Translated from *Uspekhi Khimii* **60** 1229–1254 (1991) U.D.C. 546.24.07

The structure and the electron-donating and electron-accepting properties of tellurium tetrahalides and halogen-containing σ-telluranes

I D Sadekov, L E Rybalkina, D Ya Movshovich, S B Bulgarevich, V A Kogan
Rostov-on-Don State University
Institute of Physical and Organic Chemistry at the Rostov-on-Don State University

ABSTRACT. The review gives a systematic account and surveys the available data on the structures of tellurium tetrahalides, σ-telluranes, and the complexes based on them.

The bibliography includes 167 references.

Contents

I. Introduction 628
II. The structures of tellurium tetrahalides and σ-telluranes in the crystal state and in solutions 628
III. Electron-donating properties of tellurium tetrahalides and σ-telluranes 635
IV. Electron-accepting properties of tellurium tetrahalides and σ-telluranes 636

I. Introduction

The great interest shown in the last two decades in the chemistry of organotellurium compounds is due to the possibility of using them in various branches of science and engineering[1,2] and in preparative organic chemistry.[3–5] Derivatives of tetracoordinate tellurium (σ-telluranes) of the type $RTeX_3$ and R_2TeX_2, where X is an electronegative substituent, occupy a key position in the chemistry of organotellurium compounds. It is possible to convert them comparatively readily into various types of derivatives of dicoordinate, tricoordinate, pentacoordinate, and hexacoordinate tellurium.[1,2] σ-Telluranes are distinguished by an increased stability compared with the selenium and especially sulphur compounds with analogous structures. The presence of lone electron pairs and unoccupied *d*-orbitals in the tellurium atom in these compounds as well as in tellurium tetrahalides is responsible for their electron-donating properties (in interactions with Lewis acids) and electron-accepting properties (in interactions with Lewis bases). This review gives a systematic account and surveys the available data on the structures of tellurium tetrahalides and σ-telluranes in the crystalline state and in solutions and of the complexes based on them.

II. The structures of tellurium tetrahalides and σ-telluranes in the crystal state and in solutions

1. The structure of tellurium tetrahalides in the crystal state and in solutions

In conformity with the theory of valence electron pair repulsion,[6] tellurium tetrahalides should have a trigonal bipyramidal (TBP) structure with a lone electron pair (LP) as a phantom ligand occupying one of the equatorial positions. Such a structure of the above compounds has been confirmed by studies on $TeCl_4$ in the gas phase by electron diffraction.[7] The tellurium tetrachloride molecule has the TBP structure with an average Te–Cl length of 2.33 Å. According to the authors,[7] the $Cl_{eq}-Te-Cl_{eq}$ bond angle is probably less than 120° but more than 90°, while the $Cl_{ax}-Te-Cl_{ax}$ bond angle is about 170°.

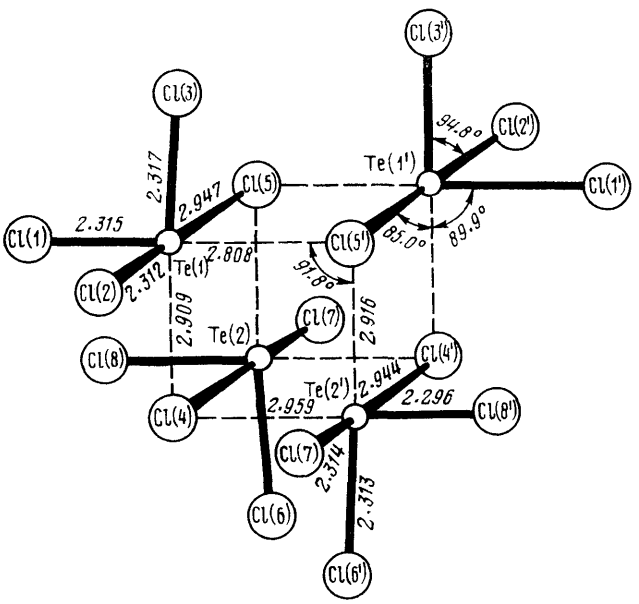


Figure 1. The structure of the tetramer Te_4Cl_{16}.[9]

However, as a consequence of secondary interactions involving tellurium atoms, the structure of tellurium tetrahalides in the crystal state is not quite so evident. Structures of all tellurium

tetrahalides have now been investigated by X-ray diffraction: the tetrachloride,[8–10] the tetrabromide,[8,11] the tetraiodide,[12–14] and the tetrafluoride.[15,16]

The crystal structure of tellurium tetrachloride is made up of isolated Te_4Cl_{16} tetramers[9,10] (Fig. 1). Each tellurium atom is joined to three terminal chlorine atoms by bonds whose average length is 2.311 Å, which is close to the Te–Cl bond length found in gaseous $TeCl_4$ (2.33 Å). The terminal chlorine atoms and the tellurium atom form a trigonal pyramid with average bond angles of 94.8°. The tellurium atom is also joined to three bridging chlorine atoms by bonds 2.929 Å long, which complete the environment around the tellurium atom to form a highly distorted octahedron. The average $Cl_{bridge}-Te-Cl_{bridge}$ bond angle is 85°.

Comparison of the data for tellurium tetrachloride with X-ray diffraction data for compounds with bonds of saturated types—ionic in $[TeCl_3]^+[AlCl_4]^-$,[17] where the tellurium atom has a distorted octahedral configuration ($Te-Cl_{term}$ = 2.276 Å, Te...Cl = 3.062 Å), and covalent in the $[TeCl_6]^{2-}$ ion[18] (Te–Cl = 2.54 Å) led the authors[10] to the conclusion that bonding intermediates between the two extreme types of bonds described above takes place in $TeCl_4$ and that there is only partial charge transfer from the bridging chlorine atoms to the tellurium atoms.

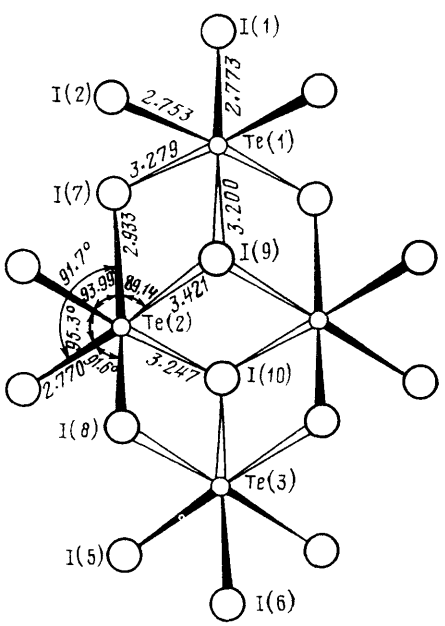


Figure 2. The structure of the tetramer $Te_{14}I_{16}$.[13]

Tellurium tetrabromide has a similar structure.[11] In the tetramers Te_4Br_{16}, the bond lengths are $Te-Br_{term}$ = 2.496 Å and $Te-Br_{bridge}$ = 3.054 Å.

Although the TeI_4 structure[13,14] (Fig. 2) is made up of $(TeI_4)_4$ tetramers, like those of $TeCl_4$ and $TeBr_4$, it is not isomorphous in relation to them. This structure consists of four edge-linked TeI_6 octahedra. As a result of this and in contrast to $TeCl_4$ and $TeBr_4$, three types of iodine atoms were detected in tellurium tetraiodide: those linked to a single tellurium atom (terminal bonds whose length is 2.769 Å), those linked to two tellurium atoms (bridged bonds whose length is 3.108 Å), and those linked to three tellurium atoms (pyramidal bonds whose length is 3.232 Å). The comparatively short intermolecular I...I bonds (3.870, 3.892, and 3.932 Å) join together separate tetramers.[14]

Tellurium tetrafluoride has a different structure.[15,16] The tellurium atom in this compound has three terminal fluorine atoms (average bond length 1.866 Å) and two bridging fluorine atoms with an average bond length of 2.181 Å. The fluorine atoms are located at the vertices of a distorted square pyramid and the individual TeF_5^- fragments are joined via the bridging fluorine atoms, forming infinite chains (Fig. 3). When account is taken of the lone pairs, the coordination around tellurium can be regarded as octahedral.

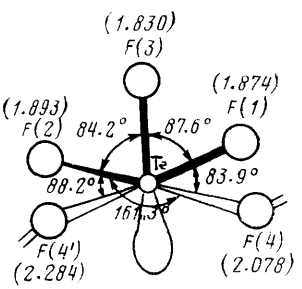


Figure 3. The structure of TeF_4.[15,16]

The availability of crystallographic data permitted the correct interpretation of spectroscopic data, in particular the ^{35}Cl NQR spectrum of $TeCl_4$,[19–21] the ^{81}Br NQR spectrum of $TeBr_4$,[21] and the ^{127}I NQR spectrum of TeI_4.[22,23] The NQR spectrum of $TeCl_4$ consists of six lines, which can be assigned to covalently linked chlorine atoms forming part of the composition of two non-equivalent $TeCl_3$ groups in the tetrameric structure (bridging chlorine atoms which are largely ionic are not manifested in the spectrum).[20,21] The ^{81}Br NQR spectrum of $TeBr_4$ is similar.[21] In the ^{127}I NQR spectrum, 10 non-equivalent iodine atoms can be detected in conformity with crystallographic data. Of these, six were identified as terminal atoms, two were identified as bridging atoms, and two were identified as pyramidal iodine atoms, which follows from their quadrupole splitting constants and the asymmetry parameters.[23]

X-Ray diffraction data for tellurium tetrahalides, and in the first place tellurium tetrachloride,[8–10] made it possible to explain the earlier extremely contradictory conclusions, obtained mainly with the aid of IR spectroscopy, concerning the structures of these compounds in the crystal state and in solutions. On the basis of the electrical conductivity of $TeCl_4$ in the melt, determined by dissociation in accordance with the scheme $TeCl_4 \rightleftarrows TeCl_3^+ + Cl^-$,[24] and also comparison of the IR and Raman bands of TeX_4 in the solid state[25–28] with the spectra of complexes of tellurium tetrahalides containing $TeCl_3^+$ ions,[17,26,28–30] it was concluded that the compound has an ionic structure ($TeCl_3^+Cl^-$)., This finding is confirmed by the results of conductimetric measurements for $TeCl_4$ solutions in a number of solvents.[29,31] Many other workers[32–34] concluded, on the basis of the same data, that tellurium tetrahalide has a covalent structure both in the solid state and in solutions.

Table 1. The average bond lengths (Å) and bond angles (degrees) in the molecules of the σ-telluranes $RTeX_3$.

