HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.

HULME, R. & SCRUTON, J. C. (1968). *J. Chem. Soc. A*, pp. 2448–2452.

HULME, R. & SZYMANSKI, J. T. (1969). *Acta Cryst.* B25, 753–761.

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KISLIUK, P. (1954). *J. Chem. Phys.* **22**, 86–92.

LINDQUIST, I. & NIGGLI, A. (1956). *J. Inorg. Nucl. Chem.* **2**, 345–347.

MENSHUTKIN, B. (1912). *Zh. Russ. Fiz. Khim. Ova*, **44**, 1079–1145.

NELSON, J. B. & RILEY, D. P. (1945). *Proc. Phys. Soc. London*, **57**, 160–177.

PARK, W. (1969). PhD Dissertation, Univ. of Louisville, Louisville, Kentucky.

PAULING, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

WILLIAMS, D. E. (1964). *A Fortran Lattice Constant Refinement Program*, US Atomic Energy Commission Report, IS-1052.

WILLIAMS, D. E. & RUNDLE, R. E. (1964). *J. Am. Chem. Soc.* **86**, 1660–1666.

The Crystal Structures of Hexahalouranates.
I. Bis(triphenylethylphosphonium) Hexachlorouranate(IV) and Bis(triphenylethylphosphonium) Hexabromouranate(IV)

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The crystal structures of the bis(triphenylethylphosphonium) hexahalouranates(IV), $[P(C_6H_5)_3C_2H_5]_2[UX_6]$ [X = (I) chlorine, (II) bromine], have been determined from three-dimensional X-ray diffraction data collected on an automatic Philips PW 1100 four-circle diffractometer using 2894 (I) and 1448 (II) structure amplitudes from independent reflexions. The compounds crystallize in the (I) triclinic $P\bar{1}$, and (II) monoclinic $P2_1/n$ space groups with the lattice constants (I): $a = 10.53$ (1), $b = 10.95$ (1), $c = 10.31$ (1) Å, $\alpha = 113.22$ (5), $\beta = 105.20$ (5), $\gamma = 80.40$ (5)°; and (II): $a = 10.45$ (1), $b = 13.51$ (1), $c = 15.46$ (1) Å, $\beta = 96.67$ (5)°. In both structures the U atoms are situated at centres of symmetry [$Z = 1$ (I) and 2 (II)]. Trial atomic coordinates, obtained by the usual heavy-atom techniques, were refined by blocked-full-matrix least-squares refinement procedures to values for the conventional R of 0.029 (I) and 0.055 (II). The mean values of the U–X bond lengths and their estimated standard deviations are U–Cl = 2.624 (1) and U–Br = 2.770 (2) Å.

Introduction

The increasing number of accurate crystal-structure determinations in recent years on oxo–halo complexes of uranium with oxidation states U^{IV} to U^{VI}, as well as those of the type UX_4L_2 (X = Cl, Br; L a neutral oxygen donor ligand) has provided sufficient structural

data to permit important conclusions to be drawn with regard to the nature of the bonding by U in such complexes. Thus, de Wet & du Preez (1977) have adduced strong evidence that the nature of the bonding between U and its coordination neighbours is predominantly ionic, since ligand–ligand repulsions can account for the observed bonding distances as well as the shifts in U–X (X = oxygen, halogen) bond lengths which accompany changes in charge density, donor strength and coordination position of the ligands. For

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example, the U^{IV}—Cl bond length varies between 2·618 (4) and 2·665 (5) Å in the UCl_4L_2 complexes (de Wet & Darlow, 1971; Bombieri, Brown & Graziani, 1975; Caira & Nassimbeni, 1977; Sommerville & Laing, 1976), while a larger variation in U^{VI}—Cl bond lengths has been reported: 2·41–2·51 (4) Å in UCl_6 (Taylor & Wilson, 1974), 2·668 (5) Å in salts of $UO_2Cl_4^{2-}$ (Brusset, Nguyen & Haffner, 1974; Bois, Nguyen & Rodier, 1976), and 2·443–2·536 (3) Å in the tetraphenylphosphonium salt of $UOCl_5^-$ (de Wet & du Preez, 1977). Similar variations may be expected for other U—halogen bonds. In view of the sensitivity of such bond lengths to the chemical environment of U, and the association between their variations and bonding relationships, it is desirable to have available bond lengths which could be used as comparison standards. If the crystallographic environment is similar for a series of U–halogen complexes, and the bonds are chemically equivalent (e.g. terminal U—X in UX_6 octahedra), then the effects that cause variability are kept constant and intercomparison is possible, both for one type of halogen in different U oxidation states, and for different halogens and the same oxidation state.

