

## Chromium Squarates: $\text{Cr}(\text{C}_4\text{O}_4)(\text{OH}) \cdot 3\text{H}_2\text{O}$ and $\text{Cr}(\text{C}_4\text{O}_4)_{3/2} \cdot 7\text{H}_2\text{O}^*$

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### Abstract

$[\text{Cr}(\text{C}_4\text{O}_4)(\text{OH}) \cdot 3\text{H}_2\text{O}]$ ,  $\text{C}_4\text{HCrO}_5 \cdot 3\text{H}_2\text{O}$ , is triclinic,  $P\bar{1}$ , with  $a = 7.490$  (2),  $b = 7.540$  (3),  $c = 8.120$  (3) Å,  $\alpha = 106.28$  (2),  $\beta = 95.16$  (2),  $\gamma = 113.86$  (2)°,  $V = 391.59$  Å<sup>3</sup>,  $Z = 2$ ,  $D_o = 1.97$ ,  $D_c = 1.99$  Mg m<sup>-3</sup>.  $R = 0.045$  for 922 reflections. Two  $\text{Cr}(\text{OH})(\text{C}_4\text{O}_4)$  units, related by a center of symmetry, exist as dimers. The Cr pairs are joined by two  $\mu$ -hydroxo bridges and by two  $\text{C}_4\text{O}_4^{2-}$  ions acting as bridging groups through adjacent O atoms. Here  $\text{C}_4\text{O}_4^{2-}$  is the dianion of 3,4-dihydroxy-3-cyclobutene-1,2-dione, or squaric acid. The O atoms of two water molecules complete the octahedral coordination of each Cr ion. Hydrogen bonds connect the dimeric units to each other and to the one remaining water molecule.  $[\text{Cr}(\text{C}_4\text{O}_4)_{3/2} \cdot 7\text{H}_2\text{O}]$ ,  $\text{C}_6\text{CrO}_6 \cdot 7\text{H}_2\text{O}$ , monoclinic,  $C2/c$ ,  $a = 14.878$  (5),  $b = 15.434$  (3),  $c = 11.500$  (3) Å,  $\beta = 112.33$  (6)°,  $V = 2442.7$  Å<sup>3</sup>,  $Z = 8$ ,  $D_o = 1.89$ ,  $D_c = 1.88$  Mg m<sup>-3</sup>.  $R = 0.044$  for 1956 reflections. One complete squarate ion exists in the asymmetric unit, and another half squarate exists in the asymmetric unit with four atoms on a twofold rotation axis. The hexaaquachromium(III) ion is hydrogen bonded to the squarate ions and to the remaining water molecule in the asymmetric unit.

### Introduction

West & Niu (1963) have described the preparation from aqueous solutions of 'isostructural' divalent metal squarates of general formula  $M\text{C}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$ , and have predicted a chelated linear polymer structure. Trivalent metal squarates of general formula  $M\text{C}_4\text{O}_4(\text{OH}) \cdot 3\text{H}_2\text{O}$ , also described as isostructural for  $M = \text{Al}$ ,  $\text{Fe}$ , and  $\text{Cr}$ , were prepared for  $M = \text{Al}^{\text{III}}$ ,  $\text{Fe}^{\text{III}}$ , and  $\text{Cr}^{\text{III}}$ . A determination for the divalent metal squarate  $\text{Ni}(\text{C}_4\text{O}_4) \cdot 2\text{H}_2\text{O}$  has been reported by Habenschuss & Gerstein (1974), which did not have the predicted structure. Few structures have been published

for other transition-metal squarates, and the possibility remains for unusual metal coordination with the delocalized  $\pi$ -electron system of the squarate anion, which has been found by Macintyre & Werkema (1964) to have essentially  $D_{4h}$  symmetry in the potassium salt. It was therefore thought to be of interest to carry out a structure determination of one of the  $M(\text{C}_4\text{O}_4)(\text{OH}) \cdot 3\text{H}_2\text{O}$  salts. Another new chromium squarate salt was also prepared.

