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EPR and X-ray Structural Study of some Tetrahalocuprates CuX_4^{2-} (X = Cl, Br) of Protonated Ammines with Thermochromic Properties

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Abstract

The EPR spectra of the tetrachlorocuprates(II) of a group of protonated ammines (n-propyl, isopropyl, n-butyl, isobutyl, octyl, lauryl-ammine, pyridine and piperidine) have been studied and the crystal structures of bis(isopropylammonium)tetrabromocuprate(II) (**1**) and of bis(piperidinium)tetrachlorocuprate(II) (**2**) have been studied by X-ray diffraction in single crystals. Compound **1** is monoclinic, space group $P2_1/n$, with unit cell parameters of 10.8137(3), 14.6227(5), 14.2048(5) Å, 106.918(2)°, D_x 1.816 g cm^{-3} and one independent formula unit. The final R factor, for the 3455 observed reflections recorded with Cu Kα radiation, was 0.052. Compound **2** is also monoclinic space group $P2_1/c$, unit cell parameters of 8.2221(2), 16.9179(7), 12.1725(3) Å, 100.542(2)°, D_x 1.507 g cm^{-3} and one independent formula unit. Final R factor is 0.055 for the 2506 observed reflections, recorded with Cu Kα radiation. In both cases the anions, $[CuBr_4]^{2-}$ and $[CuCl_4]^{2-}$, have a squashed tetrahedron structure with a range of distances Cu–Br of 2.372(1)–2.405(1) Å and Cu–Cl of 2.226(1)–2.261(1) Å, and angles, at the Cu atom, of two types, [96.74(5)–103.40(5)°] and [130.62(5)–136.50(5)°] these for both compounds. In each case the anions are involved in a network of hydrogen interactions that have as donor atoms the charged tetrahedral nitrogens of the organic cations.

Introduction

A wide variety of tetrahalocuprates CuX_4^{2-} (X = Cl, Br) are known, some of which are very interesting because they present thermocromism and this property is related with a change in the structure of the substance [1–8].

In a previous study [9] the tetrahalocuprates CuX_4^{2-} (X = Cl, Br) of bis(n-propyl-, isopropyl-, n-butyl-, isobutyl-, octyl-, lauryl-ammonium, pyridinium and piperidinium) have been synthesized and their IR, UV and visible spectra have been discussed.

In this paper we present the EPR spectra of the tetrachlorocuprates(II) previously indicated and the crystal structures of bis(piperidinium)tetrachlorocuprate(II) and of bis(isopropylammonium)tetrabromocuprate(II) in order to complete the structural study of these compounds.

Experimental

All the compounds were obtained by direct reaction of the corresponding ammine chlorhydrate or bromhydrate, and cupric chloride and bromide in relation 2:1, in ethanol solution, with small amounts of the appropriate hydrochloric or hydrobromic acid [9]. All of them (see Table I), except **II** (green), form yellow coloured crystals at room temperature and are air stable; **I**, **III**, **IV**, **V** and **VI** turn to green colour at −80 °C, **VII** and **VIII** turn to orange colour at ~95 °C. Bis(isopropylammonium)tetrabromocuprate(II) does not change colour with the change of temperature and it was not possible to obtain good EPR data because it decomposes in solution.

The EPR spectra were recorded on a Varian E-12 spectrometer at a microwave frequency of 9 GHz (X-band) equipped with a HP 5342 A frequencymeter, and a Bruker NMR Gaussmeter.

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TABLE I. EPR Parameters of the Compounds and Polar Angle Φ (°) (UV–Vis.)[a]

