ELSEVIER

Journal of Organometallic Chemistry 577 (1999) 243–248

Journal of Organo metallic Chemistry

Synthesis and characterization of monomeric tellurolato complexes of zinc and cadmium: crystal and molecular structure of bis[2-(4,4-dimethyl-2-oxazolinyl)phenyl]ditelluride

G. Mugesh [a], Harkesh B. Singh [a,*], Ray J. Butcher [b]

[a] *Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400 076, India*
[b] *Department of Chemistry, Howard University, Washington DC 20059, USA*

Received 12 August 1998

Abstract

The synthesis and characterization of homoleptic zinc(II) and cadmium(II) tellurolates incorporating the intramolecularly chelating oxazoline ligand are described. The derivatives, M[Te(Ox)]$_2$ [M = Zn (**4**) or Cd (**5**) and Ox = 2-(4,4-dimethyl-2-oxazolinyl)phenyl], are prepared in good yield via the metathesis reactions of MCl_2 with lithium arenetellurolate, $OxTe^-Li^+$ (**2**). Attempts to synthesise the mercury complex led to isolation of the corresponding ditelluride (**3**). Crystal structure of the ditelluride was determined by X-ray diffraction method. Of particular interest in the structure is the intramolecular interaction of the sp^2 nitrogen with the tellurium. The strength of the Te...N nonbonded interactions in this compound [Te(1)...N(1): 2.864(5), Te(2)...N(2): 2.694(5) Å] is found to be stronger than the similar interactions found in related compounds. The zinc and cadmium complexes are quite stable in the solid state and highly soluble in common non-polar organic solvents. The variable temperature NMR spectra of Zn[Te(Ox)]$_2$ (**4**) and Cd[Te(Ox)]$_2$ (**5**) show the complexes to be chiral at low temperatures. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Intramolecular coordination; Ditelluride; Monomeric tellurolates; Chirality

---

1. Introduction

The chalcogenolate derivatives of Group 12 elements have recently attracted considerable attention because of their potential use as single source precursors to Group 12–16 semiconductors [1]. Unfortunately, the development of the molecular chemistry of these compounds has been slow as the precursors are frequently insoluble in common organic solvents due to the formation of non-crystalline polymers through bridging of the chalcogenolate ligands, and are therefore, difficult to purify and characterize. A number of synthetic approaches have been used to reduce the ligand association and enhance the volatility of the compounds. Although the introduction of bulky substituents has proved very effective in preventing higher degrees of aggregation in metal chalcogenolato complexes of the type M(ER)$_2$ [2], the complexes are known to involve in a reductive elimination process to give the dichalcogenide and elemental metal. The other approach reported in the literature to prepare volatile precursors involves saturating the metal coordination sphere with neutral donor ligands [3]. However, although evidently even weak donor ligands are capable of producing monomeric complexes, the use of such compounds as volatile precursors is limited due to the facile dissociation in the first step of the thermolysis process.

However, the introduction of chalcogenolate ligands having covalently attached donor atoms is highly effective in reducing the ligand dissociation process and thereby increasing the volatility of the complexes [4]. In

---

* Corresponding author. Fax: +91-22-578-3480.
E-mail address: chhbsia@chem.iitb.ernet.in (H.B. Singh)

PII: S0022-328X(98)01069-9

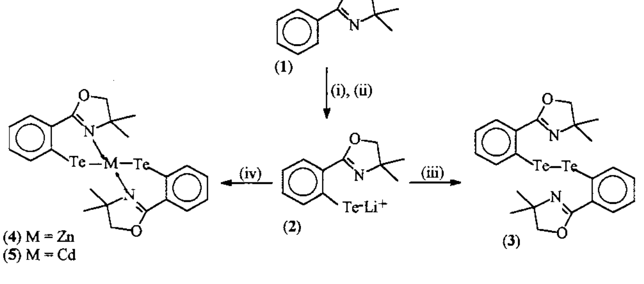
continuation of our work on intramolecularly coordinated organochalcogens [5], we have recently isolated some stable monomeric mercury selenolates using *ortho*-chelating *N*,*N*-dimethylaminobenzyl and *N*,*N*-dimethylaminoethyl ferrocenyl ligands [6] and well-characterized examples of zinc, cadmium and mercury thiolato and selenolato complexes by using a more rigid 4,4-dimethyl-2-phenyloxazoline substrate [7]. Interestingly, the zinc thiolato [7a] and selenolato [7b] complexes were found to be chiral at room temperature (r.t) and the cadmium thiolate and selenolate showed chirality at low temperatures. It was thought worthwhile to extend our approach to the heaviest chalcogen, tellurium. Although several metal thiolates and selenolates are known, the metal tellurolates are highly limited due to their instability [8,9]. In this paper we describe the synthesis and characterization of zinc and cadmium tellurolato complexes by using the more rigid 4,4-dimethyl-2-phenyloxazoline substrate. Attempts to synthesize the corresponding mercury tellurolate complex were unsuccessful.