### Experimental

The reaction of dilute solutions of aqueous chromium nitrate with squaric acid, under the conditions described by West & Niu (1963), is very slow and generally yields fine powders as product, usually only after heating of the solution mixture. However, slow evaporation (over a two-month period) of such a solution mixture in an open-ended 3 mm diameter  $\times$  500 mm Pyrex tube at *ca* 308 K eventually yielded product which was mostly fine powder, but which also contained a few crystals of barely sufficient size to be usable for single crystal structure analysis. The IR spectrum (in KBr) of this product matched that given by West & Niu for  $\text{Cr}(\text{C}_4\text{O}_4)(\text{OH}) \cdot 3\text{H}_2\text{O}$ , and our structure determination gave results that also corresponded to this formula.

It was found that if a nearly saturated solution of squaric acid, *ca* 0.25M at 308 or 313 K, is mixed with an equivalent amount of a freshly prepared solution of aqueous chromium nitrate, which presumably contains the  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  ion, an almost immediate precipitate is obtained. This is readily shown by its IR spectrum and density to be different from the previously reported compound of West & Niu. We are also reporting here the structure determination of this new compound,  $\text{Cr}(\text{C}_4\text{O}_4)_{3/2} \cdot 7\text{H}_2\text{O}$ .

Diffraction symmetries and systematic absences seen in precession photographs indicated space groups  $P1$  or  $P\bar{1}$  for  $\text{Cr}(\text{C}_4\text{O}_4)(\text{OH}) \cdot 3\text{H}_2\text{O}$ , and  $Cc$  or  $C2/c$  for  $\text{Cr}(\text{C}_4\text{O}_4)_{3/2} \cdot 7\text{H}_2\text{O}$ .

\* Squaric acid is 3,4-dihydroxy-3-cyclobutene-1,2-dione.

Intensities were measured at 291 K using a Picker-Nuclear FACS-I diffractometer, with a 20s count for each background and measurements of three standard reflections every 50 reflections using graphite-mono-chromatized Mo  $K\alpha$  radiation for data collection. In each case cell constants were determined by a least-squares procedure from 12 strong reflections centered on the Mo  $K\alpha_1$  peak, wavelength 0.7092 Å. H atom scattering factors were those of Stewart, Davidson & Simpson (1965). Scattering factors for C, O, and Cr, including real and imaginary anomalous-dispersion corrections for Cr, were taken from *International Tables for X-ray Crystallography* (1974). No absorption corrections were made. Intensity statistics strongly indicated the centrosymmetric choices for space groups in both cases. The structure solution for  $\text{Cr}(\text{C}_4\text{O}_4)(\text{OH})\cdot 3\text{H}_2\text{O}$  proceeded simply by standard heavy-atom methods. The locations of five of the seven H atoms were clearly shown in a difference Fourier map. These five H atoms were included in structure factor calculations in final least-squares refinement.

Because the Cr atom in  $\text{Cr}(\text{C}_4\text{O}_4)_{3/2}\cdot 7\text{H}_2\text{O}$  is close to the  $y = 0.0$  plane, direct methods were used in conjunction with information from the Patterson to solve the structure problem. Four atoms, O(6), C(6), O(7), and C(7) are located in special positions on the twofold rotation axis at  $x = 0.5$ ,  $z = 0.25$ . These were given occupancy factors of 0.5, and only the  $y$  coordinates were varied in the refinement. Appropriate constraints were also made in varying the anisotropic temperature factors for these four atoms. All 14 H atoms appeared in expected locations for this compound, and these 14 H atoms were also included for structure factor calculations in final least-squares refinements. No attempt was made to refine the H atom coordinates for either compound. Parameters in the weighting scheme were chosen to give reasonably uniform average values of  $w(|F_o| - |F_c|)^2$  over intervals spanning the range of  $|F_o|$  values. Table 1 gives particular details of the data collection and refinement process, and Table 2 gives the atomic coordinates after refinement for each compound and also equivalent values of anisotropic temperature factor coefficients.\* Figs. 1 and 2 show the atomic numbering scheme and bond lengths for each compound. Table 3 specifies the hydrogen-bonding interactions and the hydrogen-bonded O—O distances. Refinement of all coordinates was to convergence using block-diagonal methods. No temperature factor abnormalities were found, as evidenced by the uniformity of  $B_{\text{eq}}$  values in Table 2.

