

## The Crystal Structure of Cadmium n-Butyl Xanthate

BY H. M. RIETVELD\* AND E. N. MASLEN

*Department of Physics, University of Western Australia, Nedlands, Western Australia*

(Received 31 March 1964)

The crystal and molecular structure of cadmium n-butyl xanthate ( $C_{10}H_{18}O_2S_4Cd$ ) has been determined by a three-dimensional X-ray analysis. The space group is  $P2_1/a$  and the cell dimensions are  $a = 11.59$ ,  $b = 5.84$ ,  $c = 25.7$  Å;  $\beta = 101^\circ 44'$ . There is one molecule per asymmetric unit. The structure has been solved by the heavy atom technique and refined by least-squares methods. The shapes of the two xanthate chains are markedly different. One has the normal extended arrangement, while the other has a curled configuration.

### Introduction

Water-soluble alkali metal xanthates are widely used as collectors in the separation and concentration of ores by flotation. The xanthate adsorbs onto the mineral in such a manner that the polar xanthate group is attached to the surface, and the non-polar alkyl chain is directed outwards. Much chemical and structural work has been carried out to determine the mode of absorption and the structure of the xanthate surface species. The infrared spectra of copper and zinc alkyl xanthate suggest that the xanthate group has a C=S bond and the structure of these molecules must be  $\left[ R-O-C \begin{array}{l} \swarrow S \\ \searrow S \end{array} \right]_2 M$  where M is the metal atom (Little, Poling & Leja, 1961*a, b*). X-ray analyses of arsenious and antimonious xanthates (Carrai & Gottardi, 1960; Gottardi, 1961) have shown that the xanthate groups in these molecules have a similar structure.

The spectra of aqueous solutions of alkali metal xanthates (Little, 1963) are similar to those of the solid copper and zinc xanthates, suggesting that the C=S group persists in ion solution. However, an X-ray structure determination of solid potassium xanthate (Mazzi, 1962) shows that the two C-S groups in this molecule are equivalent. In view of this contradictory result further structural information on divalent metal xanthates is of interest.

An analysis has therefore been made of the crystal structure of cadmium n-butyl xanthate  $\left[ C_4H_9-O-C \begin{array}{l} \swarrow S \\ \searrow S \end{array} \right]_2 Cd$  by X-ray diffraction techniques.

### Experimental

Cadmium n-butyl xanthate crystals were kindly supplied by Dr D. Dale. The crystals, which had been grown by recrystallization from hexanol, were in the

form of small plates. Oscillation and zero, first and second layer Weissenberg photographs were recorded for three crystal settings. The reflexions were systematically absent for  $h0l$  reflexions with  $h$  odd, and  $0k0$  reflexions with  $k$  odd, except for a very weak 010 spot which was assumed to be a Renninger reflexion. These absences are consistent with the space group  $P2_1/a$ . The cell dimensions measured from oscillation and Weissenberg photographs are

$$a = 11.59 \pm 17, \quad b = 5.84 \pm 9, \quad c = 25.7 \pm 4 \text{ \AA}; \\ \beta = 101^\circ 44' \pm 12'.$$

The unit-cell volume is then  $1705 \pm 70$  Å<sup>3</sup>, and the molecular weight is 410.91. Assuming four molecules per unit cell this gives a calculated density of  $1.61 \pm 6$ , which agrees well with a value of  $1.66 \pm 2$  measured by flotation.

### Structure determination

A number of crystals were trimmed down to  $0.09 \times 0.05 \times 0.3$  mm<sup>3</sup>, with the long axis parallel to a crystallographic axis. Equi-inclination Weissenberg photographs were recorded with the use of multiple films and exposures, for the layers with  $k=0$  to 5 from a specimen mounted along the  $b$  axis, and for the layers with  $h=0$  to 2 from a specimen mounted along the  $a$  axis. All photographs were taken with Cu  $K\alpha$  radiation.

The intensity data did not extend to the limit of the Cu  $K\alpha$  sphere even though exposures up to six days were used, since the size of the crystal had been kept very small to reduce absorption. Corrections for this factor were still necessary, but approximate values assuming the crystals to be cylinders with a radius of 0.04 mm were sufficiently accurate. Lorentz and polarization factors were calculated and layer scaling factors were determined from the relative intensities of reflexions common to the  $a$ - and  $b$ -axis photographs. After applying the scaling factor the correlation factor

\* Present address: Reactor Centrum Nederland, Petten (N. H.), Netherlands.

$$\frac{\sum |F_b + F_a| - 2\sum |F_b - F_a|}{\sum |F_b + F_a|}$$

for the 300 common reflexions was 0.89. The  $F$  values of the common reflexions were averaged, and after the inclusion of the other reflexions 1296 values were observed out of a possible 4330 within the Cu  $K\alpha$  sphere. The small number of the observed intensities was partly due to the low reflectivity of the crystals, but also to a strong pseudosymmetry, which caused systematic near absence of reflexions with  $\frac{1}{2}h+l$  odd for  $h$  even and  $k$  even, and  $\frac{1}{2}h+l$  even for  $h$  even and  $k$  odd.

With a mean isotropic temperature factor coefficient of  $4.0 \text{ \AA}^2$  the intensity data were modified to correspond to point atoms at rest and a sharpened three-dimensional Patterson synthesis was calculated. Large peaks were observed at (0.250, 0.583, 0.483), (0.500, 0.917, 0.000) and (0.750, 0.500, 0.483), the first being approximately half the height of the other two. These correspond to a cadmium position with coordinates (0.625, 0.2945, 0.2415) which compare well with the final values of (0.623, 0.2940, 0.2436).

The cadmium contribution to the structure factors was evaluated and the phases used to calculate a Fourier synthesis, from which positions of the four sulphur atoms were obtained. The lighter atoms could not be located unambiguously from this map because of strong pseudosymmetry, caused by the closeness of the cadmium atom to the line  $(\frac{1}{8}, y, \frac{1}{4})$ . The cadmium and sulphur positions were refined by means of a differential synthesis and structure factors were evaluated. A new scale factor and a mean isotropic temperature factor coefficient ( $B=5.63 \text{ \AA}^2$ ) were determined from a plot of  $\ln F_o/F_c$  versus  $\sin^2 \theta/\lambda^2$ . The  $R$  index on the corrected structure factors was 0.29. A Fourier synthesis using these phases showed the positions of all atoms other than hydrogens clearly. There were no spurious peaks.

The structure was refined by several rounds of least squares using the block diagonal approximation and a variety of weighting systems. A scheme where the weight of each reflexion,  $\omega$ , was given by

$$\omega = \frac{1}{\sqrt{[1 + \{(F_o - b)/a\}^2]}}$$

where

$$a = 5.65e^-, \quad b = -4.0e^-$$

yielded the most satisfactory results, and was used for all the later rounds of refinement. No hydrogen atoms were included, and all unobserved reflexions were excluded from the least-squares and structure factor calculations. Atomic scattering factors were obtained from *International Tables for X-ray Crystallography* (1962). It was noticed that the  $B$  values of atoms C(13), C(14), C(15), and C(25) increased steadily during the first few cycles and then stayed nearly constant at about  $10.0 \text{ \AA}^2$ . The apparent divergence

of the temperature factors suggested that these atoms had been misplaced, so a difference synthesis was computed using structure factors on all atoms except these four. This indicated that the positions originally chosen were correct, so the refinement was resumed.

After ten rounds of refinement an examination of the structure factors showed that, for all large terms, the calculated values were larger than the observed ones, indicating the presence of secondary extinction. Approximate correction factors were calculated by determining the constants  $k$  and  $\gamma$  of the equation

$$k^2 I_o = I_c \exp(-\gamma I_c)$$

from a plot of  $\ln(I_c/I_o)$  versus  $I_c$ .  $I_o$  is the observed and  $I_c$  the calculated intensity. The values obtained were  $\gamma = 8.44 \times 10^{-7}$  and  $k = 1.042$ .

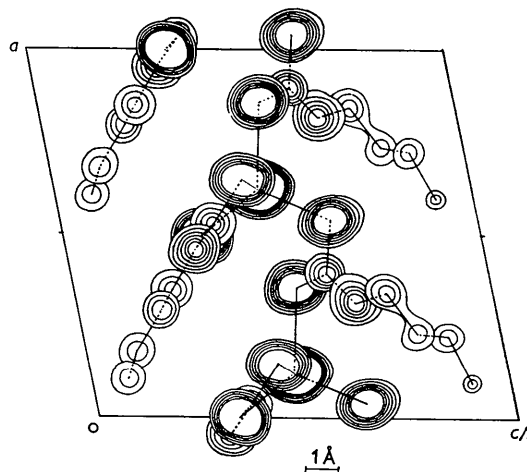


Fig. 1. Composite Fourier synthesis through the atomic peaks, projected on (010). Contour interval:  $1.0 \text{ e.\AA}^{-3}$ . Contours below  $2 \text{ e.\AA}^{-3}$  and higher than  $8 \text{ e.\AA}^{-3}$  omitted.