		Solid		Solution					Θ (°)
		$g_{\parallel}$	$g_{\perp}$	$g_{\parallel}$	$g_{\perp}$	$[A_{\parallel}]^b$	g_{iso}	$[A_{iso}]^b$	
I	$(n\text{-}C_3H_7NH_3^+)_2CuCl_4$	2.052	2.145	2.343	2.076	132.3	2.151	39.4	136.9
II	$(iso\text{-}C_3H_7NH_3^+)_2CuCl_4$	2.122		2.345	2.075	129.2	2.148	39.4	139.7
III	$(n\text{-}C_4H_9NH_3^+)_2CuCl_4$	2.056	2.144	2.345	2.073	131.4	2.150	40.2	136.9
IV	$(iso\text{-}C_4H_9NH_3^+)_2CuCl_4$	2.049	2.146	2.344	2.073	129.1	2.151	41.3	135.2
V	$(C_8H_{17}NH_3^+)_2CuCl_4$	2.058	2.146	2.346	2.073	134.3	2.149	43.2	136.9
VI	$(C_{12}H_{25}NH_3^+)_2CuCl_4$	2.053	2.152	2.353	2.072	137.3	2.150	39.6	136.9
VII	$(C_5H_5NH^+)_2CuCl_4$	2.161	2.113	2.349	2.075	134.7	2.152	40.1	137.9
	rhombic		2.073						
VIII	$(C_5H_{10}NH_2^+)_2CuCl_4$	2.210	2.106	2.347	2.074	131.5	2.149	40.3	136.9

[a]Polar angle (109.47°, tetrahedral – 180° square plane structure) see text, ref. 9. [b]In $\times 10^4$ cm^{-1} units.

Results and Discussion

EPR Spectra

The EPR spectra have been recorded in solid and solution ($CHCl_3$/toluene) at room temperature and at –160 °C. The values of the EPR parameters for all the studied complexes are reported in Table I.

The isotropic spectra in solution at room temperature present only one signal, from which the values of A_{iso} (39.4–43.2 × 10^{-4} cm^{-1}) can be calculated. In frozen solutions, the anisotropic spectra present the split commonly observed in the Cu(II) complexes, in both the parallel and perpendicular components, a hyperfine split being observed only in the parallel direction, $A_{\parallel}$, values of which are reported in table I.

The determined values of g_{iso}, A_{iso} and $A_{\parallel}$ are considerably smaller than those found in square-planar complexes of Cu(II) [10].

The principal values of the g and A tensors in relation with the coefficients of the molecular orbitals which take place in the bond, have been extensively studied in pseudotetrahedral Cu(II) complexes [10, 11].

It has been found that when the distortion grade towards the tetrahedral form increases, the value of $g_{\parallel}$ increases, while $A_{\parallel}$ decreases in relation to the square-planar complex [12, 13].

In general, small values of $A_{\parallel}$ have been found in tetrahedral complexes of Cu(II) with higher or smaller distortion grade [10].

The values found in our complexes (Table I) are in very good relation with a pseudotetrahedral environment of the Cu(II) ion. The only signal of the isotropic spectra is consistent with the small value of the hyperfine coupling constant found in these species. Furthermore, the variation of the $g_{\parallel}$ and $A_{\parallel}$ values in the indicated complexes is not very important because all of them must have a similar distortion grade as indicated by the visible [9] and X-ray data.

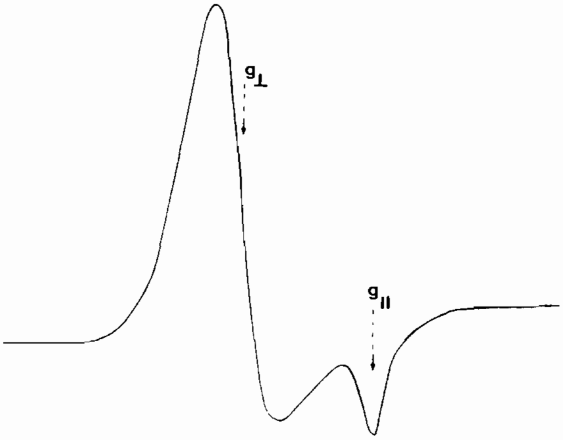

Fig. 1. Powder EPR spectra of I at room temperature.

However, in solid state, rather different EPR spectra have been obtained. The complex **II** presents only one isotropic signal with a g_{iso} value which is indicated in Table I and which agrees very well with the one described by Bloomquist *et al.* [7].

The complexes **I**, **III**, **IV**, **V** and **VI** present one axial reversed spectrum with $g_{\perp}$ higher than $g_{\parallel}$ (Fig. 1) which is analogous to the one observed in other distorted square-planar Cu(II) complexes [14, 15]. The complex **VII** presents one characteristic spectrum of Cu(II) pseudotetrahedral species with rhombic distortion [16] and $g_1 = 2.161$, $g_2 = 2.113$ and $g_3 = 2.073$, while the complex **VIII** presents one axial spectrum analogous to those found in other tetrahedral complexes of Cu(II) [17].

