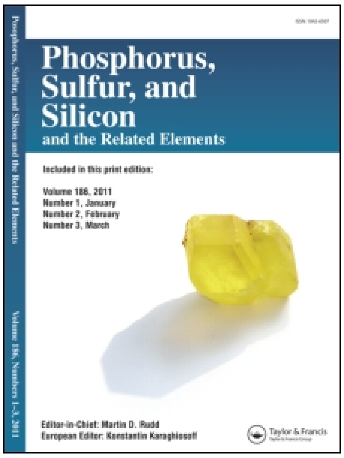

Phosphorus, Sulfur, and Silicon and the Related Elements

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Mridulata Misra; Ajai K. Singh

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BIS(2-METHYLTHIOETHYL)TELLURIDE-FIRST (Te, S_2) LIGAND AND ITS COMPLEXES WITH PALLADIUM(II), MERCURY(II) AND CADMIUM(II)

MRIDULATA MISRA and AJAI K. SINGH*

Department of Chemistry, Indian Institute of Technology, New Delhi 110016, India

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A (Te, S_2) ligand, bis(2-methylthioethyl)telluride has been synthesized by reacting Na_2Te with $ClCH_2CH_2SMe$ under a nitrogen atmosphere, as an unstable liquid which is reasonably stabilized on complexation. The complexes of this (Te, S_2) ligand having composition $[M(PPh_3)_2(L)](ClO_4)_2$ [L = (Te, S_2) ligand] where M = Pd(II), Cd(II) and Hg(II) have been synthesized. ^1H and $^{13}C\{^1H\}$ NMR, IR and FAB mass spectra have been used in conjunction with molecular weight and conductance measurements to characterize the ligand and its complexes. The potentially tridentate ligand coordinates in a bidentate mode and in solution there is an exchange between SMe of the pendent arm and the coordinated SMe group.

Keywords: Bis (2-methylthioethyl)telluride; palladium; mercury; cadmium; complexation; ligand

INTRODUCTION

The potentially tri and higher dentate telluroether ligands (including the hybrid ones) known so far are not many[1], in spite of current interest in the ligand chemistry of tellurium[2] which originates from the possible applications of metal-tellurium bond containing compounds as precursors of II-VI semiconductors.[3] Some examples of such ligands are bis [(2-aryltelluro)ethyl]amines/methylamines[4-5](1) tris(2-aryltelluroethyl)amine/dimethylamines[6](2), 2-(2-pyridoethyltelluro)ethylpyridine[7](3), bis (2-amino/dimethylaminoethyl)ditelluride[8](4), bis(2-aryltelluroethyl)ether[8](5), 1,2-bis(2-aryltelluroethoxy)ethane[8](6), N,N,N′,N′-tetrakis(2-aryltelluroe-

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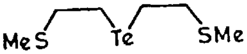
* Corresponding author: Email: aksingh@chemistry.iitd.ernet.in.

thyl)ethane-1,2-diamine[8](7) and macrocyclic Schiff bases(8) [potential (Te_2, N_4)donors][9]. However, ligation of these polydentate hybrid tellurium ligands is little explored as only few complexation reactions of **1–3** and **8** have been reported. No tridentate telluroether ligand containing sulfur atoms as co-donors is known so far. It was therefore thought worth while to design a novel (Te, S_2) ligand, bis(2-methylthioethyl)telluride (**9**), and to study its complexation behaviour. The crystal structure[10] of the platinum(II)-complex of 2-(aryltelluro)ethyl methylsulfide [a bidentate (Te, S) ligand] has shown that the *trans*-influence[10] of ArTe is somewhat greater than that of SMe group. This has prompted us to investigate the chemistry of other (Te, S_x) ligands. In the present paper, results of our investigations on a (Te, S_2) ligand **9** and its complexation with palladium(II), mercury(II) and cadmium(II) are reported.



(9).