Compound	Te–X_{term}	Te–X_{bridge}	Te–C	C–Te–X_{term}	C–Te–X_{bridge}	Type of associated species	Te...X	Refs.
$C_2F_5TeF_3$	1.872	2.193	2.20	88.8	77.6	polymer	–	[41]
$ClCH_2CH_2TeCl_3$	2.386	2.717	2.164	92.7	82.5	"	–	[42]
$C_6H_5TeCl_3$	2.377	2.755	2.122	91.68	85.46	"	–	[43]
$4\text{-}C_2H_5OC_6H_4TeCl_3$	2.396	2.749	2.12	91.0	88.2	"	–	[44]
$4\text{-}C_6H_5OC_6H_4TeCl_3$	2.374	2.768	2.111	91.3	87.2	dimer	3.702	[45]
$CH_2(TeCl_3)_2$	2.351	2.760	2.120	90.8	75.6	monomer	–	[46]
$C_6H_5TeBr_3$	2.526	2.829	2.140	92.2	85.4	polymer	–	[50]
$4\text{-}C_2H_5OC_6H_4Br_3$	2.531	2.932	2.10	93.6	88.4	dimer	4.143	[44]
$2\text{-}C_6H_5C_6H_4TeBr_3$	2.490 2.661 [a]	–	2.136	–	–	monomer	3.713	[51]
$1,2\text{-}(Br_3Te)_2\text{-cyclo-}C_6H_{10}$	2.541	2.88	2.224	92.4	83.2	"	–	[52]
$4\text{-}CH_3OC_6H_4TeI_3$	2.788	3.153	2.15	94.6	89.7	dimer	3.827	[44]
$2\text{-}C_6H_5C_6H_4TeI_3\text{-}\alpha$	2.769 2.966 [a]	–	–	–	–	monomer	[b]	[54]
$2\text{-}C_6H_5C_6H_4TeI_3\text{-}\beta$	2.748; 2.928	–	2.153	–	–	"	[c]	[55]

[a] The first figure denotes the Te–X_{eq} bond length and the second denotes the average Te–X_{ax} bond length. [b] The Te...I = 3.703 Å and I...I = 3.337 Å secondary bonds. [c] The I...I = 3.239, 3.772 Å secondary bonds.

The weak bonding of the structural units in the TeX_4 tetramers in the solid phase is responsible, according to Buss and Krebs,[10] for the ready decomposition, both homolytic and heterolytic, depending on the temperature, the nature of the solvent, and concentration. This explains many of the properties of the melt and solutions of $TeCl_4$, in particular the electrical conductivities and the solubilities in polar and non-polar solvents. In the latter (benzene, toluene), $TeCl_4$ is monomeric,[34,35] exhibiting limited association with increase in concentration, although according to the results of Greenwood et al.,[36] $TeCl_4$ and $TeBr_4$ are trimeric in the solvents indicated. Data concerning the structure of $TeCl_4$ in solutions in polar solvents are again contradictory. Some investigators[30,34,37] believe that $TeCl_4$ is not ionised in acetonitrile and propionitrile, while others[31,36] concluded that ionisation takes place in these and other polar solvents (acetone) with formation of $TeCl_3^+$ and Cl^- or of $L_2TeX_3^+$ and X^-, where L is a solvent molecule. At the same time, there is no doubt about the presence of complexes of the latter type in highly electron-donating solvents [dimethyl sulphoxide (DMSO), dimethylformamide (DMF), and pyridine].

2. The structure of σ-telluranes

Derivatives of tetracoordinate tellurium, which can be formally regarded as the products of the substitution of one ($RTeX_3$) or two (R_2TeX_2) halogen atoms in molecules of tellurium tetrahalides, have the common name σ-telluranes. The non-equivalence of the substituents at the tellurium atom in these compounds poses the problem of their preferential disposition (axial or equatorial). According to the polarity rule,[38] which has been extended to σ-telluranes,[39,40] the axial positions in the trigonal bipyramids in σ-telluranes are always occupied by the most electronegative substituents—the halogen atoms. This structure of organic derivatives of tetracoordinate tellurium has been confirmed by X-ray diffraction data.

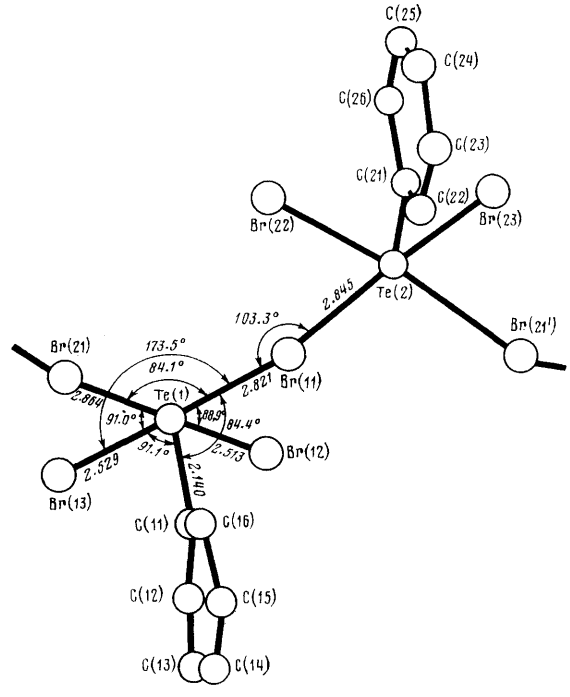


Figure 4. Geometry of the phenyltellurium tribromide molecule.[50]

(a) The structure of the σ-telluranes $RTeX_3$

The structures of a considerable number of organyl tellurium trihalides have now been investigated by X-ray diffraction: the trifluorides,[41] trichlorides,[42–49] tribromides,[44,50–53] and triiodides.[44,54,55] The principal data on the geometries of these compounds are presented in Table 1.

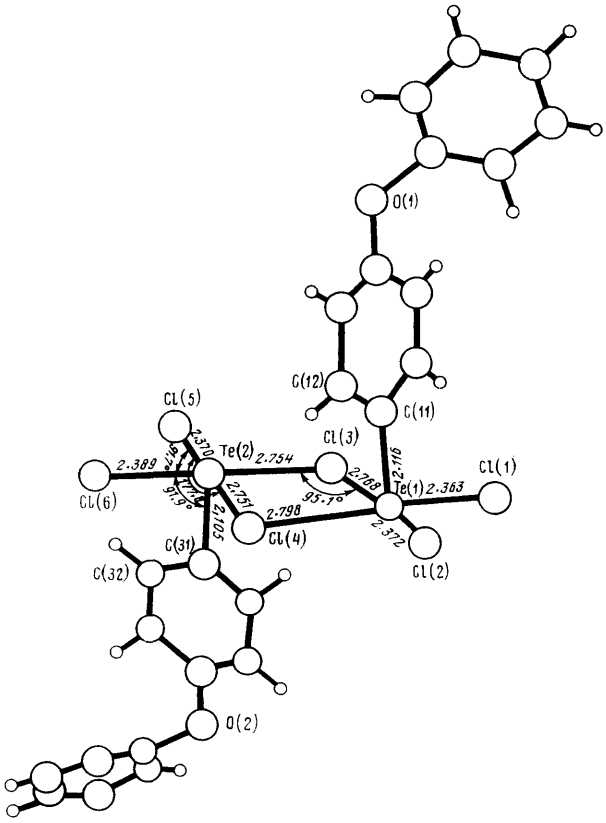


Figure 5. Geometry of the 4-phenoxyphenyltellurium trichloride molecule.[45]

As for tellurium tetrahalides, the real structure of the majority of the σ-telluranes $RTeX_3$ in the crystal state barely corresponds to the theoretically predicted trigonal bipyramidal structure. When account is taken of secondary interactions, the principal structural unit in these compounds $CTeX_4$, containing a pentacoordinate tellurium atom, has the square pyramidal configuration of the bonds around the tellurium atom with the organic group in the apical position. The tellurium atom is located virtually in the plane of the base of the square pyramid formed by the four halogen atoms, deviating slightly from it. Two halogen atoms form shorter (terminal) bonds, while the other two form longer (bridge) bonds which link the tellurium atoms of individual pyramids into polymeric or dimeric structures. The individual dimers are joined to one another by weak secondary Te...X bonds whose lengths greatly exceed those of the $Te-X_{bridge}$ bonds. The structures of typical representatives of polymeric and dimeric organyl tellurium trihalides (phenyltellurium tribromide[50] and 4-phenoxyphenyltellurium trichloride[45]) are presented in Figs. 4 and 5.

The σ-telluranes with two trihalotelluro-groups located at the same [bis(trichlorotelluro)methane[46]] (Fig. 6) or neighbouring [1,2-bis(tribromotelluro)cyclohexane][52] carbon atoms have the monomeric structure. Each tellurium atom in these compounds has a square pyramidal geometry with the exception that both Te–X bridge bonds are intramolecular. The structure of bis(trichlorotelluro)methane is presented in Fig. 6. It is noteworthy that the intermolecular Te...Te contacts in the above compounds are much shorter than in the σ-telluranes with a single TeX_3 group and amount to 3.417 Å in bis(trichloro)methane, for example.

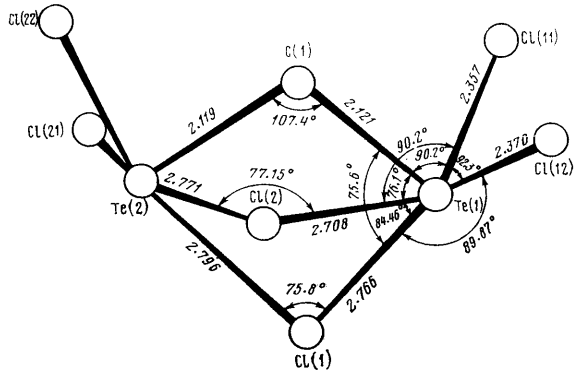


Figure 6. Geometry of the bis(trichlorotelluro)methane molecule.[46]

2-Biphenylyltellurium trihalide, containing the bulky 2-biphenylyl group, also has a monomeric structure with a trigonal-bipyramidal disposition of the ligands around the tellurium atom.[51,54,55] The geometry of the 2-biphenylyltellurium tribromide molecule[51] is illustrated in Fig. 7. The axial positions in the trigonal-bipyramidal structures of these compounds are occupied by halogen atoms, the angles between which are 178.5° for the tribromide, 176.5° for the α-modification of 2-biphenylyltellurium triiodide, and 176.0° for the β-modification. In other words, electronegative axial ligands are repelled to a greater extent from the lone pair than from the organic groups. It is of interest to note that, in conformity with the polarity rule,[38] the axial Te–X bonds are much longer than the equatorial bonds (Table 1). Short intermolecular Te...C contacts are observed in the molecules of 2-biphenylyltellurium trihalides, their length being 2.945 Å for the tribromide and 3.32 and 3.18 Å for the α- and β-triiodides respectively (the sum of the van der Waals radii of tellurium and carbon is 3.90 Å [56]). These contacts are responsible for the ease of the conversion of 2-biphenylyltellurium trihalides into 5,5-dihalodibenzotellurophenes on heating.[57] Intermolecular Te...X contacts have been detected in 2-biphenylyltellurium trihalides: 3.713 Å for the tribromide and 3.703 Å for the β-triiodide. Although they are smaller than the sums of the van der Waals radii of the corresponding elements (4.15 Å for Te and Br and 4.35 Å for

Te and I), they greatly exceed the lengths of the Te–X_{bridge} bonds (Te–Br = 2.829–2.932 Å, Te–I = 3.153 Å). The structures of the α- and β-modifications of 2-biphenylyltellurium triiodide are similar, differing only in the intermolecular contacts involving heavy atoms. Whereas β-modification contains, together with the Te...I secondary contacts, also I...I contacts whose length is 3.337 Å,[55] I...I contacts, whose lengths are 3.239 Å and 3.772 Å, were found in the α-modification.[54] The difference between the natures of these intermolecular interactions affects the colour of the compounds: the crystals of the β-modification are red and those of the α-modification are black.

