Synthesis of Dimorpholino-di-, -tri-, and -tetra-selane, and Dipiperidino-tetraselane. Crystal and Molecular Structures of the Two Tetraselanes

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The title compounds have been prepared by heating black selenium powder with morpholine or piperidine in the presence of Pb_3O_4. Dimorpholino- and dipiperidino-tetraselane, $Se_4(NC_4H_8O)_2$ (1) and $Se_4(NC_5H_{10})_2$ (2), form isomorphous tetragonal crystals, space group $I4_1/a$ (no. 88), $Z = 8$, with $a = b = 13.074(1)$, $c = 16.798(3)$ Å for (1) and $a = b = 13.262(1)$, $c = 17.713(4)$ Å for (2). The crystal structures have been determined by *X*-ray diffraction from Mo-K_α diffractometer data and refined by full-matrix least squares to *R* 0.037 and 0.035 for 803 and 871 observed reflections respectively. The molecules lie across crystallographic two-fold axes. The N–Se–Se–Se–Se–N chains occur in the *trans-trans* form, with the dimensions in (1) and (2) respectively: N–Se 1.836(6) and 1.824(6), Se–Se (terminal) 2.336(2) and 2.327(2), Se–Se (central) 2.356(2) and 2.347(2) Å; N–Se–Se 106.8(2) and 106.9(2), Se–Se–Se 102.1(1) and 104.1(1), NSeSe–SeSeSe 90.2 and 88.5, SeSeSe–SeSeSe 75.7 and 76.4°. The organic groups occur in the chair form, with N–Se equatorial. The shortest intermolecular Se · · · Se contact occurs in (1) and is 3.658(2) Å.

THE purpose of this work was to explore the feasibility of a new way to synthesize selenopolythionates, which are compounds built up of chains of bivalent selenium atoms terminated at each end by sulphite or thiosulphate groups.[1] In the sulphur, *i.e.* polythionate, series the way is known: diamino-mono- and -di-sulphanes derived from secondary aliphatic amines react with aqueous sulphurous acid to give tri- and tetra-thionates,[2] and dipiperidino-mono- and -di-sulphane react with acidified thiosulphate to give solutions of penta- and hexa-thionate,[3] the amino-groups being replaced by sulphite or thiosulphate. Furthermore, the work on the synthesis of the starting materials, *i.e.* diaminoselanes, gained interest in its own right, due to the findings: that such compounds can be prepared from selenium and the amine in a simple, direct way; that dipiperidino- and dimorpholino-tetraselane, the first organic tetraselanes to be isolated in a pure state, possess excellent crystallizing properties and high stability as solids; and that dipiperidinotetraselane with carbon disulphide produced a new allotrope of selenium.[4]

The diaminomonoselanes $Se(NMe_2)_2$ and $Se(NEt_2)_2$ have been prepared.[5] The only other reference to diaminoselanes appears to be a patent,[6] describing the reaction of heterocyclic amines with dichlorodiselane in benzene, and where, in the one example given, the product is a brick red solid of m.p. 90—95 °C thought essentially to be dimorpholinotriselane. Diamino-mono- and -di-sulphanes are usually prepared from the dichlorosulphane and the secondary amine.[7] By use of dichloropolysulphanes, Goebell [8] recently extended the piperidine and morpholine series, $S_n(NC_5H_{10})_2$ and $S_n(NC_4H_8O)_2$, up to and including $n = 6$. However, the first synthesis of diaminopolysulphanes ($n > 2$) was achieved by a different method: Levi [9] in 1931 prepared dipiperidino-tri- and -tetra-sulphane, and the dimethyl- and diethyl-aminotrisulphane analogues, from sulphur and the amine in benzene in the presence of an excess of lead oxide, PbO. The reaction was later used by others,[10,11] and HgO was also used instead of PbO as the sulphide acceptor.[10] The reaction has not, to our knowledge, been used in selenium chemistry.

We found that black selenium powder, when heated with piperidine or morpholine in the presence of PbO, reacts to give amides of bivalent selenium. However, Pb_3O_4 was found to be markedly more effective than PbO. The yields varied with the brand of Pb_3O_4 used, probably depending on surface area and properties. In the case of piperidine, pure dipiperidinotetraselane, $Se_4(NC_5H_{10})_2$, crystallized, whereas in the case of morpholine the crude product was a greenish yellow mixture of dimorpholino-di-, -tri-, and -tetra-selane, $Se_n(NC_4H_8O)_2$ ($n = 2$, 3, or 4).

