Tellurated Schiff Bases Formed from {2-[(4-Methoxyphenyl)telluro]ethyl}amine and Bis(2-aminoethyl) Telluride with *o*-Hydroxyacetophenone: Synthesis and Complexation Reactions with Hg^{II}, Pd^{II} and Ru^{II} − Crystal Structures of the Ligands, $[Ru(p\text{-cymene})Cl\{H_2NCH_2CH_2TeC_6H_4\text{-}4\text{-}OCH_3\}]Cl\cdot H_2O$ and $[RuCl\{4\text{-}MeOC_6H_4TeCH_2CH_2NHCH(CH_3)C_6H_4\text{-}2\text{-}O^-\}]$

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{2-[(4-Methoxyphenyl)telluro]ethyl}amine and bis(2-aminoethyl) telluride on treatment with *o*-hydroxyacetophenone gave the Schiff bases 4-$MeOC_6H_4TeCH_2CH_2N{=}C(CH_3)C_6H_4$-2-OH (**L¹**) and 2-$HOC_6H_4(CH_3)C{=}NCH_2CH_2TeCH_2CH_2N{=}C(CH_3)C_6H_4$-2-OH (**L³**), respectively. The reduction of **L¹** and **L³** with $NaBH_4$ resulted in 4-$MeOC_6H_4TeCH_2CH_2NHCH(CH_3)C_6H_4$-2-OH (**L²**) and 2-$HOC_6H_4(CH_3)CHNHCH_2CH_2TeCH_2CH_2NHCH(CH_3)C_6H_4$-2-OH (**L⁴**), respectively, which have 1 or 2 chiral centers. The ^1H and ^{13}C NMR spectra of **L¹** to **L⁴** were found to be characteristic. Treatment of **L¹** with $[Ru(p\text{-cymene})Cl_2]_2$ resulted in $[Ru(p\text{-cymene})(4\text{-}MeOC_6H_4TeCH_2CH_2NH_2)Cl]Cl\cdot H_2O$ (**1**) whereas in the reaction of **L²** with $[Ru(p\text{-cymene})Cl_2]_2$, the *p*-cymene ligand is lost resulting in [RuCl(**L²**-H)] (**4**). The reactions of **L¹**, **L³** and **L⁴** with $HgBr_2$ resulted in complexes of the type $[HgBr_2\cdot(\mathbf{L})_2]$ while Na_2PdCl_4 reacted with **L¹** to give [PdCl(**L¹**-H)]. The solid-state structures of **L¹**, **L³**, **1** and **4** were determined by single-crystal X-ray diffraction studies. The very swift formation of the tellurated amine from a tellurated Schiff base (**L¹**) by hydrolysis has been observed 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 replacement of the *p*-cymene ligand with a hybrid organotellurium ligand (**L²**-H), resulting in **4**, is also a first example of its kind. The Ru center in **4** has a square-planar geometry, with the Ru–N, Ru–Te, Ru–O and Ru–Cl bond lengths being 2.041(6), 2.4983(8), 2.058(5) and 2.308(2) Å, respectively. In the crystals of **4** there are secondary intermolecular Te···Cl interactions and intermolecular N–H···O hydrogen bonds. This is the first example in which coordinated Te in a complex is engaged in two intermolecular secondary interactions.

Introduction

Schiff bases have been studied extensively as ligands but known tellurated Schiff bases are rare.[1] Some important tellurated Schiff bases reported so far are 1,6-bis[2-(butyltelluro)phenyl]-2,5-diazahexa-1,5-diene,[2] Schiff bases derived by treating bis(*o*-formylphenyl) telluride and *o*-(butyltelluro)-benzaldehyde with chiral amines (*R*)-(+)-[(1-phenylethyl)-amine] and (1*R*,2*S*)-(−)-norephedrine, respectively,[3] and macrocyclic Schiff bases.[4]

In all three instances the tellurated aldehydes were treated with amines to prepare Schiff bases. If a tellurated amine is treated with aldehydes or ketones then a wider range of Schiff-base ligands may be designed by varying the carbonyl group containing compound. We have designed $NH_2CH_2CH_2TeAr$[5] and $NH_2CH_2CH_2TeCH_2CH_2NH_2$,[6] which may be used for this purpose and it was therefore thought worthwhile to synthesize the series **L¹** to **L⁴**. Their metal complexes, in which a metal−tellurium bond is formed, are of interest and so the reactivity of these ligands with species containing Hg^{II}, Pd^{II} and Ru^{II} has been studied. Tellurium being a very "soft" donor does not coordinate with common species of the 3d transition metals. The reaction of **L¹** with $[Ru(p\text{-cymene})Cl_2]_2$ (*p*-cymene = 1-methyl-4-isopropylbenzene) resulted in $[RuCl_2(H_2NCH_2CH_2TeC_6H_4OCH_3)]Cl\cdot H_2O$ (**1**), in which the ligand seems to have been generated by hydrolysis of the Schiff base **L¹**. This is the first example of very easy hydrolysis of a tellurated Schiff base effected by traces of water present in organic solvents. The reaction of $[Ru(p\text{-cymene})Cl_2]_2$ with **L²** resulted in a complex [RuCl(**L²**-H)] (**4**) by loss of a *p*-cymene ligand. This is also the first example where *p*-cymene is replaced by a hybrid organotellurium ligand. **L¹**, **L²**, **1** and **4** have been characterized by single-crystal X-ray dif-

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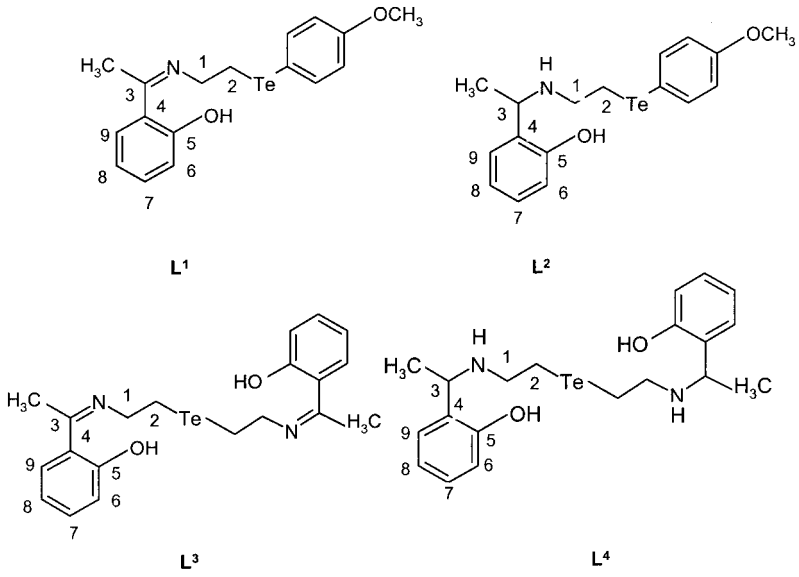

fraction studies. The results of these investigations are reported in this paper.

