

A significant feature observed in $\text{Sm}(\text{C}_5\text{H}_5)_3\text{NCCD}_3$ is the deviation from linearity of the $\text{Sm}-\text{N}=\text{C}$ arrangement: there is a bending of about 5° between the $\text{Sm}-\text{N}$ bond and the linear acetonitrile ligand as shown by the $\text{Sm}-\text{N}\equiv\text{C}$ angle (Table 2). Analogous deviations are displayed by the propionitrile derivative $(\text{C}_5\text{H}_5)_3\text{M}(\text{py})$ ($M = \text{Sm}, \text{Nd}$) (Deacon *et al.*, 1987). The deviations could result from steric hindrance in the unit-cell packing since there are some short intermolecular contacts (Table 2), less than 3.7 \AA (Pauling, 1960; Raymond & Eigenbrot, 1980), involving the acetonitrile C atoms and the cyclopentadienyl rings in $\text{Sm}(\text{C}_5\text{H}_5)_3\text{NCCD}_3$, and also in the $\text{Ln}(\text{C}_5\text{H}_5)_3\text{NCCH}_2\text{CH}_3$ complex (Spirlet *et al.*, 1987). It should be noted, nevertheless, that a nearly linear $\text{Pr}-\text{C}\equiv\text{N}$ arrangement has been observed in the isocyanide complex $(\text{C}_5\text{H}_5)_3\text{Pr}(\text{CN}-\text{C}-\text{C}_6\text{H}_{11})$ (Burns & Baldwin, 1976).

References

- BAKER, E. C. & RAYMOND, K. N. (1977). *Inorg. Chem.* **16**, 2710–2713.
- BENETOLLO, F., BOMBIERI, G., BISI CASTELLANI, C., JOHN, W. & FISHER, R. D. (1984). *Inorg. Chim. Acta*, **95**, L7–L10.
- BURNS, J. H. & BALDWIN, W. H. (1976). *J. Organomet. Chem.* **120**, 361–365.
- DEACON, G. B., GATEHOUSE, B. M., PLATTS, S. N. & WILKINSON, D. L. (1987). *Aust. J. Chem.* **40**, 907–914.
- DEACON, G. B., KOPPLICK, A. J. & TUONG, T. D. (1984). *Aust. J. Chem.* **37**, 517–520.
- ENRAF-Nonius (1986). *SDP-Plus Structure Determination Package*. Version 18. Enraf-Nonius, Delft, The Netherlands.
- NI, C., DENG, D. & QIAN, C. (1985). *Inorg. Chim. Acta*, **110**, L7–L11.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd edition. Ithaca: Cornell Univ. Press.
- RAYMOND, K. N. & EIGENBROT, C. W. (1980). *Acc. Chem. Res.* **13**, 276–280.
- REBIZANT, J., APOSTOLIDIS, C., SPIRLET, M. R. & KANELLAKOPOULOS, B. (1988). *Acta Cryst.* **C44**, 614–616.
- ROGERS, R. D., ATWOOD, J. L., EMAD, A., SIKORA, D. J. & RAUSH, M. D. (1981). *J. Organomet. Chem.* **216**, 383–388.
- ROGERS, R. D., BYNUM, R. V. & ATWOOD, J. L. (1980). *J. Organomet. Chem.* **192**, 65–69.
- SHANNON, R. D. (1976). *Acta Cryst.* **A32**, 751–754.
- SPIRLET, M. R., REBIZANT, J., APOSTOLIDIS, C. & KANELLAKOPOULOS, B. (1987). *Inorg. Chim. Acta*, **139**, 211–213.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.
- WONG, C. H., LEE, T. Y. & LEE, Y. T. (1969). *Acta Cryst.* **B25**, 2580–2587.

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Structure of a Dipotassium Tetraiodomercurate(II) Salt with Dibenzo-18-crown-6

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Abstract. Bis[(dibenzo[*b,k*][1,4,7,10,13,16]hexaoxacyclooctadeca-2,11-diene)potassium] tetraiodomercurate(II) hemiethanol solvate, $[\text{K}(\text{C}_{20}\text{H}_{24}\text{O}_6)]_2\text{[HgI}_4\text{]}\cdot 1/2\text{C}_2\text{H}_5\text{OH}$, $M_r = 1507.2$, triclinic, $P\bar{1}$, $a = 11.994$ (4), $b = 14.999$ (5), $c = 17.051$ (6) \AA , $\alpha = 63.43$ (2), $\beta = 77.91$ (3), $\gamma = 68.46$ (3) $^\circ$, $U = 2548$ (1) \AA^3 , $Z = 2$, $D_m = 1.93$ (3), $D_x = 1.96 \text{ g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.7107 \text{ \AA}$, $\mu = 56.3 \text{ cm}^{-1}$, $F(000) = 1446$, $T = 150 \text{ K}$, final $R = 0.049$ for 6154 [$I > 3\sigma(I)$] independent observed reflections. The structure of the molecule essentially consists of two potassium-crown ether cations linked through a central tetrahedral tetraiodomercurate anion with $\text{K}\cdots\text{I}$ distances of 3.520 (3) and 3.474 (3) \AA . Both the potassium ions are thus seven coordinate (six O atoms from the crown ether and one I atom from the anion). The

average $\text{K}\cdots\text{O}$ distances are 2.743 \AA in both complex cations.

Introduction. Many compounds containing the $[\text{K-DB18C6}]^+$ cation (as well as the $[\text{K-18C6}]^+$ cation) have been prepared and characterized, partly because potassium forms the most stable complex cation with crown ethers with six O atoms (Dobler, 1981). However, relatively few structures of these compounds have been reported. Those reported include the iodide (Hilgenfeld & Saenger, 1981), a series of aluminates (Atwood, Hunter, Rogers & Weeks, 1985; Zaworotko, Reid & Atwood, 1985), a complex chromium anion (Wink, Fox & Cooper, 1985), a cobaltate(II) (Fan, Zhang, Wang, Zhang & Han, 1985) and two mercurate(II) complexes (Mok,

McKee & Robinson, 1987, 1989). We report here the structure of the tetraiodomercurate(II).