2. Results and discussion

2.1. Synthesis

Synthesis of ditelluride (**3**) was accomplished by the 'ortholithiation' route. Ortholithiation of **1** with *n*-BuLi afforded the aryllithium compound which was further reacted with finely powdered tellurium powder to give the corresponding lithium arenetellurolate (**2**). Oxidative workup of **2** gave the diaryl ditelluride **3**. Synthesis of the tellurolate complexes was approached by the metathesis reaction of the lithium arenetellurolate with the corresponding MCl_2 in ether (Scheme 1) according to our recently reported method for the synthesis of metal selenolates [7b].

The 2:1 molar reactions of $OxTe^-Li^+$ (**2**) and anhydrous MCl_2 ($M = Zn$, Cd) in ether afforded the desired complexes (**4**, **5**) in good yields. The reaction of $OxTe^-Li^+$ (**2**) and $HgCl_2$ did not give the expected mercury complex, instead it gave the ditelluride (**3**). Although there was some indication of the formation of mercury tellurolate in solution, the compound decomposed upon exposure to air to give the ditelluride and elemental mercury. Recently, we have shown that pure monomeric mercury selenolate complexes were best obtained in two further steps, whereby the lithium areneselenolate was oxidized to the diselenide (which is air stable and readily purified), followed by a oxidative addition of mercury [6,7b]. However, attempts to synthesize the mercury tellurolate complex by the reaction of ditelluride (**3**) and elemental mercury were also unsuccessful. The reaction of elemental mercury with ditelluride afforded, after 24 h stirring, a yellow powder which analyzed for the ditelluride. This is in accordance with the recent reports that the oxidative addition of dichalcogenides to elemental mercury is a reversible process and the equilibrium position depends on R, the chalcogenide E and the temperature ([9]d, [10]). In some cases, for example in $Hg(TeC_6H_2i\text{-}Pr_3)_2$, even changes in solvent polarity were found to be enough to shift the equilibrium towards the left [10].



Scheme 1. Synthesis of M(II) complexes. Reagents and conditions: (i) *n*-BuLi, hexane, r.t., 1 h; (ii) Te powder, ether, 0°C, 2 h; (iii) O_2, H_2O; (iv) anhydrous, MCl_2, 0°C, 1 h and r.t., 18 h.

The complexes have excellent solubility in both nonpolar and slightly polar solvents. They are, however, almost insoluble in highly polar solvents like DMSO and methanol. In contrast to the thiolato and selenolato complexes derived from the phenyloxazoline substrate, the tellurolato complexes were found to be unstable in solution and decomposed over a period of time to give the ditelluride.

2.2. NMR spectroscopic studies

In order to confirm the monomeric nature of the complexes in solution, we have studied in detail the ^1H-, ^{13}C- and ^{125}Te-NMR spectra in $CDCl_3$. The r.t. ^1H-NMR spectrum of complex **4** contains an AB pattern for the methylene protons, indicative of an inequivalence of the geminal protons in the molecule. Although the AB pattern is not well resolved, its observation implies that the strong coordination of the imine 'hard' nitrogen with 'hard' zinc(II) removes the erstwhile enantiotopic nature of the methylene protons. The protons become diastereotopic and the complexes chiral. The broad AB pattern becomes well resolved at − 60°C. The two broad signals observed for the methyl protons also become sharper at this temperature. Upon heating above r.t. the spectrum observed for **4** collapses into two sharp singlets (Fig. 1). For the cadmium tellurolate complex **5**, the signals due to the methyl and methylene protons are very broad at r.t. and resolve into two singlets and an AB pattern, respectively at − 60°C. This indicates the existence of a 'helical' arrangement of atoms at low temperatures and fast exchange between the 'helical-' 'non-helical' arrangements at higher temperatures. This is consistent with our