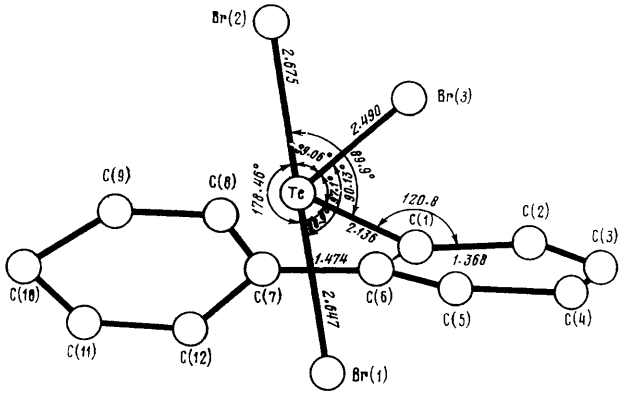


Figure 7. Geometry of the 2-biphenylyltellurium tribromide molecule.[51]

The degree of association and, what is most important, the molecular geometry of organyltellurium trihalides change significantly when they contain electron-donating atoms (oxygen, nitrogen) capable of intramolecular coordination to the tellurium atom. 8-Ethoxy-4-cyclooctenyltellurium trichloride[47] (Fig. 8) has a square pyramidal structure, like other organyltellurium trichlorides whose apex is occupied by a carbon atom. However, whereas in other σ-telluranes $RTeCl_3$ there are four chlorine atoms in the base of the pyramid, two of which are bridging, in the given compound there are three chlorine atoms, the lengths of the bonds of which with tellurium have the usual values (2.355–2.505 Å) and an O atom in the base of the pyramid. The Te...O distance (2.419 Å) is much smaller than the sum of the van der Waals radii of tellurium and oxygen (3.60 Å). Very weak secondary Te...Cl bonds, linking the molecules into dimers, were also found in the crystals. Their length (3.558 Å) is appreciably greater than those of the Te–Cl_{bridge} bonds (2.717–2.768 Å) observed in other organyltellurium trichlorides. 7-Ethoxycycloheptyltellurium tribromide probably has a similar structure.[53]

Another representative of the σ-telluranes $RTeX_3$, in which strong intramolecular Te ← N coordinate bonds were found is 2-(phenylazophenyl-C,N′)tellurium trichloride[48] (Fig. 9). Its bonds around the tellurium atom have an octahedral configuration. The apical Cl atoms (the Te–Cl bond lengths are 2.483 and 2.491 Å) form an angle of 171.7° with one another; the equatorial positions are occupied by the third Cl atom (the Te–Cl bond length is 2.406 Å), the bidentate organic ligand (the Te–C bond length is 2.114 Å), and the lone pair. The intramolecular Te ← N coordinate bond is of special interest. Its length (2.417 Å) is much smaller than the sum of the van der Waals radii (3.70 Å) and approaches the lengths of the usual Te–N covalent bonds. The molecule is monomeric and no Te...Cl contacts shorter than the sum of the van der Waals radii were detected in it.

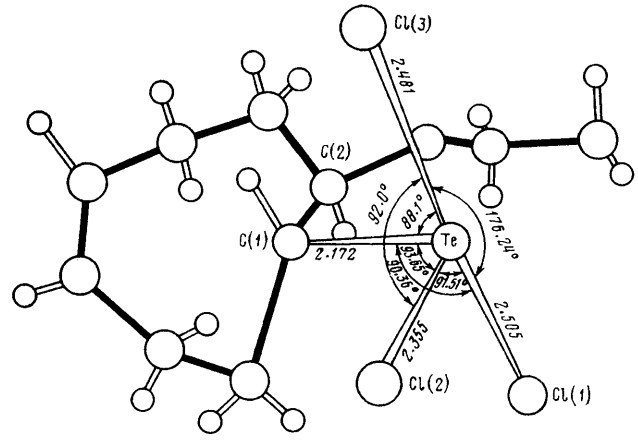


Figure 8. Geometry of the 8-ethoxy-4-cyclooctenyltellurium trichloride molecule.[47]

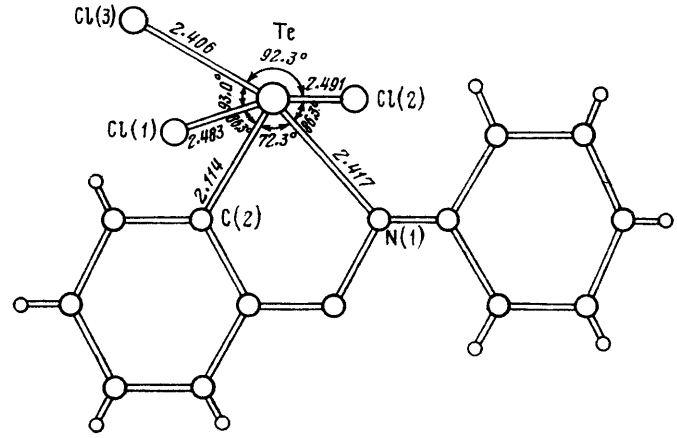


Figure 9. Geometry of the (2-phenylazophenyl-*C,N′*)tellurium trichloride molecule.[48]

The polydenticity of the organic ligand in 2,6-diacetylpyridinetellurium trichloride[49] leads to a structure of a new type which had not been encountered previously in the series of organyltellurium halides (Fig. 10). The coordination polyhedron of

the tellurium atom can be described as a distorted pentagonal bipyramid with two axial Te–Cl bonds (2.492 and 2.500 Å); the equatorial positions are occupied by a Cl atom (Te–Cl_{eq} = 2.431 Å), the lone pair, and the three atoms of the tridentate organic group: the carbon atom (Te–C = 2.129 Å), the nitrogen atom (Te...N = 2.402 Å), and the oxygen atom (Te...O = 2.878 Å).

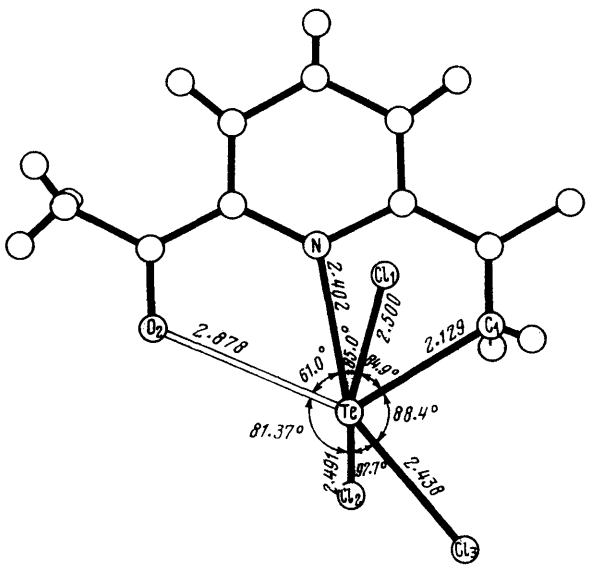


Figure 10. Geometry of the 2,6-diacetylpyridinetellurium trichloride molecule.[49]

Although the lengths of the neighbouring two bonds do exceed the sums of the covalent radii of the corresponding elements (2.07 Å for Te and N and 2.03 Å for Te and O), nevertheless they are much smaller than the sum of the van der Waals radii of these elements (3.70 Å for Te and N and 3.60 Å for Te and O [56]). The presence of the Te–N and Te–O coordinate bonds has been confirmed also by IR spectroscopic data: the shift of the vibrations of the pyridine ring from 997 cm^{-1} in 2,6-diacetylpyridine to 1012 cm^{-1} in the trichloride; the two carbonyl absorption bands at 1676 and 1712 cm^{-1}, observed in the spectrum of free 2,6-diacetylpyridine, are replaced in tellurium trichloride by a single vibration at 1707 cm^{-1}.[49] It is also of interest that the presence of coordinate bonds in the given trichloride increases significantly its resistance to hydrolysis.

The IR and Mössbauer spectra of organyltellurium trihalides, mainly the aryl derivatives, examined in Refs. 58–63 and 64–67 respectively, in general agree with X-ray diffraction data. By virtue of the wide variety of the Te–Hal bonds found in the σ-telluranes $RTeX_3$, they are of interest for NQR spectroscopy. However, the NQR spectroscopic data for these compounds are so far lacking in the literature.

The question of the aggregation of organyltellurium trihalides in solutions is important for the chemistry of the complexes based on them. Conductimetric data for solutions in acetonitrile, acetone, and nitrobenzene show that organyltellurium trichlorides do not dissociate into ions.[68–71] Organyltellurium tribromides and triiodides dissociate in the same solvents into ions ($RTeX_2^+$ and X^-) according to Khandelwal and co-workers,[70,71] although it has been claimed[61] that CH_3TeBr_3 is a non-electrolyte in nitrobenzene. On the other hand, aryltellurium trihalides containing amino(or dimethylamino)-groups in the ring, behave as 1:1 electrolytes in the solvents listed above regardless of the nature of the halogen.[63,72] This is probably due to the greater polarity of the Te–Hal bonds in the latter compounds owing to the presence in them of strong electron donors — the amino(or dimethylamino)-groups.

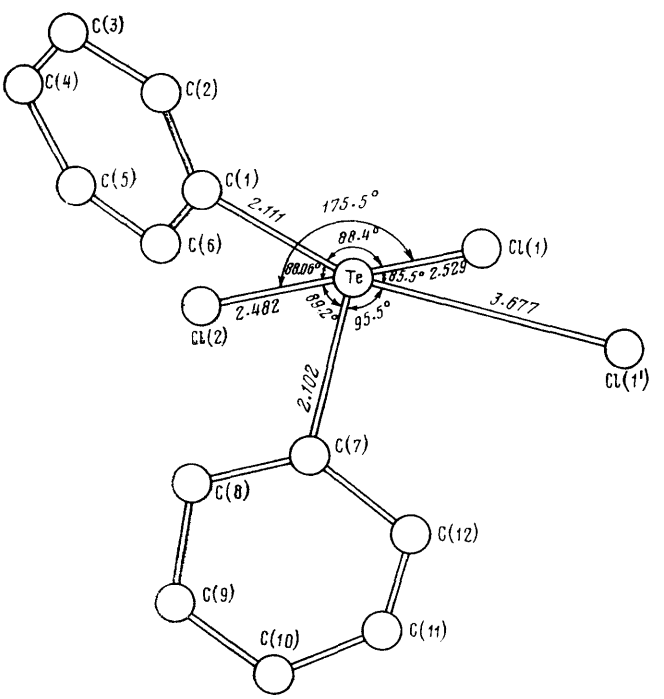


Figure 11. Geometry of the diphenyltellurium dichloride molecule.[43]

The results of cryoscopic studies on organyltellurium trihalides in general agree with conductimetric data. Aryltellurium trichlorides are monomeric in solutions [with the exception of amino(dimethylamino)-derivatives], exhibiting a weak association with increase in concentration,[39,68–70] while the tribromides and triiodides are partly dissociated.[63,70–72] On the other hand, in the case of the methyltellurium trihalides there is a monomer–dimer equilibrium in solution in benzene,[60,61] methyltellurium tribromide being more associated than its chlorine analogue.

(b) The structure of the σ-telluranes R_2TeX_2

Among diorganyltellurium dihalides, diorganyltellurium dichlorides have been most thoroughly investigated by X-ray diffraction.[43,73–81] Other tellurium dihalides (difluorides,[82] dibromides,[83] and diiodides[84,85]) are represented by single examples.

Table 2. The average bond lengths (Å) and bond angles (degrees) in the molecules of the σ-telluranes R_2TeX_3.