\* Lists of structure factors, anisotropic thermal parameters, and coordinates of the unrefined H atoms used in structure factor calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35851 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Details of the intensity-data collection and the least-squares refinement*

	$\text{Cr}(\text{C}_4\text{O}_4)(\text{OH})\cdot 3\text{H}_2\text{O}$	$\text{Cr}(\text{C}_4\text{O}_4)_{3/2}\cdot 7\text{H}_2\text{O}$
$M_r$	235.10	346.17
Crystal size (mm)	0.10 × 0.10 × 0.03	0.12 × 0.25 × 0.35
$\mu(\text{Mo } K\alpha)$ (mm <sup>-1</sup> )	1.42	0.979
$\theta$ interval (°)	4–22.5	4–25
Scan type	$\omega$	$\theta-2\theta$
Number of unique reflections	1026	2160
Criterion for zero weight ( $\sigma_{F_c}$ based on counting statistics)	$ F_o  < 2.0 \sigma_{F_c}$	$ F_o  < 2.33 \sigma_{F_c}$
Number of reflections used in final refinements	922	1956
Number of parameters refined	118	183
$R = \sum   F_o  -  F_c   / \sum  F_o $	0.045	0.044
$R_w = \left[ \sum w( F_o  -  F_c )^2 / \sum w F_o ^2 \right]^{1/2}$	0.061	0.060
Refinement minimized		
$\sum w( F_o  -  F_c )^2$ , where $w^{-1} = A + B F_o  + C F_o ^2$		
A	1.537	0.3020
B	-0.200	-0.01132
C	0.00910	0.0003101
$F(000)$	238	1424

Table 2. *Atomic coordinates (× 10<sup>4</sup>), with e.s.d.'s, and equivalent values of anisotropic temperature factors*

$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$ , with  $\beta_{ij}$  defined by the temperature factor  $\exp(-\sum_i \sum_j \beta_{ij} h_i h_j)$  (Hamilton, 1959).

	x	y	z	$B_{\text{eq}}$ (Å <sup>2</sup> )
(a) $\text{Cr}(\text{C}_4\text{O}_4)(\text{OH})\cdot 3\text{H}_2\text{O}$				
Cr	3135 (1)	3060 (1)	3960 (1)	1.33
O(1)	8187 (4)	6970 (5)	4071 (4)	1.83
O(2)	4096 (4)	2698 (4)	1765 (4)	1.76
O(3)	5799 (5)	2734 (5)	-1701 (4)	1.93
O(4)	9763 (4)	7065 (5)	611 (4)	1.91
O(5)	2367 (5)	88 (5)	3524 (4)	2.09
O(6)	562 (5)	2438 (6)	2493 (4)	2.67
O(7)	4207 (4)	6063 (4)	4582 (4)	1.44
O(8)	7219 (5)	1123 (5)	3599 (4)	2.18
C(1)	7508 (6)	5735 (7)	2483 (6)	1.60
C(2)	5730 (6)	3852 (6)	1472 (5)	1.44
C(3)	6466 (7)	3841 (7)	-120 (5)	1.67
C(4)	8263 (7)	5803 (7)	929 (5)	1.68
(b) $\text{Cr}(\text{C}_4\text{O}_4)_{3/2}\cdot 7\text{H}_2\text{O}$				
Cr	2509 (0)	-72 (0)	4198 (0)	1.40
O(8)	2481 (1)	1107 (1)	3567 (2)	2.30
O(9)	2546 (1)	-1272 (1)	4800 (2)	2.36
O(10)	3365 (1)	-413 (1)	3349 (2)	2.06
O(11)	1638 (1)	266 (1)	5047 (2)	1.98
O(12)	3618 (1)	246 (1)	5726 (2)	1.99
O(13)	1380 (1)	-327 (1)	2645 (2)	1.93
O(14)	2458 (1)	1558 (1)	6638 (2)	2.15
O(1)	4973 (1)	1217 (1)	5600 (2)	2.53
C(1)	5021 (2)	2030 (2)	5731 (2)	1.84
O(2)	3605 (1)	2687 (1)	6053 (2)	2.33
C(2)	4405 (2)	2693 (2)	5924 (2)	1.83
O(3)	5158 (1)	4164 (1)	6046 (2)	2.51
C(3)	5118 (2)	3354 (2)	5934 (2)	1.95
O(4)	6532 (1)	2657 (1)	5603 (2)	2.38
C(4)	5730 (2)	2681 (2)	5727 (2)	1.74
O(5)	3561 (1)	2157 (1)	2793 (2)	2.32
C(5)	4344 (2)	2149 (2)	2628 (2)	1.82
O(6)	5000	670 (2)	2500	2.40
C(6)	5000	1477 (2)	2500	1.89
O(7)	5000	3627 (2)	2500	2.89
C(7)	5000	2810 (2)	2500	1.82

