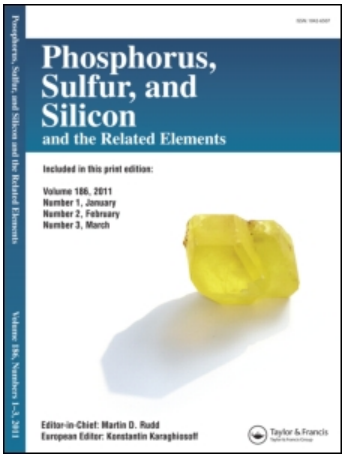

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Aravamudan, G. , Janakiram, Chhaya and Sejekan, B. G.(1978) 'COMPLEXES OF Te(IV), Te(II) AND Se(II) WITH METHYL β-HYDROXYETHYLDITHIOCARBAMATE', Phosphorus, Sulfur, and Silicon and the Related Elements, 5: 2, 185 — 188
To link to this Article: DOI: 10.1080/03086647808069883
URL: http://dx.doi.org/10.1080/03086647808069883

Phosphorus and Sulfur
1978, Vol. 5, pp. 185–188

COMPLEXES OF Te(IV), Te(II) AND Se(II) WITH METHYL β-HYDROXYETHYLDITHIOCARBAMATE

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(*Received May 8, 1978*)

Novel complexes of methyl β-hydroxyethyldithiocarbamate $\begin{matrix} H_3C \\ HOH_2CH_2C \end{matrix}\!\!>\!NCSS^-$, L, with Te(IV), Te(II) and Se(II) having composition TeL_3X, where $X = Cl^-$, Br^-, NCS^- and $O_{0.5}$, TeL_2I_2 and TeL_2 and SeL_2 were isolated and characterized through molecular weight, conductance, magnetic, x-ray and spectral (uv, ir) measurements.

INTRODUCTION

The dithiocarbamate group $\left[\begin{matrix} R_1 \\ R_2 \end{matrix}\!\!>\!N\!-\!C\!<\!\begin{matrix} S \\ S \end{matrix}\right]^-$ derived from the interaction of carbon disulfide with a secondary amine $\begin{matrix} R_1 \\ R_2 \end{matrix}\!\!>\!NH$ is one of the most important chelating sulfur ligands in transition and post-transition metal chemistry.[1] Extensive literature is available on the preparation, structure and properties of diethyldithio-carbamate complexes, where R_1 and R_2 are both ethyl groups. The Scandinavian School of Foss, Husebye and others[2] has contributed greatly to studies on sulfur-ligand complexes of Te(IV), Te(II) and Se(II). The diethyldithiocarbamate ($(C_2H_5)_2NCSS^-$, Et_2Ddtc) and morpholine-4-carbadithioate (morph.Ddtc, $O\!<\!\!>\!NCSS^-$) have been shown to form complexes $Te(Et_2Ddtc)_4$,[3] $PhTe(Et_2Ddtc)_3$,[4] $Te(Et_2Ddtc)_?$,[5] $Se(Et_2Ddtc)_2$,[6] $Te(morph.Ddtc)_4$,[7] $Te(morph.Ddtc)_2$,[8] and $Se(morph.Ddtc)_2$.[9] Crystal structure work has shown that in all the complexes the dithiocarbamate group acts as a bidentate chelating ligand. However, there is an unequal participation in the bonding of two sulphur atoms from the same group. The tetrakis(diethyldithiocarbamato) and morpholine-4-carbodithioate complexes of Te(IV) are extraordinarily stable towards the displacement reactions. To date, there has been only one report of a mixed ligand complex, namely, $PhTe(Et_2NCS_2)_3$.[4] However, by suitably altering the R_1 and R_2 groups in the dithiocarbamate moiety one can expect to modify, from the steric and the electronic considerations, the ligating characteristics of the dithiocarbamate to such an extent that possibilities are created for the formation of mixed ligand complexes featuring dithiocarbamate in combination with other ligands coordinated to Te(IV). Recent work[10] with 2,2′-iminodiethanoldithiocarbamate (DEADTC, $(HOCH_2CH_2)_2NCSS^-$, where $R_1 = R_2 = CH_2CH_2OH$) afforded for the first time two such complexes, namely, $Te(DEADTC)_3I$ and $Te(DEADTC)_2I_2$; this dithiocarbamate, however, did not yield other mixed ligand complexes. Our investigation with methyl-β-hydroxyethyldithiocarbamate $\begin{matrix} CH_3 \\ (L,HOCH_2CH_2 \end{matrix}\!\!>\!NCSS^-$, where $R_1 = CH_3$, $R_2 = -CH_2CH_2OH$), however, gave a large number of Te(IV)-L complexes featuring a variety of additional ligation, namely O^{2-}, NCS^-, Cl^-, Br^- and I^-. These are the first complexes of such kind in Te(IV)-dithiocarbamate chemistry. The preparation and characteristics of these complexes as well as of those of L with the Te(II) and Se(II) oxidation states are described in the present paper.