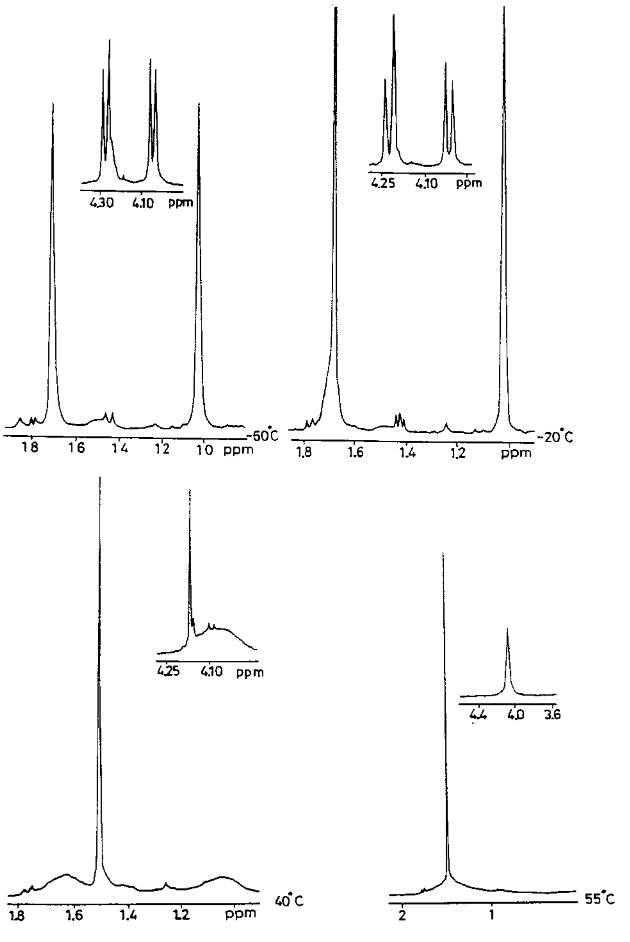


Fig. 1. Variable temperature ^{1}H-NMR ($CDCl_3$, 300 MHz) spectra (in part only) of **4**. At -60°C, the signals due to the $-CH_2-$ and $-CH_3$ protons split into an AB pattern and two singlets, respectively.

recent report that the zinc selenolate showed 'helical' chirality at r.t. whereas the cadmium selenolate showed chirality only at low temperatures [7].

The chemical shift values in all the complexes are observed almost in the same region and there is no drastic change in the chemical shift values by changing the metal atom. However, the signals due to methyl and methylene protons are shifted upfield compared with the corresponding ditelluride (**3**) probably due to the d^{10} configuration of the metals. The ^{13}C-NMR spectra of the complexes are not very informative. The chemical shift values for methyl and methylene carbons are almost equal to the values observed for the ditelluride. In order to understand the effect of coordination on the tellurium chemical shifts, we have recorded ^{125}Te-NMR for the complexes **4**, and **5** as ^{125}Te is a very sensitive NMR nucleus and it is easily influenced by its chemical environment. The ^{125}Te chemical shifts for the tellurolato complexes (**4** and **5**) are in the range δ 164.3–215.5 ppm. The chemical shifts for these complexes are shifted upfield compared with the ditelluride (417.03 ppm). Interestingly, for complex **4**, two signals appear at 164.3 and 164.4 ppm relative to Me_2Te at r.t. and indicate non-equivalence of the two tellurium atoms present in the complex. It is worth mentioning that the analogous zinc selenolate complex also showed two signals in the ^{77}Se-NMR spectrum [7b]. For the Cd complex (**5**), the singlet at 215.5 ppm is indicative of the equivalence of the tellurium nuclei and hence 'non-helical' environment at r.t. In complex **5**, coupling of ^{125}Te to the 12.3% abundant ^{113}Cd ($I = 1/2$) was observed at r.t. ($J_{^{125}Te-^{113}Cd}$: 317.5 Hz).

From the above observations it is clear that the zinc and cadmium complexes are monomeric in solution. Although the complexes (**4** and **5**) are very stable in the solid state these are found to be unstable in solution if the solution is kept for long time. The complexes decomposed over a period of ca. 2 h to give signals for the ditelluride.