Table 3. Hydrogen-bonded O—O pairs and distances (Å)

(a)  $\text{Cr}(\text{C}_4\text{O}_4)(\text{OH}) \cdot 3\text{H}_2\text{O}$ 

O(7)—O(3 <sup>ii</sup> )	2.735 (5)	O(6)—O(4 <sup>ii</sup> )	2.654 (5)
O(5)—O(8 <sup>iii</sup> )	2.772 (5)	O(8)—O(3 <sup>vi</sup> )	2.735 (4)
O(5)—O(4 <sup>iv</sup> )	2.673 (3)	O(8)—O(7 <sup>i</sup> )	2.858 (5)
O(6)—O(8 <sup>v</sup> )	2.638 (5)		

## Symmetry operations

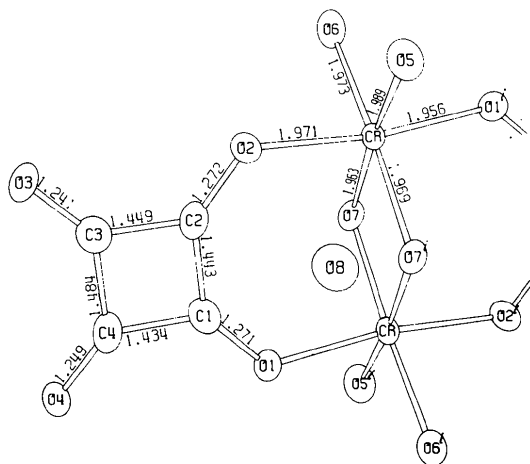
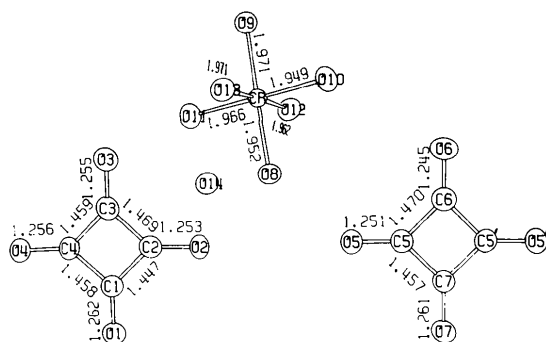
(i) $1 - x, 1 - y, 1 - z$	(iv) $x - 1, y - 1, z$
(ii) $1 - x, 1 - y, -z$	(v) $x - 1, y, z$
(iii) $1 - x, -y, 1 - z$	(vi) $1 - x, -y, -z$

(b)  $\text{Cr}(\text{C}_4\text{O}_4)_{3/2} \cdot 7\text{H}_2\text{O}$ 

O(8)—O(5)	2.662 (3)	O(11)—O(14)	2.667 (3)
O(8)—O(2 <sup>i</sup> )	2.609 (3)	O(12)—O(1)	2.560 (3)
O(9)—O(4 <sup>ii</sup> )	2.674 (3)	O(12)—O(6 <sup>iii</sup> )	2.683 (2)
O(9)—O(4 <sup>iii</sup> )	2.630 (3)	O(13)—O(3 <sup>vi</sup> )	2.714 (2)
O(10)—O(1 <sup>iii</sup> )	2.617 (3)	O(13)—O(7 <sup>ii</sup> )	2.567 (3)
O(10)—O(14 <sup>iv</sup> )	2.608 (3)	O(14)—O(5 <sup>v</sup> )	2.722 (3)
O(11)—O(3 <sup>i</sup> )	2.635 (3)	O(14)—O(2)	2.697 (3)

## Symmetry operations

(i) $0.5 - x, 0.5 - y, 1 - z$	(iv) $x, -y, z - 0.5$
(ii) $x - 0.5, y - 0.5, z$	(v) $0.5 - x, 0.5 - y, 1 - z$
(iii) $1 - x, -y, 1 - z$	(vi) $x - 0.5, 0.5 - y, z - 0.5$

