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The Hemi-Adduct of Bis(diethyldithiocarbamato-*S*,*S*′)tellurium(II) with 4,4′-Bipyridyl

S. RAJASHREE,[a] R. KRISHNA KUMAR,[a] M. R. UDUPA,[a] R. SESHASAYEE[b] AND G. ARAVAMUDAN[a]*

[a]*Department of Chemistry, Indian Institute of Technology, Madras 600 036, India, and* [b]*Department of Physics, Indian Institute of Technology, Madras 600 036, India*

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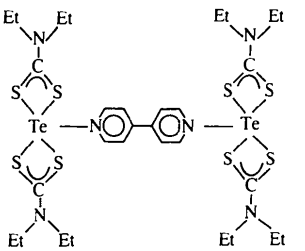
Abstract

In the structure of bis(diethyldithiocarbamato-*S*,*S*′)-tellurium(II)–4,4′-bipyridyl (2/1), $[Te(C_5H_{10}NS_2)_2]\cdot\frac{1}{2}C_{10}H_8N_2$, the bipyridyl molecule was found to bridge two bis(diethyldithiocarbamato)tellurium moieties centrosymmetrically, *i.e.* μ-(4,4′-bipyridyl-*N*:*N*′)-bis(diethyldithiocarbamato-*S*,*S*′)tellurium. The N atom of the bipyridyl is very weakly coordinated to tellurium and this is the first instance of Te—N coordination observed in a tellurium–dithiocarbamate complex. Each Te atom has an unusual planar-pentagonal arrangement of ligands around it.

Comment

The structure of TeL_2 (L = diethyldithiocarbamate) (Fabiani, Spagna, Vaciago & Zambonelli, 1971) reveals the geometry around the Te atom to be essentially trapezoidal, with the two S atoms from each of the dithiocarbamate groups bonded to the Te atom in a highly anisobidentate manner. In addition, the Te atom exerts a very weak interaction in the same plane with an S atom from a neighbouring TeL_2 moiety leading to a bridged dimer. In order to examine whether other ligands could possibly occupy this fifth coordination site, the reactions of TeL_2 with the nitrogen bases pyridine, 1,10-phenanthroline, 2,2′-bipyridyl and 4,4′-bipyridyl were carried out. We were successful in the isolation of an adduct with 4,4′-bipyridyl only, (I), and its structure is presented here.



(I)

The structure determination of (I) reveals the title compound to be a binuclear species bridged centrosymmetrically by a 4,4′-bipyridyl molecule, as shown in Fig. 1. The dithiocarbamate ligand is bound in an anisobidentate manner, with two short and two long Te—S bonds. The two short bond distances are 2.624 (1) for Te—S(1) and 2.573 (1) Å for Te—S(4), while the two long Te—S(2) and Te—S(3) bonds are 2.826 (1) and 2.720 (1) Å, respectively. The Te—S distances are longer than the sum of the covalent radii of the individual atoms (2.41 Å; Pauling, 1960). The average short Te—S distance of 2.599 Å is longer, while the average long Te—S distance of 2.773 Å is shorter, compared with the average short and long Te—S distances observed in TeL_2 (2.519 and 2.861 Å). Within the chelated dithiocarbamate ligands, the S—Te—S angles are 65.37 (2) and 67.04 (2)°. The angle at Te between the two closest S atoms, S(1) and S(4), is 80.2 (2)°, while that between the two distant S atoms, S(2) and S(3), is 147.4 (2)°. In the adduct, the Te—N bond replaces the weak fifth Te—S bond observed in the structure of TeL_2. The Te—N(3) vector bisects the S(2)—Te—S(3) angle almost equally [angles S(2)—Te—N(3) and S(3)—Te—N(3) are 74.0 (1) and 73.6 (1)°, respectively]. The Te—N distance of 2.700 (2) Å in the title compound is much greater than the sum of the individual covalent radii of Te and N (2.04 Å). This distance is also greater than the Te—N distance observed in the Te^{II} complex $[Te\{N(SiMe_3)_2\}_2]$ (2.05 Å; Bjoergvinsson, Roesky, Pauer, Stalke & Sheldrick, 1990) and in many other compounds, where it ranges between 1.98 and 2.10 Å (Johnson, Maclean, Passmore & White, 1989; Bjoergvinsson & Roesky, 1991). A similar weak Te—N interaction is seen in the previously reported

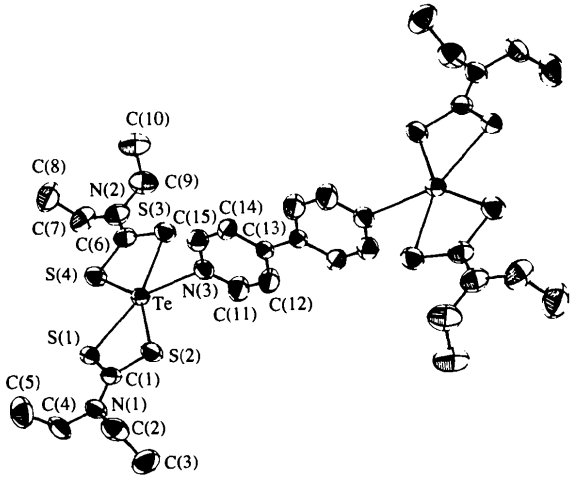


Fig. 1. *ORTEP* plot (Johnson, 1965) of the hemi-adduct of TeL_2 with 4,4′-bipyridyl, drawn with 50% probability ellipsoids. H atoms are omitted for clarity.

hemi-adduct of 4,4′-bipyridyl with bis(diethylxanthato)-tellurium(II) (Hoskins, Oliver & Winter, 1984).