2.3. Mass spectroscopic studies

The mass spectra of compound **4** and **5** are indicative of the presence of a higher molecular species in the gas phase. **4**; m/z 671, $Zn(TeOx)_2^+$; m/z 972, $Zn(TeOx)_3^+$, m/z 1036, $Zn_2(TeOx)_3^+$; **5**; m/z 718, $Cd(TeOx)_2^+$, m/z 1021; $Cd(TeOx)_3^+$, m/z 1133, $Cd_2(TeOx)_3^+$. This is not surprising because the structurally characterized monomeric zinc and cadmium selenolates also showed similar behavior under mass spectroscopic conditions [7b]. The primary organic product Ox–Te–Ox was observed in the mass spectrum and indicates the formation of MTe (M = Zn, Cd) under mass spectroscopic conditions. The molecular ion peaks and the peaks due to other fragments containing Te and M exhibit the expected isotope patterns.

2.4. Molecular structure of compound 3

An ORTEP [11] view of compound **3** with atom numbering is shown in Fig. 2. Some details of data collection and refinement are given in Table 1. Selected bond distances and angles are in Table 2. Compound **3**

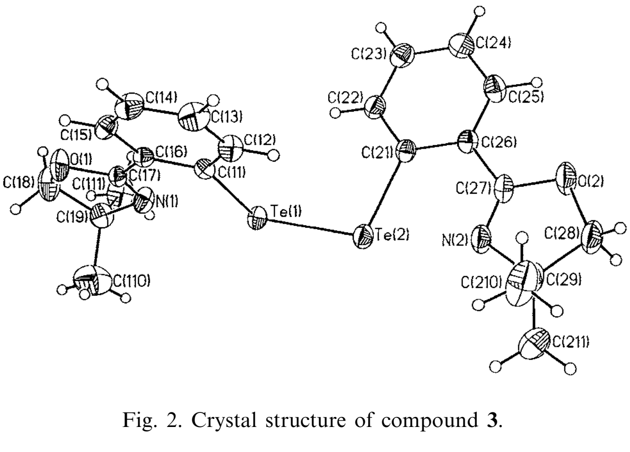


Fig. 2. Crystal structure of compound **3**.

Table 1
Crystal data and structure refinement for **3**

	Compound
Empirical formula	$C_{22}H_{24}N_2O_2Te_2$
Formula weight	603.63
Crystal system	Rhombohedral
Space group	$R\overline{3}$
Unit cell dimensions	
a (Å)	34.180(2)
b (Å)	34.180(2)
c (Å)	10.6640(11)
α (°)	90
β (°)	90
γ (°)	120
V (Å^3)	10789.3(14)
Z	18
$D_{\mathrm{calc.}}$ (Mg m^{-3})	1.672
Temperature (K)	293(2)
λ (Å)	0.71073
Absorption coeff. (mm^{-1})	2.451
Observed reflections [$I > 2\sigma$]	5631
Final $R(F)$ [$I > 2\sigma$]^a	0.0409
wR (F^2) indices [$I > 2\sigma$]	0.0838
Data/restrains/parameters	5631/0/281
Goodness of fit on F^2	1.04

[a] Definitions: $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR(F_o^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_c^2)^2\}^{1/2}$.