After applying these corrections to the observed structure factors it was found necessary to recalculate the inter-layer correlation factors. The  $R$  index on the rescaled data was 0.122. Further rounds of refinement failed to reduce either  $R$  or  $\sum \omega(F_o - F_c)^2$ , and the refinement was terminated. A Fourier synthesis calculated on the final structure factors is well resolved, but the heights of the peaks for the carbon atoms are rather low, presumably because of their large temperature factors. A summary of this synthesis projected down the  $b$  axis is shown in Fig. 1. The observed and calculated structure factors are listed in Table 1.

## Discussion

The final parameters, and the standard deviations for the coordinates calculated from the diagonal elements of the inverse to the normal equations matrix, are listed in Tables 2 and 3. The final bond lengths and angles are listed in Tables 4 and 5 and are

Table 1. *Observed and calculated structure factors*

| <i>h k l</i> | <i>F<sub>o</sub></i> | <i>F<sub>c</sub></i> | <i>h k l</i> | <i>F<sub>o</sub></i> | <i>F<sub>c</sub></i> | <i>h k l</i> | <i>F<sub>o</sub></i> | <i>F<sub>c</sub></i> | <i>h k l</i> | <i>F<sub>o</sub></i> | <i>F<sub>c</sub></i> |       |     |
|--------------|----------------------|----------------------|--------------|----------------------|----------------------|--------------|----------------------|----------------------|--------------|----------------------|----------------------|-------|-----|
| 0 0 1        | -                    | 22.8                 | -5           | 20.4                 | 29.7                 | 6            | -52.0                | -57.2                | 11           | -59.3                | -65.8                |       |     |
| 2            | -350.8               | -346.8               | 6            | 33.4                 | 35.8                 | 7            | 27.3                 | 32.4                 | 12           | -                    | 1.4                  |       |     |
| 3            | -19.5                | -23.4                | -7           | -57.2                | -64.3                | 8            | 49.3                 | 51.0                 | 13           | 63.1                 | 66.0                 |       |     |
| 4            | 92.3                 | 133.5                | -8           | -18.9                | -20.6                | 9            | -29.0                | -27.1                | 14           | 12.6                 | 15.8                 |       |     |
| 5            | 24.5                 | 20.9                 | 9            | 23.6                 | 25.0                 | 10           | -49.2                | -48.8                | 15           | -38.8                | -36.0                |       |     |
| 6            | -85.2                | -112.1               | 10           | -59.9                | -31.6                | 11           | 8.0                  | 11.9                 | 16           | -35.1                | -30.0                |       |     |
| 7            | -23.5                | -21.7                | 11           | -39.5                | -44.1                | 12           | 45.2                 | 44.7                 | 17           | 9.6                  | 13.6                 |       |     |
| 8            | 66.8                 | 72.5                 | 12           | 49.0                 | 52.3                 | 13           | -                    | -                    | 18           | 31.4                 | 29.3                 |       |     |
| 9            | 48.1                 | 41.5                 | 13           | 33.3                 | 41.9                 | 14           | -32.7                | -29.4                | 19           | -                    | 4.0                  |       |     |
| 10           | -128.5               | -149.1               | 14           | -48.7                | -47.7                | 15           | -                    | -5.3                 | 20           | -23.4                | -20.1                |       |     |
| 11           | -60.0                | -60.6                | 15           | -31.1                | -30.2                | 16           | 18.7                 | 17.8                 | 21           | -                    | 2.1                  |       |     |
| 12           | 105.0                | 121.5                | 16           | 22.4                 | 18.1                 | 17           | -                    | -7.6                 | 22           | 11.7                 | 8.8                  |       |     |
| 13           | 57.6                 | 58.4                 | 17           | 18.9                 | 20.5                 | 18           | -13.8                | -15.2                | -1           | -111.2               | -113.7               |       |     |
| 14           | -94.2                | -91.9                | 1 2 0        | -113.9               | -115.3               | 19           | -                    | 4.1                  | 2            | -69.2                | -64.5                |       |     |
| 15           | -48.1                | -45.0                | 1            | -108.1               | -111.5               | 20           | 10.3                 | 13.9                 | -3           | 85.0                 | 87.9                 |       |     |
| 16           | 46.3                 | 39.0                 | 2            | 92.8                 | 89.0                 | -1           | 49.0                 | 48.7                 | -4           | -                    | 3.2                  |       |     |
| 17           | 18.4                 | -                    | 3            | 59.5                 | 62.7                 | 2            | -62.1                | -64.6                | -5           | -94.8                | -97.0                |       |     |
| 18           | -                    | -2.0                 | 4            | -75.7                | -89.3                | -3           | -61.7                | -59.5                | -6           | 16.0                 | 11.5                 |       |     |
| 19           | -                    | -3.4                 | 5            | -30.8                | -33.9                | -4           | 25.8                 | 28.8                 | -7           | 115.8                | 125.1                |       |     |
| 20           | -                    | 0.7                  | 6            | 70.9                 | 82.8                 | -5           | 40.4                 | -                    | -8           | -                    | 3.5                  |       |     |
| 21           | -                    | 0.9                  | 7            | 35.5                 | 43.9                 | -6           | -10.1                | -                    | -9           | -94.2                | -109.6               |       |     |
| 22           | -                    | -10.1                | 8            | -29.4                | -35.1                | -7           | -23.0                | -24.7                | 10           | -34.7                | -36.1                |       |     |
| 23           | -12.1                | -10.1                | 9            | -12.1                | -11.9                | -8           | 8.2                  | 10.4                 | 11           | 54.3                 | 61.0                 |       |     |
| 0 1 0        | 0.0                  | 0.0                  | 10           | -28.1                | -24.4                | -9           | 22.1                 | 24.0                 | 12           | 43.9                 | 45.9                 |       |     |
| 1            | -176.9               | -180.9               | 11           | 33.2                 | 33.3                 | -10          | -                    | -9.6                 | 13           | -31.9                | -28.7                |       |     |
| 2            | 23.7                 | 45.7                 | 12           | 29.5                 | 21.4                 | -11          | -27.1                | -25.8                | 14           | -34.4                | -35.0                |       |     |
| 3            | 110.3                | 152.5                | 13           | -45.7                | -44.0                | -12          | -                    | -7.1                 | 15           | 20.8                 | 17.7                 |       |     |
| 4            | -75.7                | -91.1                | 14           | -                    | -2.1                 | -13          | 27.4                 | 30.7                 | 16           | 19.7                 | 16.7                 |       |     |
| 5            | -138.4               | -184.1               | 15           | 28.4                 | 21.1                 | -14          | -                    | -14.8                | 17           | -25.1                | -24.7                |       |     |
| 6            | 25.9                 | 27.2                 | 1 1          | 95.3                 | 92.7                 | -15          | -25.1                | -27.5                | -18          | -                    | -11.4                |       |     |
| 7            | 63.8                 | 84.0                 | -2           | 119.5                | 120.7                | -16          | -                    | -3.1                 | 19           | 30.6                 | 27.3                 |       |     |
| 8            | 21.9                 | 21.8                 | -3           | -55.2                | -55.2                | -17          | 6.5                  | 17.6                 | 20           | -                    | 16.8                 |       |     |
| 9            | -80.2                | -95.1                | -4           | -83.5                | -90.4                | 2 0 0        | 34.2                 | 34.7                 | 21           | -20.0                | -18.2                |       |     |
| 10           | -80.1                | -60.9                | -5           | -34.2                | -33.8                | 1            | -91.1                | -95.6                | 0            | 87.4                 | 84.4                 |       |     |
| 11           | 84.1                 | 87.8                 | -6           | 150.5                | 115.5                | -2           | -88.3                | -94.7                | 2 3 0        | 2                    | 1                    | -     | 3.6 |
| 12           | 23.0                 | 20.4                 | -7           | 38.7                 | 36.9                 | 3            | 82.7                 | 86.3                 | 3            | -79.1                | -82.4                |       |     |
| 13           | -73.1                | -77.4                | -8           | -98.4                | -114.0               | 4            | 51.4                 | 43.7                 | 3            | -                    | 4.4                  |       |     |
| 14           | -8.8                 | -9.9                 | -9           | 18.7                 | 25.3                 | 5            | -146.2               | -159.3               | 4            | 96.1                 | 102.2                |       |     |
| 15           | 95.6                 | 56.3                 | 10           | 79.1                 | 87.2                 | 6            | 29.1                 | 26.4                 | 5            | 30.3                 | 27.8                 |       |     |
| 16           | 12.3                 | 12.3                 | 11           | -23.7                | -25.8                | 7            | 95.5                 | 114.6                | 6            | -83.5                | -95.0                |       |     |
| 17           | -39.7                | -34.2                | 12           | -69.2                | -74.8                | 8            | 17.8                 | 8.9                  | 7            | -21.4                | -21.0                |       |     |
| 18           | -                    | -8.2                 | 13           | -                    | 8.8                  | 9            | -102.8               | -111.8               | 8            | 66.4                 | 73.4                 |       |     |
| 19           | 30.8                 | 27.3                 | 14           | 43.0                 | 44.1                 | 10           | -97.7                | -98.0                | 9            | 31.4                 | 30.4                 |       |     |
| 20           | 21.8                 | 15.6                 | 15           | 8.8                  | 8.8                  | 11           | -27.5                | -28.2                | 10           | 64.5                 | 64.9                 |       |     |
| 21           | -21.9                | -17.1                | 16           | -25.4                | -22.6                | 12           | 106.8                | 104.3                | 11           | -28.1                | -25.8                |       |     |
| 22           | -19.6                | -13.9                | 17           | 2.2                  | 2.2                  | 13           | -18.0                | -15.6                | 12           | 40.6                 | 42.3                 |       |     |
| 2 2 0        | -17.2                | -15.6                | 18           | 20.7                 | 16.7                 | 14           | -72.3                | -75.8                | 13           | -                    | 2.8                  |       |     |
| 0 2 0        | -7.5                 | -10.6                | 19           | -                    | -4.4                 | 15           | 32.4                 | 28.1                 | 14           | -22.0                | -19.7                |       |     |
| 1            | 64.5                 | 99.4                 | 20           | -14.1                | -11.9                | 16           | 49.0                 | 37.1                 | 15           | -                    | -1.1                 |       |     |
| 2            | -11.8                | -9.8                 | 1 3 0        | 62.6                 | 62.5                 | 17           | -27.5                | -28.2                | 16           | -                    | 5.5                  |       |     |
| 3            | -107.2               | -158.6               | 1            | 62.6                 | 62.5                 | 18           | -36.5                | -28.0                | 17           | -                    | 7.3                  |       |     |
| 4            | -25.6                | -31.7                | 2            | 28.7                 | 33.4                 | 19           | 29.0                 | 20.5                 | 18           | -13.9                | -12.8                |       |     |
| 5            | 105.6                | 147.7                | 3            | -69.2                | -74.8                | 20           | -27.6                | -26.0                | 19           | -7.9                 | -7.9                 |       |     |
| 6            | -88.8                | -112.8               | 4            | -38.7                | -53.6                | 21           | -17.9                | -14.7                | 1            | 18.3                 | 11.4                 |       |     |
| 7            | -41.8                | -46.9                | 5            | 47.1                 | 58.9                 | 22           | -26.7                | -17.9                | -2           | -119.7               | -118.1               |       |     |
| 8            | 41.3                 | 43.0                 | 6            | -38.3                | -32.3                | 23           | -                    | 2.3                  | -3           | -16.5                | -4.8                 |       |     |
| 9            | 27.7                 | 29.6                 | 7            | -38.4                | -39.3                | 24           | 23.2                 | 14.8                 | -4           | 102.1                | 105.3                |       |     |