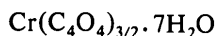
Fig. 1. Bond lengths (Å) for  $\text{Cr}(\text{C}_4\text{O}_4)(\text{OH}) \cdot 3\text{H}_2\text{O}$ . Maximum bond-length e.s.d. (from least-squares refinement) Cr—O, 0.003; C—O, 0.005; C—C, 0.007 Å.Fig. 2. Bond lengths (Å) for  $\text{Cr}(\text{C}_4\text{O}_4)_{3/2} \cdot 7\text{H}_2\text{O}$ . Maximum bond-length e.s.d. (from least-squares refinement) Cr—O, 0.002; C—O, 0.005; C—C, 0.004 Å.

## Description and discussion of structures

 $\text{Cr}(\text{C}_4\text{O}_4)(\text{OH}) \cdot 3\text{H}_2\text{O}$ 

Two  $\text{Cr}(\text{C}_4\text{O}_4)(\text{OH}) \cdot (\text{H}_2\text{O})_2$  units are bound together as a dimer by di- $\mu$ -hydroxo-di- $\mu$ -squarato bridging (Fig. 1). These units are related by the crystallographic center of symmetry at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . The separation of the O(1) and O(2) squarato bridging atoms is a bit too long to accommodate the hydroxy bridging system without O—Cr—O angle deformation. This is seen in the O(2)—Cr—O(1<sup>i</sup>) angle of  $171.2^\circ$  and the O(7)—Cr—O(7<sup>i</sup>) angle of  $80.7^\circ$ , with the O(2)—Cr and O(1<sup>i</sup>)—Cr bonds being bent back from the center of the dimer unit. This may be compared with the O—Cr—O angle of  $85^\circ$  found by Flood, Marsh & Gray (1969) for the di- $\mu$ -hydroxo bridging O atoms in  $[\text{Cr}_4(\text{OH})_6(\text{en})_6] \cdot (\text{N}_3)_6 \cdot 4\text{H}_2\text{O}$ . The average length of the six Cr—O bonds is  $1.970 \text{ \AA}$ , with a sample standard deviation for the six values of  $0.011 \text{ \AA}$ . This is twice the C—O bond length e.s.d. of  $0.005 \text{ \AA}$  obtained from coordinate uncertainties, and no consistent structural explanation for the most deviant values is obvious. Flood (1969) found  $1.98 \text{ \AA}$  for the average of five bonds between  $\text{Cr}^{\text{III}}$  and the oxygens of  $\mu$ -hydroxo bridging units. Values of  $1.975 \text{ \AA}$  (Evans, 1968) and  $1.94 \text{ \AA}$  (Bacon & Gardner, 1958) have been reported for the bond length between  $\text{Cr}^{\text{III}}$  and the O of coordinated water. The C—O bonds with the coordinated squarato oxygens, O(1) and O(2), average  $1.272 \text{ \AA}$ , or  $0.03 \text{ \AA}$  longer than the average of  $1.245 \text{ \AA}$  found for the C—O bonds involving O(3) and O(4), which are subject only to intermolecular hydrogen-bonding interactions. This difference is probably real and reflects a lower C—O bond order for the O atoms coordinated to  $\text{Cr}^{\text{III}}$ . The C—O bond length of  $1.259(9) \text{ \AA}$  has been reported by Macintyre & Werkema (1964) for potassium squarate monohydrate. However, van Ooijen, Reedijk & Spek (1979) found essentially the same distance [ $1.251(2) \text{ \AA}$ ] for C—O squarate bond lengths with both uncoordinated O and with an O coordinated to  $\text{Ni}^{\text{II}}$ . The average of  $1.45 \text{ \AA}$  for the four C—C bond lengths also agrees well with the average of  $1.456(10) \text{ \AA}$  given by Macintyre & Werkema (1964) for the squarate ion. The C(3)—C(4) bond is  $0.03 \text{ \AA}$  longer than the average as may be expected from the coordination of the squarate ion. These values are all slightly less than the average of  $1.467(5) \text{ \AA}$  reported by van Ooijen *et al.* (1979). The slow rate of formation of this compound is understood in terms of the inertness of the  $\text{Cr}^{\text{III}}$  ion with respect to inner-sphere substitution, since four Cr—O links must be broken for the formation of each bridged dimer unit, assuming  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  as the starting unit in the synthesis. The seventh water molecule is involved in four hydrogen bonds: two with the coordinated water molecules, one with a free O on a squarate and one with the O of the bridging hydroxy group. The O—O distances for the