Results and Discussion

All the tellurated Schiff bases and their reduction products $\mathbf{L^1}$ to $\mathbf{L^4}$ are stable and can be stored under ambient conditions up to 6 months. They have good solubility in $CHCl_3$, CH_2Cl_2, CH_3CN, EtOH and acetone. In MeOH the solubility is moderate for $\mathbf{L^3}$ but good for the other three ligands. In hexane all four ligands either are partially soluble or insoluble. Complexes **1** and **4** are stable under ambient conditions and soluble in $CHCl_3$, CH_2Cl_2, CH_3CN, EtOH, MeOH and acetone but insoluble in hexane. Complex **2** and the mercury complexes of $\mathbf{L^1}$ and $\mathbf{L^3}$ are poorly soluble in $CHCl_3$ and CH_2Cl_2 and insoluble in hexane, acetone, and acetonitrile. $[HgBr_2{\cdot}(\mathbf{L^4})_2]$ is soluble in $CHCl_3$, CH_2Cl_2 and acetonitrile. All the mercury complexes, however, decompose in DMSO. All the ligands as well as **4** are non-electrolytes. The molecular weights were found to be consistent with the monomeric nature of $\mathbf{L^1}$ and $\mathbf{L^2}$. The molar conductivity of **1** was found to be lower than that of a 1:1 electrolyte probably due to association in the solution. **4** is a non-electrolyte but molecular weight measurement suggests intermolecular association in solution. The IR spectra of $\mathbf{L^1}$ and $\mathbf{L^3}$ are characteristic and show >C=N stretching vibrations at 1612 cm^{-1}, which are absent in the spectra of $\mathbf{L^2}$ and $\mathbf{L^4}$. The Te−C(alkyl) vibrations are observed in the IR spectra at 513 to 518 cm^{-1}, whereas Te−C(aryl) vibrations appear at 292 cm^{-1}. In all mercury complexes the potentially polydentate ligands appear to coordinate through the tellurium atom alone since the $-TeCH_2$ signal is deshielded ($\delta \approx 0.4-0.5$ ppm). The ν(Hg−Br) resonance appears in the IR spectra at 278 or 288 cm^{-1}. In complex **2**, the palladium atom appears to be coordinated to a monoanionic tridentate $\mathbf{L^1}$ since both $-TeCH_2$ and $-NCH_2$ are deshielded ($\delta \approx 0.36$ and 0.25 ppm, respectively) and the protons *ortho* and *para* to the oxygen atom are shielded ($\delta \approx 0.2$ ppm). This is corroborated by the $^{13}C\{^1H\}$ NMR spectrum of **2** and a red shift (ca. 17 cm^{-1}) in the >C=N− stretching frequency. Unfortunately, crystals of complexes **2**, **3**, **5** and **6** suitable for X-ray diffraction could not be obtained. In the course of the reaction of $\mathbf{L^1}$ with $[Ru(p\text{-cymene})Cl_2]_2$; the ligand is first hydrolyzed by traces of water present in the solvents resulting in $NH_2CH_2CH_2TeC_6H_4$-4-OMe, which generates complex **1**. This hydrolysis appears to be catalyzed by metallic species since in their absence it was not observed. This is the first example where a tellurated Schiff base is hydrolyzed by traces of water present in the solvent so rapidly and this is probably induced by the metal. Such metal-induced hydrolysis has also been reported earlier for common Schiff-base ligands.[7] The reaction of $\mathbf{L^2}$ with $[Ru(p\text{-cymene})Cl_2]_2$ resulted in the replacement of the *p*-cymene ring with the Te,N,O ligand. So far no hyrbrid organotellurium ligand has been able to displace this ring[1,8] and this is the first example of such behaviour. However, the replacement of the *p*-cymene ring in $[Ru(p\text{-cymene})Cl_2]_2$ has been reported earlier with some polydentate hybrid phosphanes.[9] The reactions of $\mathbf{L^3}$ and $\mathbf{L^4}$ with $[Ru(p\text{-cymene})Cl_2]_2$ and $[Ru(DMSO)_4Cl_2]$ gave intricate mixtures which are very difficult to separate.

Molecular Structures of $\mathbf{L^1}$ and $\mathbf{L^3}$

The structures of $\mathbf{L^1}$ and $\mathbf{L^3}$ are shown in Figures 1 and 2 with selected bond lengths and angles given in Table 1. In $\mathbf{L^1}$, Te−C(11) [2.111(3) Å] is shorter than Te−C(10) [2.142(3) Å]. For $\mathbf{L^3}$, Te−C(10A) and Te−C(10B) are 2.143(4) and 2.148(4) Å, respectively. These values are closer to that of Te−C(10) in $\mathbf{L^1}$ and consistent with the earlier reports that Te−C(aryl) bonds are shorter than Te−C(alkyl) bonds.[10] In $\mathbf{L^1}$ the angle C(11)−Te(1)−C(10) is 94.29(11)° which is consistent with the