Compound	Te—X	Te—C	X—Te—X	C—Te—C	Te...X[a]	Te...X/Te—X[b]	Type of associated species	Refs.
$(C_6H_5)_2TeF_2$	2.006	2.115	173.1	96.1	3.208	1.60	A[c]	[82]
$(CH_3)_2TeCl_2$	2.511	2.09	172.3	98.2	3.46–3.52	1.39	A	[73, 74]
$(CH_3CHClCH_2)_2TeCl_2$	2.501	2.149	169.1	98.2	footnote[d]	–	A	[75]
$(C_6H_5)_2TeCl_2$	2.506	2.107	175.54	99.01	3.677	1.47	A	[43]
$C_6H_5TeCl_2C_6H_4Br$-4	2.513	2.114	176.3	95.05	3.413–3.723	1.41	B	[76]
$(4\text{-}BrC_6H_4)_2TeCl_2$	2.500	2.131	178.24	96.1	4.67–5.54	1.86	A[e]	[77]
$(4\text{-}CH_3OC_6H_4)_2TeCl_2$	2.519	2.112	178.35	96.45	3.446–3.675	1.41	B	[78]
$(4\text{-HO-3-}CH_3C_6H_3)_2TeCl_2$	2.518	2.104	174.8	99.2	3.884	1.54	A[f]	[79]
$(2\text{-Cl-cyclo-}C_6H_{10})_2TeCl_2$	2.493	2.19	177.6	103.0	footnote[d]	–	–	[80]
$(2\text{-Cl-cyclo-}C_6H_{10})TeCl_2-C_6H_4CH_3$-4	2.485	2.16	176.4	101.0	footnote[d]	–	–	[81]
$(C_6H_5)_2TeBr_2$	2.682	2.16	182.2	95.35	3.93	1.47	A	[83]
$(CH_3)_2TeI_2$	2.924	2.127	177.9	95.0	3.659–4.030	1.33	A	[84]
$(4\text{-}ClC_6H_4)_2TeI_2$	2.935	2.115	173.5	101.1	4.13–4.46	1.46	A	[85]

[a] The extreme limits of the bond lengths are quoted in a number of instances for the secondary bonds. [b] The arithmetical mean lengths of individual types of bonds have been adopted. [c] A, infinite chains; B, tetramers. [d] Data are lacking. [e] The chains are formed as a result of the Te...Br secondary interactions (3.71, 3.80 Å). [f] The chains are formed via O—H...Cl intermolecular hydrogen bonds (2.45 Å).

This review does not deal in detail with cyclic σ-telluranes, information about which can be found in other publications.[2,86,87] The most important structural characteristics of diorganyl tellurium dihalides are presented in Table 2.

The σ-telluranes R_2TeX_2 are characterised by the trigonal-bipyramidal disposition of the ligands around the tellurium atom, the halogen atoms always occupying axial positions. The X—Te—X angles are less than 180°, which shows that the halogen atoms are more strongly repelled from the lone pair of tellurium than from the equatorial organic groups. Diphenyltellurium dibromide, for which the Br—Te—Be angle exceeds 180°, is an exception.[83] The steric interactions between the bromine atoms and the phenyl rings[83] cannot be the cause of the increase in the angle, since in di(4-chlorophenyl)tellurium diiodide,[85] containing the more bulky iodine atoms, the I—Te—I bond angle is less than 180°. The structure of diphenyltellurium dichloride[43] is presented in Fig. 11.

In the majority of the σ-telluranes R_2TeX_2 investigated secondary Te...X interactions have been observed, the weakest being those in the difluorides. The lengths of these bonds are smaller than the sums of the van der Waals radii with the corresponding elements but greatly exceed the lengths of the Te—X bridge bonds in the σ-telluranes $RTeX_3$. The halogen atoms involved in the secondary bonds supplement the coordination around tellurium to the octahedral configuration. These interactions bind the individual molecules into infinite chains or tetramers. The bond length ratio Te...X/Te—X makes it possible to estimate roughly the degree of intermolecular association of the corresponding diorganyltellurium dihalides. Difluorides are least associated; dialkyltellurium dihalides are more associated than the diaryl derivatives.

In certain σ-telluranes R_2TeX_2, the Te...X secondary interactions are insignificant and the secondary bonds involving other atoms are shorter. In di(4-bromophenyl)tellurium dichloride,[7] the shortest linkages arise due to the Te...Cl interactions (4.67 and 5.54 Å), but they exceed significantly the sum of the van der Waals radii of Te and Cl (4.0 Å [56]). The individual molecules of this compound are linked by weak secondary Te...Br interactions (3.71 and 3.80 Å), the corresponding bond lengths being smaller than the sum of the van der Waals radii of Te and Br (4.15 Å [56]). The Te...Cl secondary interactions (3.884 Å) do not play an important role also in di(4-hydroxy-3-methylphenyl)tellurium dichloride.[79] The O—H...Cl intermolecular hydrogen bonds (2.45 Å) are energetically more favourable.

The secondary interactions with participation of heavy atoms (tellurium and iodine) in the molecules of diorganyltellurium dihalides are of special interest. The colour of these compounds, which varies from orange to dark-violet, is determined by the nature of the intermolecular bonds (Te...I or I...I). The compounds less coloured in the crystalline state have only the intermolecular Te...I bonds, while the dark-violet compounds contain in the main the I...I intermolecular bonds. Indeed, in the dark-violet di(4-chlorophenyl)-tellurium diiodide[85] and 1,1-diiodo-1-thia-4-telluracyclohexane[88] the intermolecular bonds are of the I...I type, whose lengths are 3.85 and 4.14 Å for the first compound and 3.66 and 3.90 Å for the second. On the other hand, in the yellow-orange 1,1-diiodo-3,4-benzo-1-telluracyclopentane[89,90] (Te...I = 3.653, 3.878 Å), the pale-red 1,1-diiodo-1-oxa-4-telluracyclohexane[91] (Te...I = 3.692, 3.814 Å), 10,10-diiodophenoxatellurin[92] (Te...I = 3.74, 3.79 Å),

and the red 5,5-diiododibenzotellurophene[93] (Te...I = 3.696, 3.617 Å), the secondary Te...I bonds are observed.

The IR spectra of the σ-telluranes R_2TeX_2 [58,94–97] agree with the trigonal-bipyramidal structure of the molecules of these compounds.[94,96,97] The Mössbauer spectra of diorganyltellurium dihalides, indicating that, regardless of the nature of the halogens these compounds have the same structure in the crystalline state, have been examined in a number of studies.[64–67,98]

The available information about the NQR spectra of compounds of the type R_2TeX_2 is extremely limited.[99,100] Two resonance lines have been observed in the ^{35}Cl NQR spectrum of dimethyltellurium dichloride,[99] while only one such line has been found in the NQR spectra of the diphenyl derivatives $(C_6H_5)_2TeX_2$ (X = Cl, Br, I).[100] While the first result agrees with X-ray diffraction data[73,74] (non-equivalence of the Te–Cl bonds), the data for diphenyltellurium dihalides do not. According to the results of Kondo et al.,[99] the Te–Cl bond in $(CH_3)_2TeCl_2$ is more ionic than in $TeCl_4$.

In contrast to organyltellurium tribromides and triiodides, which dissociate in solution into $RTeX^+$ and X^-, the σ-telluranes R_2TeX_2 are not electrolytes according to conductimetric data.[61,69–71] This is also indicated by the results of the determination of the molecular weights. An exception is 1,1-diiodo-3,4-benzo-1-telluracyclo-pentane,[89] the conductivity of which in dimethylformamide is typical for a 1:1 electrolyte and the observed molecular weight of this compound is appreciably lower than the theoretical value, indicating its existence in the ionic form.

III. Electron-donating properties of tellurium tetrahalides and σ-telluranes

Tellurium tetrachloride and its organic derivatives exhibit electron-donating properties in their reactions with Lewis acids. One of two alternative structures is usually attributed to the complexes formed: the donor–acceptor structure (I) or the ionic structure (II):

$$TeCl_4 + MX_n \rightarrow Cl_4Te \cdot MX_n, \quad \text{(I)}$$

$$TeCl_4 + MX_n \rightarrow [TeCl_3]^+ [MX_nCl]^-. \quad \text{(II)}$$

The conclusions concerning the existence of structures (I) or (II) are based mainly on vibrational spectroscopic data.[17,29,30,101,102–104] Bands in the range 343–345 cm^{-1}, characteristic of the $AlCl_4^-$ anion, have been observed in the Raman spectra of the complex of $TeCl_4$ with $AlCl_3$ in the melt and in the solid phase. This supports the structure (II).[101] The structure is also indicated by X-ray diffraction data for the complex.[17] The structure of the complex is made up of layers formed by highly distorted octahedra in which three terminal chlorine atoms are much closer to the tellurium atom than the other three, which are in their turn part of the composition of the $AlCl_4^-$ tetrahedra (Fig. 12).

Analysis of the vibrational spectra led to the conclusion that the crystalline complexes $TeCl_3^+ . AlCl_4^-$, $TeCl_3^+ . SbCl_6^-$, $TeCl_3^+ . AsF_6^-$, and $PCl_6^- . TeCl_7^+$ [actually $TeCl_4 . PCl_5$ in Ref. 30 (Ed. of Translation)] and their solutions in solvents of different polarity (benzene and acetonitrile) are ionic.[30] However, more detailed study of the Raman spectra of the complex $TeCl_4 . SbCl_5$ in the solid state[102] showed that its structure resembles that of the molecular complex $SeCl_4 . SbCl_5$ and is of the donor–acceptor type. In the highly polar nitromethane, it dissociates into the ions $TeCl_4^+$ and $SbCl_6^-$. It is of interest to note that the solid, freshly prepared, complex $TeCl_4 . SbCl_5$ is ionic and metastable. Its prolonged exposure to room temperature entails the disappearance of the bands characteristic of the $SbCl_6^-$ ion.[102]

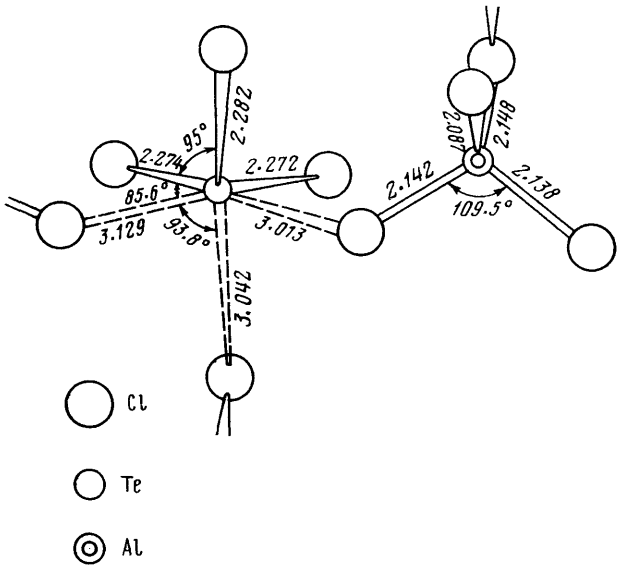


Figure 12. The crystal structure of the complex $TeCl_4 . AlCl_3$.[17]

The complexes of $TeCl_4$ with BCl_3 in polar solvents exhibit an electrical conductivity typical for 1:1 electrolytes,[104] which indicates the presence of the ions $TeCl_3^+$ and BCl_4^-. This has been confirmed by IR spectroscopic data.[105] It is of interest to note that $TeCl_4$ and BBr_3 afford $TeBr_4$ quantitatively on interaction, but the latter does not react with BBr_3.[106]

The interaction of TeF_4 with SbF_5 [107] leads to the formation of trifluorotelluro(IV)-μ-fluorobis[pentafluoroantimonate(V)], which also has the ionic structure $TeF_3^+ . Sb_2F_{11}^-$ with appreciable interaction between the ions via the fluorine atoms. On the other hand, the interaction of $TeCl_4$ with Group III metal halides ($AlBr_3$, $GaBr_5$, $GaCl_3$) [108] results in the formation of stable, highly polar, 1:1 electron-donating complexes.

