

- MOK, K. F., MCKEE, V. & ROBINSON, W. T. (1987). *Acta Cryst.* C43, 2093–2096.
- MOK, K. F., MCKEE, V. & ROBINSON, W. T. (1989). *Acta Cryst.* C45, 201–204.
- POONIA, N. S. & BAJAJ, A. V. (1979). *Chem Rev.* 79, 389–445.
- ROGERS, R. D. & ATWOOD, J. L. (1984). *J. Cryst. Spectrosc. Res.* 14, 1–11.
- SHELDRIK, G. M. (1984). *SHELXTL Users Manual*. Revision 4.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.
- SHELDRIK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Federal Republic of Germany.
- VAN ECK, C. L., VAN P., WOLTERS, H. B. M. & JASPERS, W. J. M. (1956). *Recl Trav. Chim. Pays-Bas*, 75, 802–808.
- WINK, D. J., FOX, J. R. & COOPER, N. J. (1985). *J. Am. Chem. Soc.* 107, 5012–5014.
- ZAWOROTKO, M. J., REID, C. & ATWOOD, J. L. (1985). *Organometallics*, 4, 238–241.

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Structure of Bis(diisopropylthiocarbamato)tellurium(II)

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Abstract. Bis(diisopropylthiocarbamodithioato- κ^2S,S')-tellurium(II), [Te(C₇H₁₄NS₂)₂], $M_r = 479$, orthorhombic, *Pbca*, $a = 12.411$ (1), $b = 13.679$ (9), $c = 25.579$ (1) Å, $V = 4342.59$ Å³, $D_m = 1.50$, $D_x = 1.467$ Mg m⁻³, $Z = 8$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.619$ mm⁻¹, $F(000) = 1935.97$, $T = 293$ K, final $R = 0.036$, $S = 0.83$ for 1969 unique reflections. Both the dithiocarbamate ligands are bound asymmetrically to the central Te atom. Around Te there is a tendency towards five coordination with one S atom from the neighbouring molecule making a short Te...S contact.

Introduction. Dithiocarbamates undergo redox complexation reactions (Bode, Tusche & Wahrhausen, 1962; Schnabel, Deuten & Klar, 1980). The title compound was prepared as part of our study of divalent tellurium complexes of dithiocarbamates. The structure determination was carried out to study the effect of the bulkiness of the ligand and the effect of the tellurium lone pairs of electrons on the stereochemistry. Other structures of Te(ligand)₂ complexes which have been reported are those of bis(*O*-ethylxanthato)tellurium(II) (Husebye, 1967), bis(morpholinylthiocarbamato)tellurium(II) (Husebye, 1970), bis(*N,N*-diethylthiocarbamato)tellurium(II) (Fabiani, Spagna, Vaciago & Zam-

bonelli, 1971), bis[bis(2-hydroxyethyl)dithiocarbamato]tellurium(II) (Rout, Seshasayee, Radha & Aravamudan, 1983) and bis(dipropylthiocarbamato)tellurium(II) (Ganesh, Seshasayee, Chidambaram, Aravamudan, Goubitz & Schenk, 1989).

Experimental. The title compound was prepared from the tetrakis complex, Te^{IV}L₄ ($L =$ diisopropylthiocarbamate). TeL₄ was initially prepared as a yellow solid on addition of 50 ml of 2*M* acetic acid to 30 ml of 2*M* sodium hydroxide containing 4 mmol of sodium tellurite and 100 mmol of the sodium salt of diisopropylthiocarbamic acid. The yellow solid was washed with water and air dried. 1 mmol (0.831 g) of TeL₄ was dissolved in 10 ml of dichloromethane and 5 ml of acetonitrile added. In solution TeL₄ breaks down to Te^{II}L₂ and *L-L*, the thiuram disulfide. The disulfide was removed by washing with hexane. TeL₂ was formed as red crystals; dimensions 0.52 × 0.52 × 0.52 mm, D_m by flotation in acetone-carbon tetrachloride mixture, Enraf-Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, graphite monochromator; cell parameters by least squares from setting angles of 40 reflections with $26 \leq 2\theta \leq 34^\circ$; 3513 reflections collected with $4 \leq 2\theta \leq 46^\circ$ and $0 \leq h \leq 13$, $0 \leq k \leq 14$, $0 \leq l \leq 28$ using $\omega-2\theta$ scan, three standard reflections measured every hour showed no significant change, correction for Lorentz and polarization effects; 1969 reflections with $I > 3\sigma(I)$