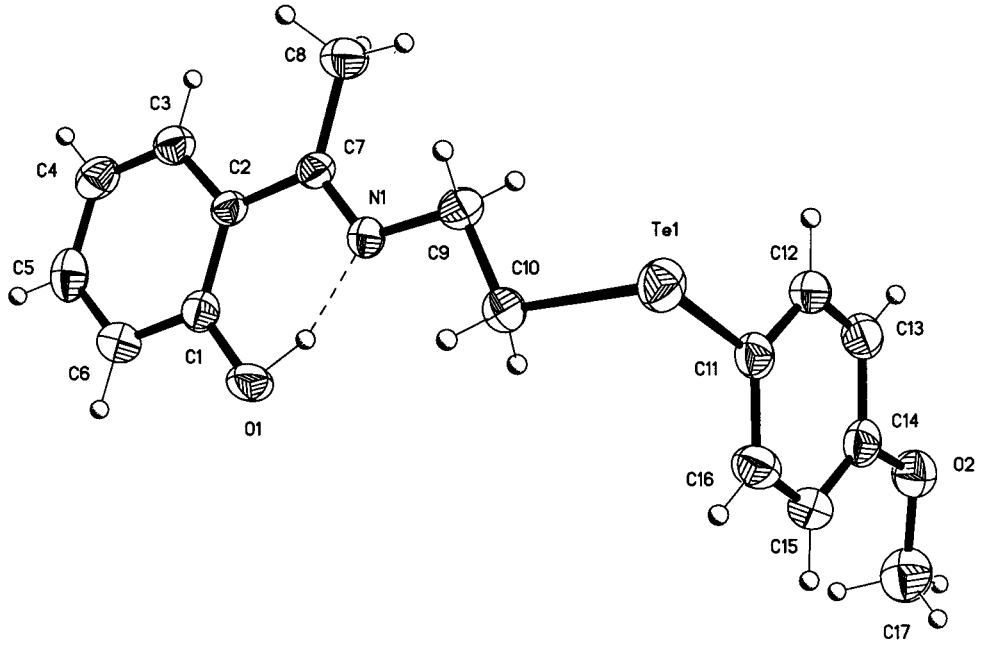

Figure 1. Molecular structure of **L**[1]

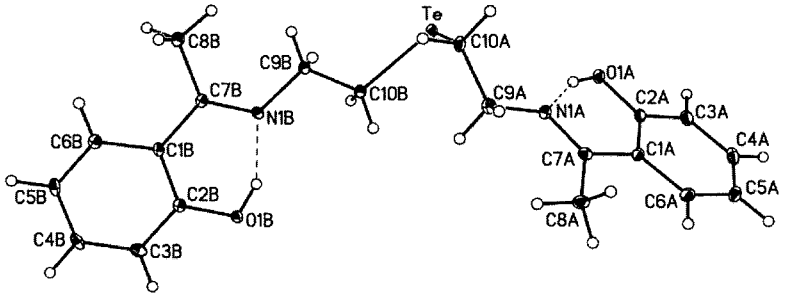

Figure 2. Molecular structure of **L**[3]

C(10A)−Te−C(10B) angle of 94.88(14)° in **L**[3] as well as other related values reported in the literature.[10] The molecules of both these ligands have intramolecular hydrogen bonding. The azomethine bond length is nearly the same in both ligands, N(1)−C(7) is 1.284(3) Å, with N(1B)−C(7B) and N(1A)−C(7A) both being 1.287(4) Å.

Molecular Structures of 1 and 4

The molecular structure of **1** is shown in Figure 3 and selected bond lengths and angles are given in Table 1. In the lattice of **1** there is one water molecule per molecule of the complex. The Ru−N bond length is 2.142(3) Å (sum of covalent radii ca. 1.95 Å) and consistent with literature reports of 2.056(6) Å in $[Ru(bipy)_3][PF_6]_2$,[11] 2.042(5)−2.154(6) Å in Ru^{II} complexes of 2-(arylazo)pyridines,[12] 1.990(3)−2.087(5) Å for Ru^{II} complexes of tetradentate ligands based on 2,6-bis(pyrazol-1-yl)pyridine,[13] 2.060(5) and 2.079(4) Å for [Ru(*p*-cymene)Cl{2,3-bis(2-pyridyl)pyrazine}]BF_4 [14] and 2.077(3)−2.113(3) for Ru^{II} complexes of oxazoline-based ligands. The Ru−Te bond length is 2.6371(4) Å which is consistent with earlier reports [2.619(8)−2.656(8) Å] of Ru^{II} complexes of hybrid organotellurium ligands.[15] The bond angles at the Ru center are normal. The bond angles at Te and the coordinating N atom are consistent with their nearly trigonal-pyramidal [92.28(11)−106.82(9)°] and tetrahedral [120.0(2)°] geometries, respectively.

The molecular structure of **4** is shown in Figure 4 and selected bond lengths and angles are given in Table 1. The Ru−N bond length is 2.041(6) Å which is shorter than that of **1** but consistent with the literature reports mentioned above. The Ru−Te bond length 2.4983(8) Å is significantly shorter than that of **1** and also shorter than the sum of covalent radii of 2.62 Å. The Ru−O bond length is 2.058(5) Å (sum of covalent radii ca. 1.91 Å) and agrees with the values of 2.034(5)−2.232(5) Å reported for complexes of Ru^{II} with a variety of ligands.[16] The Ru−Cl bond length of 2.308(2) Å (sum of covalent radii ca. 2.24 Å) is somewhat shorter than the reported range of 2.404(3)−2.434(1) Å for complexes of the [Ru(*p*-cymene)Cl_2] moiety with hybrid organotellurium ligands.[15] There are two interesting features of the structure of **4**. The first is the intermolecular second-

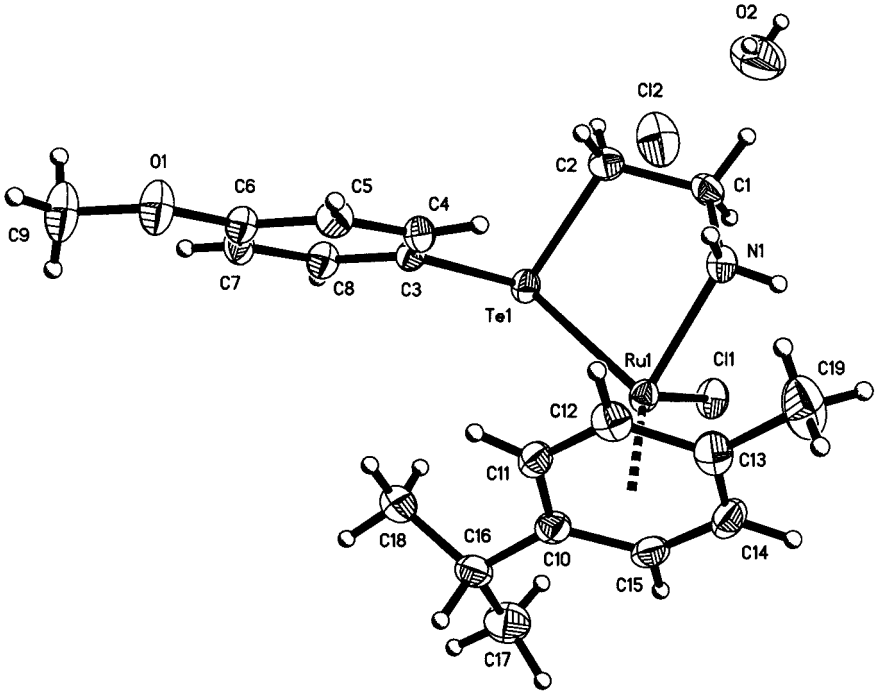

Figure 3. Molecular structure of [Ru(*p*-cymene)Cl($H_2NCH_2CH_2TeC_6H_4OCH_3$)]Cl·$H_2O$ (**1**)