Conclusions concerning the structure of the complexes of σ-telluranes with Lewis acids are also as a rule based on the analysis of the vibrational spectra and these systems are regarded as ionic.[109,110] The possibility of the formation of the cations $RTeCl_2^+$ has been demonstrated by a series of complexes of

organyltellurium trichlorides with $SbCl_5$, which are insoluble in non-polar solvents.[109] The ionic structure of these complexes, whose composition is $RTeCl_3.SbCl_5$, follows from the similarity of their IR spectra to those of the ionic complexes $RSeCl_3.AlCl_3$ [109] and from the observation of bands characteristic of the $SbCl_6^-$ ion.[110]

The interaction of $RTeCl_3$ with $AlCl_3$ is of special interest. The formation of compounds of the type $[RTeCl_2]^+[AlCl_4]^-$ has been postulated in a series of studies. Indeed $C_6H_5TeCl_3$ does not interact with benzene to form $(C_6H_5)_2TeCl_2$,[111] while 2-trichlorotellurodiphenylmethane does not cyclise to 10,10-dichlorotelluroxanthene in the absence of $AlCl_3$.[112] On the other hand, the addition of $AlCl_3$ makes it possible to achieve the above reactions by virtue of the enhancment of the electrophilic nature of the trichlorotelluro-groups in the above aryltellurium trichlorides probably as a result of the formation of the complexes $[RTeCl_2]^+[AlCl_4]^-$.

Thus in the majority of the studies quoted, carried out using vibrational spectroscopy, it was concluded that the complexes of $TeCl_4$ and σ-telluranes with Lewis acids are ionic. It is believed[30,101,102,104,109,110] that the complexes are formed as a result of the transfer of a Cl^- ion from the tellurium-containing donor to the acceptor. However, this mechanism cannot be regarded as the only one possible. Much depends on the strength of the Lewis acid and the nature of the medium in which the complexes are present. Thus, according to IR and UV spectroscopic and mass-spectrometric data, the complexes of R_2TeI_2 with I_2 have a distorted octahedral structure in the crystalline state and are donor–acceptor compounds.[113,114] This conclusion also follows from a study[115] in which the crystal and molecular structures of dimethyltellurium tetraiodide were investigated. It has the structure of a molecular adduct in which the individual $(CH_3)_2TeI_2$ and I_2 molecules are linked mainly by the $-I\ldots I-I$ intermolecular bonds. The interaction of dialkyltellurium diiodides with mixed halides also results in the formation of the molecular complexes $R_2TeI_2.IX$ (X = Cl, Br).[116]

The above data refer to the structure of the complexes of $TeCl_4$ and σ-telluranes with Lewis acids in the crystalline state or in solution in highly polar solvents. However, on passing to non-polar solvents, these systems acquire a qualitatively different structure. The dipole moments of the complexes of $TeCl_4$ with Group IIIA metal halides, having the composition $TeCl_4.MX_3$ (MX = $AlBr_3$, $GaCl_3$, $GaBr_3$), are in the range 6–10 D.[35] Such polarity precludes the attribution of the structure of ion pairs to these complexes. On the other hand, the bridged structures, whose formation cannot be ruled out *a priori*, should have significantly smaller dipole moments. On the basis of these data and the absence of electrical conductivity in benzene, it has been concluded that these are donor–acceptor complexes.[35] The bond in them is formed via the lone pair of the tellurium atom and the unoccupied orbitals of the central atom of the Lewis acid and, judging from calorimetric data and dielectric constant measurements, it is fairly strong and polar. Comparison of the IR spectra of solutions of these complexes in benzene with those of typical donor–acceptor systems $R_2S.MX_3$ [117] reveals a virtually complete identity of the spectra in the region corresponding to the absorption by the acceptor. Other studies[118,119] have led to a similar conclusion about the nature of the bond in the complexes of the σ-telluranes $RTeX_3$ and R_2TeX_2 with $SbCl_5$ in benzene.[118,119] A characteristic feature of the latter systems is also the formation of the complexes $D.3SbCl_5$ (D = donor molecule).[118] An exception is the $(C_6H_5)_2TeI_2$ + $SbCl_5$ system in which halogen exchange probably takes place.[119] The results obtained by combined thermal analysis indicate the molecular nature of the complexes formed.[119] The dipole moments of the 1:1 complexes are in the range 6–8 D, while those of the 1:3 complexes are in the range 10–13 D, which indicates the ionic structure of the latter.[118] The electrical conductivity of the complexes having the simplest composition, observed in nitrobenzene,[118] does not rule out the possibility that they are donor–acceptor in nature. Judging from the heats of formation of the complexes, the electron-donating capacity of the tellurium atom in the σ-telluranes is determined primarily by the number of aromatic groups and their nature.[119,120]

IV. Electron-accepting properties of tellurium tetrahalides and σ-telluranes

1. Electron-accepting properties of tellurium tetrahalides

The relatively low-lying unoccupied *d* orbitals of the tellurium atom are responsible for the electron-accepting properties of its tetracoordinate derivatives, the subject of numerous investigations. A considerable proportion of them involve the study of the electron-accepting properties of tellurium tetrahalides, which are moderately strong Lewis acids in relation to various N-, P-, O-, S-, and Se-containing organic donors. The complexes have been, as a rule, isolated in the solid state and investigated by various physicochemical methods.

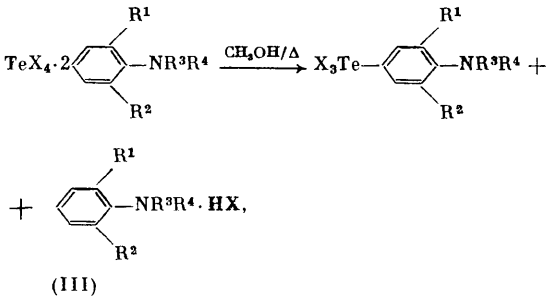
(a) Complexes with N-donors

In the literature devoted to the study of the electron-accepting properties of tellurium tetrahalides, most attention has been devoted to their interaction with N-containing bases. The reactions of TeF_4 with aliphatic amines (trimethylamine and tetramethylethylenediamine) result in the formation of crystalline 2:1† and 1:2 adducts.[121] Bands characteristic of the TeF_5^- anion have been detected in the IR spectra of these systems,[122] which made it possible to attribute to them the ionic structures $[TeF_3.L_2]^+[TeF_5]^-$ and $[TeF_3.L]^+[TeF_5]^-$ respectively. An octahedral structure has been proposed for the cation $[TeF_3.L_2]^+$, in which the tellurium atom is surrounded by three fluorine atoms, two electron-donating ligand atoms in the *cis*-positions, and the lone pair at one of the vertices. The nature of the relative positions of the monodentate ligands in the complexes has not been elucidated.[121]

On interaction with TeX_4 (X = Cl, Br, I), aromatic amines[72,123–126] form 2:1 complexes which are sparingly soluble in the usual organic solvents. However, after prolonged heating of these complexes in dry methanol, electrophilic substitution of one of the aromatic rings takes place in the *p*-position (relative to the amino-groups) with formation of tellurium trihalides (III) or, if the *p*-position is

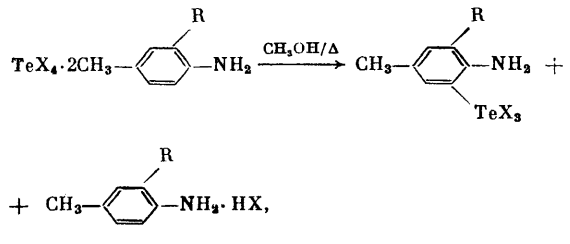
† In the designation of the composition of the complexes, here and henceforth the first figure denotes the number of electron-donating molecules and the second denotes the number of electron-accepting molecules.

occupied, substitution in the *o*-position takes place with formation of compounds (IV):[72,123]



(III)

$R^1 = R^2 = R^3 = R^4 = H$; $R^1 = R^2 = R^3 = H$; $R^4 = CH_3$; $R^1 = R^2 = H$; $R^3 = R^4 = CH_3$; $R^1 = R^3 = R^4 = H$, $R^2 = CH_3$; $R^1 = R^2 = CH_3$, $R^3 = R^4 = H$,



(IV)

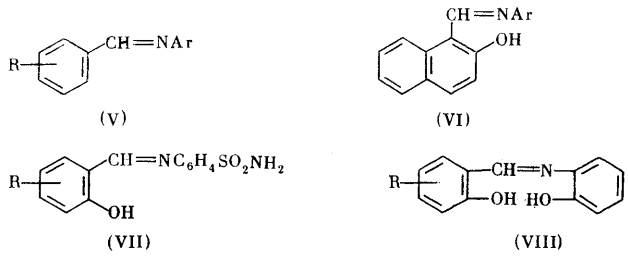
R = H, CH_3.

The interaction of $TeCl_4$ with heterocycles containing an sp^2-hybridised nitrogen atom results in the formation of mainly 2:1 complexes.[29,127–130] The reaction with the bidentate 2,2′-bipyridyl results in the formation of a 1:1 adduct[128] and the formation of complexes of both compositions has been noted only for pyridine.[29,31] According to conductimetric and vibrational spectroscopic data, these complexes are ionic.[29] The anion is Cl^-, while the cation, $[TeCl_3.L_2]^+$, is a pseudo-octahedron with a lone pair at one of the vertices. X-Ray diffraction demonstrated the *trans*-octahedral structure of the 2:1 adduct of $TeCl_4$ with pyridine.[131] In this case, the lone pair of the tellurium atom is not stereoactive.

In contrast to $TeCl_4$, the reaction of TeF_4 with pyridine affords only a 1:1 adduct.[132] Its treatment with aqueous HF results in the formation of more complex fluorides: $C_6H_5NH.TeF_5$ and $(C_6H_5NH)_2.TeF_6$.

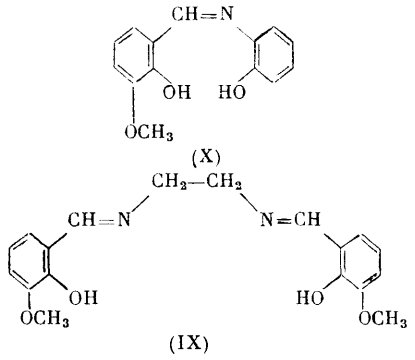
Thiopicolinamides[130] react with $TeCl_4$ to form 2:1 complexes. It follows from the analysis of IR and ^1H NMR spectroscopic data that the tellurium atom is coordinated to the pyridine nitrogen atom and the nitrogen atom of the thioamide group. Judging from the molar conductances in solutions in DMF, these complexes can be regarded as 1:2 electrolytes.

Tellurium tetrachloride exhibits electron-accepting properties also in relation to hydrazones[133] and Schiff bases (V)–(VIII),[134–136] with which it forms mainly 2:1 complexes. The complexes with type (VII) azomethines possess antibacterial properties.[135]



(V) (VI) (VII) (VIII)

However, the reaction of $TeCl_4$ with the azomethines (IX) and (X) affords 1:1 complexes. The reason for the conflict between the results of the above studies[136,138] is obscure, since the electron-donating compounds (VIII) and (IX) employed in these investigations have very similar structures.



