*Inorganica Chimica Acta, 105* (1985) 171–176

# The Preparation and Characterization of Mixed Dithiolate Ligand Complexes: the Crystal and Molecular Structure of (*O*-ethylxanthato)(*N*,*N'*-diethyldithiocarbamato)tellurium(II)

BERNARD F. HOSKINS, EDWARD R. T. TIEKINK and GEORGE WINTER

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

Received April 5, 1985

## Abstract

The preparation and spectroscopic characterization of a number of mixed ligand complexes involving both xanthate and dithiocarbamate ligands are reported for the main group elements Sn(IV), Sb(III), Bi(III), and Te(II). The crystal structure of Te(exa)(dedtc) shows that the tellurium atom is in a trapezoidal planar environment and that the dithiocarbamate ligand is more tightly bound than the xanthate ligand. Crystals of Te(exa)(dedtc) are monoclinic, $P2_1/n$, $a$ = 8.942(2), $b$ = 7.365(2), $c$ = 22.415(5) Å, and $\beta$ = 92.68(2)°, with $Z$ = 4. The structure was refined by a least squares method with final $R$ = 0.042 and $R_w$ = 0.045 for 1593 reflections with $I \geqslant 2\sigma(I)$.

## Introduction

During studies concerning the chemistry of complexes involving the xanthate ion $ROCS_2^-$, a number of attempts have been made to isolate mixed xanthate complexes for which xanthate ligands with different R groups are present in the one complex. Since these were unsuccessful, there has been some doubt as to the likelihood of their existence. However, evidence was recently obtained from tin-119 NMR data for the formation, by ligand exchange, of species of the type $Sn(exa)_x(iprxa)_{4-x}$ (where exa is *O*-ethylxanthate, iprxa is *O*-isopropylxanthate, and x = 1, 2, 3) when dichloromethane solutions of $Sn(exa)_4$ and $Sn(iprxa)_4$ are mixed [1]; attempts to isolate these complexes in crystalline form have proved unsuccessful. Although mixed xanthate/dithiocarbamate compounds of the general formula $M(dtc)_2(xan)$ have been previously prepared for the elements Sb(III) [2], Bi(III) [3], and Fe(III) [4], no structural features have so far been reported.

The recent synthesis of haloxanthates for Sn(IV) [5], Sb(III) [6], Bi(III) [6], and Te(II) [7] has suggested a pathway for the preparation of mixed dithiolate complexes by metathesis. Whilst the isolation of mixed xanthate species was again unsuccessful for Sn(IV) it has been possible to prepare and characterize mixed exa/mexa complexes for Sb(III), Bi(III), and Te(II) (where mexa is *O*-methylxanthate). Using a similar procedure mixed xanthate/dithiocarbamate complexes of Te(II), Sb(III), Bi(III), and Sn(IV) also have been obtained. A single crystal structure analysis of Te(exa)(dedtc) was performed for the purpose of examining the effect on the immediate environment of the central tellurium atom by the coordination of two different dithiolate ligands.

## Results and Discussion

### *Mixed Xanthate Complexes*

The vibrational absorption spectra of the recrystallized mixed ligand complexes differ markedly (Table

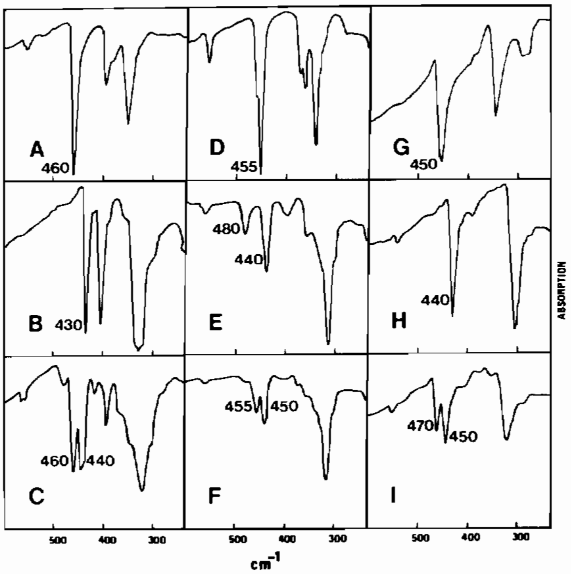

Fig. 1. Infrared absorptions for the mixed exa/mexa complexes in the region 500–300 $cm^{-1}$: **A**, $Sb(mexa)_3$; **B**, $Sb(exa)_3$; **C**, $Sb(exa)_2(mexa)$; **D**, $Bi(mexa)_3$; E, $Bi(exa)_3$; **F**, $Bi(exa)_2(mexa)$; **G**, $Te(mexa)_2$; **H**, $Te(exa)_2$; **I**, Te(exa)(mexa).

