)—O(4)	1.92 (2)	Mo(5)—O(5)	1.93 (2)
Mo(1)—O(6)	1.85 (2)	Mo(5)—O(7)	2.43 (2)
Mo(1)—O(8)	2.25 (2)	Mo(5)—O(16)	1.87 (2)
Mo(1)—O(9)	2.52 (2)	Mo(5)—O(17)	2.31 (2)
Mo(1)—O(12)	1.67 (2)	Mo(5)—O(23)	1.62 (3)
Mo(1)—O(13)	1.64 (2)	Mo(5)—O(24)	1.69 (2)
Mo(2)—O(3)	1.88 (2)	S(1)—O(7)	1.46 (2)
Mo(2)—O(11)	1.73 (3)	S(1)—O(8)	1.49 (2)
Mo(2)—O(15)	2.38 (2)	S(1)—O(14)	1.40 (2)
Mo(2)—O(16)	1.87 (2)	S(1)—O(15)	1.49 (2)
Mo(2)—O(17)	2.45 (2)	S(2)—O(9)	1.47 (2)
Mo(2)—O(20)	1.67 (2)	S(2)—O(17)	1.48 (2)
Mo(3)—O(3)	1.90 (2)	S(2)—O(19)	1.43 (2)
Mo(3)—O(6)	1.91 (2)	S(2)—O(22)	1.41 (2)
Mo(3)—O(8)	2.38 (2)	N(2)—C(11)	1.56 (5)
Mo(3)—O(10)	1.64 (2)	N(2)—C(13)	1.56 (7)
Mo(3)—O(21)	1.61 (2)	N(2)—C(15)	1.37 (6)
Mo(3)—O(22)	2.35 (2)	N(2)—C(17)	1.49 (5)
Mo(4)—O(4)	1.83 (2)	C(11)—C(12)	1.37 (6)
Mo(4)—O(5)	1.89 (2)	C(13)—C(14)	1.52 (8)
Mo(4)—O(7)	2.43 (2)	C(15)—C(16)	1.61 (9)
Mo(4)—O(9)	2.38 (2)	C(17)—C(18)	1.59 (7)
Mo(4)—O(18)	1.67 (3)	C(41)—C(47)	1.20 (8)
Mo(4)—O(25)	1.66 (3)	C(47)—N(5)	1.03 (10)

O(4)—Mo(1)—O(6)	148.2 (9)	Mo(1)—O(4)—Mo(4)	131 (1)
O(12)—Mo(1)—O(13)	103 (1)	Mo(4)—O(5)—Mo(5)	126 (1)
O(3)—Mo(2)—O(16)	140.7 (8)	Mo(1)—O(6)—Mo(3)	128 (1)
O(11)—Mo(2)—O(20)	103 (1)	Mo(2)—O(16)—Mo(5)	131 (1)
O(3)—Mo(3)—O(6)	143.7 (8)	C(11)—N(2)—C(13)	110 (3)
O(10)—Mo(3)—O(21)	102 (1)	C(11)—N(2)—C(15)	105 (3)
O(4)—Mo(4)—O(5)	146.1 (9)	C(11)—N(2)—C(17)	108 (3)
O(18)—Mo(4)—O(25)	101 (1)	C(13)—N(2)—C(15)	113 (4)
O(5)—Mo(5)—O(16)	148.0 (8)	C(13)—N(2)—C(17)	106 (3)
O(23)—Mo(5)—O(24)	103 (1)	C(15)—N(2)—C(17)	115 (3)
O(7)—S(1)—O(14)	110 (1)	N(2)—C(11)—C(12)	114 (4)
O(8)—S(1)—O(14)	112 (1)	N(2)—C(13)—C(14)	113 (4)
O(14)—S(1)—O(15)	112 (1)	N(2)—C(15)—C(16)	114 (4)
O(9)—S(2)—O(19)	109 (1)	N(2)—C(17)—C(18)	112 (3)
O(17)—S(2)—O(19)	113 (1)	C(42)—C(41)—C(47)	112 (4)
O(19)—S(2)—O(22)	112 (1)	C(46)—C(41)—C(47)	128 (4)
Mo(2)—O(3)—Mo(3)	152 (1)	C(41)—C(47)—N(5)	167 (9)

The input to the program *LAUESCALE* is the list of reflection intensities (or structure factors) measured for one film pack, together with the wavelength of measurement and film coordinates of each, and the list of calculated structure factors from the isotropic structure refinement. The program carries out alternate cycles of (a) determination and refinement of the wavelength-normalization curve, $f(\lambda)$, and (b) fitting of a polynomial function to the two-dimensional absorption 'surface', until convergence is reached.

For each film pack of this compound, two cycles of normalization and absorption-surface fitting were carried out, finishing with another normalization, and using polynomials of order 6 and 6 respectively (the user may choose this order). The resulting absorption surface for one film pack is illustrated in Fig. 2. Finally, the seven film packs were merged (*SHELX*) to give 2811 reflections, $R_{\text{merge}} = 0.046$.