The geometry around the Te atom is pentagonal planar, composed of the four S atoms of the two dithiocarbamate ligands and an N atom of the bipyridyl molecule. The two lone pairs of electrons of the Te atom lie above and below this plane in accordance with the VSEPR (valence-shell electron-pair repulsion) theory (Gillespie, 1972). The two Te atoms which are bridged by the two bipyridyl N atoms are 12.42 Å apart in comparison with a Te···Te separation of 6.32 Å in the sulfur-bridged TeL_2 structure. In TeL_2, the two TeS_5 groups are coplanar and correspondingly, in the hemi-adduct, the two TeS_4N groups are almost coplanar, with the r.m.s. deviation from the mean plane being 0.136 Å. The Te atoms are not, however, collinear with the two N atoms, but instead are tilted at an angle of 167.5 (6)° and are *trans* to the N(3)···C(13)—C(13′)···N(3′) axis. The plane of the bipyridyl and any one of the TeS_4N planes make a dihedral angle of 77.9°.

In accordance with the weak Te—N interaction, TeL_2 separates as a red solid on addition of excess hexane to a solution of the adduct in dichloromethane. It has been observed that bis(diisopropyldithiocarbamato)tellurium(II) also yields a hemi-adduct with 4,4′-bipyridyl, which is less prone to incongruent dissolution relative to the title compound.

Experimental

For the preparation of the title compound, 0.5 mmol (0.212 g) of red-coloured TeL_2 dissolved in 10 ml of dichloromethane was mixed with 1.0 mmol (0.192 g) of 4,4′-bipyridyl dihydrate dissolved in 20 ml of dichloromethane. On controlled evaporation of the solvent, orange-coloured needle-shaped crystals of the adduct were obtained in addition to the white crystals of 4,4′-bipyridyl. The unreacted bipyridyl was removed by rapid washing with ethyl acetate. The orange crystals were found by analysis to be $TeL_2.\frac{1}{2}$bipy. Analysis found C 35.7, N 8.21, H 4.80, S 25.3, Te 25.08%; $C_{15}H_{24}N_3S_4Te$ requires C 35.87, N 8.37, H 4.82, S 25.53, Te 25.41%. The presence of the bipyridyl moiety was also confirmed by IR and ^1H NMR spectroscopic analysis. The density D_m was measured by flotation in $CCl_4/CHBr_3$ solution.

Crystal data

$C_{15}H_{24}N_3S_4Te$
$M_r = 502.18$
Triclinic
$P\bar{1}$
$a = 7.869\ (4)$ Å
$b = 9.677\ (3)$ Å
$c = 14.602\ (3)$ Å
$\alpha = 82.09\ (2)°$
$\beta = 84.16\ (2)°$
$\gamma = 77.12\ (3)°$
$V = 1070.74$ Å^3
$Z = 2$
$D_x = 1.56$ Mg m^{-3}
$D_m = 1.61$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10–15°$
$\mu = 1.646$ mm^{-1}
$T = 298$ K
Needle
0.5 × 0.3 × 0.1 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (Fair, 1990)
$T_{min} = 0.784$, $T_{max} = 0.997$
4069 measured reflections
3688 independent reflections
3467 observed reflections $[F > 6\sigma(F)]$
$R_{int} = 0.006$
$\theta_{max} = 25°$
$h = 0 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -17 \rightarrow 17$
2 standard reflections monitored every 100 reflections
intensity decay: <5%

Refinement

Refinement on F
$R = 0.027$
$wR = 0.030$
$S = 0.620$
3467 reflections
304 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F) + 0.02590F^2]$
$(\Delta/\sigma)_{max} = 0.009$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.70$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Liberman (1970)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Te	0.09980 (2)	0.85235 (1)	0.76567 (1)	0.0373 (4)
S(1)	0.3745 (1)	0.6420 (1)	0.7822 (1)	0.0472 (17)
S(2)	0.1200 (1)	0.6400 (1)	0.6478 (1)	0.0514 (19)
S(3)	−0.0829 (1)	1.1010 (1)	0.8255 (1)	0.0535 (19)
S(4)	0.2602 (1)	0.9439 (1)	0.8822 (1)	0.0533 (19)
C(1)	0.3083 (4)	0.5601 (3)	0.6959 (2)	0.045 (7)
N(1)	0.4083 (3)	0.4394 (2)	0.6710 (2)	0.052 (6)
C(2)	0.3547 (5)	0.3617 (3)	0.6035 (3)	0.067 (10)