0020-1693/85/$3.30

TABLE I. Infrared Frequencies (cm$^{-1}$) in the C–N, C–O, and C–S regions.[a]

| Compound | Region | Frequency | Reference[b] |
|---|---|---|---|
| Sb(mexa)$_3$ | (C–O) | 1225(s), 1205(s) | |
| | (C–S) | 1045(m), 1030(s) | |
| Bi(mexa)$_3$ | (C–O) | 1225(sh), 1215(sh), 1205(s) | |
| | (C–S) | 1040(m), 1030(s) | |
| Te(mexa)$_2$ | (C–O) | 1220(s) | |
| | (C–S) | 1044(s) | |
| Sn(exa)$_4$ | (C–O) | 1250(s), 1210(s) | 8 |
| | (C–S) | 1055(s), 1033(s) | |
| Sb(exa)$_3$ | (C–O) | 1230(s) | 9 |
| | (C–S) | 1029(s) | |
| Bi(exa)$_3$ | (C–O) | 1210(s), 1190(s) | 9 |
| | (C–S) | 1032(s) | |
| Te(exa)$_2$ | (C–O) | 1240(s), 1220(s) | |
| | (C–S) | 1030(s) | |
| Sb(exa)$_2$(mexa) | (C–O) | 1285(sh), 1265(sh), 1218(s), 1195(s) | |
| | (C–S) | 1045(sh), 1020(s), 1005(sh) | |
| Bi(exa)$_2$(mexa) | (C–O) | 1285(sh), 1270(w), 1210(s), 1190(s) | |
| | (C–S) | 1040(sh), 1020(s), 1005(sh) | |
| Te(exa)(mexa) | (C–O) | 1285(sh), 1240(s), 1220(s) | |
| | (C–S) | 1035(sh), 1025(sh), 1018(s), 995(w) | |
| Sn(exa)$_2$(dedtc)$_2$ | (C–N) | 1518(s) | |
| | (C–O) | 1278(m), 1215(s), 1200(s) | |
| | (C–S) | 1037(s), 1008(w), 990(m) | |
| Sb(exa)$_2$(dedtc) | (C–N) | 1507(s) | |
| | (C–O) | 1270(m), 1210(sh), 1202(s) | |
| | (C–S) | 1040(s), 1002(w), 993(w) | |
| Bi(exa)$_2$(dedtc) | (C–N) | 1492(s) | |
| | (C–O) | 1270(m), 1200(s), 1185(s) | |
| | (C–S) | 1030(s), 1020(s), 995(m) | |
| Te(exa)(dedtc) | (C–N) | 1495(s) | |
| | (C–O) | 1298(m), 1270(s), 1215(s) | |
| | (C–S) | 1013(s), 1002(sh) | |
| Sn(dedtc)$_4$ | (C–N) | 1507(s) | 11 |
| | (C–S) | 989(s) | |
| Sb(dedtc)$_3$ | (C–N) | 1485(s), 1478(s) | |
| | (C–S) | 985(s) | |
| Bi(dedtc)$_3$ | (C–N) | 1489(s), 1478(s) | |
| | (C–S) | 983(s) | |
| Te(dedtc)$_2$ | (C–N) | 1495(s), 1485(s) | |
| | (C–S) | 982(s) | |

[a] w = weak, m = medium, s = strong intensity, sh = shoulder. [b] This work unless otherwise stated.

I) from those of the corresponding simple xanthates. The differences are particularly pronounced in the M–S region, [as illustrated in Fig. 1 for antimony(III), bismuth(III), and tellurium(II)], providing evidence that substitution had taken place. In harmony with this are the proton NMR spectra, Table II, where the ratio of 2:1 for the Group V complexes and the ratio 1:1 for the tellurium(II) complex were found in $CDCl_3$ solution for the $CH_3$ protons of the ethyl and methyl groups.

