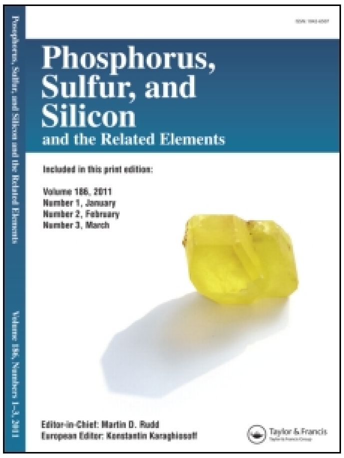

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Organotellurium Ligands & Their Metal Complexes: Recent Developments

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Organotellurium Ligands & Their Metal Complexes: Recent Developments

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*The ligand chemistry of telluroethers, halotellurium ligands, and polytellurides has received good attention in the last decade. Tellurium-containing species have been used to design clusters. In the recent past the ligation of di and tri-telluroethers (including bis(4-methoxyphenyltelluro)methane) has been studied. Hybrid organotellurium ligands, N-[2-(4-methoxyphenyltelluro)propyl]phthalimide (**L^1**), 2-(4-ethoxyphenyltelluromethyl)-tetrahydro-2*H*-pyran (**L^2**), 2-(2-{4-ethoxyphenyl} telluroethyl)-1,3-dioxane (**L^3**), N-{2-(4-methoxyphenyltelluro)ethyl}morpholine (**L^4**), N-{2-(4-methoxyphenyltelluro)ethyl}-pyrrolidine (**L^5**), bis{2-(pyrrolidine-N-yl)ethyl}telluride (**L^6**), 1-(4-methoxyphenyltelluro)-2-[3-(6-methyl-2-pyridyl) propoxy]ethane (**L^7**), and 2-[2-(4-methoxyphenyltelluro)ethyl]thiophene (**L^8**) have been designed recently and studied for their complexation reactions. The (Te, N) and (N, Te, N) ligands, **L^5** and **L^6**, coordinate with Hg(II) through Te and N both, but the bonding with N is some what weak. The morpholine nitrogen of **L^4** does not coordinate with Pd(II) or Pt(II) along with Te. The **L^7** behaving as a (Te, N) ligand has formed 20-membered metallomacrocycle ring with Pt(II). Tellurated Schiff bases $4\text{-MeOC}_6H_4TeCH_2CH_2N{=}C(CH_3)C_6H_4\text{-2-OH}$ (**L^9**) and $2\text{-HO-}C_6H_4\text{-}(CH_3)C{=}NCH_2CH_2TeCH_2CH_2N{=}C(CH_3)C_6H_4\text{-2-OH}$ (**L^{10}**) and their reduction products $4\text{-MeOC}_6H_4TeCH_2CH_2NHCH(CH_3)C_6H_4\text{-2-OH}$ (**L^{11}**) and $2\text{-HO-}C_6H_4\text{-}(CH_3)CHNHCH_2CH_2TeCH_2CH_2NHCH(CH_3)C_6H_4\text{-2-OH}$ (**L^{12}**) respectively have been synthesized and studied for ligation behaviour. The **L^9** on reaction with the $[Ru($p-cymene$)Cl_2]_2$ results in $[Ru($p-cymene$)(4\text{-MeOC}_6H_4\text{-}TeCH_2CH_2NH_2)Cl]Cl\cdot H_2O$ whereas in the reaction of **L^{10}** with $[Ru($p-cymene$)Cl_2]_2$, p-cymene ligand is lost resulting in $[RuCl(L^{10}\text{-}H)]$. The recent developments, particularly designing of **L^1** to **L^{12}** and their ligand chemistry, are reviewed in the present paper.*