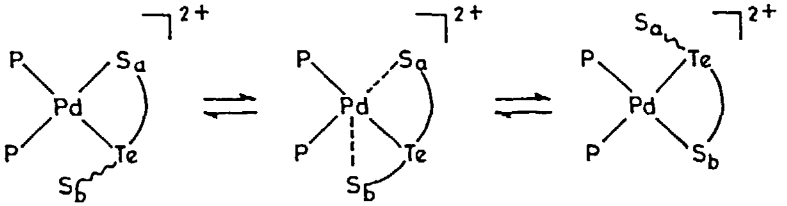
RESULTS AND DISCUSSION

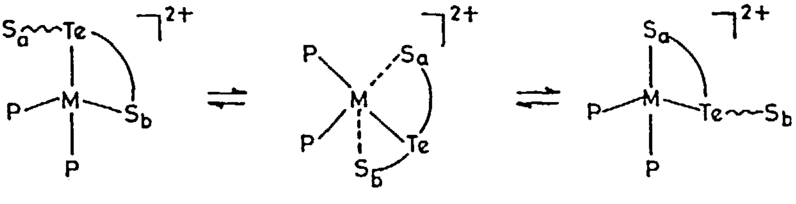
The (Te, S_2) ligand **9** was synthesized as an orange yellow viscous liquid by reactions given in equation 1. It is soluble in common organic solvents like chloroform,

$$Te \xrightarrow[NaOH]{NaBH_4} Na_2Te \xrightarrow{2ClCH_2CH_2SMe} 9 \qquad (1)$$

ethanol, acetone etc. but very unstable in pure form as well as in solution, as signs of its decomposition (deposition of black elemental tellurium) begin to appear within 2–3 h of its isolation. We have attempted to stabilize **9** by converting it into its palladium(II), mercury(II) and cadmium(II) complexes having stoichiometry, $[(PPh_3)_2M(9)](ClO_4)_2$ (M = Pd, Hg or Cd). The complexes are more stable than the ligand but mercury and cadmium complexes can not be stored more than a week and after one month they become black, due to extensive decomposition. For none of these three complexes single crystals suitable for X-ray diffraction could be grown. The molecular weight of the Pd-complex in chloroform has been found to be 376, or nearly one third of the calculated value, 1108. This is in agreement with its 1:2 electrolyte character, which is also reflected by its molar conductance $\Lambda_M = 232\ \mathrm{Ohm^{-1}\ cm^2\ mol^{-1}}$ in acetonitrile.

The ^1H NMR spectrum of **9** is characteristic, but in comparison to a related compound[11], $ArTeCH_2CH_2SMe$, the signal of CH_2Te is shielded, most probably due to greater electron releasing property of an alkyl group in comparison to that of an aryl group. However, the ^1H NMR spectrum of **9** should be recorded immediately after its dissolution as it is more unstable in solution and its aerial oxidation results in the formation of $(MeSCH_2CH_2)_2TeO$ which gives CH_2 signals in the range 3.26 – 3.42 ppm. The signals of CH_2Te and CH_2S in the $^{13}C\{^1H\}$ NMR spectrum of **9** also appear shielded in comparison to that of $ArTeCH_2CH_2SMe$ due to the difference in electronic effects of alkyl and aryl groups. ^1H NMR spectra of the three complexes $[(PPh_3)_2M(\mathbf{9})](ClO_4)_2$ [M = Pd(**10**), Hg(**11**) and Cd(**12**)] are also characteristic, but each spectrum has three distinct SMe signals. This indicates the existence of the following equilibria, presuming usual square planar environment of ligands around palladium and a tetrahedral one around mercury and cadmium.





M ≡ Cd / Hg, P ≡ PPh3

In the $^{13}C\{^1H\}$ NMR spectrum of the palladium complex **10**, also three SMe and four-CH_2S signals are present supporting the above mentioned equilibria. The four SCH_2 signals in ^{13}C NMR may be due to nonequivalence of Pd-S_b and Pd-S_a interactions, which is able to separate CH_2S signals of transition state but not of CH_3. This is supported by the fact that SMe signal at 2.00 ppm in ^1H NMR spectrum of **10** and at **19**. 85 ppm in its ^{13}C NMR are somewhat broader relative to other SMe signals. In the aryl region of this spectrum the presence of sixteen signals has been noticed which also concurs with the equilibria proposed above. Most probably there is a secondary interactions[11] between sulfur and tellurium of **9**, which breaks down on complex formation. Consequently the ^1H NMR signal due to the free SMe group appears shielded and that of coordinated SMe slightly downfield with respect to that of free ligand **9**. The CH_2Te signal in ^1H NMR spectra of all the complexes appears deshielded with respect to that of the free ligand, but merges with signals of CH_2S which are broad due to the equilibria mentioned above and the fact that the signal of coordinated CH_2S is somewhat deshielded and CH_2S of the pendent arm undergoes shielding. The FAB mass spectrum of the palladium complex has a molecular ion peak as well as the fragmentation pattern expected for this compound, thus supporting its stoichiometry. In the IR spectra of all the complexes the presence of bands at 630/635 and 1100 cm^{-1}suggest that ClO_4 groups are not coordinated[12]. The $\nu_{Te\text{-}C(alkyl)}$ appears in the complexes around 355 cm^{-1} as reported earlier[13]. All these observations suggest that bis(2-methylthioethyl)telluride can be reasonably stabilized in complexes of soft metal ions having PPh_3 as a co-ligand, but the stability of the palladium complex is much greater than those of mercury and cadmium. The pendent arm containing SMe makes the M-S bond hemilabile which may be further explored for catalytic possibilities.

