SHORT PAPER

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Synthesis and crystal structures of two new (Te, N,) type hybrid organotellurium ligands

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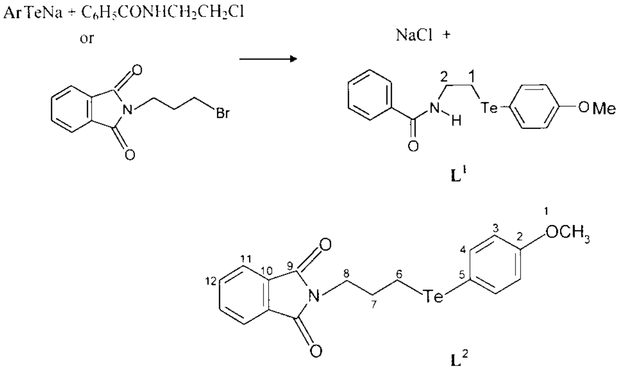
The reaction of N-(2-chloroethyl)benzamide and N-[3-bromopropyl]phthalimide with $ArTe^- Na^+$ generated *in situ* by borohydride reduction of Ar_2Te_2, has resulted in N-[2-(4-methoxyphenyltelluro)ethyl] benzamide (**L**^{1}) and N-[2-(4-methoxyphenyl telluro)propyl] phthalimide (**L**^{2}) respectively, which are potentially (Te, N)-type ligands. Their NMR (^{1}H and ^{13}C) spectra are characteristic and single crystal structures are solved. The Te-C(alkyl) distance [2.140(8)/2.151(4) Å] is longer than Te-C(aryl) distance [2.107(8)/2.128(5) Å].

Keywords: hybrid organotellurium ligands

Several hybrid organotellurium ligands[1–4] have been designed in the recent past. However, the designing of most of the (Te, N)-type of hybrid organotellurium ligands has been carried out so far by tellurating aliphatic amines[1,5,6] and pyridine derivatives.[7] No hybrid tellurium ligand containing an amide functionality is known so far and the telluration of imide derivatives has been reported[3b,c] scantly. It was therefore thought worthwhile to synthesise N-[2-(4-methoxyphenyltelluro) ethyl]benzamide (**L**^{1}) and N-[2-(4-methoxyphenyltelluro) propyl] phthalimide (**L**^{2}). Their synthesis and crystal structures are now reported.



Scheme 1

The ligands **L**^{1} and **L**^{2} were prepared according to the reaction given in Scheme 1. They are stable under ambient conditions and soluble in common organic solvents. In the IR spectrum of **L**^{1}, the bands appearing at 1641 cm^{-1} and 3384 cm^{-1} may be assigned to CO and NH vibrations of monosubstituted amide. The band at 441 cm^{-1} seems to originate from Te–C (aliphatic) vibrations. In the ^{1}H NMR spectrum of compound **L**^{1}, H_1 appears as a triplet at 3.00–3.05 ppm, whereas the signals of H_2 protons merge with that of OCH_3 and appear as multiplet at 3.77–3.82 ppm. The broad peak at 6.52 ppm in the spectrum of **L**^{1} disappears with D_2O and therefore may be assigned to NH. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **L**^{2} are characteristic and their assignments are supported by HETCOR spectra. The molecular structure of **L**^{1} is shown in Fig. 1. Selected bond lengths and angles are given in Table 1. It can be seen from the molecular structure of **L**^{1} that it should act as a (Te, N) donor easily. The Te–C(1)/(2.107(8)Å) is shorter than the Te–C(8) distance (2.140(8) Å), as is generally found[8–10] for Te–C(aryl) in comparison to that of Te–C(alkyl). The C(1)–Te–C(8) angle (98.8(3)°) is consistent with the literature reports on alkyl aryl tellurides.[8–10] The C–C bond lengths and C–C–C bond angles of aryl groups are normal (average values 1.372(4) to 1.377(4) Å and 119.96(1)° respectively). The molecular structure of **L**^{2} is shown in Fig. 2. The possibility of coordinating in a bidentate mode (*i.e.* as a (Te, N) donor] is apparent for **L**^{2} as in the case of **L**^{1}. The selected bond lengths and angle for **L**^{2} are given in Table 2. The Te–C(alkyl) bond length is longer than Te–C(aryl) in this case also as observed for **L**^{1}. The C(1)–Te–C(8) angle is 94.9(4)° and consistent with the value observed for **L**^{1}. The average