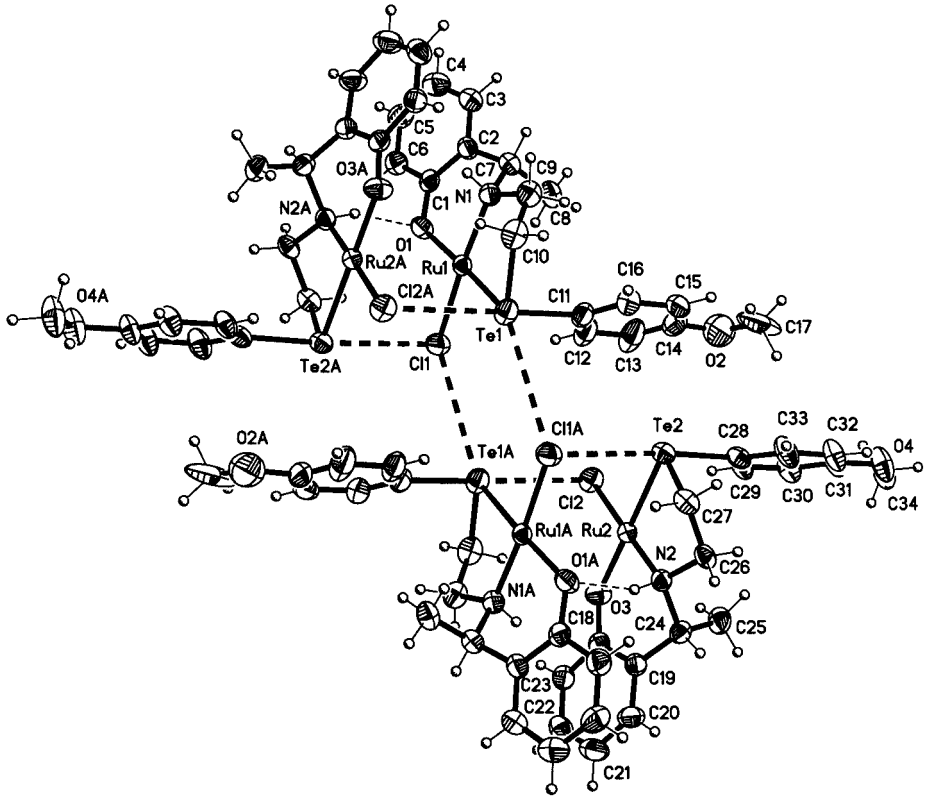

Figure 4. Molecular structure of **4**

ary interactions between each Te and two Cl atoms of neighboring molecules [Te···Cl distances of 3.322(2)−3.805(2) Å are less than the sum of van der Waals radii of 4.0 Å], which makes the geometry around the Te center distorted pseudo-octahedral. The second feature of interest is the intermolecular N−H···O hydrogen bond. The bond angles at Ru (Table 1) suggest that the N, O, Te and Cl centers are arranged around it in an almost square-planar

Table 1. Selected bond lengths [Å] and angles[°]; symmetry transformation used to generate equivalent atoms: #1: $-x+1,-y+1,-z+1$

L^1			
Te(1)−C(11)	2.111(3)	C(11)−Te(1)−C(10)	94.29(11)
Te(1)−C(10)	2.142(3)	C(7)−N(1)−C(9)	122.6(2)
N(1)−C(7)	1.284(3)	N(1)−C(7)−C(8)	122.6(3)
N(1)−C(9)	1.470(3)	N(1)−C(9)−C(10)	108.2(2)
C(9)−C(10)	1.506(4)	N(1)−C(7)−C(2)	117.6(3)
O(1)−C(1)	1.330(3)	C(16)−C(11)−Te(1)	120.2(2)
O(1)−H(1)	0.91(3)	C(12)−C(11)−Te(1)	122.1(2)
H(1)···N(1)	1.64(3)	O(1)−H(1)···N(1)	155(3)
O(1)···N(1)	2.496(3)		
L^3			
Te−C(10A)	2.143(4)	C(10A)−Te−C(10B)	94.88(14)
Te−C(10B)	2.148(4)	C(7A)−N(1A)−C(9A)	120.6(3)
N(1B)−C(9B)	1.466(4)	C(7B)−N(1B)−C(9B)	121.9(3)
N(1B)−C(7B)	1.287(4)	N(1A)−C(7A)−C(1A)	116.5(3)
N(1A)−C(7A)	1.287(4)	N(1A)−C(7A)−C(8A)	124.4(3)
N(1A)−C(9A)	1.468(5)	N(1B)−C(7B)−C(1B)	117.2(3)
O(1B)−C(2B)	1.347(4)	N(1B)−C(7B)−C(8B)	123.8(3)
O(1A)−C(2A)	1.337(4)	N(1B)−C(9B)−C(10B)	109.1(3)
O(1A)−H(1A)	0.72(4)	N(1A)−C(9A)−C(10A)	110.5(3)
O(1B)−H(1B)	0.91(5)	C(9B)−C(10B)−Te	113.0(2)
C(9A)−C(10A)	1.512(5)	C(9A)−C(10A)−Te	115.5(2)
C(9B)−C(10B)	1.524(5)	O(1A)−H(1A)···N(1A)	144(5)
H(1A)···N(1A)	1.89(5)	O(1B)−H(1B)···N(1B)	152(4)
H(1B)···N(1B)	1.68(5)		
O(1A)···N(1A)	2.510(4)		
O(1B)···N(1B)	2.516(4)		
1			
Ru (1)−N(1)	2.142(3)	N(1)−Ru(1)−Te(1)	82.48(9)
Ru(1)−Te(1)	2.6371(4)	Cl(1)−Ru(1)−Te(1)	82.42(2)
Te(1)−C(3)	2.110(3)	N(1)−Ru(1)−Cl(1)	85.33(10)
Te(1)−C(2)	2.149(4)	C(2)−Te(1)−C(3)	97.40(15)
N(1)−C(1)	1.481(5)	C(3)−Te(1)−Ru(1)	106.82(9)
		C(2)−Te(1)−Ru(1)	92.28(11)
		C(1)−N(1)−Ru(1)	120.0(2)
4			
Ru(1)−N(1)	2.041(6)	Ru(2)−N(2)	2.048(6)
Ru(1)−O(1)	2.058(5)	Ru(2)−O(3)	2.041(5)
Ru(1)−Cl(1)	2.308(2)	Ru(2)−Cl(2)	2.3116(19)
Ru(1)−Te(1)	2.4983(8)	Ru(2)−Te(2)	2.5030(7)
Te(1)−C(11)	2.113(8)	Te(2)−C(28)	2.109(7)
Te(1)−C(10)	2.132(8)	Te(2)−C(27)	2.117(7)
Te(1)···Cl(2)#1	3.416(2)	Te(2)···Cl(1)#1	3.322(2)
Te(1)···Cl(1)#1	3.805(2)	O(3)−C(18)	1.328(8)
O(1)−C(1)	1.323(8)	O(4)−C(31)	1.351(9)
O(2)−C(17)	1.231(12)	O(4)−C(34)	1.411(9)
O(2)−C(14)	1.530(14)	N(2)−C(26)	1.501(8)
N(1)−C(9)	1.501(9)	N(2)−C(24)	1.513(9)
N(1)−C(7)	1.508(9)		
N(1)−Ru(1)−O(1)	89.5(2)	O(3)−Ru(2)−N(2)	92.1(2)
N(1)−Ru(1)−Cl(1)	175.66(18)	N(2)−Ru(2)−Cl(2)	178.89(18)
O(1)−Ru(1)−Cl(1)	91.66(14)	O(3)−Ru(2)−Cl(2)	88.99(14)
N(1)−Ru(1)−Te(1)	90.18(18)	N(2)−Ru(2)−Te(2)	88.84(17)
O(1)−Ru(1)−Te(1)	174.59(14)	O(3)−Ru(2)−Te(2)	178.94(14)
Cl(1)−Ru(1)−Te(1)	89.03(6)	Cl(2)−Ru(2)−Te(2)	90.05(6)
C(11)−Te(1)−C(10)	97.0(3)	C(28)−Te(2)−C(27)	93.4(3)
C(11)−Te(1)−Ru(1)	97.4(2)	C(28)−Te(2)−Ru(2)	96.07(19)
C(10)−Te(1)−Ru(1)	87.3(2)	C(27)−Te(2)−Ru(2)	89.46(18)
C(11)−Te(1)−Cl(1)#1	80.3(2)	C(28)−Te(2)−Cl(1)#1	171.4(2)
C(10)−Te(1)−Cl(1)#1	131.5(2)	C(27)−Te(2)−Cl(1)#1	78.1(2)
Ru(1)−Te(1)−Cl(1)#	141.28(4)	Ru(2)−Te(2)−Cl(1)#1	85.18(4)
Cl(2)#1−Te(1)−Cl(1)#1	97.06(5)	C(18)−O(3)−Ru(2)	125.7(4)
C(1)−O(1)−Ru(1)	126.8(5)	C (31)−O(4)−C(34)	117.4(7)
C(17)−O(2)−C(14)	103.9(13)	C(26)−N(2)−C(24)	110.0(5)
C(9)−N(1)−C(7)	111.3(6)	C(26)−N(2)−Ru(2)	117.6(4)
C(9)−N(1)−Ru(1)	117.6(5)	C(24)−N(2)−Ru(2)	111.9(4)
C(7)−N(1)−Ru(1)	110.4(4)		