| 10           | -28.1                | -24.2                | 8            | -41.6                | -44.1                | 25           | -                    | -1.9                 | -5           | -72.7                | -72.3                |       |     |
| 11           | -7.3                 | -                    | 9            | 14.5                 | 14.5                 | -1           | 193.7                | 181.1                | -6           | -77.4                | -14.8                |       |     |
| 12           | 36.9                 | 36.8                 | 10           | 20.1                 | 23.5                 | -2           | -56.1                | -36.5                | -7           | 54.6                 | 61.1                 |       |     |
| 13           | 20.1                 | 21.5                 | 11           | -21.1                | -15.9                | -3           | -212.2               | -208.2               | -8           | -                    | 8.3                  |       |     |
| 14           | -38.1                | -38.4                | 13           | 27.1                 | 24.2                 | -4           | -100.3               | -103.7               | -9           | -40.2                | -40.7                |       |     |
| 15           | -33.0                | -36.2                | 14           | -                    | 7.0                  | -5           | 226.9                | 231.3                | 10           | -                    | -2.8                 |       |     |
| 16           | 41.3                 | 36.3                 | 15           | -25.2                | -21.3                | -6           | 233.0                | 265.5                | 11           | 32.5                 | -                    |       |     |
| 17           | 34.8                 | 29.8                 | 16           | -20.1                | -21.1                | -7           | -129.8               | -152.3               | 13           | -                    | 11.3                 |       |     |
| 18           | -24.0                | -18.5                | 17           | 11.7                 | 8.0                  | -8           | 91.0                 | 45.1                 | 14           | -27.8                | -25.8                |       |     |
| 19           | -19.8                | -18.7                | 18           | 26.9                 | 27.2                 | -9           | -67.3                | -61.2                | 15           | -22.0                | -20.0                |       |     |
| 0 3 0        | 0.0                  | 0.0                  | 19           | -                    | 3.5                  | -10          | -77.8                | -88.6                | 16           | 61.0                 | 58.3                 |       |     |
| 1            | 43.1                 | 47.6                 | 20           | -20.9                | -19.8                | -12          | -46.4                | -51.4                | 1            | -30.1                | -32.3                |       |     |
| 2            | 21.4                 | 28.9                 | 21           | -                    | 8.9                  | -13          | 74.1                 | 77.3                 | 2            | -                    | 2.0                  |       |     |
| 3            | -43.9                | -57.6                | 22           | 13.3                 | 10.7                 | -14          | 33.1                 | 34.2                 | 3            | 10.5                 | 6.0                  |       |     |
| 4            | 45.7                 | -55.4                | -1           | -13.3                | -21.2                | -15          | -85.4                | -68.5                | 4            | -30.9                | -30.7                |       |     |
| 5            | 42.4                 | 59.2                 | -2           | 13.1                 | 7.2                  | -16          | -47.6                | -46.6                | 5            | -18.6                | -18.4                |       |     |
| 6            | 37.2                 | 49.3                 | -3           | 23.7                 | 24.8                 | -17          | 31.3                 | 29.3                 | 6            | 28.1                 | 28.1                 |       |     |
| 7            | -66.1                | -83.3                | -4           | -37.2                | -44.7                | -18          | 44.8                 | 42.1                 | 7            | 42.0                 | 40.2                 |       |     |
| 8            | 54.1                 | 64.9                 | -5           | -39.1                | -47.7                | -19          | -60.5                | -19.0                | 8            | -                    | -13.9                |       |     |
| 9            | 23.4                 | 25.6                 | -6           | 61.8                 | 73.3                 | -20          | -39.8                | -34.4                | 9            | -44.3                | -47.5                |       |     |
| 10           | -11.5                | -14.3                | -7           | 60.8                 | 73.8                 | -21          | -                    | 4.1                  | 10           | -                    | -                    |       |     |
| 11           | -37.5                | -42.6                | -8           | -42.8                | -47.0                | -22          | 26.6                 | 23.0                 | 11           | 27.3                 | 29.3                 |       |     |
| 12           | 39.0                 | 39.4                 | -9           | -62.4                | -74.9                | -23          | -                    | -10.9                | -11          | 60.7                 | 58.2                 |       |     |
| 13           | -                    | -10.1                | -10          | 29.0                 | 26.7                 | -24          | -                    | -10.2                | -12          | -36.1                | -34.7                |       |     |
| 14           | -                    | -10.1                | 11           | 49.6                 | 54.2                 | -25          | -                    | -111.7               | -13          | -61.1                | -51.9                |       |     |
| 15           | -                    | -10.1                | 12           | -17.9                | -19.8                | 2 1 0        | -116.0               | -120.1               | -4           | -                    | 10.1                 |       |     |
| 16           | -30.3                | -311.9               | 13           | -37.8                | -42.7                | 1            | -26.7                | -20.1                | -5           | -                    | 45.6                 |       |     |
| 17           | 9.9                  | 13.9                 | 14           | -                    | 7.2                  | 2            | 81.5                 | 88.9                 | -6           | 50.3                 | -                    |       |     |
| 18           | 21.1                 | 20.3                 | 15           | 27.1                 | 25.7                 | 3            | 15.5                 | 14.2                 | -7           | -30.5                | -29.0                |       |     |
| 19           | -16.2                | -15.8                | 16           | -                    | -6.2                 | 4            | -88.8                | -92.6                | -8           | -                    | 3.8                  |       |     |
| 0 4 0        | 0.0                  | 0.0                  | 17           | -23.1                | -22.9                | 5            | -28.5                | -26.9                | -9           | -                    | -7.4                 |       |     |
| 1            | 21.0                 | 22.0                 | 18           | 10.6                 | 18.4                 | 6            | 73.8                 | 79.1                 | -10          | 14.3                 | 18.0                 |       |     |
| 2            | -                    | -10.6                | 19           | 25.8                 | 27.2                 | 7            | 33.0                 | 32.4                 | -9           | -                    | -13.8                |       |     |
| 3            | -28.1                | -37.0                | 20           | -                    | -10.4                | 8            | -70.8                | -75.7                | 11           | -13.6                | -13.3                |       |     |
| 4            | -                    | -7.7                 | 21           | -21.5                | -22.2                | 9            | -29.4                | -31.7                | 12           | 22.0                 | 27.1                 |       |     |
| 5            | 17.1                 | 21.4                 | 22           | -                    | 1.5                  | 10           | 56.6                 | 67.3                 | 13           | 22.8                 | 29.2                 |       |     |
| 6            | 15.6                 | 20.2                 | 23           | 11.2                 | 14.6                 | 11           | 22.9                 | 24.0                 | 14           | -22.9                | -26.9                |       |     |
| 7            | 15.9                 | 12.2                 | 1 4 0        | 59.3                 | 48.9                 | 12           | -36.2                | -31.4                | 15           | -31.4                | -32.1                |       |     |
| 8            | -                    | -10.6                | 1            | 47.1                 | 46.3                 | 13           | -25.1                | -21.8                | 16           | -                    | -3.6                 |       |     |
| 9            | -22.5                | -23.3                | 2            | -44.2                | -48.7                | 14           | 49.0                 | 42.7                 | 17           | 12.1                 | 17.6                 |       |     |
| 10           | -24.3                | -23.2                | 3            | 66.4                 | 73.7                 | 15           | 36.4                 | 31.7                 | 2 5 0        | 1                    | -46.4                | -40.5 |     |
| 11           | -                    | -11.4                | 4            | 26.8                 | 27.2                 | 16           | -44.3                | -38.8                | 2            | 2.7                  | 2.7                  |       |     |
| 12           | 28.5                 | 27.3                 | 5            | 64.1                 | 78.7                 | 17           | -28.0                | -24.8                | 3            | 46.8                 | 42.0                 |       |     |
| 13           | 13.8                 | 19.0                 | 6            | -16.9                | -23.4                | 18           | 29.5                 | 22.3                 | 4            | -                    | 3.8                  |       |     |
| 14           | -17.6                | -20.3                | 7            | -58.4                | -67.8                | 19           | 23.9                 | 17.6                 | 4            | -43.0                | -41.0                |       |     |
| 15           | -20.2                | -22.6                | 8            | 21.1                 | 29.5                 | 20           | -22.1                | -17.9                | 5            | -                    | -7.4                 |       |     |
| 16           | 12.7                 | 12.9                 | 9            | 48.1                 | 55.1                 | 21           | -17.8                | -16.6                | 6            | 26.8                 | 27.7                 |       |     |
| 17           | -                    | 16.5                 | 10           | -34.0                | -37.6                | 22           | 13.5                 | 12.9                 | -1           | -                    | -5.5                 |       |     |
| 18           | -11.5                | -8.8                 | 11           | -36.9                | -33.3                | 23           | 24.6                 | 14.3                 | -2           | 30.7                 | 21.8                 |       |     |
| 0 5 0        | -                    | 0.0                  | 12           | 21.9                 | 26.2                 | 24           | -                    | -6.1                 | 3 1 0        | 0                    | 84.6                 | 72.3  |     |
| 1            | -                    | -17.1                | 13           | 27.1                 | 31.6                 | 25           | -17.7                | -11.4                | 1            | -51.6                | -48.0                |       |     |
| 2            | 12.1                 | 4.7                  | 14           | -12.9                | -2.1                 | -1           | -31.8                | -24.7                | 2            | -                    | -18.0                |       |     |
| 3            | -                    | 10.8                 | 15           | -24.4                | -31.9                | -2           | 24.3                 | 15.6                 | 3            | -                    | -11.6                |       |     |
| 4            | -16.2                | -24.5                | 16           | -                    | -6.2                 | -3           | 17.9                 | 14.9                 | 4            | -                    | -1.5                 |       |     |
| 5            | -9.4                 | -15.3                | 17           | 24.0                 | 26.3                 | -4           | -63.9                | -63.9                | 5            | -                    | -6.5                 |       |     |
| 6            | -13.1                | -13.1                | 18           | -                    | 6.8                  | -5           | -25.6                | -24.2                | 6            | 28.1                 | 27.3                 |       |     |
| 7            | 24.6                 | 9.4                  | 19           | -15.1                | -19.1                | -6           | 103.9                | 111.0                | 7            | 37.8                 | 37.9                 |       |     |
| 8            | -                    | 22.7                 | 20           | -                    | -1.7                 | -7           | 22.4                 | 17.6                 | 8            | -28.3                | -28.1                |       |     |
| 9            | -25.7                | -7.2                 | 21           | 12.5                 | 11.6                 | -8           | -90.8                | -103.7               | 9            | -19.8                | -17.3                |       |     |
| 10           | -                    | -24.5                | -1           | -51.4                | -68.8                | -9           | -24.9                | -23.0                | 10           | -14.3                | -4.7                 |       |     |
| 11           | 8.8                  | 2.5                  | -2           | -63.3                | -58.9                | -10          | 101.0                | 119.9                | 11           | -                    | 37.3                 |       |     |
| 12           | 62.3                 | 66.9                 | -3           | 42.8                 | 42.5                 | -11          | 51.6                 | 55.9                 | 12           | 25.0                 | 21.4                 |       |     |
| 13           | -29.3                | -59.6                | -4           | 50.8                 |                      |              |                      |                      |              |                      |                      |       |     |