C(3)	0.2545 (6)	0.2515 (5)	0.6498 (4)	0.088 (13)
C(4)	0.5797 (4)	0.3745 (3)	0.7078 (2)	0.064 (9)
C(5)	0.7280 (5)	0.4197 (5)	0.6454 (3)	0.086 (12)
C(6)	0.0897 (5)	1.0896 (3)	0.8895 (2)	0.051 (8)
N(2)	0.0953 (4)	1.1883 (3)	0.9438 (2)	0.061 (8)
C(7)	0.2441 (5)	1.1823 (4)	0.9961 (2)	0.071 (11)
C(8)	0.3840 (6)	1.2514 (5)	0.9442 (4)	0.102 (15)
C(9)	−0.0534 (6)	1.3101 (4)	0.9532 (3)	0.076 (11)
C(10)	−0.0473 (7)	1.4341 (5)	0.8803 (3)	0.084 (12)
N(3)	−0.1833 (3)	0.9373 (2)	0.6656 (2)	0.048 (6)
C(11)	−0.3175 (4)	0.8707 (4)	0.6766 (2)	0.066 (9)
C(12)	−0.4403 (4)	0.8919 (4)	0.6137 (2)	0.063 (9)
C(13)	−0.4338 (3)	0.9866 (3)	0.5344 (2)	0.037 (6)
C(14)	−0.2938 (4)	1.0558 (3)	0.5233 (2)	0.048 (7)
C(15)	−0.1752 (4)	1.0277 (3)	0.5892 (2)	0.051 (8)

Table 2. *Selected geometric parameters (Å, °)*

Te—S(1)	2.624 (1)	S(1)—C(1)	1.755 (3)
Te—S(2)	2.826 (1)	S(2)—C(1)	1.686 (3)
Te—S(3)	2.720 (1)	S(3)—C(6)	1.701 (4)
Te—S(4)	2.573 (1)	S(4)—C(6)	1.723 (3)
Te—N(3)	2.700 (2)	C(1)—N(1)	1.329 (3)
C(6)—N(2)	1.333 (5)		
S(1)—Te—S(2)	65.37 (2)	Te—S(4)—C(6)	89.9 (1)
S(3)—Te—S(4)	67.04 (2)	S(2)—Te—N(3)	74.0 (1)
Te—S(1)—C(1)	90.9 (1)	S(3)—Te—N(3)	73.6 (1)
Te—S(2)—C(1)	85.7 (1)	S(1)—C(1)—S(2)	118.0 (1)
Te—S(3)—C(6)	85.6 (1)	S(3)—C(6)—S(4)	117.4 (2)

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: local program. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). Molecular graphics: *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a packing diagram, have been deposited with the IUCr (Reference: DE1011). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Sesterterpene Lactone from *Petrosaspongia nigra* sp. nov.

RICHARD C. CAMBIE, ALLICK R. LAL AND CLIFTON E. F. RICKARD

Chemistry Department, University of Auckland, Private Bag 92019, Auckland, New Zealand

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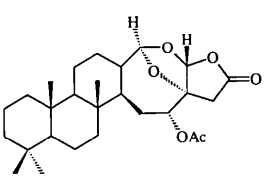
Abstract

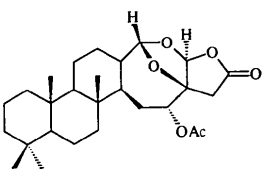
A sponge from the new genus *Petrosaspongia* has yielded two new isomeric sesterterpene lactones. We report here the structure of one of these lactones, [4a*S*-(4aα,4bβ,6aα,7β,8aα,11aβ,12β,13aβ,13bα,15aβ)]-12-acetoxyoctadecahydro-1,1,4a,13b-tetramethyl-7,11a-epoxy-2*H*-furo[2,3-*b*]phenanthro[1,2-*f*]oxocin-10(11*H*)-one, $C_{27}H_{40}O_6$.

Comment

As part of a search for biologically active compounds from South Pacific sponges, extracts from *Petrosaspongia nigra* sp. nov. yielded two sesterterpene lactones, (1) and (2). Preliminary details have been published elsewhere (Lal, Cambie, Rickard & Bergquist, 1994) in which the sponge was incorrectly assigned to the genus *Dactylospongia*. Further investigations have confirmed that the sponge belongs to a new genus (Bergquist, 1995). The NMR spectra of these compounds were almost identical with those recorded (Kernan *et al.*, 1989) for cyclization products of luffolide, a novel anti-inflammatory sesterterpene from the sponge *Luffariella* sp., but which had been assigned different structures. In order to confirm our structure assignments and relative stereochemistries, a single-crystal X-ray crystallographic analysis was carried out on our lactone, (2).



(1)



(2)

An *ORTEP*II (Johnson, 1976) diagram showing the numbering scheme is given in Fig. 1. The molecule is shown to be hexacyclic with an acetal function and a γ-lactone. The *A*, *B* and *C* rings show the usual *trans*-fused arrangement and ring *D* is also *trans* fused. An ideal *trans*-fused *A*, *B*, *C* ring system has torsion angles C3—C4—C5—C6, C2—C1—C10—C9 and C6—C7—C8—