The *X*-ray crystal structures of the compounds have been determined.[4a] The chains of selenium atoms, *N*-bonded at the ends, are unbranched and non-planar. We report here the crystal structures of the two tetraselanes. These are the first crystal structures of diaminoselanes, and the first, generally, of compounds containing tetraselenium chains.

EXPERIMENTAL

Black selenium powder (Merck) was used, and laboratory grade piperidine and morpholine. The m.p.s were determined in a preheated bath, and are corrected.

Selenium and Piperidine.—Selenium (40 g), piperidine (50 cm³), and Pb_3O_4 (23—30 g), in a 300 cm³ Erlenmeyer flask covered with a watch glass, were heated close to the b.p. of the amine with magnetic stirring for 30—60 min. The hot mixture was filtered with suction and the black residue was washed with hot MeOH (2 × 50 cm³). On mixing with the orange-red main filtrate, the MeOH washings caused a red oil to form and settle on the bottom of the beaker. Overnight crystals deposited and the oil also changed into crystals. They were all filtered off and washed with MeOH; yield of *dipiperidinotetraselane*, 7—13 g (see Table 1), m.p. 90—91 °C (decomp.) (Found: Se, 65.1. $C_{10}H_{20}N_2Se_4$ requires Se, 65.2%). The highest yield, 13.28 g, corresponds to *ca.* 26% based on selenium (40 g) and the tentative equation below (piperidine and Pb_3O_4 present in excess). Another 2—3 g, not quite pure, could be obtained by evaporating the filtrate nearly to dryness in a stream of air, and adding MeOH (25 cm³).

$$19\,Se + 8\,C_5H_{10}NH + Pb_3O_4 \longrightarrow 4\,Se_4(NC_5H_{10})_2 + 3\,PbSe + 4\,H_2O$$

Selenium and Morpholine.—Selenium (40 g), morpholine (50 cm^3), and Pb_3O_4 (Baker Analyzed) (23 g) were heated as above for 1 h. Hot cyclohexane (2 × 50 cm^3) instead of MeOH was used for washing, the morpholine–cyclohexane filtrate was allowed to cool to room temperature and was further cooled in a refrigerator, before filtering and washing with freezer-cold MeOH; yield, 8—10 g. The greenish yellow product consisted of a mixture of dimorpholino-di-, -tri-, and -tetra-selane, and had a selenium content of 55.4—56.6%, corresponding to an average of 2.71—2.84 selenium atoms in the chain. A further crop, with a slightly lower selenium content (54.5—55.1%), was obtained on evaporating the filtrate nearly to dryness in a stream of air, adding freezer-cold MeOH (25 cm^3), and filtering; total yield, 16—17 g.

TABLE 1

Yields of dipiperidinotetraselane, from selenium (40 g), piperidine (50 cm^3), and Pb_3O_4

Pb_3O_4		Heating	
Amount/g	Brand *	time/min	Yield/g
23	A	30	10.79
23	B	30	7.21
30	B	30	9.38
23	C	30	7.74
23	D	30	6.82
23	D	60	9.94
30	D	30	7.68
30	D	60	13.28

*A, B.D.H. Lab. Reagent, for manganese test; B, B.D.H. Lab. Reagent; C, Baker Analyzed; D, Merck *p.a.*

Dimorpholinotetraselane. This compound was obtained from the crude product by treatment with MeOH (15 cm^3 per g). The tetraselane is slightly soluble in hot MeOH whereas the tri- and di-selane are readily soluble, and hot MeOH promotes disproportionation of the lower members leading to the formation of more tetraselane, which crystallizes on cooling. The mixture was heated to the b.p. of MeOH, and allowed to cool; the cycle was repeated a few times, and the mixture was then filtered while at 35—40 °C. The crystals were washed with MeOH; yield, 60—65% of the weight of crude product used, m.p. 123—124 °C (decomp.) (Found: Se, 64.4. $C_8H_{16}N_2O_2Se_4$ requires Se, 64.7%).