(X)

(IX)

The shift of the stretching vibration bands of the C=N bond in the IR spectra of the adducts compared with the initial Schiff bases has led to the conclusion[134,135,137] that N → Te coordinate bonds are formed via the lone pairs of the azomethine nitrogen atoms.

(b) Complexes with O-donors

Tellurium tetrachloride exhibits electron-accepting properties in relation to the oxygen atom in the C=O, N → O, P → O, and S → O groups. The interaction of $TeCl_4$ with acetamide and its derivatives[138] and 2-hydroxybenzylideneacetophenones[139] results in the formation of 2:1 complexes, in which, judging from IR spectroscopic data, the tellurium atom is coordinated to the carbonyl oxygen atom. The electrical conductivities of solutions of the complexes of $TeCl_4$ with acetamide and its derivatives are characteristic of 1:1 electrolytes and made it possible to attribute the structure $[TeCl_3L_2]^+Cl^-$ to the complexes.[138]

Pyridine[31] and 2,6-lutidine[140] *N*-oxides form 2:1 complexes on interaction with $TeCl_4$ (pyridine *N*-oxide also gives rise to a 1:1 complex). Conductimetric measurements and analysis of the IR spectra indicated that the complexes of pyridine *N*-oxide, containing Cl^- as the anion, have an ionic structure.[31] The splitting of the stretching vibration bands of the N → O group in the IR spectrum of the complex of 2,6-lutidine, similar to that observed for the *cis*-octahedral complexes $MCl_4.2L$ (M = Hf, Ta, Th; L = R_nYO,

Y = N, P, S, etc., n = 2, 3), made it possible to postulate a *cis*-disposition of the ligands also in the 2,6-lutidine complex.[140]

Dialkyl sulphoxides react with $TeCl_4$ to form 2:1 and 1:1 complexes. This is particularly characteristic of dimethyl sulphoxide.[20] The complex with the simplest composition is a molecular compound both in solution and in the crystalline state. This follows from the dipole moment determined in benzene and the ^{35}Cl NQR spectrum in the solid phase. On the other hand, conductimetric data for the 2:1 complexes indicate the ionic structure $[TeCl_3.2(CH_3)_2SO]^+Cl^-$. It has been postulated[20] that the structures of complexes of both types are made up of octahedra, one of the vertices of which in the 1:1 complex is occupied by the lone pair of the tellurium atom. Dicyclohexyl sulphoxide reacts with $TeCl_4$ to form the complex having the simplest composition.[120] The complexes of $TeCl_4$ with diethyl and dibutyl ethers, investigated by the dielectric constant titration method, have a similar composition.[35]

According to the dielectric constant titration data, under isomolar series concentration conditions in solutions in benzene, $TeCl_4$ reacts with $(C_6H_5)_3PO$ to form complexes having only two compositions: 1:1 and 2:1.[141] Judging from the dipole moments, they are donor–acceptor complexes. One of the vertices of the octahedron in the 1:1 complex is probably occupied by the lone pair of tellurium, while the octahedral 2:1 complex has the *cis*-structure.

(c) Complexes with S-donors

According to the dipole moment and calorimetric titration data, $TeCl_4$ reacts with the dialkyl sulphides $(C_3H_7)_2S$ and $(C_7H_{15})_2S$ to form 1:1 complexes.[20,35] The dipole moments of the complexes (5–9 D) and the low electrical conductivities in benzene demonstrate their donor–acceptor nature. Complexes with the simplest composition are formed also on interaction of $TeCl_4$ with the sulphides $RS(CH_2)_nSR$ (R = alkyl, n = 2–10) [142] despite the presence of two sulphur atoms in the latter.

Much attention has been devoted to the study of complexes in which an sp^2-hybridised sulphur atom functions as the donor centre. Both $TeCl_4$ and $TeBr_4$ form 2:1 complexes with tetramethylthiourea (TMTU).[143–145] It has been established by X-ray diffraction[143–145] that these complexes have an octahedral structure in which the sulphur atom is in the equatorial plane in the *trans*-position. The structure of the complex $TeBr_4.2TMTU$ is illustrated in Fig. 13. The slight distortions of the coordination unit are treated as a consequence of packing effects[144] or of the influence of the lone pair of the tellurium atom.[145]

Comparison of the long-wavelength IR spectra of the complexes of TMTU in the solid state and in solution[128] in the light of X-ray diffraction data[143–146] indicated that the *trans*-octahedral structure is retained also in solutions. The determination of the molecular weights in solution in tetramethylene sulphone and of the electrical conductivity in solutions in nitrobenzene and tetramethylene sulphone led to the conclusion that these complexes are monomeric and weakly ionised.[128]

N,N'-Substituted thioureas also form 2:1 complexes with $TeCl_4$ which are non-conducting in DMF and DMSO.[147] The shift of the bands in the range 600–700 cm^{-1}, referring to the vibrations of the C=S groups, led to the conclusion that the adducts have an octahedral structure with the apical S-coordination of the organic bases.

It is of interest to note that TMTU reduces tellurium(IV) derivatives in acid solutions, which leads to the formation of the complexes $Te^{(III)}:Te(L)Cl_2$.[143]

Various thiones can also function as S-containing donors. The 2:1 complex of $TeCl_4$ with benzimidazolethione has the *cis*-configuration with coordination to the sulphur atoms according to X-ray diffraction data.[149] On the other hand, the analogous complex with benzothiazolethione, isolated from solution in dioxane, has the *trans*-octahedral structure.[150]

Adducts of the type $TeX_4.L_2$ have also been obtained by the reaction of TeX_4 (X = Cl, Br, I) with thiazolidine-2-thione. IR spectroscopic data in the solid state have lead to the hypothesis that the complexes have an octahedral structure[151] in which the tellurium atom is coordinated to the nitrogen atom of one of the ligand molecules and the sulphur atom of the other.

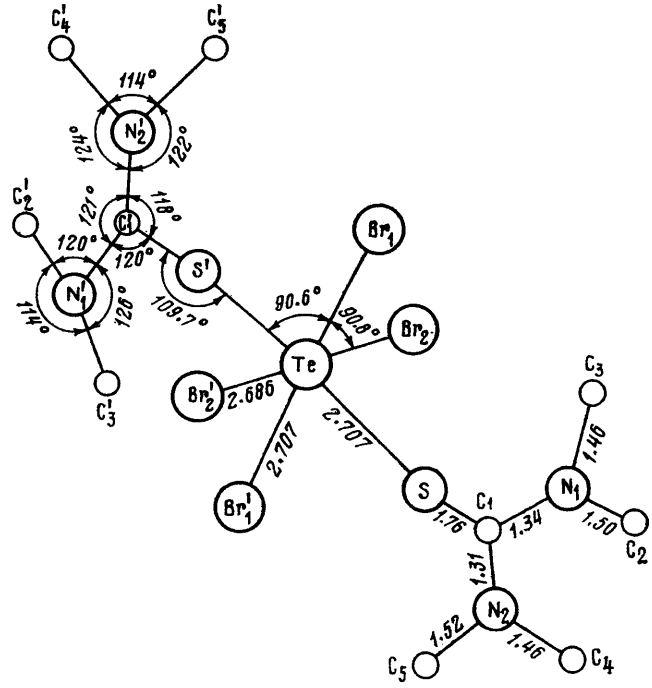


Figure 13. The structure of the adduct $TeCl_4.2TMTU$.[143,144]

Measurements of the electrical conductivities of the above systems showed that these are 1:1 electrolytes and the low electrical conductivities in solution in DMF have been explained by the tight bond between the cation and the anion.

Tetramethyl(ethyl)dithiooxamides constitute another type of sulphur-containing donors forming 1:1 complexes with $TeCl_4$ and $ArTeCl_3$.[152,153] The long-wavelength IR and the Raman spectra indicate an octahedral structure of the complexes containing bidentate ligands coordinated to the sulphur atoms of the thiocarbonyl groups.

The complex formation reaction of tetramethylthiuran disulphide is unusual. The interaction of this donor with TeX_4 (X = Cl, Br, I) results in the elimination of one sulphur atom and the formation of 1:1 complexes between tetramethylthiuram sulphide and TeX_4.[154] It follows from the IR spectra that tellurium is coordinated to the thione sulphur atoms.

Complexes of $TeCl_4$ with the thiosemicarbazones and semicarbazones of benzaldehyde, salicylaldehyde, acetophenone, and 2-hydroxyacetophenone, having the 1:1 structure, have also been described.[155] The IR and NMR spectra confirm the coordination of the tellurium atom via the azomethine nitrogen atom, the sulphur atom of the C=S/O group, and the phenolic oxygen atom (if it is present in the benzene ring).

The interaction of $TeCl_4$ with $(C_6H_5)_3PS$ leads to the complex with the simplest composition whose structure is analogous to that of the complex of $TeCl_4$ with $(C_6H_5)_3PO$ described above.[141]

2. Electron-accepting properties of the σ-telluranes $RTeX_3$

In contrast to tellurium tetrahalides, a characteristic feature of which is the formation of 2:1 adducts, organyltellurium trichlorides form mainly 1:1 complexes.

Aryltellurium trichlorides react with pyridine (Py), 4-picoline, and 4-picoline *N*-oxide to form 1:1 complexes.[68] The first two complexes which behave in solution in nitromethane as 1:1 electrolytes, have the structure $[ArTeCl_2.L]^+Cl^-$. The complex of 4-picoline *N*-oxide is a weak electrolyte and its formula is $ArTeCl_3.L$.

According to IR spectroscopic and conductimetric data, an octahedral structure has been attributed to the 1:1 complexes of $ArTeCl_3$ with the bidentate ligands bipyridyl and phenanthroline and to the 2:1 complexes of 4-phenoxyphenyltellurium trichloride with the monodentate pyridine, pyridine *N*-oxide and tri(*n*-octyl)-phosphine oxide.[156] The complexes of aryltellurium trichlorides with a series of N-, P-, and O-containing bases (trimethylamine, pyridine, benzimidazole, triphenylphosphine, triphenylphosphine oxide, and dimethyl sulphoxide), isolated in a pure state, have been described.[157–159] The complexes have the 1:1 composition and are apparently dissociated in acetonitrile judging from the electrical conductivities of the solutions. The composition and enthalpy of formation of the complex of $C_6H_5TeCl_3$ with $(C_6H_{13})_2SO$ have been investigated by calorimetric titration in benzene.[120]

Organyltellurium trichlorides exhibit electron-accepting properties also in relation to S-containing bases. In the study[154] quoted above, it was shown that the aryltellurium trihalides $4\text{-}C_2H_5OC_6H_4TeX_3$ (X = Cl, Br, I) as well as tellurium tetrahalides interact with tetramethylthiuram disulphide. This entails the elimination of one sulphur atom and the formation of 1:2 tetramethylthiuram sulphide complexes. However, no conclusions were reached about the structure of these complexes.

