International Journal of Science and Research (IJSR)
ISSN: 2319-7064
Impact Factor 2025: 7.089

Diethyl Tellurium Morpholine Dithiocarbamate: Synthesis, Structural Elucidation and Te-C bond Cleavage

Vikas Singh

Department of Chemistry, National P.G. College, Lucknow 226001, India
Corresponding Author Email: *vikasnpgc2013[at]gmail.com*

Abstract: ***Sulfur-ligated tellurium complexes continue to attract considerable attention owing to their intriguing stereochemical behaviour and supramolecular associations. In this work, diethyl tellurium diiodide, [$(C_2H_5)_2TeI_2$] was reacted with ammonium salt of morpholine dithiocarbamates in dichloromethane. Remarkably, morpholine dithiocarbamates led to Te–C bond cleavage, yielding $Te(C_4H_{10}NO)$. The complexes were characterized by elemental analysis, FT-IR, ^1H, ^{13}C NMR spectroscopy, and single-crystal X-ray diffraction. Spectroscopic studies confirmed the presence of monodentate dithiocarbamate coordination in the bis-complexes. X-ray analyses revealed that $Te(C_4H_{10}NO)$ features Te–H agostic interactions and C–H···O hydrogen bonds leading to a hexameric supramolecular association. These findings provide the structural evidence for Te–C bond cleavage in acyclic diethyl tellurium (IV) systems, highlighting new pathways for organotellurium transformations and supramolecular assembly formation.***

Keywords: Sulfur tellurium complexes, supramolecular association, morpholine dithiocarbamate

1. Introduction

The sulfur ligated complexes of tellurium continue to be of great interest for their steriochemical aspects and supramolecular associations.[(1)] The complexes of tellurium in both its di- and tetravalent states with dithiocarbamates are well known.[(2-11)] Several reports on organotellurium(IV) compounds with 1,1-dithioligands have appeared on N,N-dialkyl dithiocarbamates,[(12-21)] but reports on related halo derivatives of the type Me_2TeXL have been limited to a few N,N-dialkyl dithiocarbamates.[(19)] The synthesis and characterization through the X-ray crystal structures of $Me_2TeX(S_2CNEt_2)$ (X=Cl, Br, I) were reported by Drake et.al.[(22)] The crystal molecular structure and solution NMR data of $MeTeI(S_2CNEt_2)_2$ have been reported by Dakternieks et. al.[(12)]

The reactions of organotelluriums involving cleavage of Te-C bonds are known but they are restricted to organotellurium(II) complexes. McWhinnie et al.[(23)] described the lability of organic groups from tellurium on reaction of organotellurium (II) with a series of metal compounds. Uemura et al.[(24)] reported a palladium catalysed cross coupling reaction between organic tellurides and alkenes involving cleavage of Te-C bonds. Recently Singh et al.[(25)] reported Te-C bond cleavage in the reactions of organotellurium(II) compounds with $HgCl_2$ and $Pt(COD)Cl_2$. The Te-C bond cleaved product was first reported by our group[(26)] through substitution reactions of organo (heterocyclic) tellurium(IV) derivatives.

Recently our group reported on diethyl tellurium bis(N,N-dialkyl dithiocarbamate) and cleavage of Te-C (acyclic) bond in the substitution reactions of diethyl tellurium diiodide[(27)]. We herein describe the synthesis, characterization and (FT-IR, ^1H, ^{13}C and ^{125}Te NMR) spectral studies of dithiocarbamate derivatives of diethyl tellurium diiodide [$(C_2H_5)_2TeI_2$]. The unusual Te-C scission occurs in the reaction between diethyl tellurium diiodide [$(C_2H_5)_2TeI_2$] and ammonium morpholine dithiocarbamate ($NH_4S_2CNC_4H_8O$) (1:2 molar ratio) and yields Te-C bond cleaved product $Te(C_4H_{10}NO)$. The structures of $Te(C_4H_{10}NO)$ have been determined through single crystal X-ray diffraction studies.

