Journal of Organometallic Chemistry, 120 (1976) 381—388

THE SOLID STATE STRUCTURE OF TRIPHENYLTELLURONIUM CYANATE-CHLOROFORM($\frac{1}{2}$)

DONALD D. TITUS *, JUNG-SI LEE
Department of Chemistry, Temple University, Philadelphia, Pa. 19122 (U.S.A.)

and RONALD F. ZIOLO
Xerox Corporation, Webster Research Center, Xerox Square 114, Rochester, New York 14644 (U.S.A.)

(Received April 16th, 1976)

Summary

Three-dimensional X-ray crystal structure analysis shows that the organotelluronium salt, triphenyltelluronium cyanate-chloroform(1/2), exists as a tetramer in the solid state with both end-to-end and terminally bridging NCO groups. The oligomer is predominantly ionic with tellurium—nitrogen and tellurium—oxygen distances significantly shorter than respective van der Waals distances. Refinement of the structure, based on 3817 reflections collected by automatic diffractometry, converged to a conventional R factor of 4.9% and a weighted R factor of 4.2%. Crystal data for $Ph_3Te(NCO) \cdot \frac{1}{2} CHCl_3$ are as follows: $a = 12.083(6)$Å, $b = 12.900(12)$Å, $c = 13.878(10)$Å, $\alpha = 95.83(7)°$, $\beta = 103.47(7)°$, $\gamma = 98.87(6)°$, $V = 1901$Å^3 (temperature = 23°C) and $Z = 4$.

Introduction

Organo—telluronium salts, R_3TeX, have been known for nearly one hundred years and are generally believed to be ionic and of a simple $R_3Te^+X^-$ form [1,2,3]. The only reported structure of a telluronium salt, however, is that of $[(CH_3)_3Te]^+[CH_3TeI_4]^-$ which shows four weak tellurium—iodine interactions [4]. Recently we synthesized several pseudohalide compounds of the triphenyltelluronium cation, Ph_3Te^+, and obtained infrared and Raman spectroscopic [5] and crystallographic data [6,7], suggesting complex solid state structures for these compounds. In view of the complexity and novelty of the situation, we have determined the crystal and molecular structure of the triphenyltelluronium cyanate.

(continued on p. 384)

TABLE 1

POSITIONAL AND THERMAL PARAMETERS OF THE NON HYDROGEN ATOMS [a,b,c]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Tc(1)	3900(.5)	4243(.4)	2873(.4)	92(1)	51(1)	66(1)	14(1)	36(1)	16(1)
Tc(2)	1775(.5)	7084(.4)	4102(.4)	92(1)	53(1)	73(1)	27(1)	47(1)	21(1)
C(1)	7116(9)	3634(7)	3310(7)	99(11)	73(8)	72(8)	16(7)	53(8)	14(6)
N(1)	7814(8)	3156(7)	3813(6)	138(10)	124(8)	97(7)	65(8)	58(7)	49(6)
O(1)	6379(7)	4143(5)	2802(6)	166(9)	97(6)	123(7)	35(6)	43(7)	28(5)
C(2)	4897(8)	6659(6)	4629(6)	52(8)	42(5)	195(5)	4(5)	−2(5)	1(4)
N(2)	4128(9)	6465(6)	3901(8)	166(12)	88(7)	103(8)	8(8)	6(8)	15(6)
O(2)	5844(8)	6954(6)	5458(6)	205(11)	121(7)	140(8)	37(7)	79(8)	55(6)
C(11)	2064(8)	4266(6)	2672(7)	107(10)	38(6)	76(8)	−2(6)	52(8)	4(5)
C(12)	1786(9)	4060(7)	3496(8)	139(12)	81(8)	125(10)	37(8)	80(9)	31(7)
C(13)	5633(12)	4008(7)	3369(10)	190(17)	78(8)	137(12)	37(9)	116(12)	30(8)
C(14)	−337(10)	4182(8)	2422(11)	123(12)	76(8)	160(12)	21(8)	88(11)	−8(8)
C(15)	−55(10)	4416(8)	1611(9)	126(13)	113(10)	124(11)	32(9)	63(10)	3(8)
C(16)	1152(9)	4460(8)	1710(7)	109(11)	106(9)	78(8)	29(8)	46(8)	13(7)
C(17)	3349(7)	2609(6)	2007(6)	85(9)	61(6)	61(7)	21(6)	26(6)	9(5)
C(18)	2420(8)	1914(7)	2081(7)	97(10)	65(7)	102(8)	10(7)	49(8)	16(6)
C(19)	2096(10)	855(7)	1553(8)	148(12)	61(8)	109(9)	6(8)	47(9)	13(7)
C(110)	2681(10)	515(7)	977(8)	161(14)	61(8)	109(10)	19(8)	55(10)	−7(7)
C(111)	3609(10)	1205(9)	904(8)	134(13)	102(10)	100(9)	35(9)	52(9)	−3(8)
C(112)	3973(9)	2281(7)	1433(8)	126(11)	68(8)	104(9)	10(7)	56(8)	1(6)
C(113)	3785(8)	4955(7)	1493(7)	87(9)	74(7)	75(8)	27(6)	38(7)	24(6)
C(114)	4478(9)	5942(7)	1675(8)	117(11)	80(8)	122(9)	19(8)	63(8)	42(7)
C(115)	4480(10)	6400(9)	796(12)	138(13)	128(11)	162(14)	44(10)	91(12)	85(11)