Results and discussion

Fig. 3 shows two views of the heavy ion. This consists of a pentagonal array of molybdenum atoms linked by oxygen bridges, and each with two terminal oxygen atoms. Tetrahedral sulfate groups sit above and below the heavy-atom plane; three

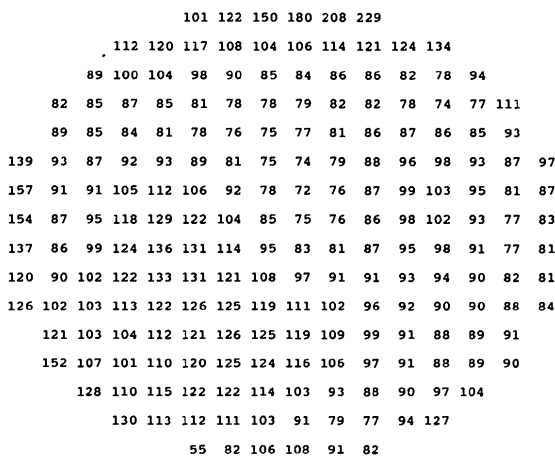


Fig. 2. Example of the absorption surface for one film pack, fitted from 570 reflections; the grid, covering the exposed area of the film, is in equal intervals of the angles $\tan^{-1}(xf/CF)$ and $\tan^{-1}(yf/CF)$, where CF is the crystal to film distance. All values have been multiplied by 100.

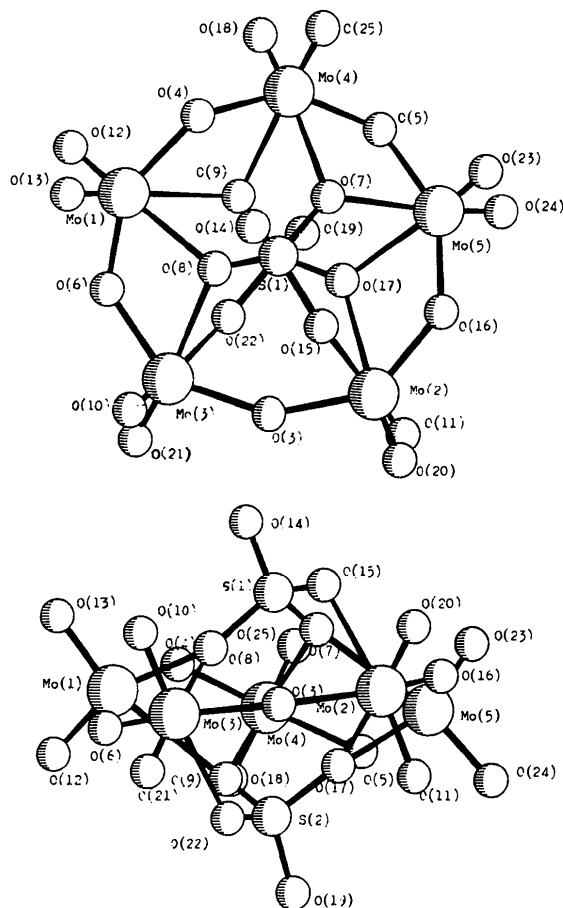


Fig. 3. The heavy ion, drawn by *PLUTO* (Motherwell & Clegg, 1978).

oxygens on each sulfate interact with the metal atoms. Assuming the metal atoms are molybdenum(V), the whole group has a total charge of $4-$. The analogous phosphate anion, $[\text{Mo}_5\text{P}_2\text{O}_{23}]^{6-}$, is known (Strandberg, 1973); the two ions are isostructural. However, in the phosphate case, the counterion is sodium, and that structure contains 13 water molecules which interact with the heavy ion; thus the crystals are not isostructural.

Intensity data measured by the Laue method have again allowed solution of the structure of a crystal too small for conventional diffractometer intensity measurements. Its power has been more dramatically demonstrated because the chemical constitution was quite unknown. Although the R factor and e.s.d.'s of bond lengths and angles are higher than usual, there is in this case no ambiguity about the chemistry (although reliable location of H atoms would not have been practicable). Solution by direct methods was possible here, despite the absence of axial and low-resolution reflection data. The question of sample absorption has been addressed and a satisfactory technique for its correction has been designed, implemented and demonstrated. However, the final R factor of 0.107 is still not as low as one would wish, or as low as has been achieved with Laue data for organic compounds (e.g. $R = 0.082$, Gomez de Anderez *et al.*, 1989; $R = 0.053$, Helliwell, Gomez de Anderez *et al.*, 1989; $R = 0.076$, Maginn, 1989). The variation of atomic scattering factors with wavelength, through the anomalous-dispersion terms f' and f'' , has still not been taken into account in the structure-factor calculations. This is likely to be significant and will be addressed shortly.

Furthermore, although for this compound, measurements with monochromatic radiation were used

initially to determine the unit-cell dimensions, procedures have now been developed for determining the axial ratios and cell angles (Carr, Cruickshank & Harding, 1992) and even absolute values of cell lengths (Carr, Dodd & Harding, 1993) from Laue diffraction patterns.

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Experimental Charge Density and Electrostatic Potential in Adenine Hydrochloride Hemihydrate at 123 K

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Abstract

The charge-density distribution in adenine hydrochloride hemihydrate has been determined from X-ray diffraction data collected to $(\sin\theta/\lambda) = 1.32 \text{ \AA}^{-1}$ at 123 K. Some significant differences in molecular geometry are observed when compared with the earlier room-temperature study

by Kistenmacher & Shigematsu [*Acta Cryst.* (1974), **B30**, 166–168]. Several multipole refinement strategies were evaluated. The electrostatic potential, isolated from the crystal lattice, and the deformation density in the nucleobase have been calculated following multipole refinements based on the rigid pseudoatom model of Stewart; they show features similar to those observed in