EXPERIMENTAL

2-Chloroethyl methyl sulfide (Aldrich, USA) was used as received. $(Ph_3P)_2PdCl$ was obtained from Aldrich, USA and used without further purification. Published methods were used to synthesize $(Ph_3P)_2HgCl_2$ and $(Ph_3P)_2CdCl_2$[14]. The C and H analyses were carried out with a Perkin Elmer elemental analyzer 240C. Tellurium was estimated volumetrically[15]. The ^1H NMR spectra were recorded on a JEOL JNR FX-100 FT NMR spectrometer at 99.55 MHz. ^{13}C $\{^1H\}$ NMR spectra were recorded on a Bruker Spectrospin DPX – 300 NMR spectrometer at

75.47 MHz. IR spectra were recorded in the range 200 – 4000 cm^{-1} on a Nicolet 5DX FT-IR spectrometer using CsI pellets. FAB mass spectra were recorded on a JEOL SX – 102/DA – 6000 mass spectrometer using argon (6kV, 10 mA) as the FAB gas. Molecular weights were determined on a Knauer Vapour pressure osmometer model A028 and for conductance measurement an ORION conductivity meter model 162 was used.

Synthesis of Bis (2-methylthioethyl)telluride (9)

Tellurium (1.28 g; 10 mmol), sodium borohydride (0.9 g, 24 mmol) dissolved in 10 cm^3 of 2 M NaOH and 50 cm^3 of water were mixed and refluxed for 2 h under a nitrogen atmosphere. To this colorless suspension was added dropwise a solution of $ClCH_2CH_2SMe$(1.96 cm^3, 20 mmol) in 5 cm^3 of ethanol under dinitrogen atmosphere with constant stirring. The reaction mixture was refluxed for 2 h, cooled to room temperature (25 °C) and poured into 100 cm^3 of water. Then **9** was extracted into chloroform from this aqueous mixture. The extract was washed with water and dried over anhydrous sodium sulfate. The ligand **9** was obtained from the dry extract as an orange – yellow viscous liquid after removing solvent under reduced pressure.

Yield 70%. Analysis : Found : C, 26.27; H, 5.25; Te, 45.82; Calcd. for C_6H_{14}, S_2Te ; C, 25.89; H, 5.03; Te, 46.04%. NMR (^1H, $CDCl_3$, 25°C) ; δ, 2.15 (s, 6H, SMe) 2.75 (t, 4H, CH_2Te) 2.92 (t, 4H, CH_2S) ; ($^{13}C\{^1H\}$, $CDCl_3$, 25°C); δ, 1.96 (CH_2Te), 15.27 (SMe) ; 29.7 (CH_2S).

Synthesis Of $[(PPh_3)_2Pd(9)](ClO_4)_2$ (10)

A suspension of $[(PPh_3)_2PdCl_2]$ (0.84 g; 1.2 mmol) in acetonitrile (30 cm^3) was mixed with a solution of $AgClO_4$(0.4976 g ; 2.4 mmol) in 10 cm^3 of acetonitrile. The mixture was stirred for 30 min. and a suspension of **9** (0.33g ; 1.2 mmol) in acetonitrile (10 cm^3) was added . The reaction mixture was stirred further for 2 h and AgCl filtered off. The orange filtrate was concentrated to 10 cm^3 and mixed with hexane (10 cm^3). The resulting orange precipitate of **10** was filtered, washed with a hexane – chloroform (2:1) mixture, recrystallized from a chloroform – hexane (1:1) mixture and dried in *vacuo*.