X-ray Crystallography Procedures

The main characteristics of the analysis are given in Table II. The cell parameters were obtained by least-squares fit to the angular position of 93 reflections for **1** and 88 for **2** ($2 \leqslant \theta \leqslant 45°$). Intensity data were collected on a Philips PW 1100 diffracto-

TABLE II. Crystal Analysis Parameters at Room Temperature for Compounds 1 and 2

Crystal data		
Formula	$C_{12}H_{32}N_2Br_4Cu$ (**1**)	$C_{10}H_{24}N_2Cl_4Cu$ (**2**)
Crystal habit	black prism	yellow prism
Crystal size (mm)	0.13 × 0.33 × 0.47	0.07 × 0.30 × 0.50
Symmetry	monoclinic, $P2_1/n$	monoclinic, $P2_1/c$
Unit cell	10.8137(3), 14.6227(5), 14.2048(5) Å 90, 106.918(2), 90°	8.2221(2), 16.9179(7), 12.1725(3) Å 90, 100.542(2), 90°
Packing, V and Z	2148.9(1) Å^3, 4	1664.6(1) Å^3, 4
$D_c, M, F(000)$	1.816 g cm^{-3}, 587.56, 1148	1.507 g cm^{-3}, 377.67, 780
μ-coefficient	101.86 cm^{-1}	77.72 cm^{-1}
Experimental		
Technique	$\omega/2\theta$ scans, scan width 1.5°, detector apertures 1° × 1°, θ(max) × 65°, 1 min/reflection	
No. of reflections		
Independent	3646	2839
Observed	3455 ($3\sigma(I)$)	2506 ($3\sigma(I)$)
Max.–min. transmission	1.649–0.716	1.847–0.785
Solution and refinement		
Parameters		
No. of variables	280 + 20 fixed for H	250
Degrees of freedom	3175	2256
Ratio of freedom	12.3	10.0
Final shift/error	0.16	0.10
Max. thermal value	U_{11} (C4) = 0.14(1) Å^2	U_{11} (C3) = 0.093(5) Å^2
Final ΔF peaks	0.79 e Å^{-3}	0.52 e Å^{-3}
Final R and R_w factors	0.052, 0.066	0.055, 0.064

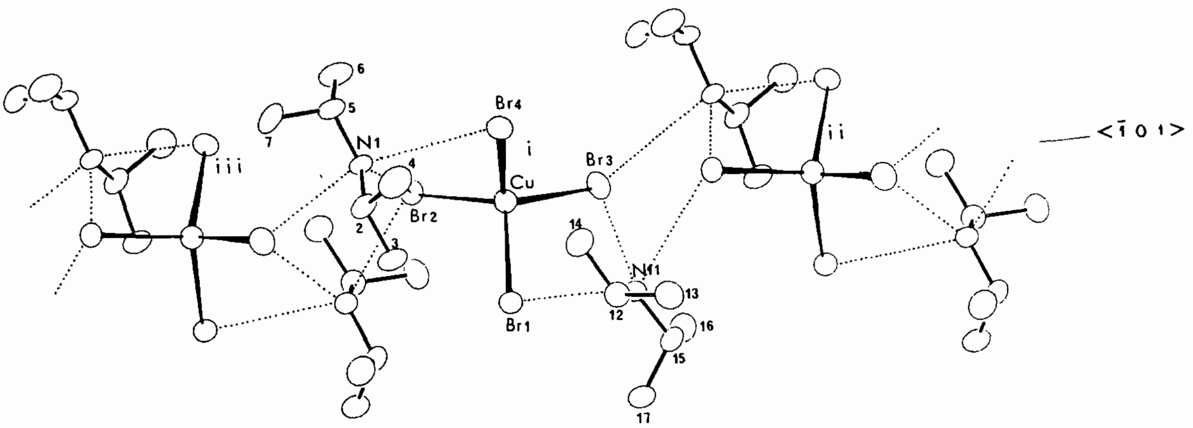

Fig. 2. An ORTEP [27] view of the structure of compound 1 showing the network of hydrogen interactions and the numbering scheme. Roman numbers stand for the symmetry operations: (i) x, y, z; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$.

meter, Cu Kα radiation and graphite monochromator. No decay was observed during collection. Absorption was corrected empirically [23]. The structures were solved by Patterson and Fourier methods and refined by one block matrix least-squares on F_{obs} only. In compound 1 20 hydrogen parameters had to be kept fixed, although all hydrogen atoms were found in difference maps.