*Xanthate/Dithiocarbamate Complexes*

In the infrared spectra of the mixed xanthate/dithiocarbamates strong absorptions are observed around 1500 cm$^{-1}$ which are characteristic for the dithiocarbamate ligand [12]. Absorptions in this region have been attributed to vibrations of a partial C–N double bond resulting from a significant contribution to the overall structure of the resonance form $^{2-}\mathrm{S_2C{=}\overset{+}{N}}$ [12] (*cf.* Fig. 2, **A**) which accounts for the greater stability of dithiocarbamate complexes compared with xanthate complexes where there is only a minor contribution of the analogous canonical form; see Fig. 2, **B**. The partial replacement of dithiocarbamate ligands by xanthate ligands results in a slight but significant shift of the $\nu$(C–N) absorption to higher frequencies; see Table I. These observations are believed to be a manifestation of changes

TABLE II. Proton NMR Chemical Shifts (ppm).[a]

| Compound | Ligand | Chemical Shifts |
|---|---|---|
| Sb(exa)$_2$(mexa) | exa | 1.47(t, 6H, CH$_3$), 4.64(q, 4H, CH$_2$) |
| | mexa | 4.21(s, 3H, CH$_3$) |
| Bi(exa)$_2$(mexa) | exa | 1.52(t, 6H, CH$_3$), 4.73(q, 4H, CH$_2$) |
| | mexa | 4.24(s, 3H, CH$_2$) |
| Te(exa)(mexa) | exa | 1.49(t, 3H, CH$_3$), 4.66(q, 2H, CH$_2$) |
| | mexa | 4.23(s, 3H, CH$_3$) |
| Sn(exa)$_2$(dedtc)$_2$ | exa | 1.48(t, 6H, CH$_3$), 4.60(q, 4H, CH$_2$) |
| | dedtc | 1.35(t, 12H, CH$_3$), 3.72(q, 8H, CH$_2$) |
| Sb(exa)$_2$(dedtc) | exa | 1.45(t, 6H, CH$_3$), 4.63(q, 4H, CH$_2$) |
| | dedtc | 1.32(t, 6H, CH$_3$), 3.83(q, 4H, CH$_2$) |
| Bi(exa)$_2$(dedtc) | exa | 1.50(t, 6H, CH$_3$), 4.70(q, 4H, CH$_2$) |
| | dedtc | 1.36(t, 6H, CH$_3$), 3.97(q, 4H, CH$_2$) |
| Te(exa)(dedtc) | exa | 1.47(t, 3H, CH$_3$), 4.65(q, 2H, CH$_2$) |
| | dedtc | 1.32(t, 6H, CH$_3$), 3.78(q, 4H, CH$_2$) |

[a] s = singlet, t = triplet, and q = quartet.

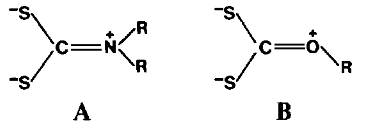

Fig. 2. Corresponding resonance forms for the dithiocarbamate (A) and the xanthate (B) anions; cf. ref. [12].

in the charge distribution around the central metal which results in an increase in the double bond character of the C–N bond. In contrast, the absorptions of the ν(C–O) band in the mixed exa/dedtc complexes is shifted to lower frequencies compared to the parent xanthate complexes. No definite trend was evident in the infrared spectra for the positions of the absorptions in the C–S region.

The proton NMR showed the expected resonances due to the ethyl groups of the exa and dedtc ligands (see Table II). The integration of the multiplets in the NMR spectrum yielded results expected from the predicted stoichiometries. The resonances due to the CH$_2$ and CH$_3$ hydrogen atoms of exa are at higher field relative to those resonances of the CH$_2$ and CH$_3$ protons of dedtc. This observation reflects the different inductive effects due to the presence of nitrogen and oxygen atoms in the dedtc and exa ligands respectively.

### *Description of the Structure for Te(exa)(dedtc)*

Crystals of Te(exa)(dedtc) consist of discrete molecules of Te(exa)(dedtc) (the geometry of which is shown in Fig. 3) with four molecules comprising the unit cell; a [010] projection of the crystal structure is shown in Fig. 4. Important intramolecular distances and angles are given in Tables III and IV respectively; the numbering scheme is shown in Fig. 3.

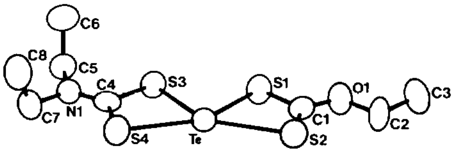

Fig. 3. The molecular structure of Te(exa)(dedtc); the numbering scheme is also shown.