RESULTS AND DISCUSSION

The analytical data and some of the physical characteristics of the complexes are presented in Table I. The electronic spectra in methanol solution are recorded in Table II.

TABLE I

Elemental analyses of complexes and some physical properties

Compound†	Color and m.p. (°C)	Conductance (cm^2/ohm)	MW††	Elemental analyses %					
				M	C	H	N	S	X
TeL_3Cl	Yellow, 110°	11.25	640.0 (613.8)	20.76 (20.79)	23.40 (23.48)	4.0 (3.94)	6.70 (6.84)	30.80 (31.34)	5.81 (5.78)
TeL_3Br	Yellow, 135°	13.53	670.1 (658.2)	19.75 (19.39)	22.0 (21.90)	3.50 (3.68)	6.40 (6.38)	28.93 (29.23)	12.76 (12.14)
TeL_3NCS	Orange-yellow, 140°	14.03	656.0 (634.4)	20.62 (20.04)	24.40 (24.52)	3.90 (3.80)	8.95 (8.80)	36.10 (35.27)	— —
$(TeL_3)_2O$	Yellow, 165°	—	not detd.	21.17 (21.77)	24.40 (24.58)	4.20 (4.13)	7.75 (7.63)	31.44 (32.82)	—
TeL_2I_2	Orange, 100°	21.4	694.0 (681.9)	19.00 (18.71)	14.20 (14.09)	2.40 (2.36)	4.00 (4.11)	18.53 (18.84)	35.50 (37.22)
TeL_2	Pinkish-orange, 140°	16.7	440.0 (428.0)	29.88 (29.82)	22.50 (22.46)	3.90 (3.77)	6.60 (6.55)	29.2 (29.97)	—
SeL_2	Pale yellow (decomp.)	7.2	394.0 (370.4)	20.54 (20.81)	25.55 (25.33)	4.35 (4.25)	7.40 (7.38)	32.80 (33.82)	—

† $L = N(CH_3)(CH_2CH_2OH)CSS^-$.
†† Calculated values are given in parentheses.
X represents Cl^-, Br^-, I^- or NCS^-.

TABLE II

Electronic spectrum of tellurium and selenium dithiocarbamates in methanol

Complex	$\bar{\nu}$ in kK (ε_{max} in parentheses in mol^{-1} cm^2)				
LH†	47.68	39.52	34.84	28.6	
TeL_3Cl	49.5 (1.02×10^5)	40.3 (1.02×10^5)	37.04 (6.14×10^4)	31.64 (2.05×10^4)	23.5 (1.023×10^3)
TeL_3Br	49.97 (1.02×10^5)	41.52 (1.26×10^5)	35.72 (8.27×10^4)	33.01 (3.88×10^4)	29.85 (2.3×10^4)
TeL_3NCS	49.03 (4.699×10^4)	39.84 (6.89×10^4)	36.63 (3.76×10^4)	32.96 (1.41×10^4)	23.3 (1.18×10^3)
TeL_2I_2	48.3 (6.53×10^4)	39.5 (1.02×10^5)	36.4 (5.5×10^4)	31.75 (2.25×10^4)	23.3 (1.38×10^3)
TeL_2	46.5 (4.88×10^3)	39.7 (9.11×10^3)	36.6 (4.72×10^3)	32.5 (1.79×10^3)	21.28 (9.76×10^3)
SeL_2	49.83 (2.78×10^4)	39.98 (4.82×10^5)	36.94 (2.96×10^4)	31.25 (1.296×10^4)	25.97 (2.78×10^2)

† $LH = N(CH_3)(CH_2CH_2OH)CSSH$.

