Synthesis, Infrared and X-Ray Studies of Diphenyltellurium(IV) Nitrosocarbamylcyanmethanides. X-Ray Evidence for Stability of a Tritelluroxane Fragment $-Ph_2Te-O-Ph_2Te-O-Ph_2Te-$

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Diphenyltellurium(IV) derivatives of the types $Ph_2Te\{ACO\}_2$ (**1**), $Ph_4Te_2O\{ACO\}_2$ (**2**) and $Ph_6Te_3O_2\{ACO\}_2$ (**3**) (ACO = nitrosocarbamylcyanmethanide $^{-}ONC(CN)C(O)NH_2$) have been prepared. The IR spectroscopic data reveal that the ambidentate ligands are coordinated to the tellurium(IV) atom in a monodentate manner via the nitroso oxygen atom. The crystal and molecular structure of **3** has been determined from X-ray diffraction data (triclinic, space group $P\bar{1}$ with $a = 12.382(2)$, $b = 13.100(2)$, $c = 14.944(3)$ Å, $\alpha = 87.74(1)$, $\beta = 85.04(2)$, $\gamma = 66.29(1)°$, V = 2211.0 $Å^3$, Z = 2, R = 0.040). The structure is made up of unsymmetric molecules, in which the tellurium atoms are linked by oxo bridges to form chains Te–O–Te–O–Te (d⟨Te–O⟩ *ca.* 1.94-2.09 Å). The Te–O (nitroso group) bond lengths are in the range 2.33 - 2.36 Å.

Introduction

Reaction of diaryltellurium(IV) derivatives with aqueous sodium hydroxide leads to diaryltellurium oxides, but milder conditions of hydrolysis allow to prepare many other oxo salts [1, 2]. The ability of diorgano-tellurium(IV) to form oxo derivatives is well known [3]. Despite their relatively large number, only few oxo salts have been examined structurally [3]. The crystal structures of $Ph_4Te_2O\{X\}_2$ (X = NCS^-, CF_3COO^-) [4, 5], μ^2-oxo-bis(phenoxatellurine) dinitrate [6] and $Ph_4Te_2O\{NO_3\}_2{*}Ph_2Te(OH)\{NO_3\}$ [3] were reported earlier. These complexes belong to a group of compounds of composition $[R_2Te\{X\}]_2O$, which is of considerable interest in coordination and metallorganic chemistry and may be considered as the most simple representatives of a hypothetical "telluroxane" $X-R_2Te-[-O-TeR_2]_n-X$ family ($n = 1$). Crystal structures of new compounds of this class are of special interest in this context. In order to clarify the chemistry and structure of these compounds, we have attempted to prepare higher homologues ($n > 1$) of this family using nitrosocarbamylcyanmethanide, $^{-}ONC(CN)C(O)NH_2$ (further ACO^-), as the group X–. Lately we have investigated a number of organotin(IV) and organoantimony(V) nitrosocarbamylcyanmethanides and have found that the nitroso oxygen atoms are coordinated to the metal centres (Sn, Sb) [7, 8] forming covalent bonds. Here we describe the synthesis and IR spectra of three diorganotellurium(IV)nitrosocarbamylcyanmethanides and the results of an X-ray investigation of a new telluroxane molecule ($n = 2$). No crystal structures of such diorganotellurium(IV) derivatives were found in the literature.

Experimental

All materials were commercial products of reagent grade, used without further purification. All experiments were carried out in air.

Preparation of tellurium(IV) compounds

The starting organotellurium compound, Ph_2TeBr_2, was obtained by reacting tellurium(IV) bromide with a tetraphenyltin in boiling toluene [9], m. p. 199°C. Nitrosocarbamylcyanmethanide was prepared by the method of Ross [10] and an aqueous solution of the anionic ligand was prepared by stoichiometric reaction with a solution of Cs_2CO_3. The silver salt of nitrosocarbamylcyanmethanide, Ag{ACO}, was obtained by ion exchange reaction with $AgNO_3$. The precipitate formed was filtered off, washed with small portions of methanol and ether and dried in air.