Empirical weights, as to give no trends on $\langle w\Delta^2F\rangle$ *versus* either $\langle|F_o|\rangle$ or $\langle\sin\theta/\lambda\rangle$, were used in final cycles of refinement. The atomic scattering factors were taken from the International Tables for X-ray Crystallography [24]. All calculations were performed on a VAX 11/750 Computer and most calculations using the X-Ray 76 System [25].

Description of the Structures of 1 (Fig. 2) and 2 (Fig. 3)

Final atomic coordinates are given in Tables III and IV, for the nonhydrogen atoms. The geometrical

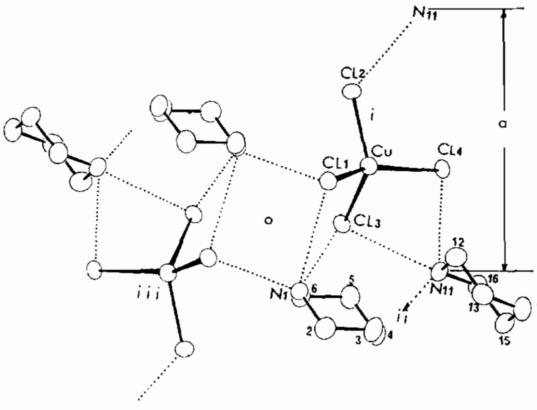

Fig. 3. Same as Fig. 2, but for compound **2**, with symmetry operations: (i) x, y, z; (ii) $x - 1, y, z$; (iii) $1 - x, -y, -z$.

TABLE III. Final Atomic Coordinates

Atom	x/a	y/b	z/c
Cu	0.25441(9)	0.23297(6)	0.01427(7)
Br1	0.08195(7)	0.26995(5)	0.08301(5)
Br2	0.12861(7)	0.20515(5)	−0.15054(5)
Br3	0.38067(8)	0.14444(6)	0.14769(6)
Br4	0.41953(7)	0.32084(6)	−0.02315(6)
N1	0.1923(7)	0.4202(4)	−0.2210(5)
C2	0.1498(8)	0.5053(5)	−0.1803(5)
C3	0.0751(10)	0.4773(6)	−0.1090(8)
C4	0.2621(15)	0.5683(8)	−0.1344(10)
C5	0.2612(8)	0.4321(6)	−0.2994(6)
C6	0.2969(19)	0.3353(11)	−0.3229(12)
C7	0.1797(13)	0.4805(8)	−0.3863(7)
N11	0.3056(5)	0.3425(4)	0.2942(4)
C12	0.3157(8)	0.4446(5)	0.2801(6)
C13	0.4029(9)	0.4875(6)	0.3737(8)
C14	0.3661(11)	0.4574(6)	0.1940(8)
C15	0.2531(8)	0.3109(5)	0.3765(6)
C16	0.2517(10)	0.2067(6)	0.3755(7)
C17	0.1201(9)	0.3513(7)	0.3646(7)

TABLE IV. Final Atomic Coordinates

Atom	x/a	y/b	z/c
Cu	0.69337(8)	0.08345(4)	0.24332(5)
Cl1	0.70290(15)	−0.03308(6)	0.15378(10)
Cl2	0.93525(14)	0.13144(7)	0.20982(11)
Cl3	0.43053(14)	0.11559(8)	0.16778(10)
Cl4	0.69005(15)	0.12213(8)	0.41766(9)
N1	0.29185(62)	−0.06514(26)	0.07179(54)
C2	0.14765(76)	−0.04615(38)	0.12457(55)
C3	0.18513(99)	−0.06904(42)	0.24565(55)
C4	0.23470(100)	−0.15545(38)	0.26048(60)
C5	0.37718(85)	−0.17316(33)	0.20234(52)
C6	0.33948(85)	−0.14981(34)	0.08144(50)
N11	0.27657(61)	0.14401(29)	0.39360(40)
C12	0.27632(81)	0.22921(35)	0.42819(63)
C13	0.13467(80)	0.24412(40)	0.48782(58)
C14	0.14126(95)	0.18948(46)	0.58594(54)
C15	0.14368(79)	0.10499(40)	0.54879(53)
C16	0.28574(77)	0.08945(38)	0.49010(49)