crystallizes in a rhombhohedral system with 18 molecules per unit cell. The coordination geometry around the tellurium atoms is distorted T-shaped with each tellurium atom bonded to a tellurium, a carbon and a nitrogen atom. The Te(1)–Te(2) distance of 2.7387(5) Å relates well to the corresponding distances reported for other ditellurides which normally range from 2.665 to 2.746 Å [12,13]. This distance is close to the distance reported for related compounds, bis(2-naphthyl)ditelluride [2.7179(6) Å] [14]. The Te–C bond lengths [Te(1)–C(11) 2.136(4), Te(2)–C(21) 2.151(5) Å] are also in agreement with the value of 2.14 Å suggested by Pauling [15] and a typical value for other ditellurides such as di(2-naphthyl) ditelluride [2.135(6), 2.127(5) Å and 8-(dimethylamino)-1-naphthyl ditelluride [2.130(5) Å, 2.126(5) Å] [12]. The interesting feature in this structure is the strong intramolecular interaction of the tertiary nitrogen with the tellurium. Atomic distances of Te(1)...N(1) and Te(2)...N(2) are 2.864(5), 2.694(5) Å, respectively, both of which are larger than the sum of their covalent radii but significantly shorter than the sum of the corresponding van der Waals radii (3.61 Å). In fact the Te...N distances in this ditelluride are shorter than those recently reported for bis[2-(hydroxyiminomethyl)phenyl] ditelluride [2.822 and 2.876 Å] where the nitrogen is also in sp^2 state [16]. It is known that diaryl ditellurides exhibit 'conformational polymorphism' in the solid state [14]. The '*cisoid*' conformations show the torsion angle C–Te–Te–C < 90° and the '*transoid*' conformations show the torsion angle C–Te–Te–C > 90°. In the case of **3**, the torsion angle C(11)–Te(1)–Te(2)–C(21) is −84.4° and, therefore, the conformation can be termed as '*cisoid*'. The unequal Te...N bond distances [Te(1)...N(1): 2.864(5), Te(2)...N(2): 2.694(5) Å] indicate that the steric effects may play an important role.

Table 2
Significant bond lengths (Å) and angles (°) for **3**

Bond lengths (Å)			
Te(1)–C(11)	2.136(4)	Te(2)–C(21)	2.151(5)
O(1)–C(17)	1.360(5)	O(1)–C(18)	1.441(7)
O(2)–C(27)	1.352(6)	O(2)–C(28)	1.457(7)
N(1)–C(17)	1.249(6)	N(l)–C(19)	1.486(6)
N(2)–C(27)	1.252(6)	N(2)–C(29)	1.475(6)
Te(1)–Te(2)	2.7387(5)		
Bond angles (°)			
C(11)–C(21)–Te(2)	119.8(3)	C(12)–C(11)–Te(1)	120.1(4)
C(11)–Te(1)–Te(2)	100.75(2)	C(16)–C(11)–Te(1)	121.4(3)
C(21)–Te(2)–Te(1)	99.08(12)	C(22)–C(21)–Te(2)	121.9(4)

3. Experimental section

3.1. General procedures

All reactions were carried out under nitrogen or argon using standard vacuum-line techniques. Solvents were purified by standard procedures [17] and were freshly distilled prior to use. Mercury and $ZnCl_2$ were purified prior to use [17]. Commercially available $CdCl_2$ and $HgCl_2$ were used as received. Melting points were recorded in capillary tubes and are uncorrected. ^{1}H-, ^{13}C- and ^{125}Te-NMR spectra were obtained at 300, 75.42 and 94.75 MHz, respectively in $CDCl_3$ on a Varian VXR 300S spectrometer. Chemical shifts are cited with respect to $SiMe_4$ as internal (^{1}H and ^{13}C) and Me_2Te (^{125}Te) as external standard. Elemental analyses were performed on a Carlo-Erba model 1106 elemental analyzer. Fast atom bombardment (FAB) mass spectrum was recorded at r.t. on a JEOL SX 102 DA-6000 mass spectrometer/data system using xenon (6 kV, 10 mV) as the bombarding gas. The acceleration voltage was 10 kV and *m*-nitrobenzyl alcohol was used as the matrix with positive-ion detection. In case of isotopic patterns the value given is for the most intense peak.

3.1.1. Synthesis of Ox_2Te_2 (**3**)

To a suspension of 4,4-dimethyl-2-oxazolinylphenyl lithium [7b] in ether (10 mmol), elemental tellurium (1.28 g, 10 mmol) was added rapidly at 0°C. After 3 h, all tellurium was consumed to give a brown solution of lithium arenetellurolate (**2**). To this, air was passed for 15 min and then the reaction mixture was poured into a beaker containing cold distilled water (50 ml) and kept for 3 h to effect complete oxidation. The resulting organic layer and ether extracts from the aqueous layer were combined, dried over anhydrous sodium sulfate and concentrated in vacuo to give a viscous yellow oil. Addition of CCl_4 to the yellow oil afforded a yellow solid of the desired product. Recrystallization of the crude from chloroform/methanol (1:1) afforded **3** as yellow needles. Yield: 1.32 g, (44%), m.p. 150–152°C;. Anal. Calc. for $C_{22}H_{24}N_2O_2Te_2$: C, 43.74; H, 3.98; N, 4.64; Found: C, 43.23; H, 3.27; N, 4.12. ^{1}H-NMR, 1.41(s), 4.29(s), 7.24–7.29(t), 7.49–7.59(t), 7.78–7.83(d), 8.32–8.36(d). ^{13}C-NMR 28.98, 68.14, 79.67, 113.82, 126.49, 128.67, 131.38, 138.25, 162.45. ^{125}Te-NMR 417.03.