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INTRODUCTION

The interest in tellurium ligands[1–11] has grown in the last decade. The increasing evidence of enhanced ligating properties of telluroether ligands compared to thioethers,[5] the availability of standardized synthetic routes to the ligands, the possibility of using metal complexes of Te-ligands as precursor for II–VI semiconductors, and the improved availability of FT-NMR for studying solution behavior of metal-tellurium bond-containing compounds are the main reasons for the growth. The ligation of ditelluroethers $RTe(CH_2)_3TeR$ (R = Me and Ph) and o-$C_6H_4(TeMe)_2$ has been explored further in the recent past[2,5] with the transition metal species which are *soft* in nature. The first structurally characterized bismuth(III) complex of telluroether, $[BiBr_3(PhTeMe)]$, has been reported[12] very recently. Tritelluroethers $Te(CH_2CH_2CH_2TeR)_2$ and $MeC(CH_2TeR)_3$ (R = Me or Ph) have been reported as ligands.[5] The ditelluroether o-$C_6H_4(CH_2TeMe)_2$ has been complexed with metal carbonyl fragments.[5] The ditelluroether $ArTeCH_2TeAr$ complexes with bivalent Pd, Pt, and Ru in a bidentate-chelating, mode much easily in comparison to that of phosphorus-analogue,[13] probaby due to its bigger bite. Lanthanide clusters having Te^{2-}, Te_2^{2-} and $(Te_5Ph)^{5-}$ ligands are reported very recently.[14] Macrocycle ligands having tellurium donor sites are explored for their ligation properties by Levason and coworkers.[5,15] Hybrid organotellurium ligands also have received considerable attention in the last few years. They generally have oxygen, sulfur, and nitrogen as the donor sites along with tellurium.[1–6] The X-ray crystal structures of complexes of tridentate S_2Te ligand, $MeSCH_2CH_2CH_2TeCH_2CH_2CH_2SMe$ with Rh(III) and Pt(II) species are reported recently.[16] The present article is a short review of the chemistry of hybrid organotellurium ligands developed in my laboratory during last five years. The ligands are N-[2-(4-methoxyphenyltelluro)propyl]phthalimide ($\mathbf{L^1}$), 2-(4-ethoxyphenlytelluro-methyl)tetrahydro-2H-pyran ($\mathbf{L^2}$), 2-(2-{4-ethoxyphenyl}telluroethyl)-1,3-dioxane ($\mathbf{L^3}$), N-{2-(4-methoxyphenyltelluro)ethyl}morpholine ($\mathbf{L^4}$), N-{2-(4-methoxyphenyltelluro)ethyl}pyrrolidine ($\mathbf{L^5}$), bis{2-(pyrrolidine-N-yl)ethyl}telluride ($\mathbf{L^6}$), 1-(4-methoxyphenyltelluro)-2-[3-(6-methyl-2-pyridyl)propoxy]ethane ($\mathbf{L^7}$) 2-[2-(4-methoxyphenyltelluro)ethyl]thiophene ($\mathbf{L^8}$), tellurated Schiff bases $4\text{-}MeOC_6H_4TeCH_2CH_2N{=}C(CH_3)C_6H_4\text{-}2\text{-}OH$ ($\mathbf{L^9}$) and $2\text{-}HO\text{-}C_6H_4\text{-}(CH_3)C{=}NCH_2CH_2TeCH_2CH_2N{=}C(CH_3)C_6H_4\text{-}2\text{-}OH$ ($\mathbf{L^{10}}$) and their reduction products $4\text{-}MeOC_6H_4TeCH_2CH_2NHCH(CH_3)C_6H_4\text{-}2\text{-}OH$ ($\mathbf{L^{11}}$), and

$2\text{-HO-}C_6H_4\text{-}(CH_3)CHNHCH_2CH_2TeCH_2CH_2NHCH(CH_3)C_6H_4\text{-}2\text{-OH}$ (**L**^{12}), respectively.

N-[2-(4-Methoxyphenyltelluro)propyl]phthalimide (L^1)

This potentially a (Te, N, O) type ligand was synthesized by reacting *N*-[3-bromopropyl]phthalimide with $ArTe^-$ generated *in situ* from Ar_2Te_2 by reduction with sodium borohydride.[17] When its single crystal was grown and structure solved by X-ray diffraction it was realized that the crystal formed was the mixed one having **L**^{1} (a) and **L**$^1H_2$ (b), with occupancies 60 and 40%, respectively (Figure 1).

The **L**$^1H_2$ (b) is formed by reduction of one carbonyl group of **L**^{1}. Most probably the formation of reduced product also occurs in the analogous synthesis of *N*-[2-(4-methoxyphenyltelluro)ethyl]phthalimide[18] which on reaction with $RuCl_3{\cdot}xH_2O$ is oxidized to a Te(IV) compound