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Table I. Analytical data and physical properties of organotellurium compounds.

Compound	Colour	m. p. [°C]	Yield [%]	Found [%]			Calcd [%]		
				C	H	N	C	H	N
1 $Ph_2Te\{ACO\}_2$	colourless	260 - 265	95	43.0	2.9	16.8	42.7	2.8	16.6
2 $Ph_4Te_2O\{ACO\}_2$	pale-yellow	212 - 215	60	44.9	3.2	10.6	44.8	3.0	10.5
3 $Ph_6Te_3O_2\{ACO\}_2{*}CH_3CN$	yellow	200 - 203	25	46.2	3.2	8.5	45.8	3.3	8.7

In the second step, the organotellurium(IV) derivatives were prepared by reacting Ph_2TeBr_2 in acetonitrile or aqueous-acetonitrile solution with $Ag\{ACO\}$ according to eqs 1 - 3.

$$Ph_2TeBr_2 + 2Ag\{ACO\} \rightarrow Ph_2Te\{ACO\}_2 + 2AgBr \quad (1)$$

$$2\,Ph_2TeBr_2 + 4Ag\{ACO\} + H_2O \rightarrow Ph_4Te_2O\{ACO\}_2 + 2H(ACO) + 4AgBr \quad (2)$$

$$3\,Ph_2TeBr_2 + 6Ag\{ACO\} + 2H_2O + CH_3CN \rightarrow Ph_6Te_3O_2\{ACO\}_2{*}CH_3CN + 4H(ACO) + 6AgBr \quad (3)$$

*Bis(nitrosocarbamylcyanmethanido)-diphenyltellurium (**1**)*

To a solution of 0.44 g (1.0 mmol) of Ph_2TeBr_2 in 15 ml of hot acetonitrile 0.44 g (2.0 mmol) of $Ag\{ACO\}$ was added. After 30 min the AgBr formed was filtered off and washed with 5 ml of acetonitrile. The colourless filtrate obtained on evaporation at room temperature gave 0.48 g (95 %) of colourless crystals of $Ph_2Te\{ACO\}_2$. The compound obtained is soluble in acetonitrile, DMF and DMSO.

*Bis(nitrosocarbamylcyanmethanido)-tetraphenylditelluroxane (**2**)*

To a hot solution of 0.44 g (1.0 mmol) of Ph_2TeBr_2 in a mixture acetonitrile-water (3:1 v/v) (20 ml) 0.44 g (2.0 mmol) of $Ag\{ACO\}$ was added. The hot mixture was stirred for 30 min and then cooled to room temperature. The precipitate of AgBr was filtered off and the clear pale-yellow solution obtained was allowed to stand at room temperature for 24 h after which pale-yellow crystals of $Ph_4Te_2O\{ACO\}_2$ separated from the solution. The crystals were filtered, washed with 2 ml of acetonitrile and dried in air. Yield 0.24 g (60 %).

*Bis(nitrosocarbamylcyanmethanido)-hexaphenyltritelluroxane (**3**)*

To a suspension of 0.88 g (2.0 mmol) of Ph_2TeBr_2 in an aqueous acetonitrile (1:1 v/v) (20 ml) 0.88 g (4.0 mmol) of $Ag\{ACO\}$ was added. The mixture was refluxed and stirred for 2 h and then the AgBr deposit was separated. The clear, pale-yellow solution obtained on standing yielded crystals suitable for X-ray diffraction of composition $Ph_6Te_3O_2\{ACO\}_2{*}CH_3CN$. They decompose slowly at about 100°C and melt at 200 - 203°C (with decomposition). The crystals are soluble in acetonitrile and DMF, but cannot be satisfactorily recrystallized. From the reaction mixture a small amount of diphenyltelluroxide was isolated, m. p. 191 - 193°C (dec.).