C(116)	3804(12)	5859(12)	—214(11)	156(16)	170(14)	124(12)	88(12)	77(12)	90(11)
C(117)	3103(11)	4849(11)	—470(8)	161(15)	149(13)	98(10)	86(12)	55(10)	42(9)
C(118)	3098(8)	4386(8)	441(8)	113(10)	102(8)	80(9)	38(8)	27(8)	33(7)
C(21)	133(7)	7340(6)	4187(6)	86(9)	61(8)	56(6)	12(6)	27(6)	9(5)
C(22)	—869(8)	6544(7)	3766(7)	95(10)	78(8)	91(8)	23(7)	42(7)	—6(6)
C(23)	—1995(8)	6635(8)	3780(8)	79(10)	88(8)	141(10)	12(7)	53(8)	2(7)
C(24)	—2093(9)	7590(8)	4232(9)	117(11)	82(8)	147(11)	33(8)	78(9)	26(8)
C(25)	—1061(10)	8431(7)	4695(9)	156(13)	64(7)	189(12)	294(8)	113(11)	8(8)
C(26)	67(8)	8318(7)	4678(8)	114(11)	61(7)	139(10)	10(7)	71(9)	7(7)
C(27)	1204(7)	7429(5)	2509(6)	103(9)	49(6)	64(6)	16(6)	32(7)	12(5)
C(28)	1931(8)	7264(6)	1996(7)	108(10)	80(7)	81(8)	31(7)	49(8)	17(6)
C(29)	1572(10)	7478(8)	956(8)	172(15)	115(9)	91(9)	29(9)	77(10)	24(7)
C(210)	510(10)	7834(8)	448(8)	156(14)	113(9)	79(8)	5(9)	46(10)	29(7)
C(211)	—223(9)	8010(7)	944(8)	118(12)	99(9)	79(9)	27(8)	19(8)	20(7)
C(212)	95(8)	7794(7)	1972(7)	131(12)	90(8)	85(8)	29(8)	52(8)	24(6)
C(213)	2940(7)	8632(6)	4870(6)	91(9)	64(6)	72(8)	21(6)	50(7)	16(6)
C(214)	2694(7)	9486(6)	4345(7)	98(10)	66(7)	85(8)	20(7)	41(7)	15(6)
C(215)	3468(9)	10498(7)	4854(8)	131(11)	64(7)	116(10)	37(8)	84(9)	18(7)
C(216)	4431(9)	10636(8)	5856(8)	127(12)	88(9)	107(10)	12(8)	64(10)	9(8)
C(217)	4654(8)	9773(8)	6359(7)	111(11)	103(10)	87(8)	12(8)	40(8)	0(7)
C(218)	3912(8)	8753(7)	5867(7)	114(11)	89(8)	82(8)	18(8)	41(8)	29(7)
Cl(1)	9360(4)	1063(4)	2191(4)	230(6)	221(5)	218(5)	61(4)	120(4)	16(4)
Cl(2)	7302(6)	—95(4)	2338(5)	582(13)	177(5)	348(8)	10(6)	359(19)	49(5)
Cl(3)	7014(4)	1542(3)	1090(3)	310(7)	207(5)	177(4)	120(5)	99(4)	17(4)
C	7984(11)	1133(9)	2275(9)	231(18)	115(10)	142(12)	44(11)	121(12)	34(9)

---

[a] All values X 10^4. [b] Values in parentheses above and in Table 2 are estimated standard deviations in the last digits as derived from the inverse matrix of the final least-squares refinement cycle. [c] The temperature factors are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Experimental

$Ph_3Te(NCO)$ was synthesized by mixing aqueous solutions of AgOCN and $(C_6H_5)_3TeCl$, removing AgCl and evaporating the water [5]. Crystals suitable for a single-crystal X-ray study were grown in chloroform, some of which is retained as solvent of crystallization.