2. Experimental

2.1 Reagents, general procedure & instrumentation

Diethyl tellurium diiodide $(C_2H_5)_2TeI_2$[(27)] was prepared by the modification of literature method developed by us in our laboratory. Melting points were recorded in capillary tubes and are uncorrected. iodoethane, Te metal, and copper turnings were commercially obtained and used as received. The organic solvents were dried by usual methods before use. Microanalysis were carried out using a Heraeus Carlo Erba 1108 analyzer. Tellurium content was estimated volumetrically. FT-IR spectra were recorded using a Shimadzu 8210 PC FT-IR spectrometer in the frequency range 4000-350 cm^{-1} with the samples in KBr discs. ^1H and ^{13}C NMR spectra were recorded at 300 MHz in $CDCl_3$ solutions containing tetramethyl silane as internal standard on a Varian DRX 300 NMR spectrometer.

2.2 Synthesis

2.2.1. Synthesis of $(C_2H_5)_2Te(S_2CNC_4H_8O)_2$ (1) & $Te(S_2CNC_4H_8O)_2$ (2)

The solution of diethyl tellurium diiodide (1.00g, 2.27 mmol) in dry dichloromethane (~ 25 ml) was added drop wise to the suspensions of freshly prepared morpholine dithiocarbamate (0.40g, 4.54 mmol). It was stirred for ~4h at room temperature. The reaction mixture was filtered to eliminate the insoluble material. The filtrate was concentrated to ~10 ml under reduced pressure and kept overnight. The few transparent crystals were obtained along with creamish compound. The creamish residue was characterized through elemental and spectral analysis and it

corresponded to $(C_2H_5)_2Te[S_2CNC_4H_8O]_2$ (**1**) yield: 0.65g (56.03%), m.p. 118 ˚C. Anal. Calc. for $C_{14}H_{26}N_2O_2S_4Te$: C, 33.0; H, 5.1; N, 5.4; Te, 24.96. Found: C, 32.9; H, 5.0; N, 5.3; Te, 24.98 %, FT-IR (KBr, cm^{-1}): 1459, 1423 (CN), 1026, 995 (CS), 552 ($TeCH_2$); ^1H NMR (δ, ppm): 3.3 (4H, q, $TeCH_2$),1.8 (6H, t, $TeCCH_3$), 4.15 (8H, t, NCH_2), 3.70 (8H, t, OCH_2); ^{13}C NMR (δ, ppm): 31.19 (4H, s, $TeCH_2$), 10.90, 11.48, 13.57 (6H, t, $TeCCH_3$), 50.86 (8H, s, NCH_2), 66.14 (4H, s, OCH_2), 1997.66 (s, S_2CN); ^{125}Te NMR (δ, ppm): 976.672. The transparent crystals were analysed through X-ray diffraction study only and corresponded to Te-C bond cleaved product *$Te(S_2CNC_4H_8O)_2$* ***(2)*** yield: 0.01 g (0.86 %), m.p. 225 °C.

2.3 X-ray crystallography

A summary of the crystallographic, data collection and refinement parameters for *$Te(S_2CNC_4H_8O)_2$* ***(2),*** is given in Table 1. The crystals of **2** was mounted on a Goniometer Xcalibur, detector: MSC-Rigaku AKC6S diffractometer using graphite-monochromatic MoKα radiation (λ=0.71073 Å). The structure of **2** was solved in space group P 1 21/c1. The data were corrected for Lorentz, polarization and absorption effects. The structures were solved by routine heavy atom and Fourier methods (SHELXL-97)[28]. Non-hydrogen atoms were refined anisotropically by full-matrix least squares refinements on F^2, using the SHELXL-97 program with hydrogen atoms in idealized positions. ORTEP diagram of compound **2** is shown in Figs. 1. The details of supramolecular motifs is given in electronic supplementary information (ESI).