These criteria are not feasible for neutral UX_6, but suitable model compounds are available for the lower oxidation states (U^{IV} and U^V) in the salts of UX_6^{n-} anions ($n = 1, 2$). This paper presents the first results in a series of accurate U—halogen bond-length determinations. The results for U^V—Cl are in part II (de Wet, Caira & Gellatly, 1978). As cations we have selected unsymmetrical phosphonium derivatives, $[P(C_6H_5)_3R]^+$ (R = benzyl, ethyl, etc.), in order to induce low crystallographic symmetry in the complex; in this way problems such as twinning (Staritzky & Singer, 1952) are avoided, and more independent bond-length estimations are possible.

Experimental

The hexachloro complex (I) was prepared by treating an ethanol–HCl solution of uranium with the stoichiometric quantity of the bromide salt of the cation; the hexabromo analogue (II) was obtained by similarly treating an acetone solution of the complex $UBr_4(CH_3CN)_4$. Both salts were recrystallized from anhydrous methyl cyanide. Intensity data were collected on a Philips PW 1100 computer-controlled four-circle diffractometer, and, in order to avoid absorption errors as far as possible, suitable crystal fragments were ground spherically to within 10% in a Hilger & Watts crystal grinder. Accurate cell dimensions were obtained by least-squares analysis of the angular data from 25 high-order reflexions. The crystal and intensity-measurement data for (I) and (II) are collected in Table 1; the criterion used to classify intensities as 'unobserved' was $|F_o| < 1.65\sigma(F_o)$; only those above this

limit were used in the structural analysis and refinement. After applying Lorentz and polarization corrections, the crystal radius for the crystal used for data collection of (II) was considered sufficiently large ($\mu r = 0.96$) to warrant additional spherical corrections for absorption; these were executed and, over the relevant θ range (0–25°), A^* varied between 3·93 and 3·72 (International Tables for X-ray Crystallography, 1967).

Structure determination and refinement

In each structure the number of formula units per unit cell requires the U atoms to lie at symmetry centres, from which it also follows that the cations are centrosymmetrically disposed around these centres. Three-dimensional electron difference syntheses, with U placed at coordinates (I) (0,0,0), and (II) (0,0,0; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$), allowed trial positional coordinates to be obtained for all nonhydrogen atoms. For both structures refinement was performed on three models with increasing parameter freedom: (i) all atoms thermally isotropic, the phenyl C atoms being constrained to an idealized benzene configuration with C—C = 1·395 Å; (ii) all atoms isotropic and free; (iii) anisotropic U, halogen and ethyl C atoms C(1) and C(2), with H atoms placed at calculated positions 1·08 Å from their parent C atoms before each cycle, and methyl, methylene and phenyl H atoms refining with a common isotropic temperature factor for each of these three types. A riding model was used for placement of the methylene and phenyl H atoms, while those of the methyl group followed from the rigid-body orientation of this moiety.

Table 1. Crystal and intensity measurement data

	(I) $C_{20}H_{20}P_2UCl_6$	(II) $C_{20}H_{20}P_2UBr_6$
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	10·53 (1)	10·45 (1)
b (Å)	10·95 (1)	13·51 (1)
c (Å)	10·31 (1)	15·46 (1)
α (°)	113·22 (5)	90
β (°)	105·20 (5)	96·67 (5)
γ (°)	80·40 (5)	90
M_r	1032·7	1299·4
U (Å^3)	1051·4	2167·9
Z	1	2
D_c (g cm^{-3})	1·631	1·990
D_m (g cm^{-3})	1·64	1·96
$F(000)$	504	1224
μ(Mo $K\alpha$) (cm^{-1})	41·3	90·9
Crystal radius (mm)	0·170	0·106
Scan mode	ω–2θ	ω–2θ
θ range (°)	3–23	3–20
Scan width (° θ)	0·9	1·0
Scan speed (° θs^{-1})	0·03	0·04
Reflexions measured	2907	2122
Reflexions observed	2894	1448

The quantity minimized was $\Sigma w\Delta^2$ ($\Delta = |F_o| - k|F_c|$). Unit weights were employed for the isotropic models, while for (iii) weights, w, were proportional to $[\sigma^2(F_o) + gF_o^2]^{-1}$; the constant g was optimized for constancy of the sampling distribution of $\langle w\Delta^2 \rangle$ after each refinement cycle. Because of computer-memory limitations, no more than 112 parameters could be refined simultaneously by the full-matrix procedure, and refinement of model (iii) proceeded by using a blocked-matrix technique. The parameter blocks were constituted so as to ensure least-squares interactions between any two parameters at least once during a series of refinement cycles.

