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The Crystal Structure of the Hemiadduct of Tellurium(II) Ethylxanthate with 4,4'-Bipyridyl: An Example of Unusual Five-coordinate Pentagonal Planar Geometry

BERNARD F. HOSKINS, PAMELA J. OLIVER and GEORGE WINTER

Department of Inorganic Chemistry, University of Melbourne, Parkville, Vic., Australia, 3052

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Apart from the complex ion $[Te(exa)_3]^-$ [1], where exa denotes the ethylxanthate anion, no other adduct of tellurium(II) xanthates has so far been reported. However, from the reaction of $Te(exa)_2$ with 4,4'-bipyridyl (bipy) in ether solution we have obtained an orange coloured crystalline product the chemical analysis of which corresponded to $Te(exa)_2$,0.5 bipy. [Found and calculated for $TeC_{11}H_{14}NO_2S_4$: C, 29.1(29.4); H, 3.4(3.1); N, 3.1(3.1); S, 28.5(28.5)]. In the C–O region of the infra-red spectrum, recorded using a KBr disc, the absorptions are 1215 and 1205 cm^{-1} compared with 1240 and 1220 cm^{-1} for the parent compound confirming the adduct formation [2]. In the C–S region the absorption occurs at 1025 cm^{-1} for the complex compared with 1030 cm^{-1} for the parent $Te(exa)_2$. The molecular weight determination, by vapour pressure osmometry in benzene, yielded a value of 370 which is well below that of 896 calculated for a bridged binuclear species as suggested by the stoichiometry of the complex, so that it must be assumed that appreciable dissociation takes place in solution.

Crystal Data

$C_{11}H_{14}NO_2S_4Te$, M = 448.1, monoclinic, $P2_1/c$ (C_{2h}^5, No. 14) a = 9.0249(9), b = 13.211(2), c = 14.347(2) Å, β = 102.3(2)°, U = 1671.5 Å^3, D_m = 1.77, Z = 4, D_c = 1.780 Mg m^{-3}, $F(000)$ = 876, Cu-K_α (Ni-filtered) radiation, λ = 1.5418 Å, μ = 193.7 cm^{-1}.

Intensity data were collected using an Enraf-Nonius CAD-4F four circle single crystal diffractometer, fitted with Cu-K_α (Ni-filtered) radiation, employing the ω:2θ scan mode. The data were corrected for Lorentz, polarization and absorption effects [3, 4] and of the 4756 measured reflections ($2\theta_{max}$ = 150°) 3428 were unique of which 2487 were considered significant on the basis of the $I \geqslant 3\sigma(I)$ criterion. The structure was solved by the usual Fourier methods and refined by a full-matrix least-squares method which minimized the function $\Sigma w\Delta^2$, where $\Delta = \| F_o | - | F_c \|$. Towards the final stages of refinement anisotropic temperature factors were applied to all the non-hydrogen atoms. All the hydrogen atoms were revealed in a difference map and these were included in the model at their calculated geometrical positions (C–H = 1.08 Å). The weighting scheme $w = [\sigma^2(F) + 0.005|F_o|^2]^{-1}$ was employed and the refinement converged with R 0.053 and R_w 0.067; $R = \Sigma\Delta/\Sigma|F_o|$ and $R_w = [\Sigma w\Delta^2/\Sigma wF_o^2]^{1/2}$. Calculations for structure determination and refinement were performed using SHELX-76 [3]. Parameters for the scattering factor curve of the neutral Te atom were taken from reference [4] and those for the remaining atoms were those collected by Sheldrick [3]. The final non-hydrogen atomic coordinates and relevant molecular dimensions are listed in Tables I and II respectively. Other details have been deposited with the Editor.

TABLE I. Fractional Atomic Coordinates for $[Te(exa)_2(bipy)_{0.5}]_2$. Coordinates of the Atoms of the Centrosymmetrically Related Component are Obtained from the Operation (1 – x, 1 – y, 1 – z).