The 1:1 complexes of $RTeCl_3$ and $RTeBr_3$ with TMTU [62,160] have a square pyramidal structure with organic substituents in the apical positions and the three halogen atoms and the S-coordinated ligand molecule in the base of the pyramid according to IR and ^1H NMR spectroscopic data. As in the case of tellurium tetrahalides, the interaction of aryltellurium trichlorides with thiourea is accompanied by the reduction of tellurium (IV) and the formation of tellurium(II) complexes.[161]

The interaction of a number of aryltellurium trichlorides with electron donors of the type $(C_6H_5)_3P=X$ (X = LEP, O, S, Se) and also with $C_6H_5PO(CH_3)_2$ has been investigated[141] by the dipole moment method under isomolar series concentration conditions in solutions in benzene. The formation of 1:1 complexes in reactions with aryltellurium trichlorides and of 1:1 and 2:2 complexes in reactions with $TeCl_4$ was observed. The dipole moments corresponding to the interaction of the components indicate the donor–acceptor nature of the bond between them. Analysis of the dipole moments shows that the coordination unit of the complex consists of a pseudo-octahedron in which the donor is in the *cis*-position relative to the lone pair of tellurium and in the *trans*-position relative to the chlorine atom. Judging from the dipole moment (13.21 D) of the octahedral complex $TeCl_4.(C_6H_5)_3PO$, the donor molecules in it are in the *cis*-position relative to one another. The decrease in the dipole moments on passing from the $TeCl_4$ complexes to the $C_6H_5TeCl_3$ complexes for the same donors shows that the electron-accepting capacity of tellurium in its tetracoordinate derivatives is determined by the number of phenyl groups linked directly to the tellurium atom. It is of interest to note[162] that, on interaction of $ArTeCl_3$ with the thiosemicarbazones (TSC) of benzaldehyde, salicylaldehyde, acetophenone, and 2-hydroxyacetophenone, ionic tricoordinate tellurium(II) complexes $[ArTe.(TSC)_2]^+Cl^-$, in which the tellurium atom is coordinated via the sulphur atom, are formed.

3. Electron-accepting properties of the σ-telluranes R_2TeX_2

The amount of data on the electron-accepting capacity of diorganyltellurium dihalides is extremely limited. The 1:1 complexes of $(C_6H_5)_2TeCl_2$ [157] and $(C_6H_5)_2Te(NO_3)_2$ [163] with certain N-, P-, O-, and S-containing Lewis bases (trimethyl- and triethyl-amines, pyridine, triphenylphosphine, pyridine *N*-oxide, tetramethylthiourea, triphenylphosphine oxide, and others) have been isolated. The 2:1 adducts of dicyclohexyltellurium dihalides,[164] α,α-bispropiophenone-tellurium dihalides,[165] and diphenacyltellurium dihalides[166] with N-containing donors such as diethylamine, pyridine, piperidine, morpholine, and pyrrolidine have been investigated. Spectroscopic studies (IR and ^1H NMR) have shown that, whereas the initial tetracoordinate tellurium compounds exhibit keto-enol tautomerism, the adducts exist mainly in the keto-form. The 1:1 complex of $(C_6H_5)_2TeCl_2$ with $(C_6H_{13})_2SO$ has been investigated by calorimetric titration in benzene.[120] Comparison of the enthalpy of formation of this complex with the analogous quantities for the complexes of $TeCl_4$ and $C_6H_5TeCl_3$ with the same donor indicates that the electron-accepting capacity of tellurium-containing compounds decreases with the increase in the number of phenyl groups in the acceptor molecule.

Data published[167] on a series of complexes of "dibenzotelluorophene dichloride" with various donors are erroneous. The compound to which the authors attributed the structure of dibenzotelluorophene dichloride is not in fact the latter.

— o0o —

The literature data presented in this review show that, despite the considerable number of studies devoted to complexes of tellurium tetrahalides and σ-telluranes, this field of coordination compounds requires further studies. Whereas the electron-accepting properties of tellurium compounds have been more or less investigated, their electron-donating capacity, especially that of σ-telluranes, has been studied to a very slight extent. Nevertheless, complexes of this type can play an important role in the chemistry of derivatives of tetracoordinate tellurium. The virtual lack of energy characteristics of the complex formation reactions of derivatives of tetracoordinate tellurium makes it essential to carry out planned and systematic studies in this field. Hitherto investigations have been limited to a narrow range of σ-telluranes. In view of this, the study of the complex formation reactions of σ-telluranes, in which the electronic and steric nature of the substituents at the tellurium atom as well as the nature of the organic donors and acceptors involved in the complex formation are varied widely, is of definite interest. Investigations of this kind make it possible to establish the rules

governing the variation of the electron-donating and electron-accepting properties of σ-telluranes as a function of the nature and number of the halogen atoms and the organic groups at the tellurium atom. The results of studies on the complex formation reactions of the σ-telluranes $RTeX_3$ and R_2TeX_2, in which the tellurium atom is involved in intramolecular interaction with an atom or groups of atoms forming part of the composition of the same molecules, may be of definite interest for the problem of competitive reactivity. The X-ray diffraction and NQR methods should be applied to an increasing extent in the study of complexes based on derivatives of tetracoordinate tellurium. Finally, it is entirely likely that certain tellurium complexes can find practical applications about which nothing is known with the exception of data on the antibacterial properties of complexes of tellurium tetrachloride with Schiff bases containing sulphamide groups.

References

1. K Irgolic *The Organic Chemistry of Tellurium,* Gordon and Breach, New York–London–Paris, 1974
2. I D Sadekov, A A Maksimenko, V I Minkin *Khimiya Telluroorganicheskikh Soedinenii* (The Chemistry of Organotellurium Compounds), Izd. Rostov. Univ., Rostov-on-Don, 328 pp
3. L Engman *Acc. Chem. Rev.,* 1985, **18** 274
4. N Petragnani, J V Commaseto *Synthesis,* 1986, 1
5. I D Sadekov, B B Rivkin, V I Minkin *Usp. Khim.,* 1987, **56**(4) 586 [English translation in *Russ. Chem. Rev.,* 1987(4)]
6. R J Gillespie *Molecular Geometry* (Translated into Russian), Mir, Moscow, 1975, 278 pp
7. D P Stevenson, V Schomaker *J. Am. Chem. Soc.,* 1940, **62** 1267
8. A W Cordes, R F Kruh *Acta Crystallogr.,* 1964, **17** 756
9. B Buss, B Krebs *Angew. Chem.,* 1970, **82** 446
10. B Buss, B Krebs *Inorg. Chem.,* 1971, **10** 2795
11. B Krebs, K Buscher *Z. Anorg. Allg. Chem.,* 1980, **463** 56
12. W R Blackmore, S C Abrahams *Acta Crystallogr.,* 1956, **9** 295
13. B Krebs, V Paulat *Acta Crystallogr.,* 1976, **32** 1470
14. V Paulat, B Krebs *Angew. Chem.,* 1976, **88** 28
15. A J Edwards, F I Hewaidi *J. Chem. Soc. A,* 1968, 2977
16. R Kniep, L Korte, R Kryschi, et al. *Angew. Chem.,* 1984, **96** 351
17. B Krebs, B Buss, D Altena *Z. Anorg. Allg. Chem.,* 1971, **386** 257
18. A C Hazell *Acta Chem. Scand.,* 1966, **20** 165
19. A Schmitt, W Zeil *Z. Naturforsch., A,* 1963, **18** 428
20. I P Gol'tshtein, E N Gur'yanova, A D Volkov, et al. *Zh. Obshch. Khim.,* 1973, **43** 1669
21. T Okuda, K Yamada, Y Furukava, et al. *Bull. Chem. Soc. Jpn.,* 1975, **48** 392
22. T Okuda, K Yamada, Y Furukava, et al., *Bull. Chem. Soc. Jpn.,* 1975, **48** 3480
23. T Okuda, K Yamada, H Negita *Bull. Chem. Soc. Jpn.,* 1980, **53** 2659
24. A Voigt, W Biltz *Z. Anorg. Allg. Chem.,* 1924, **133** 277
25. H Gerding, H Hautgraaf *Recl. Trav. Chim. Pays-Bas,* 1954, **73** 737
26. N N Greenwood, B P Straughan, A E Wilson *J. Chem. Soc. A,* 1966, 1479
27. D M Adams, P J Lock *J. Chem. Soc. A,* 1967, 145
28. J W Gorge, N Katsaros, K J Wynne *Inorg. Chem.,* 1967, **6** 903
29. R C Paul, K K Paul, K C Malhotra *Chem. Ind.,* 1968, 1227
30. I R Beattie, H Chudzynska *J. Chem. Soc. A,* 1967, 984
31. D A Couch, P S Elmes, J E Fergusson *J. Chem. Soc. A,* 1967, 1813
32. G C Hayward, P G Hendra *J. Chem. Soc. A,* 1967, 643
33. E A Robinson, J A Cirune *Can. J. Chem.,* 1968, **46** 3197
34. I R Beattie, I R Horder, P J Jones *J. Chem. Soc. A,* 1970, 329
35. M E Peisakhova, I P Gol'dshtein, E N Gur'yanova, et al. *Dokl. Akad. Nauk SSSR,* 1972, **203** 1316
36. N N Greenwood, B P Straughan, A E Wilson *J. Chem. Soc. A,* 1968, 2209
37. I R Beattie, P I Jones, M Webster *J. Chem. Soc. A,* 1969, 218
38. I Ugi, D Marquarding, H Klusacek, et al. *Acc. Chem. Res.,* 1971, **4** 288
39. V I Minkin, I D Sadekov, L M Sayapina, et al. *Zh. Obshch. Khim.,* 1973, **43** 809
40. R M Minyaev, I D Sadekov, V I Minkin *Zh. Obshch. Khim.,* 1977, **47** 2019
41. C Lau, J Passmore, E K Richardson, et al. *Can. J. Chem.,* 1985, **63** 2273
42. D Kobelt, E E Paulus *Angew. Chem.,* 1971, **83** 81
43. N W Alcock, W D Harrison *J. Chem. Soc., Dalton Trans.,* 1982, 251
44. P H Bird, V Kumar, B C Pant *Inorg. Chem.,* 1980, **19** 2487
45. R Chadha, J E Drake *J. Organomet. Chem.,* 1985, **293** 37
46. R J Batchelor, F W B Einstein, C H W Jones, et al. *Organometallics,* 1987, **6** 2164
47. J Bergman, L Engman *J. Organomet. Chem.,* 1979, **181** 335
48. M A K Ahmed, W R McWhinnie, T A Hamor *J. Organomet. Chem.,* 1985, **281** 205
49. H J Gysling, H R Luss, S A Gardner *J. Organomet. Chem.,* 1979, **184** 417
50. N W Alcock, W D Harrison *Acta Crystallogr., Sect. B,* 1982, **38** 2677
51. C Knobler, J D McCullough *Inorg. Chem.,* 1977, **16** 612
52. A C Hazell *Acta Chem. Scand.,* 1972, **26** 1510
53. T S Cameron, R B Amero, C Chan, et al. *Cryst. Struct. Commun.,* 1980, **9** 543
54. J D McCullough, C Knobler *Inorg. Chem.,* 1976, **15** 2728
55. J D McCullough *Inorg. Chem.,* 1977, **16** 2318
56. L Pauling *The Nature of Chemical Bond,* 3rd Edn., Cornell University Press, Ithaca, New York, 1960
57. J D McCullough *Inorg. Chem.,* 1975, **14** 2285
58. H P Fritz, H Keller *Chem. Ber.,* 1961, **94** 1524
59. W R McWhinnie, P Thavornyutikarn *J. Chem. Soc., Dalton Trans.,* 1972, 551
60. K J Wynne, P S Pearson *Inorg. Chem.,* 1970, **9** 106
61. M T Chen, J W George *J. Am. Chem. Soc.,* 1968, **90** 4580
62. K J Wynne, P S Peason *Inorg. Chem.,* 1971, **10** 2735
63. F J Berry, A Gupta, B L Khandelwal, et al. *J. Organomet. Chem.,* 1979, **172** 445
64. F J Berry, E H Kustan, B S Smith *J. Chem. Soc., Dalton Trans.,* 1975, 1323
65. C H W Jones, R Schultz, W R McWhinnie, et al. *Can. J. Chem.,* 1976, **54** 3234
66. F J Berry, C H W Jones *Can. J. Chem.,* 1976, **54** 3737
67. F J Berry, J Silver *J. Organomet. Chem.,* 1977, **129** 437
68. K J Wynne, A J Clark, M Berg *J. Chem. Soc., Dalton Trans.,* 1972, 2370
69. K Raina, B L Khandelwal *Indian J. Chem., Sect. A,* 1976, **15** 63