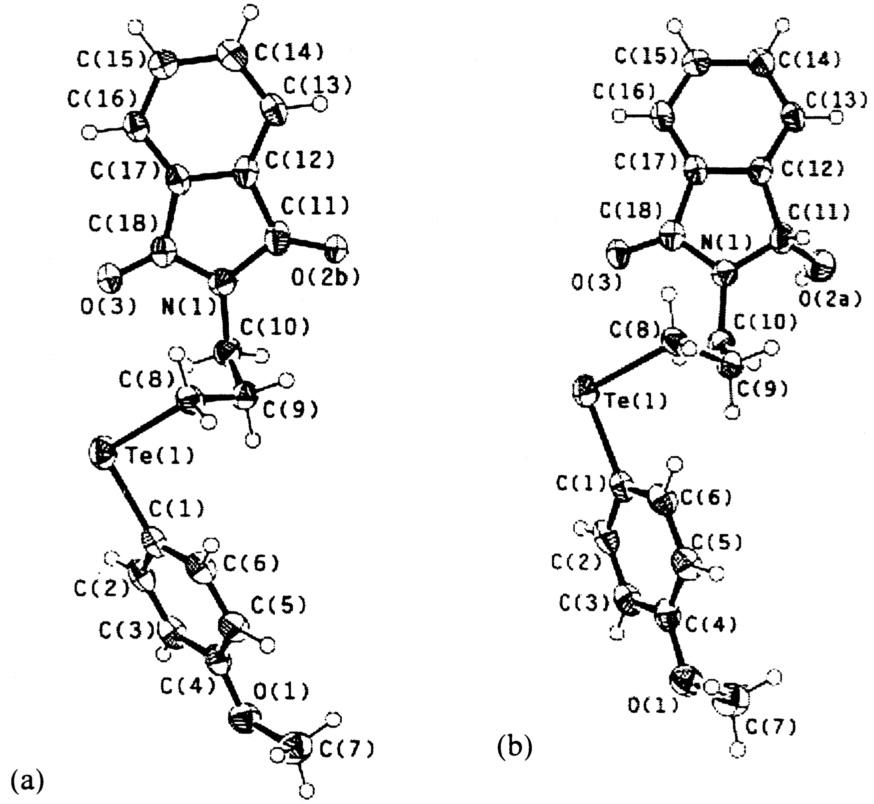


FIGURE 1 Molecular structure of **L**^{1} (a) and **L**$^1H_2$ (b).

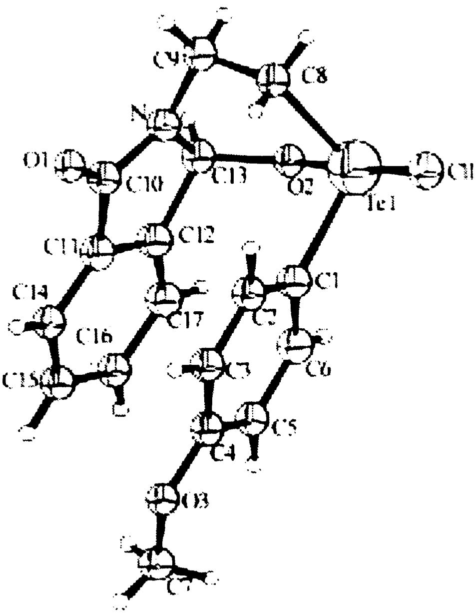


FIGURE 2 Molecular structure of *Te*-chloro,*Te*-anisyl-1a-aza-4-oxa-3-tellura-1*H*,2*H*,4*aH*-9-fluorenone.

(dichloride). The cyclization of this Te(IV) derivative by elimination of HCl between $>TeCl_2$ and OH groups finally results in *Te*-chloro,*Te*-anisyl-1a-aza-4-oxa-3-tellura-1*H*,2*H*,4*aH*-9-fluorenone (Figure 2).

However, ethyl analogue of $\mathbf{L^1}$ has been shown to coordinate with Ru(II) species only via Te.[18]

2-(4-Ethoxyphenyltelluromethyl)tetrahydro-*2H*-pyran (L^2) and 2-(2-{4-Ethoxyphenyl}telluroethyl)-1,3-dioxane (L^3)

Hemilabile (P_x, O_y) type ligands are interesting for designing catalytically active species[19–23] as their oxygen donor atoms can protect the metal by occupying its vacant coordination site until the substrate reaches it. Similar tellurium ligands of (Te_x, O_y) type are less known[3,5,24,25] and it was the motivation for designing $\mathbf{L^2}$ and $\mathbf{L^3}$ by reacting $ArTe^-$ anion with 2-(bromomethyl)tetrahydro-2*H*-pyran and 2-(2-bromoethyl)-1,3-dioxane respectively.[26] The ruthenium(II) complexes $[RuCl_2(p\text{-cymene})\cdot\mathbf{L^2}/\mathbf{L^3}]$ (Figure 3) are first examples of structurally characterized complexes having potential (Te, O) ligands. The Ru—Te bond lengths are 2.619(8) and 2.642(1) Å respectively in the complexes of $\mathbf{L^2}$ and $\mathbf{L^3}$. The Ru- - -Cl bond length is in the range