geometry. The Te···Cl secondary interaction observed in **4** has not been reported so far for coordinated Te in any complex of Te ligands. The present one is the first example of its kind.

Conclusion

Tellurated Schiff bases have been synthesized from tellurated amines and characterized structurally. This route has been rarely used, however. The reactions of 4-$MeOC_6H_4$-$TeCH_2CH_2N{=}C(CH_3)C_6H_4$-2-OH (**$L^1$**) with [Ru(*p*-cymene)$Cl_2$]$_2$ first results in the hydrolysis of **L^1** which appears to be metal-promoted. Thereafter, the tellurated amine, (4-$MeOC_6H_4TeCH_2CH_2NH_2$) forms complexes with the Ru^{II} moiety. The reaction of 4-$MeOC_6H_4TeCH_2CH_2$-$NHCH(CH_3)C_6H_4$-2-OH (**L^2**) with [Ru(*p*-cymene)Cl_2]$_2$ resulted in loss of a *p*-cymene ring. So far, in the reaction of [Ru(*p*-cymene)Cl_2]$_2$ with Te ligands, this has never been reported and the present example is the first of its kind. The Te···Cl secondary interaction observed in **4** has not been reported so far for coordinated Te in any complex of Te-based ligands and the present one is the first example.

Experimental Section

General: C and H analyses were carried out with a Perkin−Elmer elemental analyzer 240 C. Tellurium contents were estimated by atomic absorption spectroscopy. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with a Bruker Spectrospin DPX-300 NMR spectrometer operating at 300.13 and 75.47 MHz, respectively. IR spectra in the range of 4000−250 cm^{-1} were recorded with a Nicolet Protége 460 FT-IR spectrometer as KBr or CsI pellets. The conductivity measurements were carried out in acetonitrile (concentration ca. 1 mM) using an ORION conductivity meter model 162. The molecular masses (concentration ca. 5 mM) in chloroform were determined with a Knauer vapor pressure osmometer model A0280. The melting points determined in open capillary are reported as such. {2-[(4-Methoxyphenyl)telluro]ethyl}amine[5] and bis(2-aminoethyl) telluride[6] were prepared by the reported methods.

X-ray Diffraction Analyses: X-ray diffraction data for **L^3**, **1** and **4** were collected with a Bruker Smart APEX CCD diffractometer, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 293(2) K. An analytical face-indexed absorption correction was applied. The structures where solved by direct methods. Refinement was carried out using full-matrix least-squares analyses with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and refined using a riding model with fixed isotropic thermal parameters. Calculations were carried out with SMART software for data collection and data reduction and SHELXTL for solution and refinement.[17] A summary of relevant crystallographic results appears in Table 2. For **L^1**, the data were collected with a Bruker SMART 1K CCD diffractometer using X-rays of wavelength 0.71073 Å (Mo-K_α source). A semiempirical absorption correction was applied.[18] Cell refinement was done with the SMART and SAINT programs.[19] The structure was solved in a similar manner to those of **L^3**, **1** and **2** using SHELXTL.[20] CCDC-214420 (**1**), -214421 (**L^1**), -214422 (**4**) and -214423 (**L^3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at