3.1.2. Synthesis of Zn[Te(Ox)]$_2$ (4)

To a suspension of 4,4-(dimethyl-2-oxazolinyl)phenyl lithium in ether (10 mmol), elemental tellurium (1.28 g, 10 mmol) was added rapidly at 0°C. After 3 h, all tellurium was consumed to give a brown solution of lithium arenetellurolate (**2**). To this, anhydrous $ZnCl_2$ (0.68 g, 5 mmol) was added and the stirring was continued for additional 1 h at 0°C and 18 h at r.t. The resulting solution was filtered via Celite and evaporated to give a bright yellow compound. The compound could not be recrystallized due to its instability in solution. Yield: 1.0 g (30%), m.p. 180–182°C, Anal. Calc. for $C_{22}H_{24}N_2O_2Te_2Zn$: C, 39.49; H, 3.59; N, 4.19; Found: C, 38.68; H, 3.53; N, 3.85. ^{1}H-NMR 0.76(s, br), 1.46(s, br), 3.19(s, br), 3.28(s, br), 6.60–6.65(t), 6.83–6.89(t), 7.80–7.83(d), 8.41–8.44(d). ^{13}C-NMR 26.36, 69.27, 79.04, 116.70, 125.08, 130.38, 130.80, 131.88, 144.30, 168.94. ^{125}Te-NMR 164.28, 164.42. MS: *m/z* 1036 $(C_{33}H_{36}N_3O_3Te_3Zn_2)^+$, 972 $(C_{33}H_{36}N_3O_3Te_3Zn)^+$, 671 $(M^+, C_{22}H_{24}N_2O_2Te_2Zn)^+$, 605 $(C_{22}H_{24}N_2O_2Te_2)^+$, 477 $(C_{22}H_{24}N_2O_2Te)^+$, 368 $(C_{11}H_{12}NOTeZn)^+$, 304 (100%, $C_{11}H_{12}NOTe)^+$.

3.1.3. Synthesis of Cd[Te(Ox)]$_2$ (5)

Compound **5** was prepared following the method described for **4** using 1.79 g (1.75 ml, 10 mmol) of 4,4-dimethyl-2-phenyloxazoline, 6.8 ml (11 mmol) of 1.6 M solution of *n*-BuLi and 0.917 g (5 mmol) of anhydrous $CdCl_2$. The compound could not be recrystallized due to its instability in solution. Yield: 1.25 g (35%), m.p. 186–188°C, Anal. Calc. for $C_{22}H_{24}N_2O_2Te_2Cd$: C, 36.89; H, 3.35; N, 3.91; Found: C, 36.23; H, 3.34; N, 3.33. ^{1}H-NMR 1.21(s, br), 4.05(s), 6.95–7.00(t), 7.10–7.17(t), 7.57–7.60(d), 8.23–8.27(d). ^{13}C-NMR 28.06, 68.81, 79.71, 111.19, 125.54, 128.35, 130.53, 130.71, 144.70, 167.89. ^{125}Te-NMR: 215.50, ($J_{125Te-113Cd}$: 317.5 Hz), MS: *m/z* 1130, $(C_{33}H_{36}N_3O_3Te_3Cd_2)^-$; 1020, $Cd(TeOx)_3^+$; 717, $Cd(TeOx)_2^+$, 605 $(C_{22}H_{24}N_2O_2Te_2)^+$, 304 (100%), $C_{11}H_{12}NOTe^+$.

3.1.4. Attempted synthesis of Hg[Te(Ox)]$_2$

To the lithium arenetellurolate prepared as described above was added anhydrous $HgCl_2$ (1.358 g, 5 mmol) and stirring was continued for additional 1 h at 0°C, followed by 24 h at r.t. The resulting solution was filtered through Celite and evaporated to give a yellow compound which was characterized as the ditelluride (**3**). Yield: 1.8 g (60%).