The complexes containing chloride, bromide, thiocyanate and oxide as ligands constitute the first examples of their kind in tellurium(IV)-dithiocarbamate chemistry. Only two reports are available where the phenyl[4] and iodide[10] are co-ligands in Te(IV) dithiocarbamates. The formation of several mixed ligand complexes in the tellurium(IV)-methyl β-hydroxyethyldithiocarbamate (L) system is obviously due to the much weaker coordination tendency of L in comparison with diethyldithiocarbamate. This was shown by the ready quantitative conversion observed of all the Te(IV)-L mixed ligand complexes to $Te(Et_2Ddtc)_4$ on treatment with $NaEt_2Ddtc$. The oxo complex isolated in the present work, $(TeL_3)_2O$, is unique. Under similar conditions used in preparation of $(TeL_3)_2O$, addition, instead of L, of dimethyl-, diethyl-, pyrrolidine-, and bishydroxy-ethyldithiocarbamates and of morpholine-4-carbodithioate resulted in the formation of only the respective tetrakis(dithiocarbamato)Te(IV) complexes. Uranium(VI),[11–13] vanadium(IV),[14–16] molybdenum(VI) and molybdenum (IV)[17–18] form oxo-dithiocarbamates with any R_1 and R_2 substituents in the dithiocar-

bamate moiety. Te(IV) exists in acid solutions as an oxo species[19] and , therefore, separation of oxo-Te(IV)-L complex though unusual is not implausible. The separation of oxo-U(VI), V(IV) and Mo(VI) and Mo(IV) dithiocarbamates also is known to take place under acid conditions. Apart from chemical analysis, formulation of this complex as $(TeL_3)_2O$ is supported by the observation of its total conversion to TeL_3Cl on treatment with methanolic HCl; there were no side products containing tellurium in the interaction. Since iodide is a much softer ligand than O^2, Cl^-, Br^- or NCS^-, it will interact more strongly with the soft acid Te(IV) and thus it is able to bring about a larger amount of displacement of the dithiocarbamate from the Te(IV) coordination and form the TeL_2I_2 complex instead of TeL_3-type of complexes as in other cases. The chloro-, bromo-, and thiocyanato-TeL_3 complexes hydrolysed to give the $(TeL_3)_2O$ complex. Addition of dilute HCl, HBr, and acidified thiocyanate solution converted the $(TeL_3)_2O$ to the respective original complexes quantitatively. This indicates the moderate stability of the TeL_3 unit in all these complexes.

All the complexes reported in Table I were stable. Except for $(TeL_3)_2O$ which was insoluble in all solvents, the others were soluble in methanol and other polar solvents to varying extents. Conductance measurements in methanol showed them to be non-electrolytes. Molecular weight measurements given in Table I, showed them to be monomeric in solution. All the complexes of tellurium(IV) were as expected found to be diamagnetic; the observed diamagnetism of SeL_2 and TeL_2 could also be explained on the basis of Foss's interpretation for similar complexes.[2]

Infrared data showed that the characteristic C—N stretching frequency of the dithiocarbamate moiety was observed in all the complexes in the range 1470–1500 cm^{-1}. The $\nu_{(C-N)}$ band is sensitive to environmental changes, different substituents in dithiocarbamate ligand, the changes in oxidation state of the central metal ion and the stereochemistry of the complexes.[1] In the presently reported complexes, it is difficult to draw conclusions from infrared data as to whether the dithiocarbamate group in the complexes is bidentate or monodentate owing to the reasons elaborated earlier.[10] X-ray work[20] of the interesting complexes reported here is being undertaken and initial results have shown that L is bidentate in TeL_3Br in analogy with the x-ray results of all the previous dithiocarbamate complexes of Te(IV). It was difficult to pick out the Te—S, Te—Cl, Te—Br, Te—O and Te—N frequencies from the large number of bands observed in the far infrared region. In the complex TeL_3NCS, the thiocyanate band occurs at 2080 cm^{-1} which is indicative of the presence of the N-bonded thiocyanate group.[21,22] One would have expected the thiocyanate to be bonded through sulfur to Te(IV). That this does not occur in TeL_3NCS is attributed to the steric crowding of the three dithiocarbamate groups around Te(IV), forcing the thiocyanato to be coordinated through the smaller-sized nitrogen atom in preference to the larger-sized sulfur atom. This type of inversion of coordination of ambidentate ligands due to steric considerations has been reported and discussed for other soft B metal ions, such as palladium and platinum.[22]