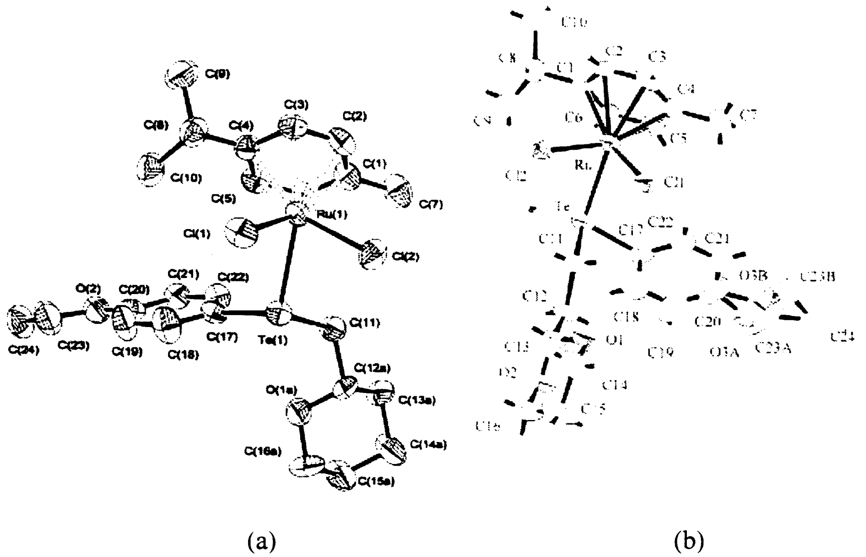


FIGURE 3 Molecular structures of [$RuCl_2$(*p*-cymene)·$\mathbf{L}^2$/$\mathbf{L}^3$] (a/b).

2.404(3)–2.420(6) Å. The reaction of these complexes with equimolar amounts of $AgClO_4$ results in [RuCl(*p*-cymene)·$\mathbf{L}^2$/$\mathbf{L}^3$]ClO_4, in which $\mathbf{L}^2$ and $\mathbf{L}^3$ are found to exhibit hemilabile behavior.

The 1:1 complexes of copper(I) and mercury(II) with $\mathbf{L}^2$ and $\mathbf{L}^3$ are characterized only by spectroscopic methods only.[26]

Hybrid Organotellurium Ligands $\mathbf{L}^4$ to $\mathbf{L}^8$

The five (Te, n/s) or (N, Te, N) type ligands. $\mathbf{L}^4$ to $\mathbf{L}^8$ synthesized by reacting $ArTe^-$ with appropriate organic halide have shown interesting ligation behavior. The morpholine nitrogen of $\mathbf{L}^4$ does not coordinate with Pd(II) and Pt(II) and the ligand coordinates as a monodentate ligand[27] through Te alone (Figure 4(a)). The Pt-Te bond length in *trans*-[$PTCl_2(\mathbf{L}^4)_2$] IS 2.583(2) Å somewhat longer than the expected value due to *trans* influence of tellurium.[3] The ligand bis{2-(N-morpholino} ethyl telluride, closely related to $\mathbf{L}^4$, also forms a complex with Pd(II) in which nitrogen of morpholine does not coordinate.[28] The reason for nonparticipation of morpholine nitrogen is not very apparent but may be steric. The [$HgBr_2$·$\mathbf{L}^4$] only is characterized spectrpscopically.[29] The pyrrolidine nitrogen of $\mathbf{L}^5$ and $\mathbf{L}^6$ coordinates along with Te, even with Hg(II) (Figure 4(b)) The Hg—N bond length in [$HgBr_2$·$\mathbf{L}^5$], 2.457(4) Å, is within the range of values reported in