3.2. X-ray crystallographic studies

The diffraction measurements for compound **3** were performed at r.t. (293 K) on a Siemens R3 m/V diffractometer using graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.7170$ Å). The unit cell was determined from 25 randomly selected reflections using the automatic search index and least-squares routine. For **3**, the θ range for data collection was from 2.64 to 28.00°. The index range for **3** was $0 \le h \le 42$, $-45 \le k \le 0$, $0 \le l \le 14$. The data were corrected for Lorentz, polarization and absorption effects. The maximum and minimum transmission values of the correction factors for compound **3** (dimensions $0.18 \times 0.80 \times 0.20$ mm) were 0.6984 and 0.5075, respectively. The data were monitored by measuring two standard reflections every 60 min of X-ray exposure time. The structure **3** was solved and refined using SHELXTL program [18]. The hydrogens were partially located from difference electron-density maps and the rest were fixed at calculated positions. Scattering factors were from common sources [19].

Acknowledgements

We are grateful to the Board of Research in Nuclear Sciences (BRNS), Department of Atomic Energy, Bombay and Department of Science and Technology (DST), New Delhi, for funding this work. Additional help from the Regional Sophisticated Instrumentation Centre (RSIC), Indian Institute of Technology (IIT), Bombay for the 300 MHz NMR spectroscopy and Tata Institute of Fundamental Research (TIFR), Bombay for the 500 MHz NMR spectroscopy is gratefully acknowledged. R.J. Butcher wishes to acknowledge the DoD-ONR program for funds to upgrade the diffractometer.

References

[1] (a) J. Arnold, J.M. Walker, K.M. Yu, P.J. Bonasia, A.L. Seligson, E.D. Bourret, J. Cryst. Growth, 124 (1992) 647. (b) P. O'Brien, Chemtronics 5 (1991) 61. (c) J.G. Brennan, T. Siegrist,

P.J. Carroll, S.M. Struczynski, L.E. Brus, M.L. Steigerwald, J. Am. Chem. Soc. 111 (1989) 4141. (d) K. Osakada, A. Yamamoto, Inorg. Chem. 30 (1990) 2328. (e) K. Osakada, T. Yamamoto, J. Chem. Soc. Chem. Commun. (1987) 1117. (f) R.J. Kern, J. Am. Chem. Soc. 75 (1953) 1865. (g) M.E. Peach, J. Inorg. Nucl. Chem. 35, (1973) 1046. (h) M.E. Peach, J. Inorg. Nucl. Chem. 41 (1979) 1390. (i) D. Craig, I. Dance, R. Garbutt, Angew. Chem. Int. Ed. Engl. 25 (1986) 165. (j) I. Dance, R. Garbutt, D. Craig, M. Scudder, Inorg. Chem. 26 (1987) 4057. (k) H.B. Singh, N. Sudha, Polyhedron 15 (1996) 745.

[2] (a) M. Bochmann, K. Webb, M. Harman, M.B. Hursthouse, Angew. Chem. Int. Ed. Engl. 29 (1990) 638. (b) M. Bochmann, K.J. Webb, J. Chem. Soc. Dalton Trans. (1991) 2325. (c) A.L. Seligson, J. Arnold, J. Am. Chem. Soc. 115 (1993) 8214. (d) J.J. Ellison, K Ruhlandt-Senge, H.H. Hope, P.P. Power, Inorg. Chem. 34 (1995) 49. (e) P.J. Bonasia, J. Arnold, Inorg. Chem. 31 (1992) 2508. (f) P.P. Power, S.C. Shoner, Angew. Chem. Int. Ed. Engl. 29 (1990) 1403. (g) M. Bochmann, G.C. Bwembya, R. Grinter, J. Lu, K.J. Webb, M.B. Hursthouse, M.A. Mazid, Inorg. Chem. 32 (1993) 532. (h) M. Bochmann, K.J. Webb, M.B. Husthouse, M.A. Mazid, J. Chem. Soc. Dalton Trans. (1991) 2317.

[3] (a) M. Bochmann, G.C. Bwembya, R. Grinter, A.K. Powell, K.J. Webb, M.B. Hursthouse, K.M.A. Malik, M.A. Mazid, Inorg. Chem. 33 (1994) 2290. (b) D.E. Gindelberger, J. Arnold, Inorg. Chem. 33 (1994) 6293.