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Table 1. Positional parameters and U_{eq} values (\AA^2) for non-H atoms with *e.s.d.*'s in parentheses

	x	y	z	U_{eq}
Te	0.43254 (3)	0.05443 (3)	0.90058 (2)	0.0521 (4)
S1	0.5280 (1)	0.2167 (1)	0.8902 (1)	0.057 (1)
S2	0.3500 (1)	0.1122 (1)	0.8160 (1)	0.060 (1)
S3	0.5647 (1)	0.1053 (1)	0.9861 (1)	0.068 (1)
S4	0.2817 (2)	0.9235 (1)	0.8570 (1)	0.083 (1)
N1	0.6527 (4)	0.2821 (4)	0.9670 (2)	0.065 (4)
N2	0.1897 (4)	0.0059 (3)	0.7751 (2)	0.058 (3)
C1	0.1174 (5)	-0.0840 (5)	0.7737 (3)	0.068 (5)
C2	0.1638 (5)	0.0833 (5)	0.7366 (3)	0.064 (4)
C3	0.1247 (6)	0.1777 (5)	0.7610 (3)	0.078 (5)
C4	0.5899 (4)	0.2082 (4)	0.9514 (3)	0.056 (4)
C5	0.2537 (6)	0.0996 (6)	0.6965 (3)	0.080 (5)
C6	0.7060 (6)	0.2835 (5)	1.0187 (3)	0.076 (4)
C7	0.2650 (4)	0.0115 (4)	0.8115 (2)	0.052 (4)
C8	0.1206 (7)	-0.1304 (6)	0.7203 (4)	0.101 (6)
C9	0.7909 (6)	0.2037 (6)	1.0252 (3)	0.092 (6)
C10	0.0029 (7)	-0.0571 (5)	0.7901 (4)	0.097 (6)
C11	0.6738 (7)	0.3679 (5)	0.9325 (3)	0.092 (6)
C12	0.7977 (9)	0.3723 (9)	0.9217 (5)	0.157 (10)
C13	0.6266 (12)	0.4594 (7)	0.9547 (4)	0.139 (9)
C14	0.6254 (8)	0.2913 (7)	1.0641 (3)	0.107 (7)

Table 2. Bond lengths (\AA) and angles ($^\circ$) involving non-H atoms with *e.s.d.*'s in parentheses