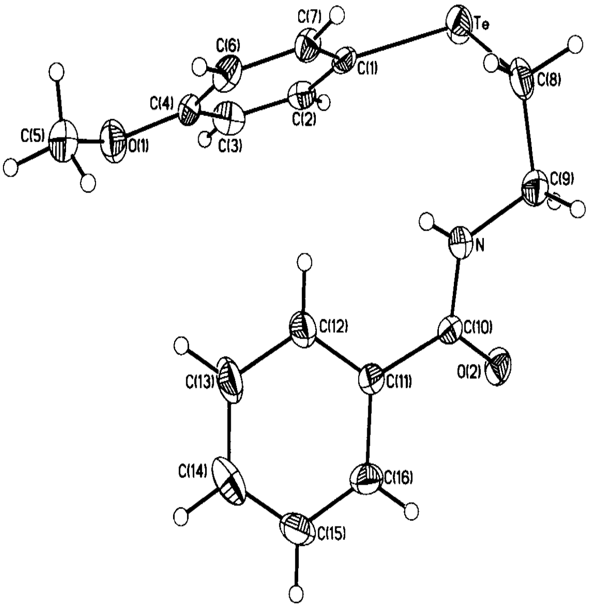


Fig. 1 Molecular structure of **L**^{1}.

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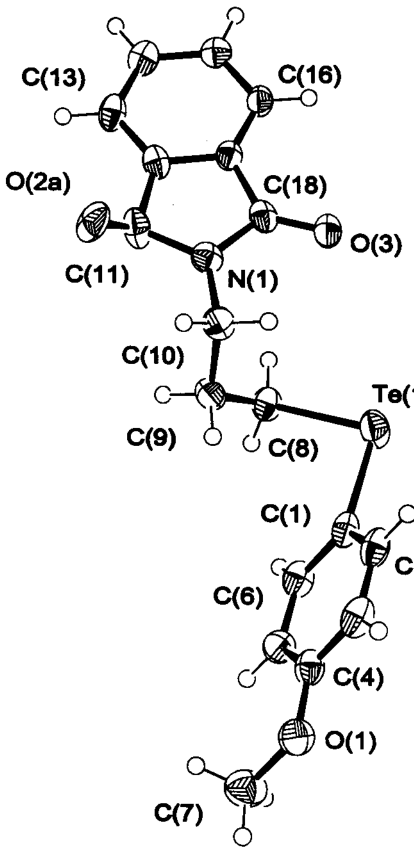

Fig. 2 Molecular structure of **L**^{2}.

C–C bond lengths and C–C–C bond angles of the corresponding substituted phenyl group are normal (1.384(1) Å and 120.0(1)°).

Table 1 Selected bond lenghts (Å) and angles (°) for **L**^{1}

Te–C(1)	2.107(8)	Te–C(8)	2.140(8)
O(1)–C(4)	1.369(9)	O(1)–C(5)	1.416(13)
O(2)–C(10)	1.215(9)	N–C(10)	1.345(10)
C(10)–C(11)	1.507(1)	C(8)–C(9)	1.490(12)
N–C(9)	1.451(10)		
C(1)–Te–C(8)	98.8(3)	C(4)–O(10–C(5)	118.9(8)
C(10)–N–C(9)	122.1(8)	C(6)–C(4)–O(1)	124.4(8)
C(2)–C(1)–Te	118.2(6)	C(7)–C(1)–Te	123.5(6)
O(1)–C(4)–C(3)	116.1(8)	C(9)–C(8)–Te	114.0(7)
N–C(9)–C(8)	111.4(8)	O(2)–C(10)–N	124.4(7)
O(2)–C(10)–C(11)	121.0(7)	N–C(10)–C(11)	114.7(7)
C(16)–C(11)–C(10)	118.2(8)	C(12)–C(11)–C(10)	123.5(7)