The proposed preparation mode can be used in general to prepare this type of organotellurium compounds. Attempts to synthesize higher 'telluroxanes' by this way were not successful. In boiling water only diphenyltelluroxide, H(ACO) or products of unstoichiometric composition were obtained.

The analytical data and melting points of the complexes are presented in Table I.

Table II. Vibrational frequences in the infrared spectra and their assignments, cm^{-1}.

Assignment	1	2	3	Cs {ACO}	Ph_4Sb {ACO}[a]
$\nu_{(CN)}$	2225	2215	2205	2205	2215
$\nu_{(C=O)}$	1680	1680	1685	1675	1685
$\rho(NH_2)$	1595	1585	1590	1610	1580
$\nu_{(NO)}$	1030	1095	1095	1260	1070
$\nu_{(CH)}$	3050	3050	3050	—	3060
C_6H_5, out-of-plane C-H deformation	690	690	690	—	695
ν_{asym}(Te–O–Te)[b]	—	635	595	—	—
ν_{sym}(Te–O–Te)[b]	—	445	445	—	—
Te–C stretch[b]	465	470	465	—	—

[a] In accordance with [8]; [b] assignments are in accordance with [3].

Measurements

IR spectra were recorded on a Carl Zeiss (Jena) UR-10 spectrometer in KBr pellets and Nujol mulls (400 - 4000 cm^{-1}). The characteristic IR absorptions of the tellurium complexes, the corresponding free ligand and the tetraphenylantimony complex [8] are presented in Table II. The assignments of the vibrational frequencies of the CNO-group in the nitrosocarbamylcyanmethanide were based on the isotope splitting effect of the ^{15}N-enriched samples.

X-ray diffraction data were collected using an Enraf Nonius CAD-4 diffractometer. Accurate unit cell

Table III. Selected bond lengths (Å) for $Ph_6Te_3O_2\{ACO\}_2{*}CH_3CN$.

Te(1)–O(5)	1.940(4)	O(1)–N(1)	1.328(8)
Te(1)–C(13)	2.115(8)	N(1)–C(1)	1.304(9)
Te(1)–C(7)	2.101(7)	N(2)–C(2)	1.14(1)
Te(1)–O(1)	2.358(5)	N(3)–C(3)	1.33(1)
Te(2)–O(6)	2.074(4)	N(4)–C(4)	1.305(8)
Te(2)–O(5)	2.095(4)	N(5)–C(5)	1.151(9)
Te(2)–C(19)	2.118(5)	N(6)–C(6)	1.32(1)
Te(2)–C(25)	2.12(1)	C(1)–C(2)	1.43(1)
Te(3)–O(6)	1.953(4)	C(1)–C(3)	1.47(1)
Te(3)–C(31)	2.104(7)	C(4)–C(5)	1.42(1)
Te(3)–C(37)	2.124(7)	C(4)–C(6)	1.474(9)
Te(3)–O(3)	2.326(4)	N(3)–H(N3.1)	0.96(9)
O(2)–C(3)	1.223(9)	N(3)–H(N3.2)	0.73(9)
O(3)–N(4)	1.320(7)	N(6)–H(N6.1)	0.91(9)
O(4)–C(6)	1.230(8)	N(6)–H(N6.2)	0.78(10)

Table IV. Selected angles (°) for $Ph_6Te_3O_2\{ACO\}_2{*}CH_3CN$.