$Ph_3Te(NCO) \cdot \frac{1}{2} CHCl_3$ crystallizes in the triclinic system, space group $P\bar{1}$, with a unit cell of dimensions $a = 12.083(6)$ Å, $b = 12.900(12)$ Å, $c = 13.878(10)$ Å, $\alpha = 95.83(7)°$, $\beta = 103.47(7)°$, $\gamma = 98.87(6)°$ and $V = 1901$ Å^3 (23°C) (Fig. 1). Reductions using the algorisms of Balashov and Ursell [8] and of Delaunay [9] revealed no hidden symmetry. The cell axes represent the three shortest noncoplanar translations (Dirichlet triplet), and the Dirichlet and Delaunay reduced cells are identical. The measured density of 1.60(4) g/cm^3 agrees with the calculated value of 1.61 g/cm^3 for four formula units per unit cell.

A complete set of independent intensity data was collected by the $\theta - 2\theta$ scan techniques on a Syntex $P\bar{1}$ automatic diffractometer using graphite monochromatized Mo-K_α radiation * and a crystal prism measuring 0.3 × 0.3 × 0.4 mm. Intensities and standard deviations of intensities were calculated using the following formulas:

$$I = S(c - RB) \text{ and } \sigma(I) = [S^2(c + R^2B) + (pI)^2]^{1/2},$$

where S in the scan rate, c is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count, and p, here set equal to 0.07, a factor introduced to downweight intense reflections. The intensities of 5157 reflections were measured; solution and refinement of the structure were based on the 3817 reflections having $F > 3\,\sigma(F)$. The intensities were corrected for Lorentz and polarization effects but not for absorption. The calculated linear absorption coefficient (Mo-K_α), μ, is 18.4 cm^{-1}.

The structure was solved by Patterson and Fourier techniques and was refined by least-squares methods. The scattering factors were taken from the compilation of Hanson, et al. [11]; those for Te and Cl were corrected for the real and imaginary components of anomolous dispersion using the values of Cromer [10]. The function minimized in the least-squares refinement was $\Sigma\, w(|F_{obs}| - |F_{calc}|)^2$ where $w = 0.04\, F/\sigma^2(F)$. Anisotropic thermal parameters were used for all of the non-hydrogen atoms. The refinement converged to a

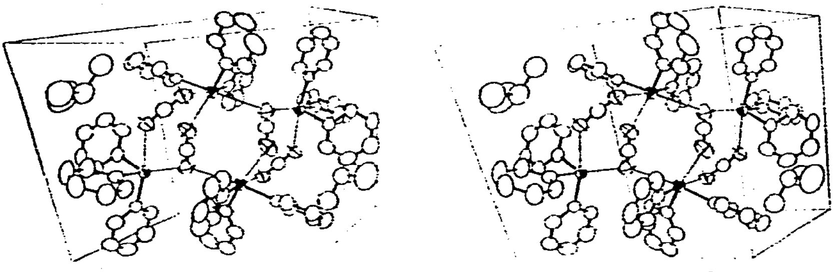

Fig. 1. Stereoscopic view of the unit cell contents of $Ph_3Te(NCO) \cdot \frac{1}{2}CHCl_3$.

---

* Data set collected by Molecular Structure Corp., College Station, Texas 77840.

final R factor $(\Sigma||F_{\mathrm{obs}}| - |F_{\mathrm{calc}}||/\Sigma\, |F_{\mathrm{obs}}|)$ of 4.9% and a weighted R factor $\Sigma w\, (|F_{\mathrm{obs}}| - |F_{\mathrm{calc}}|)^2/\Sigma\, w|F_{\mathrm{obs}}|^2)$ of 4.2%. The goodness of fit, $[\Sigma w(F_{\mathrm{obs}} - F_{\mathrm{calc}})^2/(\text{no. of reflections} - \text{no. of variables})]^{1/2}$, equals 1.06. The hydrogen atom contributions to the calculated structure factors were included as fixed contributions in the final cycles of refinement. Hydrogen atoms were positioned 0.95Å from the ring carbon atoms in the planes of the phenyl rings. Prior to their inclusion, a difference Fourier map showed electron density in all of the expected hydrogen atom positions.