Table 2. Crystal data and structural refinements for L^1, L^3, **1** and **4**

	L^1	L^3	**1**	**4**
Empirical formula	$C_{17}H_{19}NO_2Te$	$C_{20}H_{24}N_2O_2Te$	$C_{19}H_{29}Cl_2NO_2RuTe$	$C_{17}H_{20}ClNO_2RuTe$
Formula mass	396.93	452.01	603.00	534.46
Color	yellow	yellow	orange	orange
Crystal size [mm]	0.262 × 0.076 × 0.066	0.02 × 0.02 × 0.66	0.126 × 0.126 × 0.114	0.218 × 0.214 × 0.194
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$
Unit cell dimensions [Å, °]	a = 16.399(1)	a = 14.6456(12)	a = 10.2639(4)	a = 14.725(1)
	b = 7.5318(4)	b = 18.8812(15)	b = 19.459(1)	b = 13.276(1)
	c = 13.368(1)	c = 6.9923(5)	c = 10.964(1)	c = 20.562(2)
	β = 101.909(1)	β = 98.902(2)	β = 95.202(2)	β = 99.052(2)
Volume [Å^3]	1615.6(2)	1910.3(3)	2180.9(2)	3969.6(6)
Z	4	4	4	8
Density (calcd.) [Mg·m^{-3}]	1.632	1.572	1.837	1.789
Absorption coefficient [mm^{-1}]	1.845	1.572	2.288	2.372
F(000)	784	904	1184	2064
θ range [°]	2.54−25.01	2.16−24.73	1.99−24.99	1.83−25.03
Index ranges	$-19 \le h \le 19$	$-16 \le h \le 17$	$-12 \le h \le 12$	$-17 \le h \le 17$
	$-8 \le k \le 8$	$-22 \le k \le 21$	$-23 \le k \le 23$	$-15 \le k \le 15$
	$-15 \le l \le 15$	$-8 \le l \le 8 \le$	$-13 \le l \le 13$	$-24 \le l \le 24$
Reflections collected	12714	11272	17640	32038
Independent reflections	2832 [R(int) = 0.0441]	3255 [R(int) = 0.0513]	3825 [R(int) = 0.0440]	7012 [R(int) = 0.0570]
Completeness to maximum θ [%]	99.8	99.8	99.9	100.0
Max./min. transmission	0.8970/0.7222	0.928019/0.782123	0.8165/0.6977	0.6831/0.6116
Data/restraints/parameters	2832/0/195	3255/0/236	3825/0/351	7012/0/425
Goodness-of-fit on F^2	0.959	0.992	1.033	0.997
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0283, $wR2$ = 0.0524	$R1$ = 0.0278, $wR2$ = 0.0574	$R1$ = 0.0265, $wR2$ = 0.0408	$R1$ = 0.0478, $wR2$ = 0.1067
R indices (all data)	$R1$ = 0.0415, $wR2$ = 0.0551	$R1$ = 0.0480, $wR2$ = 0.0636	$R1$ = 0.0342, $wR2$ = 0.0423	$R1$ = 0.0722, $wR2$ = 0.1159
Largest diff. peak/hole [e·Å^{-3}]	0.541/−0.243	0.610/−0.387.	0.473/−0.416	1.027 (0.83 Å from Ru2)/−0.572

www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Synthesis of L^1: {2-[(4-Methoxyphenyl)telluro]ethyl}amine (1.39 g, 5.0 mmol) was stirred in dry ethanol (20 mL) at room temperature for 0.5 h. *o*-Hydroxyacetophenone (0.68 g, 5.0 mmol), dissolved in dry ethanol (20 mL), was added to the above solution dropwise with stirring. The mixture was stirred at room temp. for a further 2 h. The solvent was evaporated in a rotary evaporator resulting in a yellow precipitate. The precipitate, on recrystallization from chloroform/hexane (1:1), afforded yellow single-crystals of L^1. Yield 1.61 g (85%); m.p. 82−83 °C. Λ_M = 0.9 cm^2·mol^{-1}·ohm^{-1}. $C_{17}H_{19}NO_2Te$ (396.9): calcd. C 51.44, H, 4.82, N 3.53, Te 32.15; found C 51.26, H 4.81, N 3.16, Te 31.86. Molecular mass: calcd. 396.6; found 399.0. ^{1}H NMR ($CDCl_3$, TMS, 25 °C): δ = 2.27 (s, 3 H, CH_3), 3.13 (t, 2 H, 2-H), 3.81 (s, 3 H, OCH_3), 3.92 (t, 2 H, 1-H), 6.76−6.82 (m, 3 H, ArH *m* to Te and 7-H), 6.945 (d, J = 8.4 Hz, 1 H, 9-H), 7.30−7.32, (m, 1 H, 8-H), 7.505 (d, J = 8.1 Hz, 1 H, 6-H), 7.745 (d, J = 8.4 Hz, 2 H, ArH *o* to Te), 16.00 (br. s, 1 H, OH) ppm. ^{13}C{1H} NMR ($CDCl_3$, 25 °C, TMS): δ = 8.32 (CH_3), 14.54 (C-2), 50.87 (C-1), 55.11 (OCH_3), 99.67 (ArCTe), 115.21 (ArC *m* to Te), 117.11 (C-6), 118.63 (C-8), 119.10 (C-4), 127.97 (C-9), 132.40 (C-7), 141.34 (ArC *o* to Te), 159.90 (Ar-$COCH_3$), 163.53 (C-5), 171.38 (C-3) ppm.