O(5)-Te(1)-C(13)	91.6(2)	C(37)-Te(3)-O(3)	83.9(2)
O(5)-Te(1)-C(7)	90.3(2)	N(1)-O(1)-Te(1)	105.2(4)
C(13)-Te(1)-C(7)	96.2(3)	N(4)-O(3)-Te(3)	104.1(3)
O(5)-Te(1)-O(1)	171.6(2)	Te(1)-O(5)-Te(2)	124.2(2)
C(13)-Te(1)-O(1)	86.6(3)	Te(3)-O(6)-Te(2)	124.2(2)
C(7)-Te(1)-O(1)	81.7(2)	C(1)-N(1)-O(1)	115.9(7)
O(6)-Te(2)-O(5)	167.4(2)	C(4)-N(4)-O(3)	114.8(5)
O(6)-Te(2)-C(19)	83.9(2)	N(1)-C(1)-C(2)	120.8(7)
O(5)-Te(2)-C(19)	84.2(2)	N(1)-C(1)-C(3)	120.1(7)
O(6)-Te(2)-C(25)	90.3(4)	C(2)-C(1)-C(3)	119.1(7)
O(5)-Te(2)-C(25)	87.3(4)	N(2)-C(2)-C(1)	177(1)
C(19)-Te(2)-C(25)	98.1(4)	O(2)-C(3)-N(3)	123.1(8)
O(6)-Te(3)-C(31)	90.2(2)	N(4)-C(4)-C(6)	119.3(6)
O(6)-Te(3)-C(37)	90.6(2)	C(5)-C(4)-C(6)	118.2(6)
C(31)-Te(3)-C(37)	96.6(3)	N(5)-C(5)-C(4)	179.3(8)
O(6)-Te(3)-O(3)	170.9(2)	O(4)-C(6)-N(6)	124.0(7)
C(31)-Te(3)-O(3)	83.3(2)	N(7)-C(43)-C(44)	172(4)

parameters and the orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 24 reflections in the range $13 < \theta < 15°$. Intensity data of 7253 reflections were collected at 293(2) K in the range $1.37 < \theta < 23.97°$ using graphite monochromated MoK_α radiation ($\omega/2\theta$ scans, λ = 0.71073 Å, *hkl* range $0 \leq h \leq 14$, $-13 \leq k \leq 14$, $-17 \leq l \leq 17$). Corrections for Lorentz and polarization effects were applied. The structure was solved by direct methods and refined by full-matrix least-squares techniques in the anisotropic approximation using SHELXL-93 [11, 12]. In the refinement 6899 independent reflections (R_{int} = 0.019) were used. The NH_2 hydrogen atoms were located from the difference-Fourier syntheses and refined isotropically. The phenyl hydrogen atoms were placed at calculated positions with their isotropic U values set invariant at 0.06 Å^2. Refinement was terminated with all non-hydrogen parameter shifts $< 0.33\sigma$. Convergence was obtained at $R = 0.040$ and $wR2 = 0.111$, G. O. F. on F^2 = 1.04, based on 6383 independent reflections with $I > 2\sigma(I)$ (557 refined parameters, the data/parameters ratio is 11.5; largest peak in the final difference map = 0.68 e/Å^3). Judging by the values of the U parameter of the acetonitrile of crystallization atoms C(43), C(44), N(7) [U > 0.20 Å^2], this group is disordered, but all attempts to divide the oscillatory movement between two positions with partial occupancies of 50 % were not successful.

Crystal data for $C_{42}H_{34}N_6O_6Te_3{*}CH_3CN$: FW = 1142.6, triclinic, space group $P\bar{1}$ with a = 12.382(2), b = 13.100(2), c = 14.944(3) Å, α = 87.74(1), β = 85.04(2), γ = 66.29(1)°, V = 2211.0(7) Å^3, Z = 2, D_x = 1.72 g $*$ cm^{-3}, μ = 20.2 cm^{-1}, F(000) = 1108.

Selected bond distances and angles are listed in Tables III and IV. Full crystallographic data have been deposited at the Cambridge Crystallographic Data Centre [13].

Results and Discussion

The analytical data listed in Table I proved the stoichiometric composition of the complexes. Due to the hydrolysis of diphenyltellurium(IV) in aqueous acetonitrile both the complexes **2** and **3** contain oxo ligands.