Table I (cont.)

Table with columns for h k l, F0, Fc and multiple sets of these columns. It lists crystallographic data points for various hkl reflections, including intensity values (F0, Fc) and their corresponding Miller indices.

Table 1 (cont.)

| <i>h k l</i> | <i>F<sub>0</sub></i> | <i>F<sub>c</sub></i> | <i>h k l</i> | <i>F<sub>0</sub></i> | <i>F<sub>c</sub></i> | <i>h k l</i> | <i>F<sub>0</sub></i> | <i>F<sub>c</sub></i> | <i>h k l</i> | <i>F<sub>0</sub></i> | <i>F<sub>c</sub></i> |
|--------------|----------------------|----------------------|--------------|----------------------|----------------------|--------------|----------------------|----------------------|--------------|----------------------|----------------------|
| 19           | 9+0                  | 11+1                 | 3            | 17+5                 | 15+6                 | 5            | -                    | -10+3                | 1            | -                    | -5+6                 |
| -1           | 85+1                 | 79+1                 | 4            | -                    | -10+0                | 6            | 37+0                 | 30+8                 | 2            | 25+3                 | 22+1                 |
| -2           | -40+6                | -38+9                | 5            | -21+1                | -18+1                | 7            | -                    | 15+3                 | 3            | -                    | -8+8                 |
| -3           | -81+7                | -70+2                | 6            | -                    | 13+9                 | 8            | -18+3                | -21+2                | 4            | -21+6                | -21+9                |
| -4           | -                    | 13+2                 | 7            | -                    | 22+3                 | 9            | -5+7                 | 16+6                 | 5            | -                    | -5+8                 |
| -5           | 85+8                 | 37+5                 | 8            | -                    | -3+9                 | 10           | 8+4                  | 10+3                 | 6            | 18+4                 | 16+5                 |
| -6           | 41+0                 | 37+5                 | 9            | -21+4                | -26+2                | 11           | -                    | 15+7                 | 7            | 0+4                  | 8+2                  |
| -7           | -66+7                | -57+7                | 10           | -                    | -4+9                 | 12           | -                    | -7+3                 | 8            | -11+3                | -14+3                |
| -8           | -30+1                | -30+5                | 11           | 15+0                 | 19+4                 | 13           | -                    | -8+7                 | 9            | -                    | 8+1                  |
| -9           | 40+5                 | 32+5                 | 12           | 42+6                 | 40+3                 | 14           | 9+9                  | 13+9                 | 10           | 40+4                 | 42+5                 |
| -10          | 37+0                 | 24+9                 | 13           | -                    | -8+0                 | 15           | -                    | 6+6                  | 11           | -                    | -1+3                 |
| -11          | -46+7                | -43+2                | 14           | -65+3                | -38+7                | 16           | -11+8                | -14+3                | 12           | -41+9                | -42+6                |
| -12          | -13+8                | -15+1                | 15           | -21+6                | -22+0                | 17           | -                    | -3+1                 | 13           | -                    | -                    |
| -13          | 44+8                 | 40+8                 | 16           | 33+1                 | 26+5                 | 18           | 39+9                 | 33+3                 | 14           | 37+6                 | 40+7                 |
| -14          | -                    | 6+9                  | 17           | -37+6                | 35+1                 | 19           | -                    | -6+8                 | 15           | -                    | 5+7                  |
| -15          | -41+0                | -36+4                | 18           | -12+5                | -14+0                | 20           | -36+1                | -30+5                | 16           | -32+7                | -38+0                |
| -16          | -                    | -15+9                | 19           | -39+5                | -30+1                | 21           | -                    | 6+5                  | 17           | -                    | -12+5                |
| -17          | 23+5                 | 26+0                 | 20           | -                    | 14+1                 | 22           | 50+6                 | 48+9                 | 18           | 33+7                 | 40+4                 |
| -18          | -                    | 15+7                 | 21           | 27+7                 | 22+5                 | 23           | -7                   | 13+9                 | 19           | -                    | 18+0                 |
| -19          | -                    | -6+2                 | 22           | -                    | -17+4                | 24           | -52+7                | -50+1                | 20           | -29+1                | -35+0                |
| -20          | -12+4                | -13+8                | 23           | -17+3                | -18+1                | 25           | -22+0                | -21+0                | 21           | -14+2                | -                    |
| 6 3 0        | -76+9                | -76+9                | 24           | 13+3                 | 9+1                  | 26           | -47+6                | 45+0                 | 22           | 20+0                 | 25+6                 |
| 1            | -                    | -14+6                | 25           | 14+3                 | 19+3                 | 27           | -11                  | 21+8                 | 25+7         | 15                   | 10+6                 |
| 2            | 76+0                 | 69+9                 | 26           | -18+1                | -28+1                | 28           | -33+6                | -31+0                | 23           | -17+8                | -23+3                |
| 3            | 15+3                 | 15+3                 | 27           | 42+5                 | 36+1                 | 29           | -13                  | -                    | 24           | 1                    | 27+0                 |
| 4            | -67+8                | -61+4                | 28           | 26+3                 | 29+8                 | 30           | 13+3                 | 17+0                 | 25           | 11+7                 | 13+9                 |
| 5            | -8+8                 | -13+3                | 29           | -33+2                | -29+2                | 31           | -                    | 2+4                  | 26           | -25+8                | -32+3                |
| 6            | 33+1                 | 31+3                 | 30           | -32+7                | -33+6                | 32           | -12+5                | -17+0                | 27           | -                    | -18+7                |
| 7            | -                    | -                    | 31           | -                    | 1+8                  | 33           | 0                    | 17+0                 | 28           | 5                    | 3+6                  |
| 8            | -34+9                | -32+2                | 32           | 20+4                 | 28+6                 | 34           | 33+0                 | 27+2                 | 29           | 21+9                 | 26+3                 |
| 9            | -                    | -14+1                | 33           | -                    | -12+2                | 35           | 2                    | -                    | 30           | -                    | -12+6                |
| 10           | 32+8                 | 34+9                 | 34           | -11+0                | -12+2                | 36           | -31+4                | -29+4                | 31           | -10+1                | -18+0                |
| 11           | 20+2                 | 27+1                 | 35           | -34+3                | -28+9                | 37           | 4                    | 16+4                 | 32           | -1                   | -27+5                |
| 12           | -24+0                | -26+8                | 36           | -31+9                | -28+9                | 38           | 5                    | 25+2                 | 33           | -                    | -11+8                |
| 13           | -17+3                | -18+4                | 37           | 31+9                 | 26+7                 | 39           | 6                    | -                    | 34           | -3                   | 12+3                 |
| 14           | 22+0                 | 24+2                 | 38           | -29+0                | -27+9                | 40           | 7                    | -7+7                 | 35           | -4                   | 9+8                  |
| 15           | -                    | 10+0                 | 39           | -20+0                | -26+0                | 41           | -1                   | -4+2                 | 36           | -17+7                | -21+2                |
| 16           | 70+4                 | 68+6                 | 40           | -6+2                 | 21+2                 | 42           | -2                   | -                    | 37           | -6                   | -8+0                 |
| 17           | -                    | -4+7                 | 41           | -                    | 36+3                 | 43           | 3                    | 26+7                 | 38           | 26+4                 | 27+6                 |
| 18           | -48+2                | -38+7                | 42           | -8                   | -12+7                | 44           | -5                   | -15+0                | 39           | 4                    | 17+4                 |
| 19           | -                    | 36+2                 | 43           | -9                   | -33+3                | 45           | -5                   | -24+4                | 40           | -9                   | -27+2                |
| 20           | -                    | -17+7                | 44           | -                    | 14+6                 | 46           | -6                   | -31+2                | 41           | -                    | -1+0                 |
| 21           | -                    | -4+6                 | 45           | -                    | 21+0                 | 47           | -7                   | 28+0                 | 42           | 11                   | 23+6                 |
| 22           | 36+8                 | 29+0                 | 46           | 12                   | -                    | 48           | -8                   | 30+8                 | 43           | 12                   | 8+9                  |
| 23           | -                    | 7+3                  | 47           | 13                   | -11+4                | 49           | -9                   | -28+2                | 44           | 13                   | -13+7                |
| 24           | -32+9                | -29+9                | 48           | 14                   | 22+2                 | 50           | -10                  | -20+4                | 45           | 10 3 0               | 6+5                  |
| 6 4 0        | -12+7                | -12+7                | 49           | 15                   | 35+4                 | 51           | -11                  | 27+5                 | 46           | 1                    | 8+8                  |
| 1            | 35+1                 | 28+7                 | 50           | 2                    | -25+7                | 52           | -12                  | 0+1                  | 47           | 2                    | -17+3                |
| 2            | -                    | 10+1                 | 51           | 3                    | -26+1                | 53           | -13                  | -21+1                | 48           | 3                    | -10+7                |
| 3            | -32+3                | -33+4                | 52           | 4                    | 11+7                 | 54           | -14                  | -                    | 4            | 4                    | 20+3                 |
| 4            | -12+9                | -18+6                | 53           | 5                    | 14+6                 | 55           | -15                  | 12+9                 | 5            | 5                    | 8+2                  |
| 5            | 12+8                 | 20+4                 | 54           | 6                    | -6+2                 | 56           | 0 1 0                | 18+1                 | 6            | 6                    | -19+5                |
| 6            | -23+0                | -18+5                | 55           | 7                    | -8+9                 | 57           | 1                    | -                    | 7            | 7                    | -1+8                 |
| 7            | -2                   | 12+9                 | 56           | 8                    | -21+0                | 58           | 2                    | -10+3                | 8            | 12 0 0               | -20+3                |
| 8            | -3                   | -                    | 57           | 9                    | 7+4                  | 59           | 3                    | -                    | 9            | 1                    | -2+2                 |
| 9            | -4                   | -                    | 58           | 10                   | 32+7                 | 60           | 4                    | 31+8                 | 10           | 2                    | 19+3                 |
| 10           | -26+8                | -23+9                | 59           | 11                   | -                    | 61           | 5                    | -                    | 11           | 3                    | -                    |
| 11           | -12+9                | -16+7                | 60           | 12                   | -                    | 62           | 6                    | 37+7                 | 12           | 4                    | -19+7                |
| 12           | 40+1                 | 36+5                 | 61           | 13                   | -                    | 63           | 7                    | -33+7                | 13           | 5                    | -                    |
| 13           | 37+6                 | 31+4                 | 62           | 14                   | 20+2                 | 64           | 8                    | 27+7                 | 14           | 6                    | 15+9                 |
| 14           | -34+9                | -32+6                | 63           | 15                   | -                    | 65           | 9                    | -                    | 15           | 7                    | 4+5                  |
| 15           | -39+6                | -38+9                | 64           | 16                   | -19+4                | 66           | 10                   | 21+2                 | 16           | 8                    | -12+7                |
| 16           | -                    | -                    | 65           | 17                   | 15+5                 | 67           | 11                   | -                    | 17           | 9                    | -7+0                 |