TABLE V. Selected Geometrical Parameters for Compounds 1 and 2

(a) Bond lengths (Å)			
Cu–Br1	2.405(1)	Cu–Br3	2.372(1)
Cu–Br2	2.376(1)	Cu–Br4	2.382(1)
Cu–Cl1	2.261(1)	Cu–Cl3	2.255(1)
Cu–Cl2	2.253(1)	Cu–Cl4	2.226(1)
(b) Bond angles (°)			
Br1–Cu–Br2	98.59(4)	Br4–Cu–Br3	100.26(5)
Br1–Cu–Br3	97.61(4)	Br4–Cu–Br2	97.12(4)
Br1–Cu–Br4	133.59(5)	Br3–Cu–Br2	136.50(5)
Cl1–Cu–Cl2	96.74(5)	Cl2–Cu–Cl4	103.40(5)
Cl1–Cu–Cl3	97.40(5)	Cl3–Cu–Cl4	98.04(5)
Cl1–Cu–Cl4	136.35(5)	Cl2–Cu–Cl3	130.62(5)

parameters describing the structures are given in Table V and the networks of hydrogen interactions in Table VI.

Both structures present the $CuBr_4^{2-}$ and $CuCl_4^{2-}$ anions as flattened tetrahedra, with two angles, in nearly perpendicular planes, distinguishing their high values [130.62(5) to 136.50(5)°] from the rest [96.74(5) to 103.40(5)°]. This arrangement seems to be quite common for the $CuCl_4^{2-}$ groups [2, 17, 20, 21]. The ranges of distances within the anions are [2.372(1)–2.405(1) Å] in **1** and [2.226(1)–2.261(1) Å] in **2**, a difference of about 0.15 Å in agreement with the difference in the atomic radii [22].

Each compound has two crystallographically independent organic cations isopropylammonium in **1** and piperidinium in **2**, all having charged and tetrahedral N atoms, which present C–N–C angles higher than the tetrahedral value. In compound **1**, there is, in each cation, one terminal C–Me bond with shorter length than the others, and the cationic groups conform with internal pseudobinary axis at the N atoms, one being pseudoenantiomeric from the other. In compound **2** the pseudoenantiomeric cations conform as chairs more puckered around the N atoms.

Anions and cations pack in the crystals through networks of H-interactions (see Figs. 2 and 3 and Table VI), typical for this sort of compound [2, 4, 18–21] and without any Cu...Br/Cl intermolecular interactions [4]. All interactions except those associated with H1b and H11b in **2** appear as bifurcated into one weaker and the other stronger (see Table VI). No negative correlations appear associated between the strength of the H interaction and the

TABLE VI. Hydrogen Interactions. Those Most Likely [23] to be Hydrogen Bonds are Marked with an Asterisk, (Å, °)

X–H...Y	X...Y	X–H	H...Y	X–H...Y
(a) Compound 1				
N1–H1a–Br2	3.430(6)	0.85(8)	3.08(9)	107(6)
N1–H1a–Br3 (iii)[a]	3.474(6)	0.85(8)	2.66(8)	161(8)*
N1–H1b–Br2	3.430(6)	0.77(7)	3.05(7)	114(6)
N1–H1b–Br4	3.468(6)	0.77(7)	2.71(6)	168(7)*
N11–H11a–Br2 (ii)[a]	3.422(6)	1.01(12)	2.47(12)	159(9)*
N11–H11a–Br3	3.790(6)	1.01(12)	3.27(13)	114(7)
N11–H11b–Br1	3.428(5)	0.88(10)	2.61(10)	155(9)*
N11–H11b–Br3	3.790(6)	0.88(10)	3.18(12)	128(8)
(b) Compound 2				
N1–H1a–Cl1	3.388(5)	1.05(10)	2.42(10)	153(8)*
N1–H1a–Cl3	3.395(5)	1.05(10)	2.73(10)	121(7)
N1–H1b–Cl1 (iii)[b]	3.216(6)	1.03(8)	2.26(8)	154(5)*
N11–H11a–Cl3	3.265(5)	1.01(12)	2.38(12)	147(8)*
N11–H11a–Cl4	3.379(5)	1.01(12)	2.66(11)	129(8)
N11–H11b–Cl2 (ii)[b]	3.260(5)	0.91(7)	2.36(7)	171(6)*