Table 2 Selected bond lenghts (Å) and angles (°) for **L**^{2}

Te(1)–C(1)	2.128(5)	Te(1)–C(8)	2.151(4)
O(1)–C(4)	1.370(5)	O(1)–C(7)	1.425(5)
O(2A)–C(11)	1.296(6)	O(2B)–C(11)	1.224(8)
O(3)–C(18)	1.221(4)	N(1)–C(18)	1.379(5)
N(1)–C(10)	1.475(4)	N(1)–C(11)	1.443(5)
C(8)–C(9)	1.519(5)	C(9)–C(10)	1.496(5)
C(11)–C(12)	1.510(6)	C(12)–C(17)	1.382(5)
C(12)–C(13)	1.383(5)	C(13)–C(14)	1.394(5)
C(14)–C(15)	1.399(6)	C(15)–C(16)	1.375(5)
C(16)–C(17)	1.370(5)	C(17)–C(18)	1.473(5)
Te(1)--O(3)	3.706(4)	Te(1)--O(2A)	6.438(4)
Te(1)--O(2B)	6.316(4)		
C(1)–Te(1)–C(8)	94.9(4)	C(4)–O(1)–C(7)	117.5(3)
C(2)–C(1)–Te(1)	120.1(3)	C(6)–C(1)–Te(1)	121.0(3)
O(1)–C(4)–C(3)	115.3(4)	O(1)–C(4)–C(5)	124.5(4)
C(9)–C(8)–Te(1)	114.3(3)	C(10)–C(9)–C(8)	113.7(3)
O(2A)–C(11)–N(1)	113.7(4)	O(2B)–C(11)–N(1)	131.3(5)
O(2A)–C11)–C(12)	121.3(5)	O(2B)–C(11)–C(12)	123.1(5)
O(3)–C(18)–N(1)	125.0(4)	O(3)–C(18)–C(17)	128.8(4)
C(18)–N(1)–C(10)	122.9(4)	C(18)–N(1)–C(11)	113.8(3)
C(11)–N(1)–C(10)	123.1(3)	N(1)–C(10)–C(9)	113.2(3)
N(1)–C(11)–C(12)	101.6(4)	N(1)–C(18)–C(17)	106.1(4)
C(17)–C(12)–C(13)	120.5(4)	C(16)–C(15)–C(14)	121.4(4)
C(17)–C(12)–C(11)	110.1(4)	C(17)–C(16)–C(15)	117.9(4)
C(13)–C(12)–C(11)	129.4(4)	C(16)–C(17)–C(12)	122.1(4)
C(12)–C(13)–C(14)	118.3(4)	C(16)–C(17)–C(18)	129.6(4)
C(13)–C(14)–C(15)	119.9(4)	C(12)–C(17)–C(18)	108.3(4)

Experimental

The C and H analyses were carried out with a Perkin Elmer elemental analyzer 240 C. Tellurium was estimated volumetrically.[3c] The ^{1}H and ^{13}C{1H} NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13 and 75.47 MHz respectively. IR spectra in the range 4000–250 cm^{-1} were recorded on a Nicolet Protége 460 FT-IR spectrometer as KBr pellets. The conductance measurements were made in acetonitrile (concentration ~ 1 mM) using an ORION conductivity meter model 162. The molecular weights (concentration ~5 mM) in chloroform were determined with a Knauer vapour pressure osmometer model A0280. N-(2-Chloroethyl)benzamide and N-[3-bromopropyl]phthalimide obtained from Aldrich (USA) were used as received.

*Synthesis of N-[2-(4-methoxyphenyltelluro)ethyl]benzamide (*L^1*):* Bis(4-methoxyphenyl)ditelluride (1.87 g, 4 mmol) was dissolved in 50 cm^3 of ethanol and the solution refluxed under an oxygen free dinitrogen atmosphere. A solution of sodium borohydride (0.5 g dissolved in 10 cm^3 of 10% aqueous NaOH) was added dropwise till it became colourless. N-(2-chloroethyl)benzamide (1.46 g, 8 mmol) was added dropwise to the colourless solution kept under reflux. The reaction mixture was further refluxed for 1–2 h, cooled to 25 °C, and poured into ice cold water (200 cm^3). The ligand **L**^{1} was extracted into dichloromethane (100 cm^3). The organic extract was washed with water and dried over sodium sulfate. The solvent was evaporated off under reduced pressure on a rotary evaporator, resulting in a yellowish oil, which was dissolved in a 1:2 mixture of dichloromethane and petroleum ether (40–60 °C). The solution was kept at 0–5 °C for 24 h. The **L**^{1} was separated as fibrous white crystals, which were filtered and dried *in vacuo*. Yield 70 %; m.p. 68–70 °C A_M (ohm^{-1} cm^2 mol^{-1}) 5.3. Anal. Calc. for $C_{16}H_{17}O_2NTe$: C, 50.19; H, 44.4; N, 3.66; Te 32.50%. Found: C, 49.81; H 4.58; N, 3.17; Te, 32.70%. Mol, Wt: 375 (Calc. 382). ^{1}H NMR ($CDCl_3$ 25 °C) (δ vs TMS) 3.00–3.04 (t, 2H, H_1), 3.76–3.82 (m, 5H, H_2 and OMe), 6.52 (bs, 1H, NH), 6.72–6.75 (d, 2H, ArH *m* to Te), 7.35–7.49 (m, 3H, ArH, *p* and *m* to CO), 7.62–7.64 (d, 2H, ArH, *o* to CO), 7.69–7.72 (d, 2H, ArH *o* to Te). ^{13}C{^{1}H} NMR ($CDCl_3$ 25 °C) (δ *vs* TMS): 8.1 (C_1), 41.5 (C_2), 54.9 (OCH_3) 99.3 (ArC–Te, 115.2 (ArC *m* to Te), 126.8 (ArC, *m* to CO), 128.2 (ArC, *p* to CO), 131.7 (ArC, *o* to CO), 134.1 (ArC–CO), 140.8 (ArC *o* to Te), 160.9 (ArC *p* to Te), 167.1 (CO).