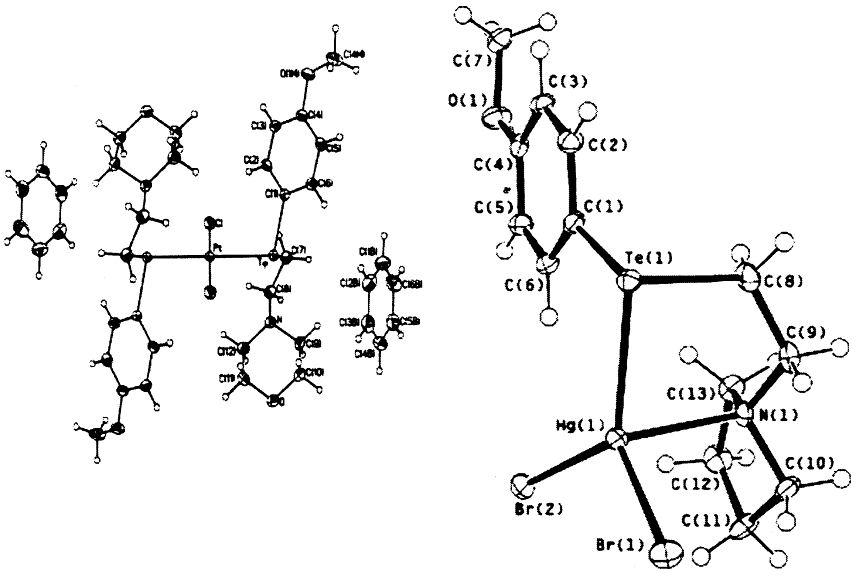


FIGURE 4 (a) *trans*-[Ptcl$_2$(**L**^{4})$_2$]; (b)[HgBr$_2$·**L**^{5}].

literature[30,31] but longer than the sum of the covalent radii of mercury and nitrogen (CA 2.23 Å), suggesting relatively weak coordination. The potentially tridentate ligand **L**^{6} also behaves as a (Te, N) ligand in [HgBr$_2$·**L**^{6}], one pyrrolidine group remains as an pendent arm. The single crystal structure of [PdCl$_2$·**L**^{5}] also has been reported.[19] The ligand 1-(4-methoxyphenyltelluro)-2-[3-(6-methyl-2-pyridyl)propoxy]ethane (**L**^{7}) designed by the reaction of nucleophile ArTe- with appropriate organic halide coordinates through N and Te both and forms a bimetallic complex with Pt(II), which has 20-membered metallomacrocycle ring structure (Figure 5).[32] The Pd(II) complexes also appears to be similar but does not give crystals suitable for X-ray diffraction. 2-[2-(4-Methoxyphenyltelluro)ethyl]thiophene (**L**^{8}) also has designed by reaction between ArTe$^-$ and 2-(2-thienyl)ethyl chloride. It forms a complex [PdCl$_2$·(**L**^{8})$_2$] which is characterized structurally and has **L**^{8} in a monodentate binding mode through tellurium.[33]

Tellurated Schiff bases

The ligands **L**^{9} and **L**^{11} have been designed by reacting 2-(4-methoxyphenyltelluro)ethylamine and bis(2-aminoethyl)telluride with *o*-hydroxyacetophenone respectively (Scheme 1).[34] Their reduction with sodium borohydride has resulted in **L**^{10} and **L**^{12}.[34] The **L**^{9}

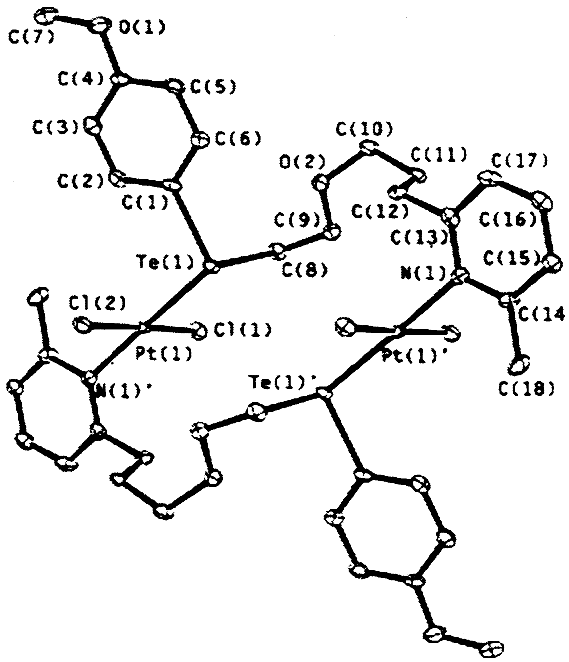
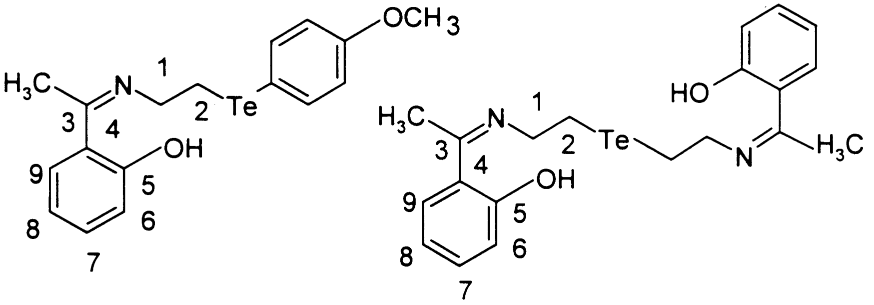