[a] ii, iii stand for the symmetry operations: $\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$ and $-\frac{1}{2} + x$, $\frac{1}{2} - y$, $-\frac{1}{2} + z$. [b] ii, iii stand for the symmetry operations: $x - 1, y, z$ and $1 - x, -y, -z$.

internal bonds in the anions [2, 18]. In compound 1 the network is formed by independent ribbons along the $\langle\bar{1}01\rangle$ direction. In 2 the network is built along the *a* axis and around the symmetry centers (see Figs. 2 and 3).

Supplementary Material

Tables of geometrical and anisotropic thermal parameters (Tables F, G, and H), parameters for the hydrogen atoms (Tables I and J) and observed and calculated structure factors (Tables K and L, 25 and 19 pages respectively).

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References

1 A. B. P. Lever, E. Mantovani and J. C. Donini, *Inorg. Chem., 10*, 2424 (1971).
2 R. L. Harlow, W. J. Wells, III, G. W. Watt and S. H. Simonsen, *Inorg. Chem., 13*, 2106 (1974).
3 R. D. Willett, J. A. Haugen, J. Lebsack and J. Morrey, *Inorg. Chem., 13*, 2510 (1974).
4 R. D. Willett, J. R. Ferraro and M. Choca, *Inorg. Chem., 13*, 2919 (1974).
5 G. Marcotrigiano, L. Menabue and G. C. Pellacani, *Inorg. Chem., 15*, 2333 (1976).
6 (a) G. Marcotrigiano, L. Menabue and G. C. Pellacani, *J. Coord. Chem., 5*, 189 (1976); (b) *9*, 141 (1979).
7 D. L. Bloomquist, R. D. Willett and H. W. Dodgen, *J. Am. Chem. Soc., 103*, 2610 (1981).
8 R. D. Willett, *J. Chem. Educ., 60*, 355 (1983).
9 A. Doadrio and M. T. Gutiérrez Ríos, *An. Quím., 75*(3), 228 (1979).
10 M. A. Hitchman, *Inorg. Chem., 24*, 4762 (1985).
11 Y. Murakani, Y. Matsuda and K. Sakata, *Inorg. Chem., 10*, 1734 (1971).
12 H. Yokoi, *Bull. Chem. Soc. Jpn., 47*, 3077 (1974).
13 W. M. Davis, A. Zask, K. Nakanishi and S. J. Lippard, *Inorg. Chem., 24*, 3737 (1985).
14 B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev., 5*, 143 (1970).
15 K. T. McGregor and W. E. Hatfield, *J. Chem. Soc., Dalton Trans.*, 2448 (1974).
16 A. C. Massabri, O. R. Nascimento, R. H. Almeida Santos, R. H. P. Francisco and J. R. Lechat, *Inorg. Chim. Acta, 72*, 127 (1983).
17 J. R. Wasson, *Spectrosc. Lett., 9*, 95 (1976).
18 D. N. Anderson and R. D. Willett, *Inorg. Chim. Acta, 8*, 167 (1974).
19 J. P. Steadman and R. D. Willett, *Inorg. Chim. Acta, 4*, 367 (1970).
20 J. Lamotte-Brasseur, L. Dupont and O. Dideberg, *Acta Crystallogr., Sect. B, 29*, 241 (1973).
21 M. R. Udupa and B. Krebs, *Inorg. Chim. Acta, 33*, 241 (1979).
22 B. K. Vainshtein, V. M. Fridkin and V. L. Indenborn, 'Modern Crystallography', Vol. II, Springer, Berlin, 1982.
23 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39*, 158 (1983).
24 'International Tables for X-Ray Crystallography', Vol. IV, Kynoch Press, Birmingham, U.K., 1974.
25 J. M. Stewart, P. A. Machin, C. W. Dickinson, H. L. Ammon, H. Heck and H. Flack, 'The X-Ray System', *Technical Report TR-446*, Computer Science Center, University of Maryland, U.S.A., 1976.
26 C. K. Johnson, 'ORTEP', *Report ORNL-3794*, Oak Ridge National Laboratory, Tenn., U.S.A., 1965.