Synthesis of N-[2-(4-methoxyphenyl telluro)propyl] phthalimide (**L**^{2}): A solution of N-[3-bromopropyl]phthalimide (1.44 g, 4.2 mmol) in THF (10 ml) was added to the refluxing colourless solution of ArTe$^-$ prepared as described above for **L**^{1}. The mixture was refluxed further for 1 h with stirring and cooled to room temperature. It then was poured into water 100 cm^3 and **L**^{2} was extracted from it into CH_2Cl_2 (50 cm^3). The organic phase was separated and dried over Na_2SO_4. Its volume was reduced to 5 cm^3 with a rotary evaporator and the concentrate was mixed with petroleum ether (40–60 °C). The resulting white crystalline solid was filtered off, washed with petroleum ether (40–60 °C) and dried *in vacuo*. Single crystals of **L**^{2} were grown from a mixture (8:2) of dichloromethane and petroleum ether (40–60 °C). Yield 80%; m.p. 102–103 °C (d) A_M 0.8 (ohm^{-1} cm^2 mol^{-1}) Anal. Calc. for $C_{18}H_{17}O_3NTe$: C, 51.13; H, 4.02; N, 3.31; Te 30.18%. Found: C, 50.60; H, 4.41; N, 3.53; Te, 30.77%. Mol. Wt 412: (Calc 423). ^{1}H NMR ($CDCl_3$, 25 °C) (δ vs TMS): 2.06–2.15 (q, 2H, H_2–C_7); 2.74–2.80 (t, 2H, H_2C–Te); 3.72–3.75 (t, 2H, H_2C–N); 3.76 (s, 3H, OCH_3); 6.73–6.76 (d, 2H, ArH *m* to Te); 7.67–7.73 (m, 4H, ArH of phthalimide ring); 7.82–7.84 (d, 2H, ArH, *o* to Te). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C) (δ vs TMS): 4.5 (C_6), 30.6 (C_7) 39.7 (C_8), 55.1 (C_1); 100.2 (C_5), 115.2 (C_3), 123.2 (C_{11}), 132.2 (C_{10}), 133.5 (C_{12}), 141.3 (C_4), 159.8 (C_2), 168.3 (C_9).

X-ray diffraction analysis: A colourless, plate crystal of **L**^{2} was mounted on glass fibre. Data were collected on an Enraf Nonius Kappa CCD area detector (ø scans and ω scans to fill Ewald sphere) at the University of Southampton EPSRC National Crystallography

Service. Data collection on **L²** (using Mo–Kα radiation of wavelength, λ = 0.71073 Å) and cell refinement[11] gave cell constants, corresponded to an orthorhombic cell. An absorption correction was applied[l2] which resulted in transmission factors range from 0.9650 to 0.7744. The structures were solved by direct methods.[13] All of the non-hydrogen atoms were treated anisotropically. One of the oxygen atoms is disordered. Hydrogen atoms were included in idealised positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached and a final cycle of full-matrix least-squares refinement[14] was made. A Bruker P4S X-ray diffractometer was used for the data collection on **L¹** using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) and employing the ω–2θ technique. The unit cell was determined from 25 randomly selected reflections using automatic search, index and least square routines. Empirical absorption correction was applied using the SHELXA programme.[15] The structure was solved by routine heavy atom/Fourier methods (using SHELXL 93[16a]/SHELX 86[16b]) and refined by full matrix least squares on F^2. The crystal data are as follows:

L¹: *Chemical formula:* $C_{16}H_{17}NO_2Te$, formula weight: 382.91, temperature: 293(2) K: crystal system: orthorhombic, space group: $P2_12_12_1$, unit cell dimensions: a = 5.410(4) Å, b = 9.915(4) Å, c = 28.760(3) Å; $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$; volume, 1542.6(15) Å^3, Z = 4; reflections collected: 1630; independent reflections: 1630 [R(int)=0.000] Final R indices [$I > 2\sigma(I)$]: R1 = 0.0572. wR2 = 0.0791.

L²: *Chemical formula:* $C_{18}H_{17}NO_3Te$, formula weight: 422.93, temperature: 150(2) K: crystal system: orthorhombic, space group: *Pbca*, unit cell dimensions: a = 14.646(3) Å, b = 5.9656(12) Å, c = 38.213(8) Å; $\alpha = \beta = \gamma = 90°$; volume, 3338.7(12) Å^3, Z = 8; reflections collected: 10807: independent reflections: 3629 [R(int) = 0.0684]; Final R indices [$I > 2\sigma(I)$]: R1 = 0.0400, wR2 = 0.0759.

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