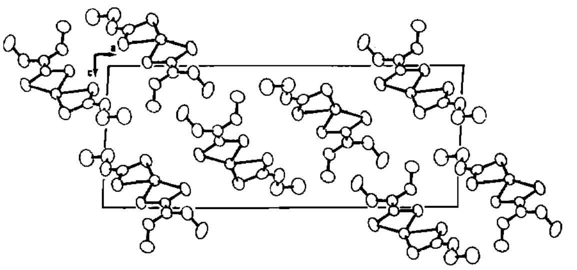

Fig. 4. The unit cell contents for Te(exa)(dedtc) viewed down the [010] direction.

The tellurium atom in Te(exa)(dedtc) is in a planar environment from the four sulphur atoms of the two unsymmetrically chelating dithiolate ligands. The overall geometry observed for the Te(exa)(dedtc) molecule is similar to those reported for both Te(exa)$_2$ [10] and Te(dedtc)$_2$ [13] which have been described as conforming to a trapezoidal planar geometry with a non-bonding pair of electrons lying above and below this plane [14].

The only significant intermolecular contact in Te(exa)(dedtc) is that of 3.679(3) Å which occurs between the tellurium atom and S(4′) [where S(4′) is related by the symmetry operation (0.5 – *x*, 0.5 + *y*, 0.5 – *z*)] so that a loosely associated dimer is formed. Similar contacts have been reported for Te(exa)$_2$ 3.61(2) Å [10] and in Te(dedtc)$_2$ 3.579(5) Å

TABLE III. Interatomic Distances (Å) for Te(exa)(dedtc).

| Atoms | Distance |
|---|---|
| Te–S(1) | 2.535(2) |
| Te–S(2) | 2.911(3) |
| S(1)–C(1) | 1.70(1) |
| S(2)–C(1) | 1.670(9) |
| C(1)–O(1) | 1.33(1) |
| O(1)–C(2) | 1.47(1) |
| C(2)–C(3) | 1.52(2) |
| S(1)···S(2) | 2.959(4) |
| Te–S(3) | 2.489(3) |
| Te–S(4) | 2.801(3) |
| S(3)–C(4) | 1.745(9) |
| S(4)–C(4) | 1.703(9) |
| C(4)–N(1) | 1.31(1) |
| N(1)–C(5) | 1.47(1) |
| C(5)–C(6) | 1.53(1) |
| N(1)–C(7) | 1.49(1) |
| C(7)–C(8) | 1.55(2) |
| S(3)···S(4) | 2.933(3) |

TABLE IV. Bond Angles (°) for Te(exa)(dedtc).

| Atoms | Angle |
|---|---|
| S(1)–Te–S(2) | 65.39(8) |
| S(1)–Te–S(3) | 81.19(9) |
| S(1)–Te–S(4) | 148.25(9) |
| S(2)–Te–S(3) | 146.41(8) |
| S(2)–Te–S(4) | 146.30(7) |
| S(3)–Te–S(4) | 67.06(8) |
| Te–S(1)–C(1) | 91.8(3) |
| Te–S(2)–C(1) | 80.2(4) |
| S(1)–C(1)–S(2) | 122.6(6) |
| S(1)–C(1)–O(1) | 113.3(7) |
| S(2)–C(1)–O(1) | 124.1(7) |
| C(1)–O(1)–C(2) | 118.2(8) |
| O(1)–C(2)–C(3) | 105.1(9) |
| Te–S(3)–C(4) | 83.5(3) |
| Te–S(4)–C(4) | 92.8(3) |
| S(3)–C(4)–S(4) | 116.6(5) |
| S(3)–C(4)–N(1) | 118.9(7) |
| S(4)–C(4)–N(1) | 124.5(7) |
| C(4)–N(1)–C(5) | 121.8(8) |
| N(1)–C(5)–C(6) | 113.2(8) |
| C(5)–N(1)–C(7) | 117.6(8) |
| C(4)–N(1)–C(7) | 120.6(7) |
| N(1)–C(7)–C(8) | 111.3(8) |

[13]. All other intermolecular contacts are at distances expected from van der Waals radii.