X-ray structure of $Te(C_4H_{10}NO)$ (2)

The X-ray structure analysis data of $Te(C_4H_{10}NO)$ at 200(2)K reveals that Te atom is bonded to one morpholine (C_4H_8O) group through N-H bond (NH_2 group). We believe that in the reaction of $(C_2H_5)_2TeI_2$ with ammonium morpholine dithiocarbamate (1:2) molar ratio; (i) $S_2CNC_4H_8O$ (morpholine dithiocarbamate) group is converted in to $H_2NC_4H_8O$ & CS_2 is given out and (ii) simultaneously cleavage of Te-C bonds as well as Te-I bonds of $(C_2H_5)_2TeI_2$ occurs giving Te metal. The free Te atom coordinates to $H_2NC_4H_8O$ through N-H bond which can be best described as agostic interaction which are very common in organo-transition metal chemistry involving coordinatively unsaturated transition metal with a C-H bond (resulting in Te---H interactions) (**Fig. 1**).

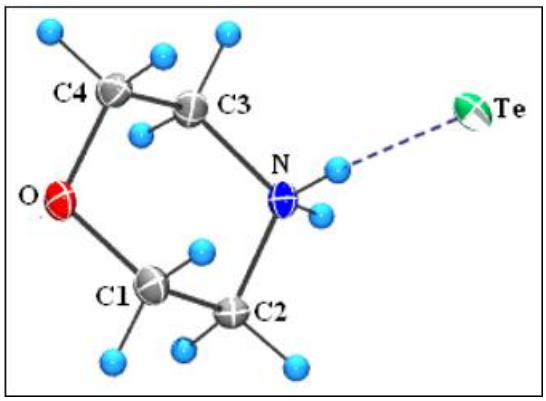

Figure 1: Crystal structure of $Te(C_4H_{10}NO)$

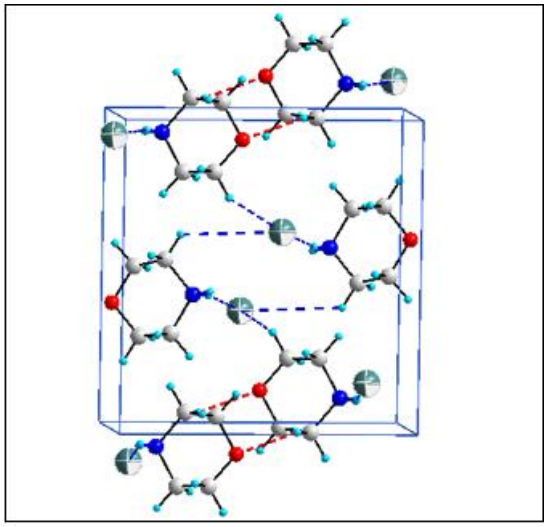

Figure 2: Hexameric supramolecular association of $Te(C_4H_{10}NO)$

In the unit cell of the complex $Te(C_4H_{10}NO)$ two types of dimers are formed through the $C(sp^3)$-H---O hydrogen bonds & intramolecular Te---H(1N) (2.648 Å) agostic interactions[29-31]. The $C(sp^3)$-H---O hydrogen bond related parameters are C(2)-O#1 = 3.615Å, H(2A)---O#1 = 2.625 Å and C(2)-H(2A)---O#1 = 150.89°. These are in close agreement with our first report on C-H---O hydrogen bonds in organotellurium complexes[32]. These dimeric units are joined together through intermolecular Te---H interactions [Te---H(2N)=3.126Å][29-31] resulting in the formation of hexameric supramolecular associations (**Fig. 2**).