The refinements proceeded as follows: For (I) three full-matrix cycles with model (i) and two with (ii) resulted in a value for the conventional R of 0·048. A further eight blocked-matrix cycles with model (iii), in which anisotropic atom parameters underwent six refinement cycles and the remainder four, gave convergence of R at 0·029. Five strong, low-order reflexions, suspected to be suffering from extinction error ($\bar{1}20$, $02\bar{1}$, $1\bar{2}1$, $1\bar{1}1$, and $\bar{2}12$), were omitted during the final four cycles. The value of g finally refined to 1·58 × 10^{-3} and the value of R_w [$=(\Sigma w|\Delta|)/\Sigma |F_o|$] was 0·032. One-way sampling of $\langle w\Delta^2 \rangle$ with respect to the variables $\sin\theta$, $|h|$, $|k|$ and $|l|$, showed no distinct trends, although the sampled means tended to decrease by about one-half over the range $|F_o| \rightarrow |F_o|_{max}$ for the variable $[F_o/F_o(max)]^{1/2}$. This was possibly due to slight residual absorption error. The mean final shift/e.s.d. ratio for the refined parameters was 0·13 and only 4·56% of the reflexions had $|\Delta| > 2\sigma(F_o)$, with $|\Delta|_{max} = 4\cdot50$. For (II) the refinement was similar, except that only one cycle was executed for model (i). The corresponding values of R were 0·082 and 0·055 (final) respectively; g refined to 8·4 × 10^{-4}, and R_w was 0·057. The sampling behaviour of $\langle w\Delta^2 \rangle$ was similar to that in (I). The final mean shift/e.s.d. ratios and percentage of reflexions with $|\Delta|$ in the range quoted for (I) were 0·03 and 5·18% respectively. Final difference syntheses revealed no peak maxima >0·6 e Å^{-3} (I) and 0·9 e Å^{-3} (II). Scattering factors were calculated analytically (for U, Cromer & Liberman, 1970; for the remaining atoms, Cromer & Mann, 1968); those for U and the halogen atoms were corrected for anomalous dispersion (Cromer & Liberman, 1970). Except for the absorption corrections, all computing was done with the program system *SHELX* (Sheldrick, 1977). Final atomic and isotropic* thermal parameters are listed in Tables 2 and 3.

Table 2. *Final non-hydrogen atomic fractional coordinates* ($\times 10^4$) *and isotropic temperature factors* ($\times 10^3$) *(deviations in parentheses)*