The electronic spectra, presented in Table II revealed typical strong intraligand transitions at ~40 kK, 35 kK and 30 kK characteristic of the dithiocarbamate moiety.[10,23,24] The band in the longer region noticed at 23 kK in all the complexes is attributed to the L → M charge transfer.

EXPERIMENTAL

Preparation of complexes

The ligand Methyl β-hydroxyethyldithiocarbamic acid $HOH_2CH_2C\diagup H_3C\diagdown NCSSH$, was prepared and used each time in solution form by mixing the N-methyl-β-aminoethanol (1.5 g, 20 mM, Riedel) and carbon disulphide (3.8 g, 50 mM, Pfizer) in a molar ratio slightly exceeding 1:1, generally in methanol solution at ice-water temperatures.

1. Chlorotris(Methyl β-hydroxyethyldithiocarbamato) tellurium (IV)[TeL_3Cl]:

Tellurium dioxide (1.6 g, 10 mM) was dissolved in 5 ml conc. HCl and the solution diluted with 50 ml water. To this 50 mM ligand in 50 ml methanol was added drop-wise with constant stirring, when a crystalline bright yellow product was separated. It was filtered, washed with dilute HCl, recrystallized from hot methanol and dried over H_2SO_4. Yield ~80%. *d* spacings (Å): 8.85s, 6.73s, 5.85s. 5.07s. 4.39m, 3.97w, 3.72s, 2.94vs, 2.69s, 2.53w, 2.49w, 2.36s, 2.23w, 2.10s, 1.95m, 1.83m, 1.68w.

2. Bromotris(-Methyl β-hydroxyethyldithiocarbamato) tellurium(IV)[TeL_3Br]

Procedure same as above excepting that HBr was used instead of HCl. Yield ~75%. *d* spacings (Å): 9.48s, 6.85s, 5.89m, 4.73s, 4.33s, 3.67w, 3.26s, 3.00w, 2.93w, 2.69m, 2.01w, 2.52m, 2.37m, 2.22m, 2.12m, 1.93w, 1.80m, 1.69w, 1.56w.

3. Thiocyanatotris(Methyl β-hydroxyethyldithiocarbamato) tellurium(IV) [TeL_3NCS]

Crystals of TeL_3Cl were dissolved in 30 ml methanol and potassium thiocyanate in methanol was added to this solution in

molar quantities of 1:5. The clear solution of TeL_3Cl immediately yielded a precipitate on this addition. The crystals were filtered, washed with methanol and recrystallized from hot methanol. Yield: ~80%. *d* spacings (Å): 6.86s, 5.64s, 4.87s, 4.39s, 3.78w, 3.25s, 2.89m, 2.68m, 2.52m, 2.49m, 2.23w, 1.01w, 1.82w.

4. μ-Oxo-bis(tris-methyl β-hydroxyethyldithiocarbamato) tellurium(IV) $[TeL_3]_2O$

5 ml conc. H_2SO_4 was added to a sodium tellurite solution (20 ml, 0.1 M) and to this solution, 50 mM ligand in methanol was added with stirring. A thick red solution resulted at first, which on continuous stirring gave a yellow solid. This was separated by filtration, washed with water, methanol and acetone and dried over $CaCl_2$. Yield 90%. *d* spacings (Å): 9.26s, 6.73s, 5.66w, 4.85m, 4.32s, 3.24s, 3.06m, 2.91w, 2.88w, 2.69m, 2.63m, 2.51s, 2.36s, 2.31s, 2.11s, 2.04w, 2.00w, 1.95m, 1.92m, 1.87w, 1.81s, 1.75w, 1.70s, 1.55m, 1.35m.