Dimorpholinotriselane. This compound often separated along with the diselane in crystallizations of the latter, and well formed crystals of it could be picked out for melting-point determination and *X*-ray work; m.p. 104—105 °C (decomp.). The compound was not obtained in analytically pure samples, probably due to ease of rearrangement.

Dimorpholinodiselane. This was obtained by treating the crude product with warm n-pentane (50 cm^3 per g), evaporating the filtrate to dryness, and recrystallizing from cyclohexane. The crystals were washed with freezer-cold MeOH; m.p. 129—130 °C (decomp.) (Found: Se, 47.4. $C_8H_{16}N_2O_2Se_2$ requires Se, 47.8%).

Remarks on Stabilities.—The tetraselanes crystallize as tetragonal bipyramids, greenish yellow to orange-red according to crystal size, dimorpholinotriselane as rhombs or elongated plates, pale green to yellowish green, and dimorpholinodiselane as prisms, colourless with a greenish tinge in the larger ones. Rather surprisingly, the stabilities of the crystals in air increase with increasing selenium content. This is probably due to a high stability of the crystal lattice of the tetraselanes, but also to the crystals of the lower members being moisture-sensitive. The crystals of dimorpholinodiselane became red after 1 d in the dark, and in light more rapidly; in dry air they are more stable. In closed bottles in the dark, the crystals of the tetraselanes have remained unchanged.

In solution, the tetraselanes are unstable and liberate selenium, markedly faster in bright daylight. The lower members, on heating in solution, rearrange giving longer selenium chains. Thus, dimorpholinodiselane (0.9 g), on rapid heating and cooling, recrystallized beautifully from MeOH (18 cm^3), but on prolonged heating (5—10 min) the pale green solution became red, and on slow cooling to room temperature well formed bipyramids of the tetraselane deposited, together with some amorphous selenium.

X-Ray Structure Analyses of the Tetraselanes.—Preliminary unit-cell and space-group data were obtained from oscillation and Weissenberg photographs taken with Cu-K_α radiation. *X*-Ray data for structure analysis were collected on a Siemens AED diffractometer using niobium-filtered Mo-K_α radiation, $\lambda = 0.710\,7$ Å. Intensities were measured by the five-value θ—2θ scan technique.[12] Three reference reflections were measured at intervals of 50 reflections, no significant trends in their intensities being detectable. Unit-cell dimensions were determined from the 2θ values of the Mo-$K_{\alpha(1)}$ peaks ($\lambda = 0.709\,26$ Å) of *ca.* 20 reflections in the $40 < 2\theta < 50°$ range, measured by an ω-scan technique.[13] $\sigma(I)$ and $\sigma(F) = \sigma(I)/2(LpI)^{\frac{1}{2}}$ were based on counting statistics, with an ' instability factor ' term [14] included, the factor derived from the reference reflections. Reflections with $I > 3\sigma(I)$ were regarded as observed and were used in the structure solution and refinement. Lorentz, polarization, and absorption corrections were applied. From comparisons of F_0 and $|F_c|$, extinction effects were not evident and were not corrected for.

Calculations were made by use of the ' *X*-Ray '72 ' programs [15] with local adaptions. Refinements were by full-matrix least squares, the sum minimized being $\Sigma w\Delta^2(F)$ with $w = 1/\sigma^2(F)$. Atomic scattering factors were from ref. 16 (from ref. 17 for H) with anomalous dispersion [18] for Se included. Anisotropic temperature factors were used for all atoms except hydrogen. Hydrogen atoms were placed geometrically by use of the ' *X*-Ray '72 ' BONDAT sub-routine, at [19] C–H 0.95 Å, and were given equal isotropic temperature factors; their parameters (positional and thermal) were not refined.

Crystal data. The crystals of dimorpholino- and dipiperidino-tetraselane are isomorphous and tetragonal with space group $I4_1/a$ (no. 88) and $Z = 8$.

(1), $C_8H_{16}N_2O_2Se_4$, $M = 488.1$, $a = b = 13.074(1)$, $c = 16.798(3)$ Å, $U = 2\,871.3$ Å^3, $D_c = 2.26$ g cm^{-3}, $F(000) = 1\,840$, μ(Mo-K_α) = 110.2 cm^{-1}, 803 observed unique reflections within $2\theta = 56°$. Absorption corrections ranged from 2.015 to 4.376. The Se atoms were located from a Patterson map and the N, C, and O atoms from subsequent Fourier maps. Refinement converged at $R = 0.037$, $R' = 0.026$, $\sigma_1 = [\Sigma w\Delta^2(F)/(n - m)]^{\frac{1}{2}} = 1.60$.