The IR data are also consistent with the formation of oxo tellurium derivatives. In **2**, peaks at 635 and 445 cm^{-1} may be assigned to ν_{asym} and ν_{sym} of the Te–O–Te bridges by comparison with oxobis(nitratodiphenyltellurium) (ν_{asym} 607, ν_{sym} 426 cm^{-1}) [3]. The features of the spectra of **3** in this region are the same (ν_{asym} 595, ν_{sym} 445 cm^{-1}, Te–O–Te) (Table II). Unlike these species the complex **1**, prepared from anhydrous acetonitrile, do not exhibit bands in this region. The vibrational frequencies of the Te-C stretching are the same for all compounds.

The IR spectra reveal substantially lower values of $\nu_{(NO)}$ in the tellurium compounds as compared with those of the ionic nitrosocarbamylcyanmethanide in its Cs^+ salt (Table II). A similar decrease of $\nu_{(NO)}$ was also observed for number of organotin [7] and organoantimony nitrosocarbamylcyanmethanides [8] (for example $Ph_4Sb\{ACO\}$), reflecting the coordination of the {ACO} group to the central atom via the nitroso oxygen atom. It is interesting to note that the $\nu_{(NO)}$ vibrational frequency of the $Ph_2Te\{ACO\}_2$ complex is lower than for the oxo compounds **2** and **3** (Table II). This suggests

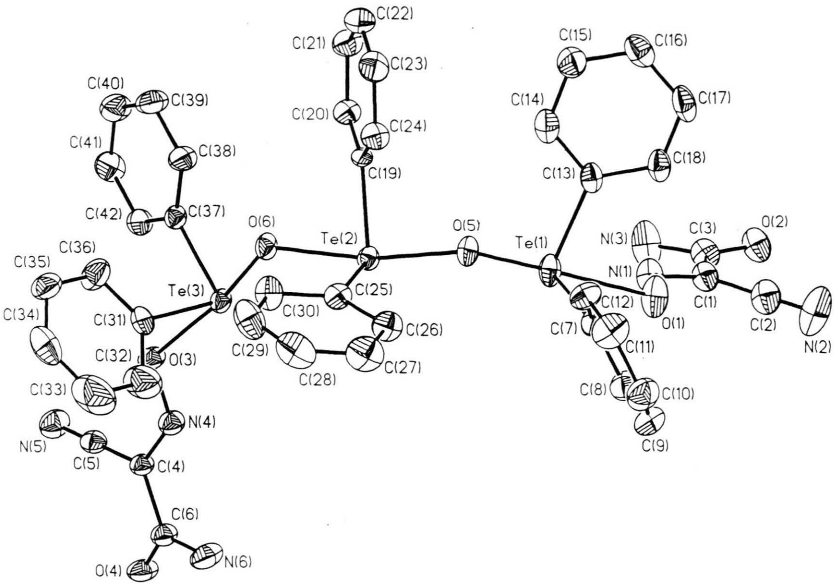

Fig. 1. Perspective view, with 40% probability ellipsoids, of the $Ph_6Te_3O_2\{ACO\}_2{*}CH_3CN$ complex, showing the atom numbering scheme. Acetonitrile of crystallization molecule [N(7)–C(43)–C(44)] and hydrogen atoms omitted for clarity.

a more covalent character for the Te-O bonds in $Ph_2Te\{ACO\}_2$ [8]. The valence vibrations of the nitrile and carbonyl groups for all species are the same and do not differ essentially from those observed for $Cs\{ACO\}$. Thus, we can conclude that the organic anions were coordinated to the tellurium in a monodentate manner via the NO oxygen atoms.

Description of the structure

The molecular and crystal structure of the complex **3** are depicted in Figures 1 - 2. The acetonitrile of crystallization is not coordinated.