5. Diiodobis(methyl β-hydroxyethyldithiocarbamato) tellurium(IV)$[TeL_2I_2]$:

Crystals of TeL_3Cl were dissolved in 30 ml methanol and potassium iodide, also in methanol, was added to this solution in molar ratio 1:5. On stirring and cooling a precipitate formed that was separated by filtration. The complex was recrystallized from hot methanol. The reddish orange crystals were dried over H_2SO_4. Yield: ~70%. *d* spacings (Å): 8.76s, 6.89s, 5.75m, 4.75m, 4.55w, 4.08s, 3.77s, 3.71w, 3.49m, 3.15m, 3.03s, 2.80vs, 2.62m, 2.47m, 2.33s, 2.24m, 2.03w, 1.85m.

6. Bis(methyl β-hydroxyethyldithiocarbamato)tellurium(II) $[TeL_2]$:

This complex was prepared by interaction of $[Te(NH_2CSNH_2)_4]Cl_2$ with methyl β-hydroxyethyldithiocarbamate. The starting material $[Te(tu)_4]Cl_2$, where tu = thiourea, was prepared as follows: 30 mM of tellurium dioxide was dissolved in 10 ml conc. HCl and diluted to 50 ml with water. The solution was treated with 100 ml of 1.5 M aq. thiourea with constant stirring. The solid $[Te(tu)_4]Cl_2$ formed was filtered and washed with 2N HCl containing 0.5% thiourea.

10 mM of the tellurium-thiourea complex was suspended in 50 ml methanol, in which was dissolved one gram of thiourea and to this were added slowly 20 ml of 20% aqueous methanol solution containing 50 mM of methyl β-hydroxyethyldithiocarbamic acid. The thiourea complex dissolved completely under these conditions and after 20–30 minutes needle shaped yellow crystals of TeL_2 were separated out. These were recrystallized from methanol and dried over H_2SO_4. Yield ~60%. *d* spacings (Å): 8.35s, 5.70s, 4.02vs, 3.41w, 3.11m, 2.86s, 2.37s, 2.29w, 2.17w, 2.02m, 1.78w, 1.66w.

7. Bis(methyl β-hydroxyethyldithiocarbamato)selenium(II) $[SeL_2]$:

0.5 mM selenium dioxide was dissolved in 5 ml acetic acid and the solution diluted to 400 ml and the pH adjusted to 4. The solution containing 4 mM of the ligand was added with stirring. A yellow crystalline solid was precipitated immediately on addition. This was filtered, washed with water, acidified by acetic acid and recrystallized from hot methanol. Yield: ~90%. As in the case of interaction of other dithiocarbamates with Se(IV), (6,9,10), the methyl β-hydroxyethyldithiocarbamic acid reduces Se(IV) to Se(II) and stabilizes the Se(II) oxidation state. *d* spacings (Å): 8.23s, 5.72s, 4.29w, 3.79s, 3.16w, 2.84s, 2.39m, 1.77w.

Physical measurements

The X-ray powder patterns of the crystalline complexes were taken in a Philips 114.6 mm diameter camera using CuK_α radiation. Conductance measurements were made in 10^{-3} M solution in methanol at 25°C using a Philips conductivity bridge, Model PR 9500. The molecular weight measurements were with a Knauer's Vapour Phase Osmometer with methanol as solvent at concentration ranges of solutes 0.01 to 0.05 M. A Gouy Balance was used to examine the magnetic characteristics. Electronic spectra were recorded in methanolic solution (10^{-3}–10^{-5} M) using a Carl Zeiss DMR-21 Recording Spectrophotometer. The infrared spectra were recorded in KBr discs using Perkin-Elmer 257 Spectrophotometer (4000–625 cm^{-1}). Far infrared spectra (600–200 cm^{-1}) were recorded using Beckman IR-12 Grating Spectrophotometer.

The elemental analyses were made using standard micro- and macro-analytical methods.

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