[4] (a) Y. Cheng, T.J. Emge, J.G. Brennan, Inorg. Chem. 35 (1996) 342. (b) Y. Cheng. T.J. Emge, J.G. Brennan, Inorg. Chem. 35 (1996) 7339. (c) Y. Cheng, T.J. Emge, J.G. Brennan, Inorg. Chem. 33 (1994) 3711.

[5] (a) H.B. Singh, N. Sudha, Coord. Chem. Rev. 135–136 (1994) 469. (b) V. Regini, R. Kaur, N. Sudha, S.C. Menon, H.B. Singh, Proc. Indian Acad. Sci. (Chem. Sci.) 107 (1995) 431. (c) R. Kaur, H.B. Singh, R.J. Butcher, Organometallics 14 (1995) 4755. (d) R. Kaur, S.C. Menon, H.B. Singh, Proc. Indian Acad. Sci. (Chem. Sci) 108 (1996) 159. (e) S.C. Menon, H.B. Singh, R.P. Patel, K. Das, R.J. Butcher, Organometallics 18 (1997) 563.

[6] R. Kaur, H.B. Singh. R.P. Patel, S.K. Kulshreshtha, J. Chem. Soc. Dalton Trans. (1996) 461.

[7] (a) G. Mugesh, H.B. Singh, R.J. Butcher, Eur. J. Inorg. Chem., submitted for publication. (b) G. Mugesh, H.B. Singh, R.P. Patel, R.J. Butcher, Inorg. Chem. 37 (1998) 2663.

[8] (a) M.L. Steigerwald, C.R. Sprinkle, J. Am. Chem. Soc. 109 (1987) 7200. (b) J.G. Brennan, T. Siegrist, P.J. Carroll, S.M. Struczynski, L.E. Brus, M.L. Steigerwald, J. Am. Chem. Soc. 111 (1989) 4141. (c) J.G. Brennan, T. Siegrist, S. Stuczynski, C. Carroll, L. Brus, M.L. Steigerwald, Chem. Mater. 2 (1990) 403.

[9] (a) M. Bochmann, A.P. Coleman, K.J. Webb, M.B. Hursthouse, M. Mazid, Angew. Chem. Int. Ed. Engl. 30 (1991) 973. (b) B.O. Dabbousi, P.J. Bonasia, J. Arnold, J. Am. Chem. Soc. 113 (1991) 3186. (c) J. Arnold, The Chemistry of Metal Complexes with Selenolate and Tellurolate Ligands, in: K.D. Karlin (Ed.), Progress in Inorganic Chemistry, vol. 43, Wiley, New York, 1995, p. 353. (d) M. Bochmann, Chem. Vap. Depos. 2 (1996) 85. (e) T. Chivers, J. Chem. Soc. Dalton Trans. (1996) 1185.

[10] Y. Okamoto, T. Yano, J. Organomet. Chem. 29 (1971) 99.

[11] C.K. Johnson, ORTEPII, Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

[12] S.C. Menon, H.B. Singh, J.M. Jasinski, J.P. Jasinski, R.J. Butcher, Organometallics 15 (1996) 1707.

[13] S. Kalyankumar, H.B. Singh, K. Das, U.C. Sinha, J. Organomet. Chem. 397 (1990) 161.

[14] D.J. Sandman, L. Li, S. Tripathy, J.C. Stark, L.A. Acampora, B.M. Foxman, Organometallics 13 (1994) 348.

[15] L. Pauling, in: The Nature of the Chemical Bond, 3rd ed., Cornell University Press, Ithaca, New York, 1960, p. 224.

[16] K.Y. Abid, N.I. Al-Salim, M.R. Greaves, W.R. McWhinnie, A.A. West, T.A. Hamor, J. Chem. Soc. Dalton Trans. (1989) 1697.

[17] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, 2nd ed., Pergamon, Oxford, 1980.

[18] G.M. Sheldrick, SHELXTL, Version 5.03, Siemens Analytical X-Ray Division, Madison, WI, 1994.

[19] International Tables for X-ray Crystallography, vol. 4, Kynoch Press, Birmingham, 1974, pp. 99, 149.