The $Ph_6Te_3O_2\{ACO\}_2$ complex adopts a polymeric structure with three oxygen-bridged tellurium atoms in the asymmetric unit, further linked by secondary coordination interaction of Te- - -N(5a) (2–*x*, 1–*y*, –*z*) to give centrosymmetric dimers (Fig. 2). The hydrogen bonding plays an important role in the molecular packing of the compound. There are two types of hydrogen bonds involving the amide groups: N(3)- - -O(2b) (1–*x*, 2–*y*, 1–*z*) 3.05(1) Å, d⟨H[N(3)]- - -O(2b)⟩ 2.20(9) Å, angle N(3)–H[N(3)]- - -O(2b) 166(8)° and N(6)- - -O(4c) (3–*x*, 1–*y*, –*z*) 2.950(9) Å, d⟨H[N(6)]- - -O(4c)⟩ 2.11(9) Å, angle N(6)–H[N(6)]- - -O(4c) 174(8)°. These interactions connect neighbouring dimers into polymeric layers.

Consideration of the {ACO} anions geometry suggests π-electron delocalization involving the nitroso, cyano and amide groups. This may be rationalized in terms of contributions by a number resonance forms [14]. It is apparent, however, that delocalization is only partial. Thus, the distances C(1)–C(2) of 1.43(1) and C(4)–C(5) of 1.42(1) Å are practically equal to the standard $C(sp^2)$–C(sp) separation (1.43 Å). The anions are practically planar and dihedral angles between cyanoxime and amide mean planes are 9.0(2)° (anion attached to Te(1)) and 7.8(2)° (Te(3)).

All phenyl groups in the complex are structurally normal. The dihedral angles between the planes of phenyl groups attached to: Te(1) 102.6(2); Te(2) 96.8(2) and Te(3) 78.6(2)°.

In the $Ph_6Te_3O_2\{ACO\}_2$ unit the coordination geometry about Te(2) is a distorted octahedron with the lone pair in the equatorial plane, comprising primary bonds Te–O of 2.074(4) and 2.095(4) Å, Te–C bonds of 2.12(1) and 2.118(5) Å (Table III), and secondary coordination interaction Te(2)- - -N(5a)

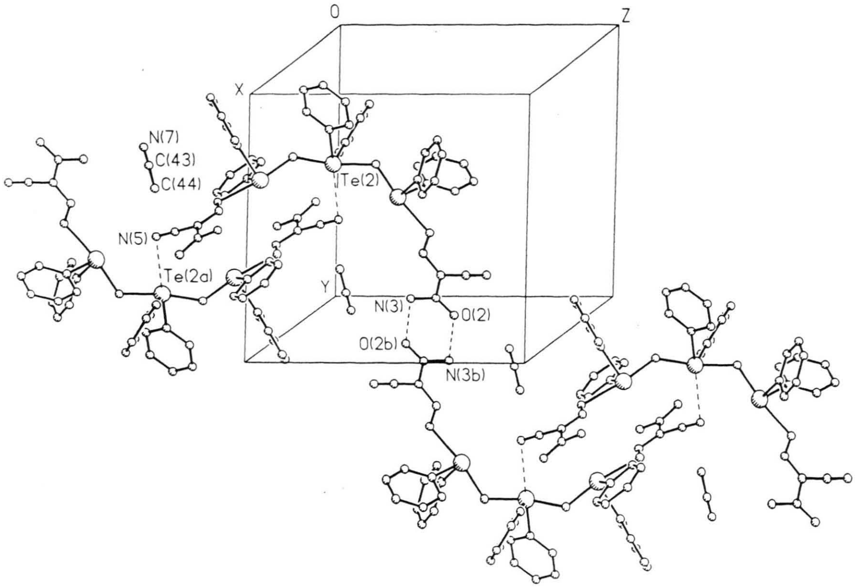

Fig. 2. Fragment of the $Ph_6Te_3O_2\{ACO\}_2{*}CH_3CN$ crystal structure.

(2–*x*, 1–*y*, –*z*) of 3.255(5) Å. The latter value agrees well with the distances of secondary Te–O and Te–N bonds reported earlier [3, 15], with angles C(19)–Te(2)–N(5a) 85.9(4) and O(6)–Te(2)–N(5a) 90.9(5)°. The tellurium atoms Te(1) and Te(2) adopt four fold coordination of a distorted trigonal-bipyramidal geometry with axial oxygens, equatorial carbons and equatorial lone pairs (Fig. 1), a fact which is consistent with previous structural studies of diorganotellurium(IV) complexes [3, 5]. This suggests a sp^3d hybridization state for the tellurium atoms Te(1) and Te(3).