Te—S(1)	2.530 (2)	C(1)—N(2)	1.522 (8)
Te—S(2)	2.520 (2)	C(2)—N(2)	1.481 (8)
Te—S(3)	2.821 (2)	C(8)—C(1)	1.51 (1)
Te—S(4)	2.821 (2)	C(10)—C(1)	1.53 (1)
S(1)—C(4)	1.747 (7)	C(3)—C(2)	1.51 (1)
S(3)—C(4)	1.693 (6)	C(5)—C(2)	1.53 (1)
S(2)—C(7)	1.740 (6)	C(9)—C(6)	1.53 (1)
S(4)—C(7)	1.687 (6)	C(12)—C(11)	1.56 (1)
C(4)—N(1)	1.337 (8)	C(13)—C(11)	1.50 (1)
C(6)—N(1)	1.48 (1)	C(7)—N(2)	1.321 (8)
C(11)—N(1)	1.491 (9)	C(6)—C(14)	1.54 (1)
S(2)—Te—S(1)	79.9 (1)	C(7)—N(2)—C(2)	125.5 (5)
S(3)—Te—S(1)	66.0 (1)	C(8)—C(1)—N(2)	110.3 (6)
S(3)—Te—S(4)	148.1 (1)	C(10)—C(1)—N(2)	110.4 (5)
S(4)—Te—S(2)	65.8 (1)	C(10)—C(1)—C(8)	112.0 (6)
C(4)—S(1)—Te	93.1 (2)	C(3)—C(2)—N(2)	113.9 (6)
C(7)—S(2)—Te	93.2 (2)	C(5)—C(2)—N(2)	113.0 (5)
C(4)—S(3)—Te	84.6 (2)	C(5)—C(2)—C(3)	112.7 (6)
C(7)—S(4)—Te	84.3 (2)	C(9)—C(6)—N(1)	113.3 (6)
C(6)—N(1)—C(4)	122.5 (5)	C(14)—C(6)—N(1)	112.6 (6)
C(11)—N(1)—C(4)	121.4 (6)	C(14)—C(6)—C(9)	114.7 (7)
C(11)—N(1)—C(6)	116.1 (5)	C(12)—C(11)—N(1)	107.9 (7)
C(2)—N(2)—C(1)	115.7 (5)	C(13)—C(11)—N(1)	111.5 (7)
C(7)—N(2)—C(1)	118.7 (5)	C(13)—C(11)—C(12)	114.8 (9)

used for structure determination; structure solved by heavy-atom method using *SHELX76* (Sheldrick, 1976); Te position from Patterson map. Successive difference Fourier maps based on Te position gave the locations of remaining non-H atoms; non-H atoms refined on *F* with anisotropic and H atoms with isotropic temperature factors; maximum electron density less than 0.3 e \AA^{-3} in final difference Fourier map, $R = 0.036$, $wR = 0.042$, $w = 1/[\sigma^2(F_o) + 0.0039|F_o|^2]$, $S = 0.83$, $(\Delta/\sigma)_{\max} = 0.02$. Scattering factors were those in *SHELX76*.

Discussion. Table 1 contains the atomic coordinates and the thermal parameters of all non-H atoms. Bond distances and angles are given in Table 2.* Fig. 1 shows the *PLUTO* (Motherwell, 1978) plot of the molecule while Fig. 2 gives the packing of the molecules in the unit cell.

The two diisopropyldithiocarbamate ligands act as bidentate chelating ligands and are asymmetrically bound to the divalent Te forming a TeS_4 trapezoid with two short and two long Te—S bonds. The Te—S bond lengths are close to those found in other TeL_2 complexes. The two centrosymmetrically related molecules bridge through S(3) and S(3'). The S(3') atom of the centrosymmetrically related molecule makes a short contact with Te of 3.628 \AA which is less than the sum of the van der Waals radii of Te and S (3.86 \AA) and longer than the sum of their covalent single-bond radii (2.36 \AA) (Alcock, 1972). The Te and the five S atoms are coplanar. The sum of the angles around Te is $359.8 (1)^\circ$. The two lone pairs of electrons on Te lie above and below this TeS_5 plane. The bond parameters in the dithiocarbamate ligands are similar to those observed in tetraisopropylthiuram disulfide (Kumar, Aravamudan & Seshasayee, 1990).

* Lists of structure factors, H-atom parameters and anisotropic thermal parameters of non-H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53079 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

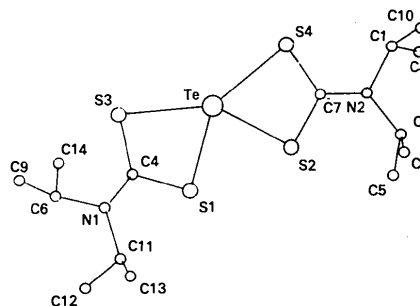
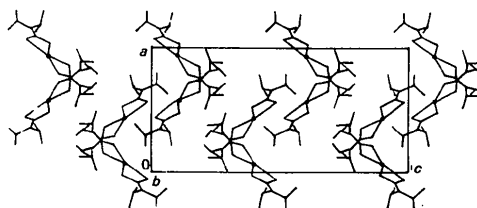
Fig. 1. *PLUTO* plot of the molecule.