(2), $C_{10}H_{20}N_2Se_4$, $M = 484.1$, $a = b = 13.262(1)$, $c = 17.713(4)$ Å, $U = 3\,115.4$ Å^3, $D_c = 2.08$ g cm^{-3}, $F(000) = 1\,840$, μ(Mo-K_α) = 101.1 cm^{-1}, 871 observed unique reflections within $2\theta = 56°$. Absorption corrections ranged from 2.185 to 2.531. The refinement began from the coordinates of the corresponding atoms in (1), and converged at $R = 0.035$, $R' = 0.028$, $\sigma_1 = 1.71$.

Maximum shift-to-error ratio in the last cycle was 0.001 3 for (1) and 0.058 for (2). Largest peaks and holes in the $\Delta(F)$ maps based on the final parameters were 1.4 and -1.7 e Å^{-3} for (1) and 1.2 and -1.1 e Å^{-3} for (2). Final co-ordinates for non-hydrogen atoms are in Table 2. Lists of structure factors, thermal parameters, and hydrogen-atom co-ordinates are in Supplementary Publication No. SUP 22695 (27 pp.).*

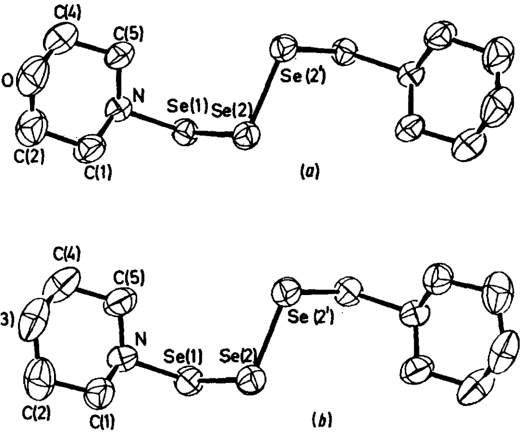
TABLE 2

Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses. Origin at a centre of symmetry

Atom	*x*	*y*	*z*
(*a*) $Se_4(NC_4H_8O)_2$			
Se(1)	987.1(7)	1 156.9(6)	663.4(5)
Se(2)	−58.5(7)	1 600.8(7)	−409.7(5)
N	2 282(5)	982(5)	264(3)
C(1)	2 428(7)	78(7)	−223(5)
C(2)	3 563(8)	−59(9)	−384(6)
O	3 973(5)	822(7)	−760(4)
C(4)	3 832(8)	1 695(9)	−285(6)
C(5)	2 711(6)	1 897(7)	−112(5)
(*b*) $Se_4(NC_5H_{10})_2$			
Se(1)	924.7(6)	1 096.1(6)	639.3(4)
Se(2)	−83.0(6)	1 619.1(6)	−362.5(5)
N	2 192(4)	912(4)	264(3)
C(1)	2 276(5)	139(6)	−305(5)
C(2)	3 369(7)	−115(7)	−469(5)
C(3)	3 958(6)	816(8)	−673(5)
C(4)	3 803(6)	1 628(7)	−89(5)
C(5)	2 700(5)	1 831(6)	40(5)

RESULTS AND DISCUSSION

Selenium does react with secondary amines in the presence of a selenide acceptor to give diaminoselanes, but is less reactive than sulphur. In experiments where tellurium was heated with morpholine or piperidine in the presence of Pb_3O_4, no reaction was observed.



(*a*) Dimorpholinotetraselane and (*b*) dipiperidinotetraselane as seen along the two-fold axes (thermal ellipsoids drawn to enclose 50% probabilities)

Structures of Dimorpholino- and Dipiperidino-tetraselane.—In the crystals, the tetraselane molecules lie across crystallographic two-fold axes (see Figure). Dimensional data, based on the atomic co-ordinates of Table 2, are in Tables 3 and 4. The N–Se–Se–Se–Se–N chains occur in the extended-helix rotameric form, the *trans-trans* form of a tetraselane or tetrasulphane derivative.[20] The space group is not enantiomorphous, so right- and left-handed forms are present. The Se–Se bond lengths along the chain alternate slightly but significantly, the central bond being 0.020 Å longer than the terminal bonds in each compound. The Se–Se bonds in (1) are 0.009 Å longer than the bonds in (2); statistically, the difference is significant [$\Delta/\sigma(\Delta) = 3.2$]. The average length of the six Se–Se bonds in the two compounds, 2.342 ± 0.010 Å, slightly exceeds the overall average, 2.335 Å, in different forms of cyclo-octaselenium.[4b,21]