The final positional and anisotropic thermal parameters for the nonhydrogen atoms are given in Table 1 [*].

Results and discussion

The structure of $Ph_3Te(NCO) \cdot \frac{1}{2} CHCl_3$ is illustrated in Fig. 2 and consists of discrete tetramers separated by van der Waals distances. The tetramers are built up through interactions between the triphenyltelluronium cations and the end-to-end and terminally bridging cyanate groups. Interatomic distances and angles are given in Table 2.

The tetramer is composed of three fused eight-membered rings with the central ring possessing a chair configuration with a dihedral angle of 132°. In

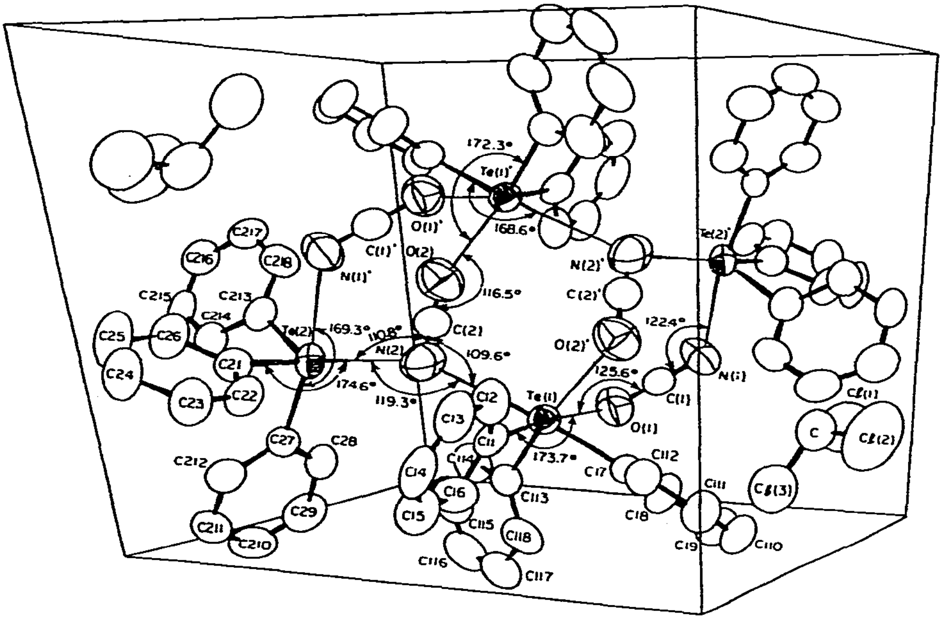

Fig. 2. The $Ph_3Te(NCO) \cdot \frac{1}{2}CHCl_3$ tetramer. The standard deviations of the angles in the Figure are approximately the same as those for similar atoms in Table 2.

---

[*] The table of structure factors has been deposited as NAPS Document No. 02876 (24 pages). Order from ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016. A copy may be secured by citing the document number, remitting $6.00 for photocopies or $3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

TABLE 2

INTERATOMIC DISTANCES (Å) AND ANGLES (DEG) [a]

Atoms	Distances	Atoms	Angles
Te(1)—O(1)	3.028(9)	N(2)—Te(1)—C(11)	75.8(3)
Te(1)—O(2)′	2.891(9)	N(2)—Te(1)—C(113)	84.9(3)
Te(1)—N(2)	3.005(9)	N(2)—Te(1)—O(1)	107.5(2)
Te(1)—Te(2)	5.329(4)	N(2)—Te(1)—O(2)′	102.2(3)
Te(1)—Te(1)′	5.441(5)	C(17)—Te(1)—C(11)	92.8(3)
Te(1)—Te(2)′	5.815(4)	C(17)—Te(1)—C(113)	96.6(3)
Te(1)—C(11)	2.130(10)	C(17)—Te(1)—O(1)	83.8(3)
Te(1)—C(17)	2.156(8)	C(17)—Te(1)—O(2)′	77.0(3)
Te(1)—C(113)	2.123(10)	C(11)—Te(1)—C(113)	98.1(4)
Te(2)—N(1)′	2.783(9)	C(11)—Te(1)—O(2)′	86.4(3)
Te(2)—N(2)	3.171(12)	O(1)—Te(1)—C(113)	77.0(3)
Te(2)—C(21)	2.102(10)	O(1)—Te(1)—O(2)′	97.9(2)
Te(2)—C(27)	2.140(8)	C(213)—Te(2)—C(21)	99.0(3)
Te(2)—C(213)	2.132(7)	C(213)—Te(2)—C(27)	93.9(3)
O(1)—C(1)	1.216(12)	C(213)—Te(2)—N(1)′	84.2(3)
C(1)—N(1)	1.148(13)	C(213)—Te(2)—N(2)	86.4(3)
O(2)—C(2)	1.203(10)	C(21)—Te(2)—C(27)	94.0(3)
C(2)—N(2)	1.017(10)	C(27)—Te(2)—N(2)	86.5(3)
		N(2)—Te(2)—N(1)′	103.8(3)
		C(21)—Te(2)—N(1)′	76.0(3)