Fig. 2. Packing of the molecules in the unit cell.

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References

- ALCOCK, N. W. (1972). *Adv. Inorg. Chem. Radiochem.* **15**, 1–58.
 BODE, H., TUSCHE, K. J. & WAHRHAUSEN, H. F. (1962). *Z. Anal. Chem.* **190**, 48–60.
 FABIANI, C., SPAGNA, R., VACIAGO, A. & ZAMBONELLI, L. (1971). *Acta Cryst.* **B27**, 1499–1504.
 GANESH, V., SESHASAYEE, M., CHIDAMBARAM, SP., ARAVAMUDAN, G., GOUBITZ, K. & SCHENK, H. (1989). *Acta Cryst.* **C45**, 1506–1509.
 HUSEBYE, S. (1967). *Acta Chem. Scand.* **21**, 42–52.
 HUSEBYE, S. (1970). *Acta Chem. Scand.* **24**, 2198–2210.
 KUMAR, V., ARAVAMUDAN, G. & SESHASAYEE, M. (1990). *Acta Cryst.* **C46**, 674–676.
 MOTHERWELL, W. D. S. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
 ROUT, G. C., SESHASAYEE, M., RADHA, K. & ARAVAMUDAN, G. (1983). *Acta Cryst.* **C39**, 1021–1023.
 SCHNABEL, W., DEUTEN, K. V. & KLAR, G. (1980). *Phosporus Sulfur*, **9**, 93–98.
 SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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Structure du Trihydrogène Hydroxy-1 Ethanedi(phosphonate)-1,1 de Sodium Monohydrate

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Abstract. Na[C(CH₃)(OH)(P₂O₆H₃)]·H₂O, $M_r = 246.03$, orthorhombic, $Pcab$, $a = 18.773$ (3), $b = 11.834$ (4), $c = 7.500$ (3) Å, $V = 1666$ (2) Å³, $Z = 8$, $D_x = 1.96$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 5.278$ mm⁻¹, $F(000) = 1008$, room temperature. The structure was solved with the direct method and refined to $R = 0.049$ for 917 independent reflections. The coordination about Na is nearly octahedral. Na is bound to one bidentate and one tridentate HEDP⁻ ligand and one water molecule. Diphosphonate ions are linked together in double chains by very strong hydrogen bonds [O...O = 2.426 (5) and 2.544 (5) Å].

Introduction. Ce travail entre dans le cadre d'une étude structurale systématique des complexes susceptibles de se former entre cations métalliques et acides

organophosphorés à fonction hydroxydiphosphonique.†

Partie expérimentale. Le complexe Na[C(CH₃)(OH)(P₂O₆H₃)]·H₂O est obtenu sous forme de monocristaux prismatiques incolores par évaporation lente à température ambiante d'une solution aqueuse d'hydroxyde de sodium et d'acide hydroxyéthylidenediphosphonique (HEDP) dans le rapport molaire NaOH:HEDP = 1.

Cristal sélectionné pour l'étude structurale de dimensions 0,75 × 0,30 × 0,25 mm. Intensités collectées sur un diffractomètre Philips PW 1100 équipé d'un monochromateur en graphite. Paramètres de la maille affinés par moindres carrés en utilisant 25

† Etude intégrée dans une Action de Recherche Coordonnée pluridisciplinaire soutenue par le PIRSEM - CNRS et l'AFME portant sur la synthèse et la mise au point de nouveaux extractants hydroxydiphosphonés à hautes performances.

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