	x	y	z	U (Å^2)
Compound (I)				
U	0	0	0	*
Cl(1)	1184 (1)	326 (2)	−1770 (2)	*
Cl(2)	184 (1)	2540 (1)	1612 (2)	*
Cl(3)	2291 (1)	−620 (1)	1450 (2)	*
C(1)	2752 (6)	5725 (6)	310 (5)	*
C(2)	1742 (6)	4688 (7)	−582 (7)	*
P	3484 (1)	5754 (1)	2107 (1)	42 (0)
C(11)	4685 (5)	6986 (5)	2978 (5)	46 (1)
C(12)	5239 (5)	7449 (5)	2189 (6)	56 (1)
C(13)	6202 (6)	8329 (6)	2896 (7)	69 (2)
C(14)	6638 (7)	8731 (7)	4363 (8)	81 (2)
C(15)	6089 (8)	8291 (8)	5179 (9)	87 (2)
C(16)	5126 (6)	7397 (6)	4467 (7)	68 (2)
C(21)	4323 (5)	4148 (5)	1997 (5)	44 (1)
C(22)	3586 (5)	3030 (5)	1489 (6)	54 (1)
C(23)	4249 (6)	1784 (6)	1302 (6)	59 (1)
C(24)	5608 (6)	1646 (6)	1593 (6)	63 (1)
C(25)	6333 (6)	2746 (5)	2087 (6)	57 (1)
C(26)	5691 (5)	4001 (5)	2297 (5)	47 (1)
C(31)	2236 (5)	6166 (5)	3141 (5)	45 (1)
C(32)	1344 (6)	7266 (6)	3119 (7)	64 (1)
C(33)	417 (6)	7654 (7)	3963 (7)	73 (2)
C(34)	357 (6)	6983 (6)	4834 (7)	66 (2)
C(35)	1230 (6)	5877 (6)	4823 (6)	63 (1)
C(36)	2168 (5)	5477 (5)	3995 (5)	52 (1)
Compound (II)				
U	0	0	0	*
Br(1)	1203 (2)	59 (2)	1683 (1)	*
Br(2)	−2184 (2)	856 (2)	547 (1)	*
Br(3)	950 (2)	1865 (2)	−329 (2)	*
C(1)	−1633 (19)	180 (17)	3026 (13)	*
C(2)	−415 (21)	533 (18)	3619 (14)	*
P	−2361 (5)	−877 (4)	3458 (3)	34 (2)
C(11)	−1175 (18)	−1862 (14)	3499 (12)	32 (5)
C(12)	−367 (21)	−2037 (18)	4240 (15)	56 (7)
C(13)	625 (24)	−2770 (18)	4210 (17)	67 (7)
C(14)	643 (27)	−3286 (22)	3451 (18)	83 (9)
C(15)	−211 (25)	−3117 (20)	2728 (18)	79 (8)
C(16)	−1163 (22)	−2378 (17)	2746 (15)	53 (6)
C(21)	−3763 (17)	−1214 (14)	2759 (12)	30 (5)
C(22)	−4609 (19)	−1915 (15)	3038 (13)	40 (6)
C(23)	−5776 (23)	−2138 (18)	2539 (15)	62 (7)
C(24)	−5991 (21)	−1684 (16)	1742 (14)	47 (6)
C(25)	−5175 (23)	−1039 (18)	1445 (16)	66 (7)
C(26)	−4047 (22)	−786 (18)	1958 (15)	61 (7)
C(31)	−2753 (16)	−598 (13)	4525 (11)	23 (5)
C(32)	−2897 (19)	−1376 (16)	5120 (13)	39 (6)
C(33)	−3274 (19)	−1149 (15)	5936 (13)	39 (6)
C(34)	−3471 (21)	−163 (15)	6169 (15)	50 (7)
C(35)	−3309 (18)	576 (16)	5592 (13)	43 (6)
C(36)	−2987 (19)	347 (16)	4785 (13)	43 (6)

* Anisotropic temperature factors for these atoms have been deposited.

Results and discussion

It is interesting that, despite chemical and geometric similarities, the two anions do not form isomorphous

Table 3. *Calculated fractional atomic coordinates* $(\times 10^3)$ *for the hydrogen atoms*

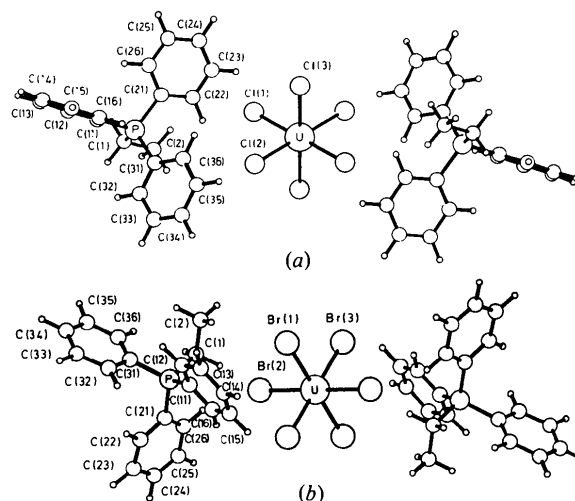|	x	y	z
Compound (I)			
H(1A)	354	552	−26
H(1B)	227	670	40
H(2A)	141	484	−159
H(2B)	92	488	−6
H(2C)	214	367	−79
H(12)	491	712	103
H(13)	662	871	229
H(14)	742	940	490
H(15)	641	864	634
H(16)	471	702	507
H(22)	252	314	125
H(23)	370	92	93
H(24)	611	67	143
H(25)	740	263	231
H(26)	626	486	269
H(32)	138	780	245
H(33)	−27	850	395
H(34)	−36	731	551
H(35)	117	532	547
H(36)	285	463	402
Compound (II)			
H(1A)	−233	78	296
H(1B)	−136	−1	239
H(2A)	−12	115	324
H(2B)	37	2	375
H(2C)	−69	80	423
H(12)	−47	−164	483
H(13)	133	−291	477
H(14)	138	−384	342
H(15)	−17	−356	215
H(16)	−185	−222	218
H(22)	−435	−229	365
H(23)	−647	−264	277
H(24)	−687	−186	133
H(25)	−540	−71	81
H(26)	−339	−26	173
H(32)	−272	−213	495
H(33)	−341	−174	639
H(34)	−375	1	680
H(35)	−344	134	577
H(36)	−291	94	433

Fig. 1. Atomic numbering schemes and views of (a) the hexa-chlorouranate and (b) the hexabromouranate compounds. In each case the view is along a trigonal axis of the anion.