| 17           | 18+1                 | 24+2                 | 66           | 18                   | 19+5                 | 68           | 12                   | -                    | 18           | 10                   | 9+9                  |
| 6 5 0        | 11+4                 | 12+1                 | 67           | 19                   | 76+5                 | 69           | 13                   | -10+3                | 19           | 11                   | 10+6                 |
| 1            | -                    | -15+2                | 68           | 20                   | 13+5                 | 70           | 14                   | 14+1                 | 20           | 12                   | -                    |
| 2            | -13+8                | -14+4                | 69           | 21                   | -65+3                | 71           | 15                   | -                    | 21           | 13                   | 21+2                 |
| 3            | -                    | -1+7                 | 70           | 22                   | -26+5                | 72           | 16                   | -                    | 22           | 14                   | -8+2                 |
| 4            | 13+4                 | 17+8                 | 71           | 23                   | 58+0                 | 73           | 17                   | -9+6                 | 23           | 15                   | -11+1                |
| 5            | -                    | 2+9                  | 72           | 24                   | 36+7                 | 74           | 18                   | -45+5                | 24           | 16                   | 13+2                 |
| 6            | -11+5                | -14+2                | 73           | 25                   | -65+4                | 75           | 19                   | -                    | 25           | 17                   | 18+4                 |
| 7            | 16+4                 | 19+4                 | 74           | 26                   | -29+0                | 76           | 20                   | 42+0                 | 26           | 18                   | -                    |
| 8            | -                    | -                    | 75           | 27                   | 66+4                 | 77           | 21                   | 18+9                 | 27           | 19                   | 8+7                  |
| 9            | -                    | -                    | 76           | 28                   | 25+9                 | 78           | 22                   | -24+1                | 28           | 20                   | -13+0                |
| 10           | -                    | -                    | 77           | 29                   | -50+0                | 79           | 23                   | -2+1                 | 29           | 21                   | -5+8                 |
| 11           | 27+3                 | 15+9                 | 78           | 30                   | -18+3                | 80           | 24                   | -17+8                | 30           | 22                   | -10+3                |
| 12           | -32+1                | -30+2                | 79           | 31                   | 30+8                 | 81           | 25                   | 12+1                 | 31           | 23                   | 6+2                  |
| 13           | -47+3                | -40+4                | 80           | 32                   | 12+6                 | 82           | 26                   | 17+0                 | 32           | 24                   | 7+9                  |
| 14           | 5                    | 24+2                 | 81           | 33                   | 12+6                 | 83           | 27                   | -11+5                | 33           | 25                   | -8+5                 |
| 15           | 30+7                 | 32+3                 | 82           | 34                   | -22+7                | 84           | 28                   | -13+5                | 34           | 26                   | -15+6                |
| 16           | -                    | -                    | 83           | 35                   | -15+8                | 85           | 29                   | -                    | 35           | 27                   | -                    |
| 17           | -                    | -                    | 84           | 36                   | 11+3                 | 86           | 30                   | 38+5                 | 36           | 28                   | 18+5                 |
| 18           | -10+6                | -14+6                | 85           | 37                   | 9+4                  | 87           | 31                   | -35+5                | 37           | 29                   | -14+5                |
| 19           | -                    | -                    | 86           | 38                   | -3+7                 | 88           | 32                   | -37+3                | 38           | 30                   | -19+8                |
| 20           | -10+4                | -14+7                | 87           | 39                   | -4+8                 | 89           | 33                   | 13+5                 | 39           | 31                   | 7+3                  |
| 21           | -                    | -                    | 88           | 40                   | -6+1                 | 90           | 34                   | -41+4                | 40           | 32                   | 14+9                 |
| 22           | 17+5                 | 18+6                 | 89           | 41                   | -87+7                | 91           | 35                   | -13+5                | 41           | 33                   | -8+7                 |
| 23           | -                    | 8+4                  | 90           | 42                   | -42+7                | 92           | 36                   | -19+3                | 42           | 34                   | -8+5                 |
| 24           | -                    | 1+8                  | 91           | 43                   | 87+8                 | 93           | 37                   | 7+7                  | 43           | 35                   | -3+8                 |
| 25           | -                    | 2+8                  | 92           | 44                   | -                    | 94           | 38                   | 21+7                 | 44           | 36                   | 13+9                 |
| 26           | -                    | -4+4                 | 93           | 45                   | -67+0                | 95           | 39                   | -7+5                 | 45           | 37                   | -                    |
| 27           | -                    | 0+0                  | 94           | 46                   | 20+4                 | 96           | 40                   | -23+3                | 46           | 38                   | 8+1                  |
| 28           | -                    | -5+1                 | 95           | 47                   | 32+4                 | 97           | 41                   | -                    | 47           | 39                   | -12+6                |
| 29           | 36+4                 | 30+9                 | 96           | 48                   | -34+4                | 98           | 42                   | 14+7                 | 48           | 40                   | -7+1                 |
| 30           | -                    | 1+5                  | 97           | 49                   | -16+5                | 99           | 43                   | 20+7                 | 49           | 41                   | 10+0                 |
| 31           | -30+5                | -28+9                | 98           | 50                   | -                    | 100          | 44                   | -                    | 50           | 42                   | 15+5                 |
| 32           | -                    | -6+5                 | 99           | 51                   | 6+1                  | 101          | 45                   | 24+0                 | 51           | 43                   | -4+0                 |
| 33           | -                    | 7+8                  | 100          | 52                   | 11+6                 | 102          | 46                   | -                    | 52           | 44                   | -9+1                 |
| 34           | -                    | 7+8                  | 101          | 53                   | 26+0                 | 103          | 47                   | -31+3                | 53           | 45                   | -7+3                 |
| 35           | -                    | 7+7                  | 102          | 54                   | -25+7                | 104          | 48                   | -                    | 54           | 46                   | 7+9                  |
| 36           | -                    | -10+1                | 103          | 55                   | -26+4                | 105          | 49                   | -6                   | 55           | 47                   | 34+5                 |
| 37           | -15+0                | -22+3                | 104          | 56                   | 18+2                 | 106          | 50                   | 21+1                 | 56           | 48                   | -9+5                 |
| 38           | -                    | 17+3                 | 105          | 57                   | 17+1                 | 107          | 51                   | -27+1                | 57           | 49                   | -2+6                 |
| 39           | -16                  | -                    | 106          | 58                   | -8+5                 | 108          | 52                   | -27+1                | 58           | 50                   | 8+2                  |
| 40           | -10+2                | -15+3                | 107          | 59                   | 18+2                 | 109          | 53                   | -                    | 59           | 51                   | 11+2                 |
| 41           | -                    | 6+7                  | 108          | 60                   | -8+5                 | 110          | 54                   | 7+6                  | 60           | 52                   | -2+5                 |
| 7 2 0        | -                    | -                    | 109          | 61                   | 52+2                 | 111          | 55                   | -20+0                | 61           | -1                   | -2+5                 |
| 1            | -                    | -                    | 110          | 62                   | -28+5                | 112          | 56                   | -                    | 62           | -2                   | -13+2                |
| 2            | -38+7                | -34+4                | 111          | 63                   | 21+7                 | 113          | 57                   | -12+1                | 63           | -3                   | -6+3                 |
| 3            | 36+1                 | 3+2                  | 112          | 64                   | -28+9                | 114          | 58                   | -10+2                | 64           | -4                   | 13+4                 |
| 4            | -13+9                | -14+7                | 113          | 65                   | 37+9                 | 115          | 59                   | 10+5                 | 65           | -5                   | -5+0                 |
| 5            | -38+6                | -34+6                | 114          | 66                   | -34+6                | 116          | 60                   | -                    | 66           | -6                   | -18+9                |
| 6            | 19+7                 | 19+2                 | 115          | 67                   | -29+8                | 117          | 61                   | 22+5                 | 67           | -7                   | -4+7                 |
| 7            | 54+9                 | 46+8                 | 116          | 68                   | 37+5                 | 118          | 62                   | -                    | 68           | -8                   | 8+3                  |
| 8            | -                    | 1+0                  | 117          | 69                   | 10+3                 | 119          | 63                   | 19+0                 | 69           | -9                   | 12+9                 |
| 9            | -31+5                | -                    | 118          | 70                   | -33+6                | 120          | 64                   | -42+1                | 70           | -                    | -                    |
| 10           | -                    | -1+2                 | 119          | 71                   | 25+3                 | 121          | 65                   | 1                    | 71           | -                    | -                    |
| 11           | -                    | -1+2                 | 120          | 72                   | -20+5                | 122          | 66                   | 2                    | 72           | -                    | -                    |
| 12           | 17+8                 | 21+9                 | 121          | 73                   | -10+5                | 123          | 67                   | 3                    | 73           | -                    | -                    |
| 13           | -                    | 1+2                  | 122          | 74                   | 10+9                 | 124          | 68                   | 4                    | 74           | -                    | -                    |
| 14           | -14+0                | -16+0                | 123          | 75                   | -59+0                | 125          | 69                   | 5                    | 75           | -                    | -                    |
| 15           | -                    | -2+5                 | 124          | 76                   | 18+2                 | 126          | 70                   | 6                    | 76           | -                    | -                    |
| 16           | -                    | 14+5                 | 125          | 77                   | -                    | 127          | 71                   | 7                    | 77           | -                    | -                    |
| 17           | -                    | 5+1                  | 126          | 78                   | -73+1                | 128          | 72                   | 8                    | 78           | -                    | -                    |
| 18           | -12+1                | -11+6                | 127          | 79                   | 25+3                 | 129          | 73                   | 9                    | 79           | -                    | -                    |
| 19           | 31+4                 | 26+6                 | 128          | 80                   | -15+8                | 130          | 74                   | 10                   | 80           | -                    | -                    |
| 20           | -                    | 7+1                  | 129          | 81                   | -6                   | 131          | 75                   | 11                   | 81           | -                    | -                    |
| 21           | -30+5                | -28+6                | 130          | 82                   | -7                   | 132          | 76                   | 12                   | 82           | -                    | -                    |
|              |                      |                      |              |                      |                      |              |                      |                      |              |                      |                      |