Synthesis of [Ru(*p*-cymene)Cl($H_2NCH_2CH_2TeC_6H_4$-4-OCH_3)]-Cl·H_2O (1): $[RuCl_2(p\text{-cymene})]_2$ (0.62 g, 1 mmol) was dissolved in dichloromethane (10 mL). A solution of L^1 (0.79 g, 2 mmol), prepared in dichloromethane (20 mL), was added with vigorous stirring. The mixture was stirred for a further 3 h. The solvent was removed in a rotary evaporator under reduced pressure. The resultant precipitate was recrystallized from chloroform/hexane (1:1). The dark-red crystals of **1** were washed immediately with dichloromethane and recrystallized again to give dark-orange single crystals. Yield ca. 0.85 g (ca. 60%); m.p. 160 °C (dec.). Λ_M = 43.0 cm^2·mol^{-1}·ohm^{-1}. Molecular mass: calcd. 603; found 648. $C_{19}H_{27}Cl_2NORuTe{\cdot}H_2O$ (603): calcd. C 39.01, H 4.65, N 2.39, Te 21.81; found C 38.97, H 4.83, N 2.56, Te, 21.22. ^{1}H NMR ($CDCl_3$, 25 °C, TMS): δ = 1.22 (d, J = 6.6 Hz, 3 H, CH_3 of *i*Pr), 1.315 (d, J = 6.6 Hz, 3 H, CH_3 of *i*Pr), 2.27 (s, 3 H, CH_3 *p* to *i*Pr), 2.69−2.74 (sept, 1 H, CH of *i*Pr), 2.69−2.72 (t, 2 H, $TeCH_2$), 3.53−3.56 (t, 2 H, NCH_2), 3.83 (s, 3 H, OCH_3), 5.13−5.96 (m, 4 H, ArH of *p*-cymene), 7.045 (d, J = 8.4 Hz, 2 H, ArH *m* to Te), 8.005 (d, J = 8.7 Hz, 2 H, ArH *o* to Te), 8.46 (br. s, 2 H, NH_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C, TMS): δ = 17.28 ($TeCH_2$), 18.89 (*p*-cymene CH_3), 24.69 and 25.73 (CH_3 of *i*Pr of *p*-cymene), 30.75, 31.41 (CH of *i*Pr of *p*-cymene), 42.55 (NCH_2), 55.36 (OCH_3), 76.58−85.13 (ArC of *p*-cymene *m* and *o* to *i*Pr), 101.51 (ArCTe), 104.75 ($ArCCH_3$ of *p*-cymene), 105.88 (ArC-*i*Pr of *p*-cymene), 115.15−116.34 (ArC *m* to Te), 138.09 (ArC *o* to Te), 161.69 (Ar-$COCH_3$) ppm. IR (KBr): nu(tilde) = 361 ν(Ru−Cl), 440 ν(Ru−N) cm^{-1}.

Synthesis of [PdCl(L^1-H)] (2): $Na_2[PdCl_4]$ (0.294 g, 1 mmol) was dissolved in water (5 mL). A solution of L^1 (0.397 g, 1 mmol) prepared in acetone (10 mL) was added with vigorous stirring. An orange precipitate of **2** was immediately obtained which was filtered and dried. The orange solid was recrystallized from chloroform/methanol/hexane to give crystals of **2**. Yield ca. 0.37 g (ca.72%); m.p. 162 °C. $C_{17}H_{18}ClNO_2PdTe$ (533.8): calcd. C 37.97, H 3.37, N 2.60, Te 23.80; found C 39.48, H 3.47, N 2.43, Te 23.65. ^{1}H NMR ($CDCl_3$, 25 °C, TMS): δ = 2.39 (s, 3 H, CH_3), 3.49 (t, 2 H, 2-H), 3.82 (s, 3 H, OCH_3), 4.17 (t, 2 H, 1-H), 6.61−6.66 (m, 3 H,

ArH *m* to Te and 7-H), 6.915 (d, J = 8.7 Hz, 1 H, 9-H), 7.12−7.14, (m, 1 H, 8-H), 7.335 (d, J = 9.0 Hz, 1 H, 6-H), 8.065 (d, J = 9.0 Hz, 2 H, ArH *o* to Te) ppm. $^{13}C\{1H\}$ NMR ($CDCl_3$, 25 °C, TMS): δ = 13.38 (CH_3), 19.29 (C-2), 62.76 (C-1), 55.01 (OCH_3), 102 (ArCTe), 115.38 (ArC *m* to Te), 115.71 (C-6), 120.86 (C-8), 125.01 (C-4), 127.68 (C-9), 130.86 (C-7), 138.58 (ArC *o* to Te), 159.90 ($ArCOCH_3$), 163.53 (C-5), 171.38 (C-3) ppm. IR (KBr): $\tilde{\nu}$ = 306 ν(Pd−Cl), 486 ν(Pd−N) cm^{-1}.

Synthesis of $[HgBr_2{\cdot}(L^1)_2]$ (3): $HgBr_2$ (0.720 g, 2 mmol) was dissolved in acetone (5 mL). A solution of $\mathbf{L^1}$ (1.588 g, 4 mmol), prepared in chloroform (10 mL), was added with stirring. The mixture was stirred for a further 0.5 h. A yellow solid separated out which was filtered, washed with acetone and dried. Yield 1.66 g (ca. 85%); m.p. 138 °C. $C_{34}H_{38}Br_2HgN_2O_2Te_2$ (1154): calcd. Te 22.8; found Te 21.6. ^1H NMR ($CDCl_3$, 25 °C, TMS): δ = 2.38 (s, 6 H, CH_3), 3.56 (t, 4 H, 2-H), 3.82 (s, 6 H, OCH_3), 4.04 (t, 4 H, 1-H), 6.80−6.83 (m, 3 H, ArH *m* to Te and 7-H), 6.925 (d, J = 9.0 Hz 1 H, 9-H), 7.505 (d, J = 7.8 Hz, 1 H, 6-H), 7.745 (d, J = 8.7 Hz, 2 H, ArH *o* to Te) ppm; signal due to 8-H merged with that of chloroform (δ = 7.26 ppm).

Synthesis of L^2: $\mathbf{L^1}$ (0.40 g, 1 mmol) and $NaBH_4$ (0.38 g, 10 mmol) were heated to reflux in dry ethanol (100 mL) for 24 h. The solution was cooled and the solvent was evaporated in vacuo. The ligand was extracted with dichloromethane and the extract dried with sodium sulfate. The solvent was removed in vacuo. $\mathbf{L^2}$ was obtained as highly viscous pale yellow oil. Yield 0.28 g (70%); Λ_M = 0.4 $cm^2{\cdot}mol^{-1}{\cdot}ohm^{-1}$. $C_{17}H_{21}NO_2Te$ (399): calcd. Te 31.98; found Te 31.31. ^1H NMR ($CDCl_3$, 25 °C, TMS): δ = 1.38 (d, J = 6.6 Hz, 3 H, CH_3), 1.87−1.97 (br. s, 1 H, NH), 2.83−2.98 (m, 4 H, 1-H + 2-H), 3.78 (s, 3 H, OCH_3), 3.83−3.88 (m, 1 H, CH), 6.71−6.79 (m, 4 H, ArH *m* to Te and 7-H + 9-H), 6.885 (d, J = 7.5 Hz, 1 H, 6-H), 7.09−7.14 (m, 1 H, 8-H), 7.655 (d, J = 8.7 Hz, 2 H, ArH *o* to Te), 11.40 (very br. s, OH) ppm. $^{13}C\{1H\}$ ($CDCl_3$, 25 °C, TMS): δ = 8.83 (C-1), 22.27 (CH_3), 47.65 (C-1), 55.09 (OCH_3), 58.19 (C-3) 99.67 (ArCTe), 115.29 116.67 (ArC *m* to Te), 118.95 (C-6), 120.20 (C-8), 126.50 (C-4), 127.90 (C-9), 128.26 (C-7), 140.23−141.07 (ArC *o* to Te), 157.12 ($ArCOCH_3$), 159.91 (C-5) ppm.