Although the mode of coordination of the exa and dedtc ligands is similar to that observed in the parent bis dithiolate tellurium(II) compounds, some interesting features are observed. A comparison of the Te–S distances, as listed in Table V, shows that the dedtc ligand in Te(exa)(dedtc) is more tightly bound than the exa ligand. Further, it is notable that the dedtc ligand inTe(exa)(dedtc) is bound at shorter Te–S distances than those reported for Te(dedtc)$_2$ [13] and that the opposite is true for the exa ligand. It is known that in general the dithiocarbamate ligand is more firmly bound to metal atoms than the xanthate ion. This has been explained in terms of the relative contributions of the resonance structures shown in Fig. 2. Chatt *et al.* [12] suggested that resonance structure **A** contributed more to the overall structure of dithiocarbamate complexes than did the corresponding resonance form **B** in xanthate complexes. This difference is enhanced in the mixed ligand compound. Thus the contribution of resonance form **B** as calculated by the method of Merlino [15] is 28% for Te(exa)$_2$ [10] and only 19% for Te(exa)(dedtc).

The geometry of the exa ligand is as expected; however, the conformation of the terminal methyl groups of the dedtc ligand is different to that observed for Te(dedtc)$_2$ [13]. In the latter, the methyl groups lie above and below the plane defined by the S$_2$CN moiety, however both substituents lie to one side of this plane in Te(exa)(dedtc).

## Experimental

### *Preparations*

Mixed Xanthate Complexes: The starting materials, [Sb(exa)$_2$Br]$_n$ [6], Bi(exa)$_2$Cl [6] and [Te(exa)Br]$_n$ [7] were prepared as previously reported. The mixed xanthates were then obtained by the reaction, in a 1:1 molar ratio, of the haloxanthate in

TABLE V. Te–S Distances (Å) in Tellurium(II) Dithiolates

| Compound | Te–S (exa) | Te–S (dedtc) | Reference |
|---|---|---|---|
| Te(exa)$_2$ | 2.48(2), 2.86(2) | | |
| | 2.49(2), 2.90(2) | | 10 |
| Te(exa)(dedtc) | 2.535(2), 2.911(3) | 2.489(1), 2.801(3) | this work |
| Te(dedtc)$_2$ | | 2.519(4), 2.830(3) | |
| | | 2.518(4), 2.893(4) | 13 |

organic solvent (chloroform for the Sb(III) and Bi(III) complexes and dichloromethane for Te(exa)-Br) with an aqueous solution of potassium methylxanthate. The product was contained in the non-aqueous layer which was separated and dried over anhydrous $Na_2CO_3$. After evaporation of the solvent the product was recrystallized from benzene for the Sb(III) and Bi(III) derivatives and dichloromethane for the Te(II) complex. Sb(exa)$_2$(mexa): large, pale yellow crystals, m.p. 88–89 °C; Bi(exa)$_2$-(mexa): microcrystalline, yellow, m.p. $\geqslant$80 °C dec.; Te(exa)(mexa): large red-brown crystals, m.p. 75–76 °C. The complexes are soluble in most common organic solvents.

### *Xanthate/Dithiocarbamate Complexes*

The mixed exa/dedtc complexes for Sb(III), Bi(III), and Te(II) were prepared from the haloxanthates (in chloroform) and the sodium salt of diethyldithiocarbamate (dedtc) in aqueous solution in an analogous manner as that described for the mixed xanthate complexes. In all cases the final products were recrystallized from dichloromethane solution. Sb(exa)$_2$(dedtc): pale yellow crystals, m.p. 72–73 °C; Bi(exa)$_2$(dedtc) yellow crystals, m.p. $\geqslant$105 °C dec.; Te(exa)(dedtc): red needles, m.p. 105–106 °C. Sn(exa)$_2$(dedtc)$_2$ was prepared from the reaction of Sn(exa)$_2$Cl$_2$ [5] in chloroform solution and the sodium salt of dedtc (water, 10 cm$^3$) in a 1:2 ratio. The product was recrystallized from chloroform. Sn(exa)$_2$(dedtc)$_2$: bright yellow, microcrystalline m.p. $\geqslant$ 98 °C dec.

### *Instrumentation*

Infrared spectra were obtained from KBr discs on a Perkin-Elmer 457 and a Jasco-A-302 spectrophotometer. NMR spectra were recorded on a JEOL FX100 spectrometer at 100 MHz using internal deuterium lock referenced against TMS.

### *Crystallography*

Crystals of Te(exa)(dedtc) suitable for X-ray analysis were grown by the slow evaporation of a dichloromethane/hexane solution of the compound.