Table 1: Crystallographic data and structure refinement details for complex **2**

	2
Formula	$C_4\ H_{10}\ N\ O\ Te$
Formula weight	215.73
T/K Wavelength (Å) Crystal system Space group	200(2) K 0.71073 Monoclinic P 1 21/c1
Unit cell dimension	
a (Å) b (Å)	6.6272(2) 10.4287(3)
c (Å)	102039(4)
α (˚)	90
β(˚)	98.885
γ(˚)	90
Volume($Å^3$)	696.76(4)
Z	4
ρ_c /Mg/m^{-3}) μ/mm^{-1} F(000) Crystal size (mm^3)	2.057 4.170 404 0.55 x 0.12 x 0.08
θ range (˚)	5.00-32.41
Reflns collected	11116
Completeness to θ_{max}(%)	98.6
Max., min. transmission	1.00000 and 0.56788
Refinement method	
Restraints/params GoF (F^2) Final R indices [I>2σ (I)] R indices (all data)	2352/0/64 0.888 R1=0.0233 wR2=0.0449 R1=0.0377 wR2=0.0467
Largest difference peak /hole (e/ Å)$^{-3}$	0.997 and -0.803

3. Conclusion

The synthesis and detailed characterization of diethyl tellurium bis (N, N-dialkyl dithiocarbamate) derivatives have revealed unprecedented Te–C bond cleavage in reactions of $[(C_2H_5)_2TeI_2]$ with ammonium piperidine and morpholine dithiocarbamates. Spectroscopic and crystallographic analyses confirm that the resultant products, $Te(S_2CNC_5H_{10})_2$ and $Te(C_4H_{10}NO)$, adopt distinct structural motifs stabilized by secondary Te···S, Te···H, and C–H···O interactions, leading to higher-order supramolecular assemblies. The study provides new insight into the reactivity of organotellurium (IV) compounds and expands the understanding of Te–C bond lability, potentially enabling the design of novel tellurium-based coordination and supramolecular systems.

Acknowledgment
The author gratefully acknowledges *National Post Graduate College, Lucknow* for providing financial support under the College Research Scheme. Sincere appreciation is also extended to the *Principal, National P.G. College, Lucknow* for providing the necessary facilities and valuable support during the course of this research work.