The Te–C distances of *ca.* 2.10 - 2.12 Å (Table III) agree satisfactorily with data reported for diphenyltellurium(IV) derivatives [15]. The Te(1)–O(5) and Te(3)–O(6) bond lengths of 1.940(4) and 1.953(4) Å respectively are typical for covalent Te-O bonds in oxo salts (*cf.* for compound $[Ph_2Te\{NCS\}]_2O$ 1.985 Å [4]). The Te-O (nitroso group) bonds are essentially longer, *ca.* 2.326(4) and 2.358(5) Å, an observation which suggests more ionic character for these Te–O bonds. The Te–O bonds in each case are practically colinear: O(1)–Te(1)–O(5) 171.6(2); O(5)–Te(2)–O(6) 167.4(2) and O(3)–Te(3)–O(6) 170.9(2)°. A small deviation from 180° may be affected by steric repulsion with equatorial lone pairs of the tellurium atoms [4].

The μ-oxo-bridging with both the O(5) and O(6) atoms is nearly symmetrical, and the Te(1)–O(5)–Te(2) and Te(2)–O(6)–Te(3) angles are found to be both *ca.* 124.2(2)° (Table IV). These values are comparable to the Te–O–Te angles found for $[Ph_2Te\{NCS\}]_2O$, 121.7° [4], and may reflect some π-interaction between the p-orbitals of these bridging oxygens and acceptor orbitals of the tellurium [3] or steric congestion (Fig. 1).

[1] K. Irgolic, The Organic Chemistry of Tellurium, Gordon and Breach, New York, London, Paris (1974).

[2] I. D. Sadekov, A. A. Maximenko, V. I. Minkin, The Chemistry of Tellurorganic Compounds (In Russ.) Rostov University Press, Rostov-on-Don (1978).

[3] N. W. Alcock, W. D. Harrison, J. Chem. Soc., Dalton Trans, 1421 (1982).

[4] C. S. Mancinelli, D. D. Titus, R. F. Ziolo, J. Organometal. Chem **140**, 113 (1977).

[5] N. W. Alcock, W. D. Harrison, C. Howes, J. Chem. Soc., Dalton Trans. 709 (1984).

[6] M. M. Mangion, M. R. Smith, E. A. Meyers, J. Heterocycl. Chem. **10**, 543 (1973).

[7] A. A. Mokhir, N. N. Gerasimchuk, E. V. Polshin, K. V. Domasevitch, Zhurn. Neorgan. Khimii (In Russ.) **39** (2), 301 (1994).

[8] K. V. Domasevitch, A. N. Chernega, S. V. Lindeman, Yu. T. Struchkov, Zhurn. Neorgan. Khimii (In Russ.) **40** (3) 426 (1995).

[9] R. C. Paul, K. K. Bhasin, R. K. Chadna, Indian J. Chem. **A14** (11), 864 (1976).

[10] J. M. Ross, W. C. Smith, J. Am. Chem. Soc. **86** (14), 2861 (1964).

[11] G. M. Sheldrick, SHELX93, a system of computer programs for X-ray structure determination, University of Göttingen, Göttingen, Germany (1993).

[12] G. M. Sheldrick, SHELXS, Acta Crystallogr. **A46**, 467 (1990).

[13] CCDC, University Chemical Laboratory, Lensfield Road, Cambridge CB 1 EW, UK.

[14] C. L. Raston, A. H. White and R. M. Golding, J. Chem. Soc., Dalton Trans. 329 (1977).

[15] I. D. Sadekov, L. E. Rybalkina, D. Ya. Movshovich, S. B. Bulgarevich, V. A. Kogan, Uspekhi Khimii (In Russ.) **60** (6) 1229 (1991).