seven hydrogen bonds linking the bridged dimer units and the single water molecule are given in Table 3. These are seen to be in the normal range, as discussed by Donohue (1968) with an average of 2.71 (8) Å for the seven hydrogen-bonded O—O distances.



In this structure the  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  unit exists with an octahedral arrangement of the six O atoms about the central metal ion, with the twelve O—Cr—O angles having a standard deviation of  $1.2^\circ$  from the  $90.0^\circ$  average. The average of the six Cr—O bond lengths is 1.962 Å, also in good agreement with the previously mentioned values. The average of 1.252 Å for the seven squarate C—O bond lengths and the value of 1.460 Å for the six C—C lengths both agree with the values found in the other compound discussed here and with the references cited for squarate ion structures. The O—C—C and C—C—C squarate ion bond angles show a standard deviation of  $0.8^\circ$  from the values of  $135^\circ$  and  $90^\circ$  expected for  $D_{4h}$  symmetry. Each of the six coordinated water molecules forms two hydrogen bonds with either squarate O atoms or with the O(14) atom of the seventh water molecule, which is subject only to hydrogen bonding. Each squarate O atom is likewise the base for two hydrogen bonds with water O—H groups. The fourteen hydrogen bonds, specified by the O—O entries in Table 3(b), show an average O—O distance of 2.65 (5) Å, also similar to the value previously discussed. The hexaaqua metal ions lie close to the planes  $y = 0$  and  $y = 0.5$ , and the squarate ions are parallel to the  $c$  face of the unit cell. Each squarate ion has a principal diagonal parallel to the  $c$  axis and close to the plane  $y = 0.25$  or  $y = 0.75$ . Thus perpendicular to the  $y$  axis are found alternating layers of hexaaqua metal and squarate ions with spacing of 0.25 between layer centers.

One complete squarate ion exists in the asymmetric unit. This ion forms a linear-chain hydrogen-bonded

structure connecting hexaaqua metal ions of adjacent layers. The *cis* squarate atoms O(1) and O(4) hydrogen bond to two *cis* coordinated water molecules, O(10) and O(9). The other two squarate O atoms O(2) and O(3) hydrogen bond to O(8) and O(11) of a hexaaqua Cr ion in the other adjacent plane of metal ions. These chains are connected by hydrogen bonds involving the remaining squarate ion. O(7), C(7), C(6), and O(6) of this ion are on a twofold rotation axis, and the corresponding rotation operation generates a complete squarate ion from the half-ion in the asymmetric unit.

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#### References

- BACON, G. E. & GARDNER, W. E. (1958). *Proc. R. Soc. London, Ser A*, **246**, 78–90.
- DONOHUE, J. (1968). *Structural Chemistry and Molecular Biology*, edited by A. RICH & N. DAVIDSON, pp. 443–465. San Francisco: Freeman.
- EVANS, H. T. (1968). *J. Am. Chem. Soc.* **90**, 3275–3276.
- FLOOD, M. T. (1969). Ph.D. Dissertation, California Institute of Technology, Pasadena, California.
- FLOOD, M. T., MARSH, R. E. & GRAY, H. B. (1969). *J. Am. Chem. Soc.* **91**, 193–194.
- HABENSCHUSS, M. & GERSTEIN, B. C. (1974). *J. Chem. Phys.* **61**, 852–860.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 72–77, 148–150. Birmingham: Kynoch Press.
- MACINTYRE, W. M. & WERKEMA, M. S. (1964). *J. Chem. Phys.* **42**, 3563–3568.
- OOIJEN, J. A. C. VAN, REEDIJK, J. & SPEK, A. L. (1979). *Inorg. Chem.* **18**, 1184–1189.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- WEST, R. & NIU, H. Y. (1963). *Inorg. Chem.* **85**, 2589–2590.