TABLE 3

Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

	$Se_4(NC_4H_8O)_2$	$Se_4(NC_5H_{10})_2$
(*a*) Bond lengths		
Se(1)–Se(2)	2.336(2)	2.327(2)
Se(2)–Se(2′) [a]	2.356(2)	2.347(2)
Se(1)–N	1.836(6)	1.824(6)
N–C(1)	1.450(12)	1.442(10)
C(1)–C(2)	1.520(14)	1.516(12)
C(2)–O	1.418(14)	
C(2)–C(3)		1.505(14)
O–C(4)	1.405(14)	
C(3)–C(4)		1.507(14)
C(4)–C(5)	1.516(13)	1.504(11)
C(5)–N	1.463(11)	1.449(10)
(*b*) Bond angles		
N–Se(1)–Se(2)	106.8(2)	106.9(2)
Se(1)–Se(2)–Se(2′)	102.1(1)	104.1(1)
Se(1)–N–C(1)	115.4(6)	114.9(5)
Se(1)–N–C(5)	114.2(5)	114.6(5)
C(1)–N–C(5)	111.9(7)	111.8(6)
N–C(1)–C(2)	108.9(8)	111.4(7)
C(1)–C(2)–O	110.7(9)	
C(1)–C(2)–C(3)		111.1(8)
C(2)–O–C(4)	110.9(8)	
C(2)–C(3)–C(4)		110.5(8)
O–C(4)–C(5)	112.1(9)	
C(3)–C(4)–C(5)		111.4(7)
C(4)–C(5)–N	108.1(8)	110.1(7)
(*c*) Dihedral angles [b]		
Se(1)–Se(2)	90.2	88.5
Se(2)–Se(2′)	75.7	76.4

[a] Se(2)–Se(2′) across molecular two-fold axis. [b] At the indicated bond of the tetraselane chain. Zero for planar *cis*.

TABLE 4

Least-squares planes of C(1), C(2), C(4), and C(5) of the morpholino- and piperidino-groups. The equations of the planes in direct space are $2.2435x - 1.3122y + 16.4623z = 0.1714$ and $1.4309x - 3.9078y + 16.8188z = -0.2518$ respectively

(*a*) Morpholino-group: distances from plane Se(2) −1.069, Se(1) 0.990, N 0.646, C(1) −0.004, C(2) 0.004, O −0.639, C(4) −0.004, C(5) 0.004 Å; angles with plane C(1)–N–C(5) 52.4, C(2)–O–C(4) 53.0, N–Se(1)–Se(2) 84.5°; angle of normal to plane with two-fold axis 11.5°

(*b*) Piperidino-group: distances from plane Se(2) −1.002, Se(1) 1.031, N 0.653, C(1) 0.010, C(2) −0.010, C(3) −0.633, C(4) 0.010, C(5) −0.010 Å; angles with plane C(1)–N–C(5) 53.7, C(2)–C(3)–C(4) 47.5, N–Se(1)–Se(2) 86.5°; angle of normal to plane with two-fold axis 18.3°

The six-membered rings of the organic groups occur in the chair form, with N–Se equatorial, *cf.* Table 4. The N–Se(1)–Se(2) plane makes an angle close to 90° with the C(1), C(2), C(3), C(4) least-squares plane, with N and Se(1) on one side of the least-squares plane and Se(2)

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

on the other side; this indicates mutually *trans* positions of the nitrogen lone pair and Se(2) relative to the N–Se(1) bond. The lengths of the N–Se bonds are apparently the first ones determined for N(amino)–Se^{II} bonds. The sum of the Pauling N–Se single-bond radii is 1.87 Å.