[a] The atom labeling scheme and additional angles are given in Fig. 2.

the terminal rings, which are highly distorted from planarity, the cyanate groups lie in a crisscross or scissor fashion relative to each other with the angle between the two groups, as projected onto a common plane, being 48°. The cyanate groups of the central ring nearly parallel to each other, and no atom deviates by more than 0.02Å from the least-squares plane of the six atoms (Table 3, plane 1).

Both five and six coordinate tellurium atoms are present. Tellurium 2 and 2′ are in a distorted square pyramidal geometry, while tellurium 1 and 1′ are in a distorted octahedral environment. The closest Te—Te approach (atoms 1 and 2) is 5.329(4)Å. Tellurium 2 is 0.579Å above the equatorial least-squares plane (Table 3, plane 2) of the square pyramid towards carbon 213. No equatorial atom deviates by more than 0.05Å from the least squares plane. The sixth

TABLE 3

LEAST-SQUARES PLANES IN $(\mathrm{Ph_3Te(NCO)} \cdot \frac{1}{2}\mathrm{CHCl_3})_4$ [a]

Plane	Atoms	Equation
1	N(2), C(2), O(2), N(1), C(1), O(1)	$10.535x - 1.921y - 11.039z + 1.212 = 0$
2	C(21), C(27), N(1)′, N(2)	$4.769x + 8.456y + 2.982z - 7.568 = 0$
3	C(11)—C(16)	$-0.715x + 11.864y + 2.949z - 5.709 = 0$
4	C(17)—C(112)	$5.022x - 5.860y + 8.640z - 1.891 = 0$
5	C(113)—C(118)	$10.993x - 6.943y - 3.556z - 0.1966 = 0$
6	C(21)—C(26)	$-0.4016x - 6.022y + 12.183z - 0.6805 = 0$
7	C(27)—C(212)	$3.144x + 10.796y + 1.108z - 8.673 = 0$
8	C(213)—C(218)	$10.884x - 3.113y - 10.145z + 4.425 = 0$

[a] Planes are defined in fractional triclinic coordinates (x,y,z) and are calculated using unit weights for all atoms.

site around tellurium 2 is unoccupied with the closest atom to the site being C(13) at 3.88(10)Å.

The Te—N and Te—O distances within the tetramer are longer than those expected for a single covalent bond, 2.02 and 1.98Å respectively, but are significantly shorter than the respective van der Waals distances of 3.61 and 3.58Å [12]. The interactions between the telluronium cations and the cyanate groups, which lead to a coordination number for tellurium higher than would be expected from the stoichiometry of the system, involve C—Te...X(X = N,O) arrangements which deviate from linearity by approximately 8° (Fig. 2). This type of interaction, called secondary bonding, is a well known occurrence in tellurium-(IV)—halide, —oxygen and —sulfur compounds and has been reviewed by Alcock [13]. To our best knowledge, $Ph_3Te(NCO) \cdot \frac{1}{2}CHCl_3$ and $Ph_3Te(NCS)$ [7] provide the first structural examples involving secondary tellurium(IV) —nitrogen interactions.