Table 2. Atomic coordinates

| Atom  | $x/a$  | $\sigma(x/a)$ | $y/b$  | $\sigma(y/b)$ | $z/c$  | $\sigma(z/c)$ |
|-------|--------|---------------|--------|---------------|--------|---------------|
| Cd    | 0.6231 | 0.0002        | 0.2940 | 0.0004        | 0.2436 | 0.0001        |
| S(11) | 0.3501 | 0.0007        | 0.1181 | 0.0015        | 0.2639 | 0.0004        |
| S(12) | 0.5377 | 0.0008        | 0.4377 | 0.0018        | 0.3222 | 0.0004        |
| O(1)  | 0.3174 | 0.0019        | 0.4029 | 0.0038        | 0.3343 | 0.0009        |
| C(11) | 0.3929 | 0.0030        | 0.3239 | 0.0054        | 0.3062 | 0.0013        |
| C(12) | 0.3421 | 0.0028        | 0.6035 | 0.0055        | 0.3707 | 0.0016        |
| C(13) | 0.2356 | 0.0050        | 0.6184 | 0.0074        | 0.3940 | 0.0017        |
| C(14) | 0.2231 | 0.0036        | 0.4255 | 0.0092        | 0.4330 | 0.0016        |
| C(15) | 0.1053 | 0.0057        | 0.4376 | 0.0129        | 0.4529 | 0.0023        |
| S(21) | 0.6471 | 0.0007        | 0.8654 | 0.0014        | 0.2253 | 0.0004        |
| S(22) | 0.4925 | 0.0008        | 0.4999 | 0.0014        | 0.1663 | 0.0004        |
| O(2)  | 0.4550 | 0.0017        | 0.9442 | 0.0030        | 0.1534 | 0.0008        |
| C(21) | 0.5275 | 0.0023        | 0.7757 | 0.0038        | 0.1811 | 0.0012        |
| C(22) | 0.3465 | 0.0027        | 0.8702 | 0.0049        | 0.1165 | 0.0013        |
| C(23) | 0.2852 | 0.0032        | 0.1097 | 0.0053        | 0.0958 | 0.0014        |
| C(24) | 0.1704 | 0.0033        | 0.0540 | 0.0074        | 0.0581 | 0.0014        |
| C(25) | 0.1026 | 0.0033        | 0.2784 | 0.0075        | 0.0428 | 0.0018        |