FIGURE 5 ORTEP plot of the molecule $[PtCl_2L^7] \cdot 2CHCl_3$.

on reaction with the $[Ru(p\text{-cymene})Cl_2]_2$ results in $[Ru(p\text{-cymene})(4\text{-}MeOC_6H_4TeCH_2CH_2NH_2)Cl]Cl \cdot H_2O$ (**1**) whereas in the reaction of $\mathbf{L^{10}}$ with $[Ru(p\text{-cymene})Cl_2]_2$, *p*-cymene ligand is lost resulting in $[RuCl(\mathbf{L^{10}}\text{-}H)]$ (**2**).



$\mathbf{L^9}$ $\mathbf{L^{11}}$

SCHEME 1

The single crystals structures of $\mathbf{L^9}$, $\mathbf{L^{11}}$, **1** and **2** are reported.[34] The very swift formation of tellurated amine back from a tellurated Schiff

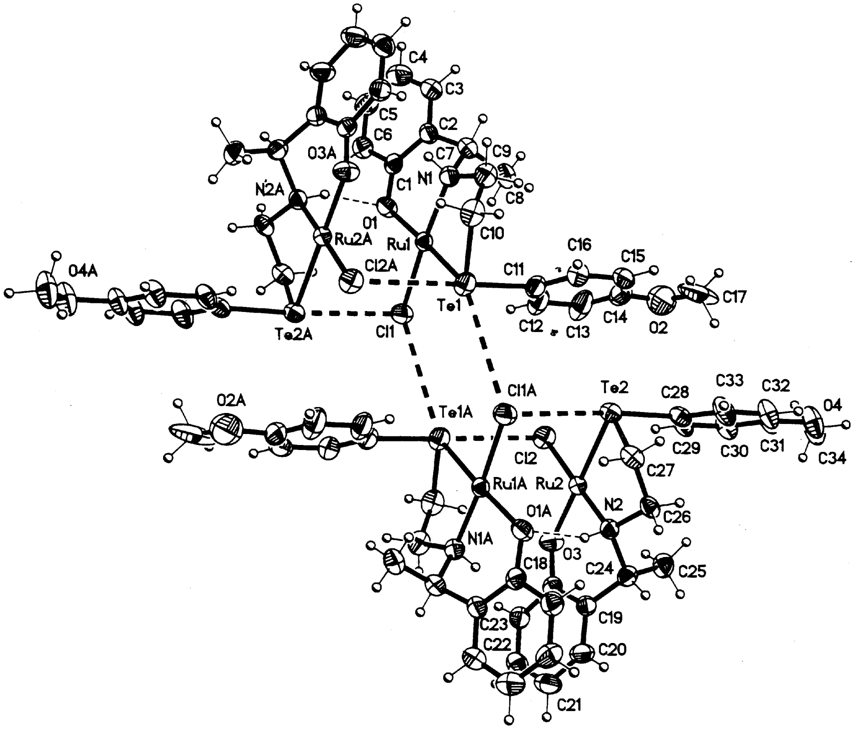


FIGURE 6 Molecular structure of **2**.

base (**L**^{9}) by its hydrolysis is noticed for the first time and has resulted in **1**. The Ru—N and Ru—Te bond lengths in **1** are 2.142(3) and 2.6371 (4) Å, respectively. The substitution of *p*-cymene ligand with a hybrid organotellurium ligand (**L**^{10}-H) resulting in **2** is also a first example of its kind. The Ru in **2** has square planar geometry. The Ru—N, Ru—Te Ru—O, and Ru—Cl bond lengths in **2** are 2.041(6), 2.4983(8), 2.058(5), and 2.308(2) Å, respectively. In the crystal of **2** there are secondary intermolecular Te· · ·Cl interactions and intermolecular N—H· · ·O hydrogen bonds (Figure 6). It is the first example where coordinated Te of a complex is engaged in two intermolecular secondary interactions.

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