Atom	*x/a*	*y/b*	*z/c*
Te	0.15978(6)	0.16904(4)	0.20170(3)
S(1)	0.1176(2)	−0.0213(2)	0.2091(2)
S(2)	0.3387(3)	0.0746(2)	0.3628(2)
S(3)	0.0859(4)	0.3449(2)	0.0877(2)
S(4)	−0.0349(3)	0.1392(2)	0.0483(2)
O(1)	0.2882(8)	−0.1225(6)	0.3387(5)
O(2)	−0.1149(8)	0.2851(5)	−0.0660(4)
C(1)	0.2564(9)	−0.0280(8)	0.3104(6)
C(2)	0.407(2)	−0.141(1)	0.4237(9)
C(3)	0.461(2)	−0.231(1)	0.4271(9)
C(4)	−0.028(1)	0.2629(7)	0.0166(6)
C(5)	−0.116(1)	0.3846(7)	−0.1040(7)
C(6)	−0.228(1)	0.389(1)	−0.1928(8)
N	0.327(1)	0.3252(6)	0.3208(6)
C(7)	0.251(1)	0.3664(7)	0.3814(6)
C(8)	0.3148(9)	0.4338(6)	0.4530(6)
C(9)	0.4637(9)	0.4644(6)	0.4617(5)
C(10)	0.539(1)	0.423(1)	0.3968(7)
C(11)	0.469(1)	0.355(1)	0.3283(8)

Crystals of the adduct consist of the molecular binuclear species $[Te(exa)_2(bipy)_{0.5}]_2$ which is situated around a centre of symmetry and the molecular structure and the numbering scheme is shown in Fig. 1; the closest intermolecular distance between non-hydrogen atoms is 3.59 Å. The most outstanding feature of the structure is the planar pentagonal nature of the coordination around the Te atom, which comprises the sulphur atoms from two bidentate xanthate ligands and one of the nitrogen atoms of the bipy, thus providing the first example of such

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TABLE II. Interatomic Distances and Bond Angles.

Atoms	Distances	Atoms	Distances
(a) Interatomic distances (A)			
Te–S(1)	2.548(3)	O(1)–C(1)	1.33(1)
Te–S(2)	2.814(3)	O(1)–C(2)	1.47(2)
Te–S(3)	2.839(3)	O(2)–C(4)	1.31(1)
Te–S(4)	2.539(2)	O(2)–C(5)	1.42(1)
Te–N	2.892(8)	C(2)–C(3)	1.27(2)
S(1)–S(2)	2.928(3)	C(5)–C(6)	1.45(2)
S(2)–N	3.362(8)	N–C(7)	1.33(1)
N–S(3)	3.592(9)	C(7)–C(8)	1.39(1)
S(3)–S(4)	2.938(4)	C(8)–C(9)	1.38(1)
S(4)–S(1)	3.220(3)	C(9)–C(10)	1.38(2)
S(1)–C(1)	1.707(8)	C(10)–C(11)	1.38(2)
S(2)–C(1)	1.65(1)	C(11)–N	1.32(2)
S(3)–C(4)	1.679(9)	C(9)–C(9′)	1.49(1)
S(4)–C(4)	1.70(1)		

C(9′) related to C(9) according to the symmetry operation 1 – x, 1 – y, 1 – z.