References

[1] I. Haiduc, R. B. King and M. G. Newton, Chem. Rev., 94 (1994) 301.
[2] C. Fabiani, R. Spagna, A. Vaciago and L. Zambonelli, Acta Cryst. B, 27 (1971) 1499.
[3] G. C. Raut, M. Seshasayee, K. Radha, G. Aravamudan, K. Goubitz and H. Schenk, Acta Cryst. C 39 (1983) 1021.
[4] V. Ganesh, M. Seshasayee, S. P. Chidambaram, G. Aravamudan, K. Goubitz and H. Schenk, Acta Cryst. C 45 (1989) 1506.
[5] V. Kumar, G. Aravamudan, M. Seshasayee, P. Selvam and K. Yvon, Acta Cryst. C 46 (1990) 2081.
[6] S. Husebye, Acta Chem. Scand., 24 (1970) 2198.
[7] S. Husebye and S. E. Svaeren, Acta Chem. Scand., 24 (1970) 2198.
[8] V. Kumar, G. Aravamudan, M. Seshasayee, P. Selvam and K. Yvon, Acta Cryst. C 46 (1990) 2100.
[9] G. C. Raut, M. Seshasayee, K. Radha, G. Aravamudan, K. Goubitz and H. Schenk, Acta Cryst. C 40 (1984) 1142.
[10] S. Husebye, Acta Chem. Scand. A 33 (1979) 485.
[11] S. Esperas and S. Husebye, Acta Chem. Scand. A 29 (1975) 185.
[12] D. Dakternieks, R. Di Giacomo, R. W. Gable and B. F. Hoskins, J. Am. Chem. Soc., 110 (1988) 6753.
[13] A. K. Singh and J. K. Asumatary, J. Organomet. Chem., 349 (1988) 305.
[14] J. H. E. Bailey, J. E. Drake, A. B. Sarkar and M. L. Y. Wong, Can. J. Chem., 67 (1989) 1735.
[15] J. H. E. Bailey, J. E. Drake, A. B. Sarkar and M. L. Y. Wong, Can. J. Chem., 69 (1991) 1948.
[16] J. E. Drake and M. L. Y. Wong, J. Organomet. Chem., 349 (1988) 305.
[17] S. Husebye, K. Maartmann-Moe and W. Steffenson, Acta Chem. Scand., 44 (1990) 139.
[18] S. Husebye, K. Maartmann-Moe and W. Steffenson, Acta Chem. Scand., 44 (1990) 579.
[19] J. H. E. Bailey and J. E. Drake, Can. J. Chem., 71 (1993) 42.
[20] D. Dakternieks, R. Di Giacomo, R. W. Gable and B. F. Hoskins, J. Organomet. Chem., 349 (1988) 305.
[21] D. Dakternieks, R. Di Giacomo, R. W. Gable and B. F. Hoskins, J. Am. Chem. Soc., 110 (1988) 6762.
[22] J. E. Drake, L. N. Khasrou, A. G. Mislankar and R. Ratnani, Inorg. Chem., 38 (1999) 3994.
[23] (a) S. A. Mbogo, W. R. McWhinnie and T. S. Lobana, J. Organomet. Chem., 384 (1990) 115.
(b) M. R. Greaves, T. A. Hamor, B. J. Howlin, T. S. Lobana, S. A. Mbogo, W. R. McWhinnie and D. C. Povey, J. Organomet. Chem., 420 (1991) 327.
(c) S. A. Mbogo, W. R. McWhinnie and T. S. Lobana, Inorg. Chim. Acta, 193 (1992) 5.
(d) S. A. Mbogo, W. R. McWhinnie and T. S. Lobana, Inorg. Chim. Acta, 172 (1990) 221.
(e) N. I. Al-Salim and W. R. McWhinnie, Polyhedron, 8 (1989) 2769.
[24] (a) Y. Nishibayashi, C. S. Cho and S. Uemura, J. Organomet. Chem., 507 (1996) 197.
(b) Y. Nishibayashi, C. S. Cho, K. Ohe and S. Uemura, J. Organomet. Chem., 526 (1996) 335.
[25] (a) S. C. Menon, H. B. Singh, R. P. Patel and S. K. Kulshreshtha, J. Chem. Soc., Dalton Trans.,(1996)1203.
(b) S. C. Menon, A. Panda, H. B. Singh and R. J. Butcher, Chem. Commun., (2000) 143.
(c) S. D. Apte, S. S. Zade, H. B. Singh and R. J. Butcher, Organometallics, 22 (2003) 5473.
[26] P. C. Srivastava, S. Bajpai, R. Lath, R. Kumar, V. Singh, S. Dwivedi, R. J. Butcher, S. Hayashi and W. Nakanishi, Polyhedron, 27 (2008) 835.
[27] V. Singh, D. Srivastava, S. Dwivedi and R. J. Butcher, Molecular Structure, 1344 (2026) 144757.
[28] G. M. Sheldrick, SHELXS 97, SHELXL 97 and SHELXTL, University of Göttingen (1987 and 1997).
[29] J. E. Huheey, E. A. Keiter, R. L. Keiter and O. K. Medhi, Inorganic Chemistry: Principles of Structure and Reactivity, 4th ed., Pearson Education, pp. 639-640.
[30] M. Brookhart and M. L. H. Green, J. Organomet. Chem., 250 (1983) 395.
[31] M. Brookhart, M. L. H. Green and G. Parkin, "Agostic interactions in transition metal compounds," Proc. Natl. Acad. Sci. U.S.A., 104 (2007) 6908.
[32] P. C. Srivastava, S. Bajpai, R. Lath, C. Ram, S. M. Bajpai, R. J. Butcher, M. Zimmer and M. Veith, J. Organomet. Chem., 649 (2002) 70.