The two crystallographically independent triphenyl telluronium cations are similar to the $(C_6H_5)_3Te^+$ and $(CH_3)_3Te^+$ cations in $(C_6H_5)_3Te(NCS)$ [7] and β-$(CH_3)_2TeI_2$ [4] respectively. The cations have a trigonal pyramidal shape, but possess no symmetry due to the conformation adopted by the phenyl rings. The mean Te—C distance is 2.130(22)Å and is within the range of other reported Te—C(aromatic) distances [14]. The mean C—Te—C angle is 95.7(8)° and is similar to the C—Te—C angle (95(2)°) in $(CH_3)_3Te^+$. These angles are smaller than those found in the corresponding selenium species: 100(1)° for $(C_6H_5)_3Se^+$ in $(C_6H_5)_3SeCl \cdot 2H_2O$ [15] and 98.5(8)° for $(CH_3)_3Se^+$ in $(CH_3)_3SeI$ [16].

Bond distances and angles within the six crystallographically independent phenyl rings appear normal. The mean value of the 36 independent phenyl C—C distances and the C—C—C angles in 1.378(92)Å and 120.0(4.5)° respectively. The rings are planar with no carbon atom deviating more than 0.010(8)Å from the least square plane of its respective phenyl ring. The least squares planes of the six phenyl rings are given in Table 3, planes 3 to 8.

The cyanate groups are essentially ionic with interatomic distances similar to those found in KNCO [17]. The N—C—O angles for groups 1 and 2 are 179.8(9)° and 174.7(1.2)° respectively. Identity of the oxygen and nitrogen atoms of the cyanate was based on the difference in the calculated C—X (X = N,O) distances with the C—N distance assumed shorter. Some difficulty, however, was encountered in refinement of the C2 atomic parameters and the distances involving this atom are probably less accurate than indicated by the least-squares estimated standard deviations. Subsequent checks on the identity of the atoms through difference Fourier calculations and least-squares refinement involving the exchange of the oxygen and nitrogen scattering factors confirmed the assignments. The two crystallographically independent NCO groups are responsible for the doublet at 2148 and 2134 cm^{-1} in the infrared spectrum of $Ph_3Te(NCO) \cdot \frac{1}{2}CHCl_3$ [5].

The two chloroform molecules are possibly hydrogen-bonded to the tetramer with a C...N(1) contact of 3.287(16)Å. Melting and decomposition of $(C_6H_5)_3$-$Te(NCO) \cdot \frac{1}{2}CHCl_3$ occur at 140°C, where $CHCl_3$ is released, 78°C above its normal boiling point [5]. The C—Cl distances and the Cl—C—Cl angles in the chloroform appear normal and have mean values of 1.727(24)Å and 108.6(1.1)° respectively.

Acknowledgment

We thank Dr. W.H.H. Günther for his interest in and support of this work, and the Temple University Computer Center for a generous allotment of computing time.

References

1 K.J. Irgolic, J. Organometal. Chem., 103 (1975) 91.
2 K.J. Irgolic, The Organic Chemistry of Tellurium, Gordon and Breach, New York, 1974.
3 W.C. Cooper, Tellurium, Van Nostrand Reinhold, New York, 1971.
4 F. Einstein, J. Trotter and C. Williston, J. Chem. Soc. A, (1967) 2018.
5 R.F. Ziolo and K. Pritchett, J. Organometal. Chem., 116 (1976) 211.
6 R.F. Ziolo and D.D. Titus, J. Appl. Crystallogr., in press.
7 J.-S. Lee, D.D. Titus and R.F. Ziolo, 170th National ACS Meeting, Chicago, Illinois, August, 1975, Abstract INOR-15; Chem. Commun., in press.
8 V. Balashov and H.D. Ursell, Acta Crystallogr., 10 (1957) 582.
9 B.N. Delaunary, Z. Kristallogr., 84 (1933) 132.
10 D.T. Cromer, Acta Crystallogr., 18 (1965) 17.
11 H P. Hanson, F. Herman, J.D. Lea and S. Skillman, Acta Crystallogr., 17 (1964) 1040.
12 A. Bondi, J. Phys. Chem., 68 (1964) 441.
13 N.W. Alcock, Advan. Inorg. Chem. Radiochem., 15 (1972) 1.
14 I.L. Karle and J. Karle, in D.L. Klayman and W.H.H. Günther (Eds.), Organic Selenium Compounds: Their Chemistry and Biology, Wiley-Interscience, New York, 1973, 989.
15 J.-S. Lee and D.D. Titus, J. Cryst. Mol. Struct., in press.
16 H. Hope, Acta Crystallogr., 20 (1966) 610.
17 E.L. Wagner, J. Chem. Phys., 43 (1965) 2728.