Table 3. Anisotropic thermal parameters

| Atom  | $b_{11}$ | $b_{12}$ | $b_{13}$ | $b_{22}$ | $b_{23}$ | $b_{33}$ |
|-------|----------|----------|----------|----------|----------|----------|
| Cd    | 0.0106   | -0.0001  | 0.0019   | 0.0232   | 0.0003   | 0.0035   |
| S(11) | 0.0094   | -0.0006  | 0.0034   | 0.0264   | -0.0034  | 0.0039   |
| S(12) | 0.0107   | -0.0175  | 0.0021   | 0.0550   | -0.0084  | 0.0041   |
| O(1)  | 0.0126   | 0.0057   | 0.0046   | 0.0340   | 0.0003   | 0.0037   |
| C(11) | 0.0148   | -0.0244  | 0.0025   | 0.0278   | -0.0014  | 0.0029   |
| C(12) | 0.0126   | -0.0341  | 0.0030   | 0.0331   | -0.0129  | 0.0051   |
| C(13) | 0.0363   | -0.0204  | 0.0094   | 0.0459   | -0.0067  | 0.0045   |
| C(14) | 0.0167   | 0.0287   | 0.0048   | 0.0982   | 0.0042   | 0.0034   |
| C(15) | 0.0365   | 0.0549   | 0.0161   | 0.1743   | 0.0080   | 0.0054   |
| S(21) | 0.0106   | 0.0028   | 0.0015   | 0.0232   | -0.0038  | 0.0047   |
| S(22) | 0.0137   | -0.0041  | -0.0008  | 0.0195   | 0.0023   | 0.0036   |
| O(2)  | 0.0112   | 0.0096   | 0.0025   | 0.0281   | 0.0010   | 0.0032   |
| C(21) | 0.0113   | -0.0010  | 0.0011   | 0.0076   | -0.0083  | 0.0036   |
| C(22) | 0.0098   | -0.0054  | -0.0001  | 0.0358   | 0.0015   | 0.0036   |
| C(23) | 0.0162   | 0.0245   | 0.0012   | 0.0417   | 0.0052   | 0.0034   |
| C(24) | 0.0146   | -0.0150  | 0.0016   | 0.0707   | -0.0002  | 0.0031   |
| C(25) | 0.0115   | 0.0036   | 0.0015   | 0.0546   | 0.0062   | 0.0060   |

also shown in Fig. 2. The C-C bond lengths of the butyl groups are consistent within the limits set by their standard deviations with the standard value of

1.54 Å for the C-C single bond (*International Tables*, 1962).

The O(1)-C(12)-C(13)-C(14) chain shows a rather unusual configuration having a *cis* oriented O(1)-C(12) bond which is not found on other xanthates (*e.g.* antimonic, arsenious or potassium xanthate). The cause of this is not clear, for there is no evidence of

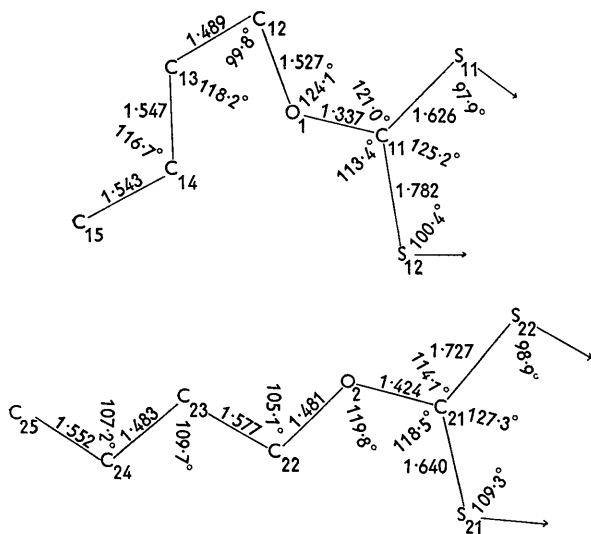


Fig. 2. Configuration of the butyl xanthate chains showing the bond lengths and angles.

Table 4. Bond lengths

| Atoms       | Bond length | e.s.d.  |
|-------------|-------------|---------|
| Cd-S(11)    | 2.619 Å     | 0.008 Å |
| Cd-S(12)    | 2.612       | 0.011   |
| Cd-S(21)    | 2.560       | 0.009   |
| Cd-S(22)    | 2.580       | 0.009   |
| S(12)-C(11) | 1.782       | 0.036   |
| C(11)-S(11) | 1.626       | 0.034   |
| C(11)-O(1)  | 1.337       | 0.041   |
| O(1)-C(12)  | 1.527       | 0.042   |
| C(12)-C(13) | 1.489       | 0.066   |
| C(13)-C(14) | 1.547       | 0.067   |
| C(14)-C(15) | 1.543       | 0.078   |
| S(22)-C(21) | 1.727       | 0.025   |
| C(21)-S(21) | 1.640       | 0.030   |
| C(21)-O(2)  | 1.424       | 0.033   |
| C(22)-C(23) | 1.577       | 0.045   |
| C(23)-C(24) | 1.483       | 0.053   |
| C(24)-C(25) | 1.552       | 0.061   |

Table 5. *Bond angles*

| Atom              | Angle | e.s.d. |
|-------------------|-------|--------|
| S(11)-Cd-S(21)    | 95.3° | 0.3°   |
| S(11)-Cd-S(12)    | 108.1 | 0.3    |
| S(11)-Cd-S(22)    | 118.1 | 0.3    |
| S(21)-Cd-S(22)    | 112.3 | 0.3    |
| S(21)-Cd-S(12)    | 121.5 | 0.3    |
| S(22)-Cd-S(12)    | 102.5 | 0.3    |
| Cd-S(12)-C(11)    | 100.4 | 1.1    |
| S(12)-C(11)-O(1)  | 113.4 | 2.4    |
| S(11)-C(11)-O(1)  | 121.0 | 2.6    |
| S(11)-C(11)-S(12) | 125.2 | 1.9    |
| C(11)-O(1)-C(12)  | 124.1 | 2.5    |
| O(1)-C(12)-C(13)  | 99.8  | 2.6    |
| C(12)-C(13)-C(14) | 118.2 | 2.5    |
| C(13)-C(14)-C(15) | 116.7 | 4.9    |
| C(11)-S(11)-Cd    | 97.9  | 1.1    |
| Cd-S(22)-C(21)    | 98.9  | 1.2    |
| S(22)-C(21)-S(21) | 127.3 | 1.8    |
| C(21)-S(21)-Cd    | 109.3 | 1.0    |
| S(22)-C(21)-O(2)  | 114.1 | 2.3    |
| S(21)-C(21)-O(2)  | 118.5 | 1.8    |
| C(21)-O(2)-C(22)  | 119.8 | 2.1    |
| O(2)-C(22)-C(23)  | 105.1 | 2.6    |
| C(22)-C(23)-C(24) | 109.7 | 3.1    |
| C(23)-C(24)-C(25) | 107.2 | 3.5    |

overcrowding when the chain would have its normal zigzag shape. It is also slightly stretched, making the C(12)-C(13)-C(14) and C(13)-C(14)-C(15) angles larger than the tetrahedral angle.

The O(2)-C(21) bond length agrees well with the value of 1.43 Å quoted in *International Tables* (1962), but there are possibly significant ( $\approx 2\sigma$ ) discrepancies from this value for the bonds O(1)-C(11), O(1)-C(12) and O(2)-C(12).

The lengths of the C-S bonds differ markedly from each other, showing clearly that one has more double bond character than the other. The average value of the C=S bond in both xanthic radicals is  $1.63 \pm 0.03$  Å and of the C-S bond  $1.75 \pm 0.03$  Å. These agree reasonably well with the values  $1.59 \pm 0.02$  Å and  $1.70 \pm 0.02$  Å for the same types of bond found in the antimonious xanthate (Gottardi, 1961). Also, the value of  $126^\circ \pm 2^\circ$  for the average S-C-S angle is

consistent with an angle of  $130.5^\circ \pm 2^\circ$  for that compound.