70. B L Khandelwal, K Kular *Synth. React. Inorg. Metal-Org. Chem.*, 1981, **11** 399
71. B L Khandelwal, K Kumar, K Raina *Synth. React. Inorg. Metal-Org. Chem.*, 1981, **11** 65
72. A Gupta, B L Khandelwal, K Raina *J. Inorg. Nucl. Chem.*, 1977, **39** 162
73. G D Christofferson, R Sparks, J D McCullough *Acta Crystallogr.*, 1958, **11** 782
74. R F Ziolo, G M Troup *J. Am. Chem. Soc.*, 1983, **105** 229
75. D Kobelt, E F Paulus *J. Organomet. Chem.*, 1971, **27** C63
76. R K Chadha, G E Drake, M A Khan *Acta. Crystallogr., Sect. C*, 1983, **39** 45
77. R K Chadha, G E Drake, G Z Hencher *Can. J. Chem.*, 1983, **61** 1222
78. R K Chadha, G E Drake *Acta Crystallogr., Sect. C*, 1984, **40** 1349
79. R H Jones, T A Hamor *J. Organomet. Chem.*, 1984, **262** 151
80. T S Cameron, R B Amero, R E Cordes *Cryst. Struct. Commun.*, 1980, **9** 533
81. T S Cameron, R B Amero, R E Cordes *Cryst. Struct. Commun.*, 1980, **9** 539
82. F J Berry, A G Edwards *J. Chem. Soc., Dalton Trans.*, 1980, 2306
83. G D Christofferson, J D McCullough *Acta Crystallogr.*, 1958, **11** 249
84. L Y Y Chan, F W B Einstein *J. Chem. Soc., Dalton Trans.*, 1972, 316
85. G Y Chao, J D McCullough *Acta Crystallogr.*, 1962, **15** 887
86. I D Sadekov, V I Minkin, A D Garnovskii *Sulphur Reports*, 1985, **4** 63
87. I D Sadekov, G M Abakarov, E I Sadekova, et al. *Sulphur Reports*, 1986, **6** 15
88. G Knobler, J D McCullough, H Hope *Inorg. Chem.*, 1970, **9** 797
89. R F Ziolo, W H H Günther *J. Organomet. Chem.*, 1978, **146** 245
90. C Knobler, R F Ziolo *J. Organomet. Chem.*, 1979, **178** 423
91. H Hope, C Knobler, J D McCullough *Inorg. Chem.*, 1973, **12** 2665
92. J D McCullough *Inorg. Chem.*, 1973, **12** 2669
93. J D McCullough *Inorg. Chem.*, 1975, **14** 1142
94. G C Hayward, P J Hendra *J. Chem. Soc. A*, 1969, 1760
95. J R Beattie, F C Stokes, L E Alexander *J. Chem. Soc., Dalton Trans.*, 1973, 465
96. W R McWhinnie, M G Patel *J. Chem. Soc., Dalton Trans.*, 1972, 199
97. N S Dance, W R McWhinnie *J. Chem. Soc., Dalton Trans.*, 1975, 43
98. S Kenneth, J S Thayer, R J Zabransky *Inorg. Nucl. Chem. Lett.*, 1975, **11** 441
99. S Kondo, E Kakiuchi, T Shimizu *Bull. Chem. Soc. Jpn.*, 1969, **42** 2050
100. V V Saadsazov, T A Khotsyanova, V P Bryukhova *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1975, **39** 2535
101. H Gerding, H Hautgraaf *Recl. Trav. Chim. Pays-Bas*, 1954, **73** 759
102. H Gerding, D J Stufkens *Rev. Chim. Miner.*, 1969, **6** 795
103. V W Brockner, A F Demiray *Z. Anorg. Allg. Chem.*, 1980, **369** 27
104. R C Paul, K K Paul, K C Malhotra *Austr. J. Chem.*, 1969, **22** 847
105. T C Waddington, F Kalnberg *J. Chem. Soc. A*, 1960, 2339
106. M T Chen, J W George *J. Inorg. Nucl. Chem.*, 1972, **34** 3261
107. A J Edwards, P Taylor *J. Chem. Soc., Dalton Trans.*, 1973, 2150
108. I P Gol'dshtein, E N Gur'yanova, M E Peisakhova, et al. *Zh. Obshch. Khim.*, 1973, **43** 2347
109. K J Wynne, P S Pearson *Inorg. Chem.*, 1971, **10** 1871
110. K J Wynne *Ann. N.Y. Acad. Sci.*, 1972, **192** 107
111. W H H Günther, J Nepywoda, J Y C Chu *J. Organomet. Chem.*, 1974, **74** 79
112. I D Sadekov, A A Ladatko, V I Minkin *Khim. Geterotsikl. Soedin.*, 1980, 1342
113. J C Thayer, K V Smith *Synth. Inorg. Met. Org. Chem.*, 1973, **3** 101
114. K V Smith, J S Thayer *Inorg. Chem.*, 1974, **13** 3021
115. W Pritzkow *Inorg. Chem.*, 1979, **18** 311
116. T N Srivastava, R C Srivastava, M Singh *Indian J. Chem., Sect. A*, 1979, **17** 615
117. I P Gol'dshtein, E N Gur'yanova, M E Peisakhova, et al. *Zhur. Obshch. Khim.*, 1973, **43** 2347
118. L E Rybalkina, S B Bulgarevich, D Ya Movshovich, et al. *Zh. Obshch. Khim.*, 1984, **54** 2281
119. D Ya Movshovich, E G Amarskii, L E Rybalkina, et al. *Zh. Obshch. Khim.*, 1987, **57** 1786
120. I P Gol'dshtein, E N Gur'yanova, I D Sadekov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 1625
121. N N Greenwood, A C Sarma, B P Straughan *J. Chem. Soc. A*, 1968, 1561
122. N N Greenwood, A C Sarma, B P Straughan *J. Chem. Soc.*, 1966, 1446
123. A K Gupta, B L Khandelwal, K Raina *J. Inorg. Nucl. Chem.*, 1977, **39** 162
124. G T Morgan, H Burgess *J. Chem. Soc.*, 1929, 1103
125. S Prasad, B L Khandelwal *J. Indian Chem. Soc.*, 1962, **39** 112
126. A Lowy, R F Dunbrook *J. Am. Chem. Soc.*, 1922, **44** 614
127. L Reichel, K Ilberg *Chem. Ber.*, **76b** 1108
128. N Katsaros, J W George *J. Inorg. Nucl. Chem.*, 1969, **31** 3503
129. N S Biradar, T M Aminabhavi, C S Patil *Inorg. Chim. Acta*, 1983, **78** 47
130. T M Aminabhavi, W E Rudzinski, N S Biradar, et al. *Inorg. Chim. Acta*, 1983, **78** 51
131. J R Beattie, M Milne, M Webster, et al. *J. Chem. Soc. A*, 1969, 482
132. E E Aynsley, N S Hetherington *J. Chem. Soc.*, 1953, 2802
133. T M Aminabhavi, N S Biradar, C S Patil *Inorg. Chim. Acta*, 1983, **78** 107
134. V G Tkalenko, A P Amarskaya, Yu V Kolodyazhnyi, et al. *Zh. Obshch. Khim.*, 1973, **43** 1943
135. W E Rudzinski, T M Aminabhavi, N S Biradar, et al. *Inorg. Chim. Acta*, 1982, **67** 177
136. W E Rudzinski, T M Aminabhavi, N S Biradar, et al. *Inorg. Chim. Acta*, 1983, **69** 83
137. T M Aminabhavi, W E Rudzinski, N S Biradar, et al. *Inorg. Chim. Acta*, 1983, **76** L131
138. K C Malhotra, K K Paul, *Curr. Sci. (India)*, 1969, **38** 266
139. W E Rudzinski, T M Aminabhavi, N S Biradar, et al. *Inorg. Chim. Acta*, 1983, **70** 175
140. N M Karayannis, A N Speca, L L Pytlewski, et al. *J. Less-Common Met.*, 1970, **22** 117
141. L E Rybalkina, D Ya Movshovich, S B Bulgarevich, et al. *Zh. Obshch. Khim.*, 1988, **58** 1561

142. M E Peisakhova, I P Gol'dshtein, E N Gur'yanova, et al. *Zh. Obshch. Khim.*, 1973, **43** 159
143. O Foss, W Johanessen *Acta Chem. Scand.*, 1961, **15** 1939
144. S Husebye, J W George *Inorg. Chem.*, 1969, **8** 313
145. S Esperas, J W George, S Husebye, et al. *Acta Chem. Scand., Ser. A*, 1975, **29** 141
146. R B Cheyne, C H W Jones *Can. J. Chem.*, 1975, **53** 1855
147. G L Tember, A S R Murty *Curr. Sci. (India)*, 1983, **52** 1013
148. O Foss, W Johannessen *Acta Chem. Scand.*, 1961, **15** 1940
149. K Deuten, W Schnabel, G Klar *Cryst. Struct. Commun.*, 1979, **8** 679
150. K Deuten, W Schnabel, G Klar *Cryst. Struct. Commun.*, 1979, **8** 221
151. E R Clark, M A Al-Turaihi *J. Inorg. Nucl. Chem.*, 1976, **38** 1443
152. E R Clark, A G Collett, D G Naik *J. Chem. Soc., Dalton Trans.*, 1973, 1961
153. E R Clark, M A Al-Turaihi *Spectrochim. Acta, Part A*, 1977, **33** 177
154. K G Karnika De Silva, W R McWhinnie, J E Stuckey *Inorg. Chim. Acta*, 1986, **122** 153
155. J K Basumatary, A K Singh, B L Khandelwal, et al. *Polyhedron*, 1988, **7** 635
156. M V Carad *Polyhedron*, 1985, **4** 1353
157. T N Srivastava, M Singh, H B Singh *Indian J. Chem., Sect. A*, 1982, **21** 307
158. T N Srivastava, R C Srivastava, M Srivastava *Indian J. Chem., Sect. A*, 1982, **21** 539
159. T N Srivastava, R K Srivastava, V K Srivastava *Indian J. Chem.*, 1983, **60** 891
160. K J Wynne, P S Pearson *J. Chem. Soc., Chem. Commun.*, 1970, 556
161. O Foss, S Hauge *Acta Chem. Scand.*, 1959, **13** 2155
162. A K Singh, J K Basumatary *J. Organomet. Chem.*, 1988, **346** 349
163. T N Srivastava, P Kumar *Nat. Acad. Sci. Lett.*, 1982, **5** 399
164. Y D Kulkarni, S Srivastava *Indian J. Chem., Sect. A*, 1985, **24** 429
165. Y D Kulkarni, S Srivastava, M Athar *Indian J. Chem., Sect. A*, 1985, **24** 1069
166. S Srivastava, A Singh, Y D Kulkarni *Indian J. Chem., Sect. A*, 1988, **27** 734
167. T N Srivastava, S Mehrotra *Synth. React. Inorg. Metal-Org. Chem.*, 1985, **15** 709