The molecular two-fold axes pass through the four-fold inversion centres of the space group. Pairs of molecules pack closely around the $\bar{4}$ centres; Se(1) and Se(2) lie 2.392 and 3.027 Å, respectively, from the centre in (1) and 2.478 and 3.099 Å from the centre in (2). The intermolecular Se · · · Se contacts generated by the $\bar{4}$ centre are Se(1) · · · Se(1) 3.658, Se(1) · · · Se(2) 4.132 and 4.866, Se(2) · · · Se(2) 5.819 Å in (1), and 3.824, 4.311 and 5.013, 5.949 Å respectively in (2); each contact occurs four times, or twice per molecule. Symmetry centres midway between the $\bar{4}$ centres generate the contacts Se(1) · · · Se(1) 4.559, Se(1) · · · Se(2) 3.828, Se(2) · · · Se(2) 4.409 Å in (1), and 4.427, 3.802, 4.488 Å respectively in (2); the first and third types, between equivalent atoms, occur once per molecule and the second twice. This gives a total of 12 intermolecular Se · · · Se contacts per molecule, each contact counted only once, with each of the four Se atoms of a molecule engaged in five contacts. Selenium being the heaviest atom in the structure and the Se · · · Se van der Waals potential well the deepest one, these Se · · · Se contacts must contribute substantially to the high stability of the lattice. There are no intermolecular N · · · Se contacts within 4.0 Å.

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REFERENCES

[1] B. Rathke, *J. prakt. Chem.*, 1865, **95**, 1; O. Foss, *Acta Chem. Scand.*, 1949, **3**, 435; J. Janickis, *Accounts Chem. Res.*, 1969, **2**, 316.

[2] H. Lecher, T. Weigel, and M. Wittwer, G.P. 517,995/1931 (*Chem. Abs.*, 1931, **25**, 2735); H. Lecher and T. Weigel, G.P. 520,857/1931 (*Chem. Abs.*, 1931, **25**, 3359).

[3] O. Foss, *Kgl. Nor. Vidensk. Selsk. Skr.*, 1945, No. 2.

[4] O. Foss and V. Janickis, *J.C.S. Chem. Comm.*, 1977, (*a*) 833; (*b*) 834.

[5] R. Paetzold and E. Rönsch, *Z. anorg. Chem.*, 1965, **338**, 22; *Spectrochim. Acta*, 1970, **A26**, 569.

[6] C. W. Christensen, U.S.P. 2,691,016/1954; *Chem. Abs.*, 1955, **49**, 662.

[7] A. Michaelis and K. Luxembourg, *Ber.*, 1895, **28**, 165; F. Lengfeld and J. Stieglitz, *ibid.*, p. 575; A. Michaelis, *ibid.*, p. 1012; E. S. Blake, *J. Amer. Chem. Soc.*, 1943, **65**, 1267; Q. E. Thompson, *Quart. Reports Sulphur Chem.*, 1970, **5**, 245.

[8] J. Goebell, Ph.D. Thesis, University of Cologne, 1963, pp. 34—48; F. Fehér and H. Münzner, *Chem. Ber.*, 1963, **96**, 1131.

[9] T. G. Levi, *Gazzetta*, 1931, **61**, 286.

[10] H. Jenne and M. Becke-Goehring, *Chem. Ber.*, 1958, **91**, 1950.

[11] K. Sharada and A. R. V. Murthy, *Z. anorg. Chem.*, 1960, **306**, 196; *Chem. Ber.*, 1960, **93**, 1251; C. N. R. Rao, R. Venkataraghavan, and T. R. Kasturi, *Canad. J. Chem.*, 1964, **42**, 36.

[12] P. G. H. Troughton, *Siemens Review*, 1970, **37**, Fourth Special Issue '*X*-Ray and Electron Microscopy News,' p. 22.

[13] K. Maartmann-Moe, *Siemens Review*, 1974, **41**, Seventh Special Issue '*X*-Ray and Electron Microscopy News', p. 54.

[14] G. H. Stout and L. H. Jensen, '*X*-Ray Structure Determination. A Practical Guide,' Macmillan, London, 1969, p. 456.

[15] The '*X*-Ray System,' Technical Report TR-192, The Computer Science Center, University of Maryland, June 1972.

[16] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[17] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[18] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

[19] M. R. Churchill, *Inorg. Chem.*, 1973, **12**, 1213.

[20] O. Foss, *Adv. Inorg. Chem. Radiochem.*, 1960, **2**, 237.

[21] O. Foss and V. Janickis, following paper.