The Cd atom is coordinated with four S atoms. Their arrangement is approximately tetrahedral and from the configuration of the outer electron shells of the ion ( $4s^2 3d^{10} 4p^6 4d^{10}$ ) it may be expected that the ( $5s5p^3$ ) orbitals are used for the  $sp^3$  hybridization. Each sulphur atom belongs to a different xanthic radical and this may cause the large deviations on some of the tetrahedral S-C-S angles. The Cd-S(11) and Cd-S(12) distances are not significantly different from their average value of  $2.615 \pm 0.009$  Å, and this

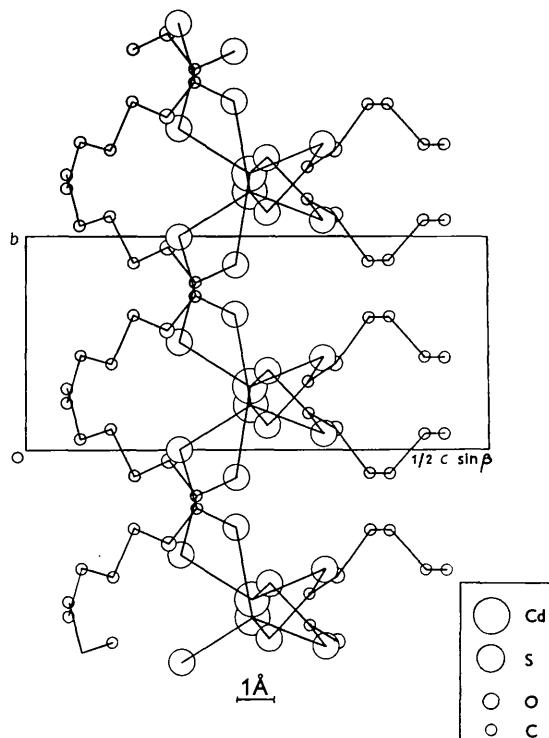


Fig. 3. Structure projected on (100), showing intermolecular coordinate linkages.

Table 6. *Mean square amplitudes of vibration* ( $\text{Å}^2$ ) *relative to orthogonal axes*  $a' = a$ ,  $b' = b$  and  $c' = c \sin \beta$

| Atom  | $U_{11}$ | $U_{12}$ | $U_{13}$ | $U_{22}$ | $U_{23}$ | $U_{33}$ |
|-------|----------|----------|----------|----------|----------|----------|
| Cd    | 0.0700   | -0.0004  | -0.0009  | 0.0417   | 0.0023   | 0.1229   |
| S(11) | 0.0622   | -0.0021  | 0.0271   | 0.0474   | -0.0267  | 0.1334   |
| S(12) | 0.0705   | -0.0601  | 0.0026   | 0.0988   | -0.0553  | 0.1462   |
| O(1)  | 0.0828   | 0.0197   | 0.0359   | 0.0612   | -0.0016  | 0.1252   |
| C(11) | 0.0977   | -0.0839  | -0.0019  | 0.0500   | 0.0062   | 0.1007   |
| C(12) | 0.0833   | -0.1173  | 0.0120   | 0.0596   | -0.0796  | 0.1795   |
| C(13) | 0.2390   | -0.0703  | 0.0449   | 0.0825   | -0.0392  | 0.1426   |
| C(14) | 0.1097   | 0.0987   | 0.0278   | 0.1765   | 0.0131   | 0.1129   |
| C(15) | 0.2401   | 0.1887   | 0.1488   | 0.3132   | 0.0249   | 0.1564   |
| S(21) | 0.0699   | 0.0096   | -0.0057  | 0.0416   | -0.0324  | 0.1699   |
| S(22) | 0.0902   | -0.0141  | -0.0497  | 0.0350   | 0.0212   | 0.1393   |
| O(2)  | 0.0734   | 0.0329   | 0.0084   | 0.0505   | 0.0012   | 0.1110   |
| C(21) | 0.0745   | -0.0033  | -0.0152  | 0.0137   | -0.0662  | 0.1309   |
| C(22) | 0.0642   | -0.0184  | -0.0290  | 0.0644   | 0.0162   | 0.1335   |
| C(23) | 0.1070   | 0.0843   | -0.0269  | 0.0749   | 0.0242   | 0.1231   |
| C(24) | 0.0961   | -0.0517  | -0.0161  | 0.1270   | 0.0091   | 0.1133   |
| C(25) | 0.0754   | 0.0122   | -0.0083  | 0.0981   | 0.0475   | 0.2155   |

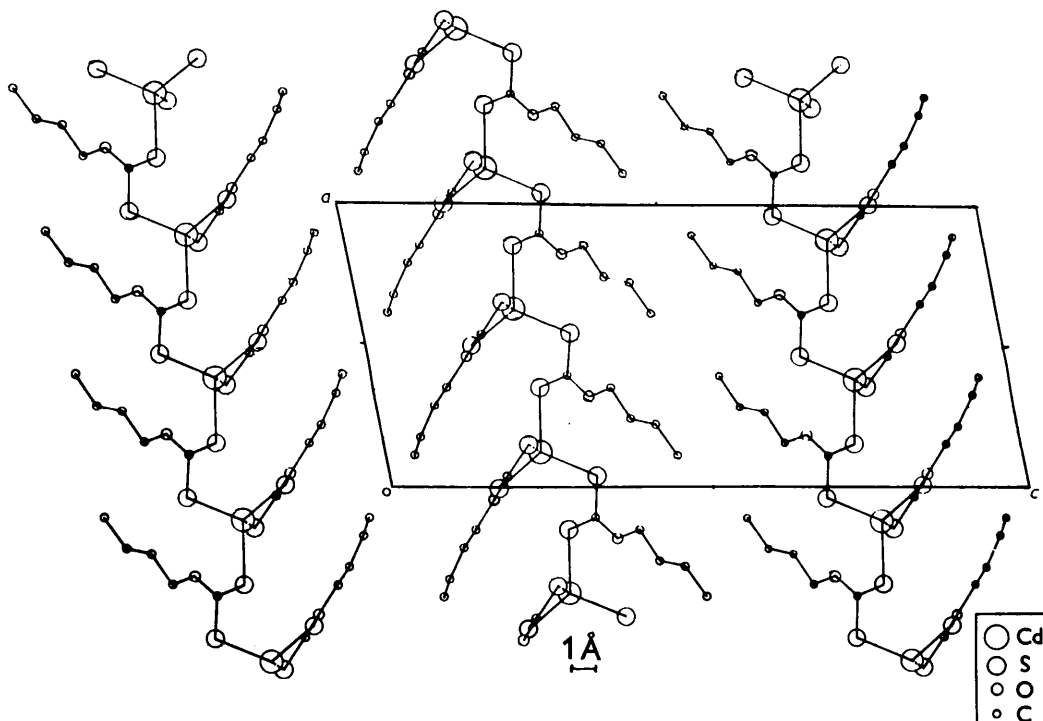


Fig. 4. Structure projected on (010), showing the intermolecular coordinate linkages.

applies also to the Cd-S(21) and Cd-S(22) distances with an average value of  $2.570 \pm 0.009$  Å. The sums of the Cd and S covalent radii are 2.52 Å and 2.42 Å for a single bonded and a double bonded sulphur atom respectively (Pauling, 1960). It can therefore be concluded that the coordinate bond is slightly longer than a 'pure' covalent bond, in agreement with the findings for the antimonious and arsenious xanthates. The difference in the coordinate bonds for atoms belonging to different xanthic radicals can possibly be explained by a change in polarization of the group due to their different configurations.

The coordinate bonds form a linkage between the xanthate groups throughout the lattice. As can be seen from Figs. 3 and 4, this causes the molecules to be strongly bonded together in a plane parallel to the (001) plane. These separate layers are held together by the weaker van der Waals forces and their orientation corresponds to the direction of the cleavage plane of the crystal.

The mean square amplitudes of the thermal vibrations for all atoms referred to the orthogonal axes  $a' = a$ ,  $b' = b$  and  $c' = c \sin \beta$  is given in Table 6. Their generally large values are probably caused by disorder in the crystal. However, there is an increase in the amplitude of thermal motion towards the end of each butyl chain, indicating that this side of the xanthate

group can move more freely than the side bonded to the heavy atom. Moreover, it is apparent that the vibrations have a maximum in the direction of the *c* axis. From this it may be concluded that the layers of bonded molecules as a whole execute thermal vibrations principally in the direction of their normal.

The authors wish to thank Dr L. Little of the Department of Chemistry, University of Western Australia and Dr D. Dale, Australian Institute of Nuclear Science and Engineering Fellow, for advice and assistance with this project.

#### References

- CARRAI, G. & GOTTARDI, G. (1960). *Z. Kristallogr.* **113**, 373.  
 GOTTARDI, G. (1961). *Z. Kristallogr.* **115**, 451.  
*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.  
 LITTLE, L. H., POLING, G. W. & LEJA, J. (1961a). *Canad. J. Chem.* **39**, 745.  
 LITTLE, L. H., POLING, G. W. & LEJA, J. (1961b). *Canad. J. Chem.* **39**, 1783.  
 LITTLE, L. H. (1963). Private communication.  
 MAZZI, F. (1962). Private communication to Dr L. H. LITTLE.  
 PAULING, L. (1960). *The Nature of the Chemical Bond*. London: Oxford University Press.