Table 4. *Interatomic distances* (Å) *with estimated standard deviations in parentheses*

Compound (I)		Compound (II)	
U–Cl(1)	2·621 (2)	U–Br(1)	2·757 (2)
U–Cl(2)	2·627 (1)	U–Br(2)	2·776 (2)
U–Cl(3)	2·623 (1)	U–Br(3)	2·777 (2)

	Compound (I)	Compound (II)
C(1)–C(2)	1·53 (1)	1·56 (3)
P–C(1)	1·80 (1)	1·79 (2)
P–C(11)	1·80 (1)	1·81 (2)
P–C(21)	1·81 (1)	1·78 (2)
P–C(31)	1·80 (1)	1·79 (2)
C(11)–C(12)	1·39 (1)	1·36 (3)
C(12)–C(13)	1·37 (1)	1·44 (3)
C(13)–C(14)	1·37 (1)	1·37 (4)
C(14)–C(15)	1·39 (1)	1·37 (4)
C(15)–C(16)	1·38 (1)	1·41 (4)
C(16)–C(11)	1·39 (1)	1·36 (3)
C(21)–C(22)	1·40 (1)	1·40 (3)
C(22)–C(23)	1·39 (1)	1·40 (3)
C(23)–C(24)	1·38 (1)	1·37 (3)
C(24)–C(25)	1·38 (1)	1·34 (3)
C(25)–C(26)	1·39 (1)	1·39 (3)
C(26)–C(21)	1·39 (1)	1·37 (3)
C(31)–C(32)	1·40 (1)	1·42 (3)
C(32)–C(33)	1·38 (1)	1·40 (3)
C(33)–C(34)	1·38 (1)	1·40 (3)
C(34)–C(35)	1·39 (1)	1·36 (3)
C(35)–C(36)	1·38 (1)	1·37 (3)
C(36)–C(31)	1·39 (1)	1·37 (3)

crystal structures, as might have been expected, although the packing densities are very similar [volumes per non-hydrogen atoms are (I) 36·3, and (II) 37·4 Å³]. The differences in conformation of the cation groups relative to the UX_6 octahedra are shown up clearly when the two structures are viewed along a common direction, e.g. a trigonal octahedral axis (Fig. 1).

Bond lengths and angles (except those involving H atoms) are listed in Tables 4 and 5 respectively. U_{iso} for the methyl, methylene, and phenyl H atoms were, respectively, for (I) 0·091, 0·068 and 0·080 Å², and for (II) 0·093, 0·009 and 0·092 Å². The overall precision of the results obtained for the chloro complex (I) is

rather better, particularly as regards constancy of the U–halogen bond lengths. At first sight the U–Br(1) bond appears to be significantly shorter (by nine e.s.d.'s) than the other two similar bonds. However,

Table 5. *Bond angles* (°) *with estimated standard deviations in parentheses*

Compound (I)		Compound (II)	
Cl(1)–U–Cl(2)	89·1 (1)	Br(1)–U–Br(2)	90·1 (1)
Cl(1)–U–Cl(3)	89·9 (1)	Br(1)–U–Br(3)	90·7 (1)
Cl(2)–U–Cl(3)	91·3 (1)	Br(2)–U–Br(3)	90·1 (1)