Synthesis of $[RuCl(L^2\text{-}H)]$ (4): $[RuCl_2(p\text{-cymene})]_2$ (0.62 g, 1 mmol) was dissolved in dichloromethane (10 mL). A solution of $\mathbf{L^2}$ (0.80 g, 2 mmol), prepared in dichloromethane (20 mL), was added with vigorous stirring. The mixture was stirred for a further 3 h. The solvent was removed in a rotary evaporator under reduced pressure. The dark orange single crystals of **4** were grown from chloroform/hexane (1:1). Yield 0.72 g (67%); m.p. 100 °C (dec.). Molecular mass: calcd. 535.41; found 1037. Λ_M = 0.9 $cm^2{\cdot}mol^{-1}{\cdot}ohm^{-1}$. $C_{17}H_{20}ClNO_2RuTe$ (534.4): calcd. C 38.21, H 3.77, N 2.62, Te 23.88; found C 39.01, H 4.20, N 2.22, Te 23.16. IR (KBr): $\tilde{\nu}$ = 361 ν(Ru−Cl), 450 ν(Ru−N) cm^{-1}.

Synthesis of L^3: Bis(2-aminoethyl) telluride (1.13 g, 2.5 mmol) was stirred at room temperature in dry ethanol (20 mL) for 0.5 h. 2-Hydroxyacetophenone (0.68 g, 5 mmol), dissolved in dry ethanol (20 mL), was added to the above solution dropwise with stirring. The mixture was stirred at room temp. for a further 6 h, was then kept at 0−5 °C for 24 h. $\mathbf{L^3}$ separated as a yellow precipitate. The precipitate was recrystallized at 0−5 °C from chloroform/hexane (1:1) to give yellow single crystals of $\mathbf{L^3}$. Yield 1.13 g (80%); m.p. 95−96 °C. Λ_M = 0.86 $cm^2{\cdot}mol^{-1}{\cdot}ohm^{-1}$. Molecular mass: calcd. 452; found 444.5. $C_{20}H_{24}N_2O_2Te$ (452): calcd. C 53.14, H, 5.35, N 6.20, Te 28.23; found C 52.52, H 5.42, N 6.74, Te 27.66. ^1H NMR ($CDCl_3$, 25 °C, TMS): δ = 2.32 (s, 6 H, CH_3), 3.02−3.07 (t, 4 H, $TeCH_2$), 3.94−3.99 (t, 4 H, 1-H), 6.75−6.80 (m, 2 H, 8-H), 6.915 (d, J = 8.1 Hz, 2 H, 9-H) 7.26−7.30 (t, 2 H, 7-H), 7.502 (d, J = 8.1 Hz, 2 H, 6-H), 15.93 (br. s, 1 H, OH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, TMS): δ = 3.49 (C-2), 14.73 (CH_3), 51.64 (NCH_2), 117.27 (C-6), 118.57 (C-8), 119.36 (C-4), 128.06 (C-9), 132.43 (C-7), 163.32 (C-5), 171.60 (C-3) ppm.

Synthesis of $[HgBr_2(L^3)_2]$ (5): $HgBr_2$ (0.360 g, 1 mmol) was dissolved in acetone (5 mL). A solution of $\mathbf{L^3}$ (0.904 g, 2 mmol), prepared in chloroform (10 mL), was added with stirring. The mixture was stirred for a further 1 h. A yellow solid separated out which was filtered, washed with acetone and dried. Yield 1.01 g (80%); m.p. 142 °C. $C_{34}H_{38}Br_2HgN_2O_2Te_2$ (1264): calcd. Te 20.25; found Te 19.88. ^1H NMR ($CDCl_3$, 25 °C, TMS): δ = 2.29 (s, 12 H, CH_3), 3.49−3.53 (t, 8 H, 2-H), 4.07−4.11 (t, 8 H, 1-H), 6.75−6.80 (t, 4 H, 8-H), 6.873 (d, J = 8.1 Hz, 4 H, 9-H), 7.22−7.27 (m, 4 H, 7-H), 7.48 (d, J = 6.9 Hz, 4 H, 6-H), 15.13 (br. s, OH) ppm.

Synthesis of L^4: $\mathbf{L^3}$ (0.452 g, 1 mmol) and $NaBH_4$ (0.38 g, 10 mmol) were heated to reflux in dry ethanol (100 mL) for 24 h. The solution was cooled and the solvent was evaporated in vacuo. The ligand was extracted with dichloromethane and the extract dried with sodium sulfate. The solvent was removed in vacuo affording $\mathbf{L^4}$ as a highly viscous pale yellow oil. Yield 0.31 g (67%); Λ_M = 0.90 $ohm^{-1}{\cdot}cm^2{\cdot}mol^{-1}$. $C_{17}H_{21}NO_2Te$ (456): calcd. Te 25.52; found Te 24.93. ^1H NMR ($CDCl_3$, 25 °C, TMS): δ = 1.361, 1.365 (2 d, J = 6.6, 9.9 Hz, 6 H, CH_3), 2.54−2.75 (m, 8 H, 1-H + 2-H), 3.83−3.84 (m, 2 H, CH), 6.67−6.74 (m, 4 H, 7-H + 9-H), 6.86 (d, J = 7.2 Hz, 2 H, 6-H), 7.03−7.08 (m, 2 H, 8-H), 11.40 (very br. s, OH) ppm.

Synthesis of $[HgBr_2(L^4)_2]$ (6): $HgBr_2$ (0.360 g, 1 mmol) was dissolved in acetone (5 mL). A solution of $\mathbf{L^4}$ (0.904 g, 2 mmol), prepared in chloroform (10 mL), was added with stirring. The mixture was stirred for a further 1 h. A yellow solid separated out which was filtered, washed with acetone and dried. Yield 1.02 g (ca.80%); m.p. 105 °C. $C_{34}H_{38}Br_2HgN_2O_2Te_2$ (1272): calcd. Te 20.12; found Te 19.35. ^1H NMR ($CDCl_3$, 25 °C, TMS): δ = 2.16 (s, 12 H, CH_3), 2.81 (br. s, 8 H, 1-H), 3.10 (br. s, 8 H, 2-H), 3.99 (m, 2 H, CH), 6.77−6.79 (m, 4 H, 7-H + 9-H), 6.99 (d, J = 6 Hz, 2 H, 6-H), 7.09−7.11 (m, 2 H, 8-H) ppm.

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