Yield 70% , m.p. 138–140°C. Analysis : Found C, 45.26 ; H, 4.20 ; Te, 12.27%. Calcd. for $C_{42}H_{44}O_8P_2S_2Cl_2PdTe$: C, 45.50 ; H, 3.97 ; Te, 11.55%. NMR (^1H, $CDCl_3$, 25°C) ; δ, 1.83, 2.00, 2.28 (3s, 6H, SMe) 2.83 (bs, 8H, $CH_2Te + CH_2S$), 7.43 – 7.67 (m, 30H, ArH). (^{13}C {^1H} , $CDCl_3$, 25°C); δ, 4.06 (CH_2Te) , 19.41, 19.85, 20.74 (SMe), 36.97, 39.97, 40.90, 47.65 (CH_2S), 128.71, 128.86, 129.48, 129.65 (C, *p* to P), 129.79, 132.27, 132.43, 132.56 (C, *m* to P), 132.87, 133.13, 133.35, 133.97 (C, *o* to P) 134.51, 134.60, 139.23, 144.67 (C bonded to P). FAB mass : m/z : 1107 (M) , 1077 (M – 2Me), 976 (M – ($2Me + ClO_4$)), 944 (M – ($Me + SMe + ClO_4$)) , 898 (M – ($2(CH_2SMe) + ClO_4$)), 799 (M – $2(CH_2SMe + ClO_4)$), 631 ($(Ph_3)_2$ Pd), 523 (PPh_2 Pd (PPh_3)) 369, (PPh_3 Pd), 261 (Ph_2Pd), 183 (Ph Pd).

Synthesis of $[(PPh_3)_2Hg(9)](ClO_4)_2$ (11)

A suspension of $(PPh_3)_2HgCl_2$ (0.9546 g; 1.2 mmol) in 30 cm^3 of acetonitrile was mixed with a solution of $AgClO_4$ (0.4976 g ; 2.4 mmol) in 10 cm^3 of acetonitrile. The mixture was stirred for 1 h and a suspension of **9** (0.33 g; 1.2 mmol) in acetonitrile (10 cm^3) was added. The reaction mixture was stirred further for 2 h and AgCl filtered off. The light yellow filtrate was concentrated to 10 cm^3 and mixed with hexane (10 cm^3). The resulting light yellow precipitate of **11** was filtered, washed with a hexane-chloroform (2:1) mixture, recrystallized from a chloroform – hexane (1:1) mixture and dried in *vacuo.*

Yield 75%, m.p 72–75 °C(d). Analysis : Found C, 42.35 ; H, 3.89 ; Te 9.90% .Calcd. for $C_{42}H_{44}O_8P_2S_2Cl_2HgTe$; C, 41.94; H, 3.66; Te, 10.6%. NMR (^1H, $CDCl_3$, 25°C); δ , 2.00, 2.10, 2.22 (3s, 6H, SMe), 2.96 (bs, 8H, $CH_2S + CH_2Te$), 7.25 – 7.65 (m, 30 H, ArH).

Synthesis of $[(PPh_3)_2Cd(9)](ClO_4)_2$ (12)

A suspension of $[(PPh_3)_2CdCl_2]$ (0.85 g; 1.2 mmol) in acetonitrile (30 cm^3) was mixed with a solution of $AgClO_4$(0.4976 g ; 2.4 mmol) in 10 cm^3 of acetonitrile. The mixture was stirred for 1 h and a suspension of **9** (0.33 g; 1.2 mmol) in acetonitrile (10 cm^3) was added. The reaction mixture was stirred further for 2 h. The yellow brown solution was separated after filtering off AgCl. The filtrate was evaporated to dryness. The yellow brown residue was thoroughly washed with hot acetonitrile and petroleum ether (40- 60°C) and dried in *vacuo.*

Yield 60%, m.p. 80–82°C. Analysis : Found C, 45.15 ; H, 3.92; Te.12.56 %. Calcd. for $C_{42}H_{44}O_8P_2S_2Cl_2CdTe$; C, 45.26; H, 3.95; Te, 11.94%. NMR (^1H, DMSO-d_6, 25°C); δ, 1.95, 2.14, 2.19 (3s, 6H, SMe), 2.96 (m, 8H, $CH_2Te + CH_2S$), 7.34 – 7.64 (m, 30H, ArH).

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