	Compound (I)	Compound (II)
C(2)–C(1)–P	115·2 (5)	112 (2)
C(1)–P–C(11)	109·3 (3)	106·3 (9)
C(1)–P–C(21)	109·2 (2)	109·5 (9)
C(1)–P–C(31)	110·1 (3)	109·3 (9)
C(11)–P–C(31)	109·3 (2)	110·6 (9)
C(21)–P–C(31)	110·8 (3)	110·8 (9)
C(11)–P–C(21)	108·2 (2)	110·2 (9)
P–C(11)–C(12)	121·7 (4)	121 (2)
P–C(11)–C(16)	118·1 (5)	115 (1)
P–C(21)–C(22)	119·6 (4)	120 (1)
P–C(21)–C(26)	120·0 (4)	121 (2)
P–C(31)–C(32)	117·7 (5)	120 (1)
P–C(31)–C(36)	122·4 (4)	122 (2)
C(11)–C(12)–C(13)	119·4 (5)	118 (2)
C(12)–C(13)–C(14)	120·5 (8)	117 (2)
C(13)–C(14)–C(15)	121·2 (7)	123 (3)
C(14)–C(15)–C(16)	118·4 (7)	120 (3)
C(15)–C(16)–C(11)	120·5 (8)	117 (2)
C(16)–C(11)–C(12)	120·0 (5)	124 (2)
C(21)–C(22)–C(23)	118·9 (5)	121 (2)
C(22)–C(23)–C(24)	120·5 (6)	116 (2)
C(23)–C(24)–C(25)	120·5 (5)	124 (2)
C(24)–C(25)–C(26)	119·9 (5)	120 (2)
C(25)–C(26)–C(21)	119·9 (5)	120 (2)
C(26)–C(21)–C(22)	120·2 (4)	119 (2)
C(31)–C(32)–C(33)	119·3 (7)	119 (2)
C(32)–C(33)–C(34)	121·3 (6)	120 (2)
C(33)–C(34)–C(35)	118·8 (7)	120 (2)
C(34)–C(35)–C(36)	120·8 (7)	120 (2)
C(35)–C(36)–C(31)	120·0 (5)	124 (2)
C(36)–C(31)–C(32)	119·8 (6)	118 (2)

blocked-matrix approximations in least-squares refinement produce underestimated standard deviations in the atomic coordinates (Cruickshank, 1965) and in any event the physical significance of e.s.d.'s of less than 0·01 Å in bond lengths should be regarded with scepticism. We consider ~0·01 Å to be a more realistic estimate of σ(U–Br) and conclude, therefore, that the three U–Br bonds are equivalent, *i.e.* in both structures the anions possess undistorted octahedral symmetry. This inference is supported by the absence of any spectroscopic data to the contrary.

The U–Br bond length determined in (II) is the first to be reported for U^{IV}, and that of U–Cl in (I), although in agreement with the mean value of 2·60 (2) Å found for hexakis(dimethyl sulphoxide)dichlorouranium(IV) hexachlorouranate(IV), $[UCl_2(OSMe_2)_6]$-$[UCl_6]$ (Bombieri & Bagnall, 1975), is probably more reliable, because of the sensitivity of the latter complex to X-rays and the rapid-scan technique which was used to minimize decomposition during data collection.

References

BOIS, C., NGUYEN, Q. D. & RODIER, N. (1976). *Acta Cryst.* B32, 1541–1544.

BOMBIERI, G. & BAGNALL, K. W. (1975). *Chem. Commun.* pp. 188–189.

BOMBIERI, G., BROWN, D. & GRAZIANI, R. (1975). *J. Chem. Soc. Dalton Trans.* pp. 1873–1876.

BRUSSET, H., NGUYEN, Q. D. & HAFFNER, F. (1974). *J. Inorg. Nucl. Chem.* 36, 791–794.

CAIRA, M. R. & NASSIMBENI, L. R. (1977). *J. Inorg. Nucl. Chem.* 39, 455–457.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* 53, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.

CRUICKSHANK, D. W. J. (1965). In *Computing Methods in Crystallography*, edited by J. S. ROLLETT. Oxford: Pergamon Press.

International Tables for X-ray Crystallography (1967). Vol. II, 2nd edition, pp. 302–305. Birmingham: Kynoch Press.

SHELDRICK, G. M. (1977). The *SHELX* system. Univ. of Cambridge, England.

SOMMERVILLE, P. & LAING, M. (1976). *Acta Cryst.* B32, 1551–1552.

STARITZKY, E. & SINGER, J. (1952). *Acta Cryst.* 5, 536–540.

TAYLOR, J. C. & WILSON, P. W. (1974). *Acta Cryst.* B30, 1481–1484.

WET, J. F. DE, CAIRA, M. R. & GELLATLY, B. J. (1978). *Acta Cryst.* B34, 1121–1124.

WET, J. F. DE & DARLOW, S. F. (1971). *Inorg. Nucl. Chem. Lett.* 7, 1041–1048.

WET, J. F. DE & DU PREEZ, J. G. H. (1977). *J. Chem. Soc. Dalton Trans.* To be published.