Intensity data were collected on an Enraf-Nonius CAD-4F diffractometer with the use of MoK$\bar{\alpha}$ radiation using the $\omega$:$2\theta$ scan technique. Accurate cell dimensions were obtained by a least squares refinement on the setting angles of 25 reflections. The inspection of the intensity values of a set of intensity control reflections, which were monitored after every 1800 seconds X-ray exposure time, showed that the values had decreased steadily during the data collection to 95% of their original values and hence the data were corrected for this variation. Correction was made for Lorentz, polarization, and absorption effects [16a] (max. and min. transmission factors 0.8293 and 0.5940). Of the 3912 reflections collected 2589 were unique and 1593 satisfied the $I \geqslant 2\sigma(I)$ criterion of observability.

### *Crystal Data*

Te(exa)(dedtc), $C_8H_{15}NOS_4Te$, M = 397.08, monoclinic, $P2_1/n$, [equivalent positions: $\pm(x, y, z$: $0.5 + x$, $0.5 - y$, $0.5 + z)$], $a = 8.942(2)$, $b = 7.365(2)$, $c = 22.415(5)$ Å, $\beta = 92.68(2)°$, $U = 1474.6$ Å$^3$, $D_{\text{meas}} = 1.77$, $Z = 4$, $D_{\text{calc}} = 1.789$ Mg m$^{-3}$, $F(000) = 776$, crystal dimensions: ±(100) 0.0938; ±(0.10) 0.15; ±(001) 0.0375 mm, MoK$\bar{\alpha}$ radiation (graphite monochromator) $\lambda = 0.71069$ Å, $\mu = 2.51$ mm$^{-1}$, $1 \leqslant \theta \leqslant 25°$, no. parameters/no. variables = 12.

The position of the tellurium atom was obtained from the three-dimensional Patterson synthesis. All non-hydrogen atoms were located in subsequent difference maps and the positional and individual isotropic thermal parameters refined, $R$ = 0.123. The structure was refined using full-matrix least-squares methods in which the function $\Sigma w \Delta^2$ was minimized where $\Delta = \| F_o | - | F_c \|$ and $w$ was the weight applied to each reflection. Anisotropic thermal parameters were introduced for all non-hydrogen atoms and a weighting scheme $w = k/[\sigma^2(F) + 0.001|F|^2]$ included. Hydrogen atoms were not included in the model. Refinement converged with $k$ = 0.99 and values of $R$ and $R_w$ equal to 0.042 and 0.045 respectively. The analysis of variance showed no significant features and the maximum residual electron density peak in the final difference map was 0.66 e Å$^{-3}$ located in the vicinity of the tellurium atom.

The scattering factors for C, H, O and S were those incorporated in the SHELX-76 program system [17] and the scattering factors for the neutral tellurium atom were from ref. 16b and these were corrected for anomalous dispersion [16c]. All calculations were

TABLE VI. Fractional Atomic Coordinates for Te(exa)-(dedtc) with e.s.d.s in parentheses.

| Atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| Te | 0.19194(7) | −0.17325(9) | −0.14514(3) |
| S(1) | 0.1603(3) | −0.2851(4) | −0.0395(1) |
| S(2) | 0.3312(3) | −0.5227(4) | −0.1181(1) |
| C(1) | 0.2615(10) | −0.4761(14) | −0.0520(4) |
| O(1) | 0.2750(8) | −0.5850(9) | −0.0046(3) |
| C(2) | 0.3648(13) | −0.7505(15) | −0.0093(5) |
| C(3) | 0.3525(16) | −0.8461(16) | 0.0503(5) |
| S(3) | 0.0298(3) | 0.0751(4) | −0.1095(1) |
| S(4) | 0.1288(3) | 0.0918(4) | −0.2323(1) |
| C(4) | 0.0317(9) | 0.1907(13) | −0.1774(4) |
| N(1) | −0.0400(8) | 0.3446(11) | −0.1830(3) |
| C(5) | −0.1206(10) | 0.4239(14) | −0.1334(4) |
| C(6) | −0.2831(12) | 0.3588(16) | −0.1316(5) |
| C(7) | −0.0425(11) | 0.4467(14) | −0.2403(4) |
| C(8) | −0.1709(17) | 0.3798(17) | −0.2839(5) |

performed on the University of Melbourne's CYBER 170-730 computer system using the SHELX-76 program [17]. Fractional atomic coordinates for Te(exa)(dedtc) are listed in Table VI and listings of anisotropic thermal parameters, least-squares planes data, and the observed and calculated structure factor tables have been deposited with the Editor-in-Chief.

## Acknowledgements

We are most grateful to the Commonwealth of Australia for a Postgraduate Research Award to one of us (E.R.T.T.) and to Miss G. Hosken for recording the NMR spectra.

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