Atoms	Angles	Atoms	Angles
(b) Bond angles (°)			
S(1)–Te–S(2)	65.98(6)	C(1)–O(1)–C(2)	119.3(9)
S(2)–Te–N	72.2(2)	C(4)–O(2)–C(5)	120.5(7)
N–Te–S(3)	77.6(2)	O(1)–C(2)–C(3)	113(1)
S(3)–Te–S(4)	65.95(8)	O(2)–C(5)–C(6)	108.3(9)
S(4)–Te–S(1)	78.56(7)	Te–N–C(7)	113.6(6)
Te–S(1)–C(1)	89.9(4)	Te–N–C(11)	129.5(7)
Te–S(2)–C(1)	82.3(3)	C(11)–N–C(7)	116.7(9)
Te–S(3)–C(4)	82.0(3)	N–C(7)–C(8)	123.7(8)
Te–S(4)–C(4)	91.4(3)	C(7)–C(8)–C(9)	119.7(7)
S(1)–C(1)–S(2)	121.6(6)	C(8)–C(9)–C(10)	115.6(8)
S(3)–C(4)–S(4)	120.7(5)	C(9)–C(10)–C(11)	121(1)
S(1)–C(1)–O(1)	112.5(7)	C(10)–C(11)–N	123(1)
S(2)–C(1)–O(1)	125.9(7)	C(10)–C(9)–C(9′)	123.1(8)
S(3)–C(4)–O(2)	125.3(7)	C(8)–C(9)–C(9′)	121.2(7)
S(4)–C(4)–O(2)	114.0(7)		

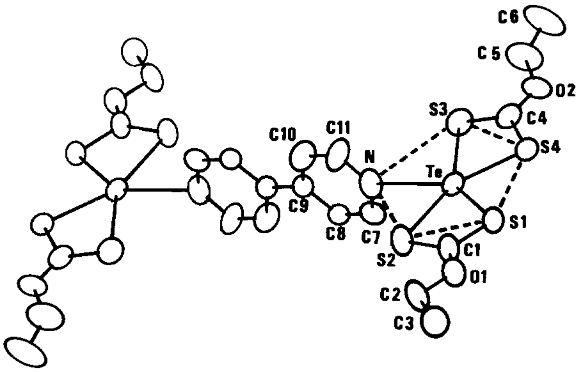

Fig. 1. Molecular structure of [Te(exa)$_2$(bipy)$_{0.5}$]$_2$ showing the bridging 4,4′-bipyridyl ligand, the pentagonal planar coordination around the tellurium atom and the essential perpendicular relationship between the 4,4′-bipyridyl and TeS_4N planes. The atom numbering scheme is also given.

geometry where a nitrogen atom is participating in the coordination sphere. The maximum displacement of any atom from the plane of best fit through the TeS_4N group of atoms is 0.111 Å which is that of the nitrogen atom; the Te atom displacement is 0.013 Å.

The gross features of the Te environment may be considered as a derivative of the pentagonal bipyramidal geometry predicted from the valence-shell electron-pair repulsion (V.S.E.P.R.) theory [5] on the basis of seven electron pairs contained in the valence shell of the Te atom with the two non-bonded electron pairs adopting the axial positions. A comparison of this complex with the bipy adducts of nickel xanthates clearly demonstrates the steric effect of the two lone pairs in the Te compound. Whereas the nickel complexes are 1:1 adducts in the form of infinite polymers [6–8] in which the nickel atom is six-coordinate, the tellurium complex is a 1:0.5 adduct where the Te atom is formally seven coordinate. This results in a weakly bridged binuclear species, as is demonstrated by the ready dissociation of the complex in benzene solution. A similar crowding effect by a lone pair has been observed previously in $[Pb(exa)_3]^-$ where the weak sulphur bridges lead to dimers with the lead atoms formally seven coordinate [9].

The observed asymmetry of the Te-S bonds in $[Te(exa)_2(bipy)_{0.5}]_2$ is similar in detail to that observed in the related anion adduct $[Te(exa)_3]^-$, the only other system so far reported with planar pentagonal geometry [1]. The dimensions of the 4,4′-bipyridyl moiety are typical of those found in similar systems; however it is interesting to note that the plane containing the bipy is essentially perpendicular to the pentagonal planar TeS_4N group of atoms; the dihedral angle is 88.1°. In all other respects the molecular dimensions are normal with the exception of the terminal C–C distances of the ethyl groups which are somewhat shorter than usual, an effect which appears to be associated with the relatively high thermal motion of the terminal carbon atoms.

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