Experimental. Compound prepared by reacting an aqueous alcohol solution of dipotassium tetraiodomercurate(II) with a solution of dibenzo-18-crown-6 in chloroform. Density by flotation in CCl_4 /petroleum ether. Crystal size approximately $0.30 \times 0.40 \times 0.44$ mm. Data collected at 150 K on a Nicolet R3m four-circle diffractometer using graphite-monochromated Mo $K\alpha$ radiation; unit-cell parameters determined by least-squares refinement of 20 accurately centred reflections in the range $13 < 2\theta < 32^\circ$; ω -scan mode at scan rate $4.88^\circ \text{ min}^{-1}$. 8979 reflections measured in the range $4 < 2\theta < 50^\circ$, h 0 to -15 , k -18 to 18 , l -21 to 21 ; statistical analysis suggested space group $P\bar{1}$. Crystal stability monitored by measuring three standards for every 97 reflections, no significant variations observed. Data corrected for Lorentz and polarization effects; empirical absorption correction based on t -scan data applied ($T_{\text{max}} = 0.93$, $T_{\text{min}} = 0.55$). 6154 data with $I > 3\sigma(I)$ used in structural analysis. Structure solved using Patterson calculation followed by tangent expansion which revealed positions of all non-H atoms. All non-H atoms except those of solvent molecule refined anisotropically. H atoms inserted at calculated positions on macrocyclic ligands, a common thermal parameter incorporated using a riding model. Solvent molecule detected in the asymmetric unit and refined at half occupancy; O atom not clearly distinguished and all solvent atoms treated as C atoms. Function minimized $\sum w(F_o - F_c)^2$ where $w = [\sigma^2(F_o) + 0.00064F_o^2]^{-1}$. Final $R = 0.049$, $wR = 0.059$, $S = 1.501$ with final max. shift/e.s.d. < 0.05 . In difference map preceding final refinement maximum and minimum heights $+2.4$ and $-1.5 \text{ e } \text{\AA}^{-3}$ located near Hg atom. Data reduction and structure refinement performed on Nova 4X computer using *SHELXTL* Version 4.0 (Sheldrick, 1984); Patterson calculation and tangent expansion used *SHELXS86* (Sheldrick, 1986). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic coordinates are given in Table 1, and details of selected interatomic distances and angles in Table 2.*

Discussion. The structure of the molecule is shown in Fig. 1. The tetraiodomercurate(II) ion is a slightly distorted tetrahedron with I—Hg—I angles in the

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a full list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53139 (59 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) and isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Hg	1196.6 (4)	6611.3 (3)	2040.8 (3)	37 (1)*
I(1)	2651 (1)	6455 (1)	575 (1)	51 (1)*
I(2)	1751 (1)	8163 (1)	2253 (1)	43 (1)*
I(3)	-1307 (1)	7306 (1)	2012 (1)	49 (1)*
I(4)	1810 (1)	4590 (1)	3384 (1)	40 (1)*
K(1)	1548 (2)	7378 (2)	-1498 (2)	41 (1)*
K(2)	1809 (2)	8069 (2)	4317 (2)	35 (1)*
O(11)	3942 (7)	6919 (5)	-2012 (5)	39 (4)*
C(12)	4487 (10)	5913 (8)	-2063 (7)	37 (5)*
C(13)	3878 (12)	5162 (8)	-1376 (7)	47 (6)*
O(14)	2678 (8)	5474 (5)	-1600 (5)	43 (4)*
C(15)	2121 (11)	4708 (8)	-1019 (7)	44 (6)*
C(16)	800 (11)	5119 (8)	-1241 (7)	43 (6)*
O(17)	219 (7)	6078 (6)	-1100 (5)	43 (4)*
C(18)	-983 (11)	6485 (8)	-1166 (7)	41 (6)*
C(19)	-1670 (12)	6120 (10)	-1418 (8)	55 (7)*
C(20)	-2887 (15)	6572 (11)	-1406 (9)	72 (9)*
C(21)	-3457 (14)	7391 (11)	-1136 (9)	63 (7)*
C(22)	-2768 (12)	7786 (9)	-907 (7)	50 (6)*
C(23)	-1535 (12)	7353 (8)	-916 (6)	41 (6)*
O(24)	-760 (8)	7715 (5)	-740 (5)	45 (4)*
C(25)	-1281 (11)	8678 (8)	-616 (7)	46 (6)*
C(26)	-334 (11)	8984 (8)	-453 (7)	44 (6)*
O(27)	518 (7)	9134 (5)	-1196 (5)	44 (4)*
C(28)	1347 (12)	9567 (9)	-1102 (8)	51 (7)*
C(29)	2202 (13)	9732 (8)	-1886 (7)	51 (6)*
O(30)	2878 (7)	8726 (5)	-1926 (5)	45 (4)*
C(31)	3769 (10)	8705 (8)	-2573 (7)	33 (5)*
C(32)	4112 (11)	9562 (8)	-3166 (7)	40 (6)*
C(33)	4998 (10)	9473 (9)	-3831 (7)	41 (6)*
C(34)	5549 (11)	8525 (10)	-3882 (8)	45 (6)*
C(35)	5228 (10)	7625 (9)	-3261 (7)	37 (6)*
C(36)	4328 (11)	7734 (8)	-2639 (7)	43 (6)*
O(41)	2357 (6)	5975 (5)	5278 (4)	35 (3)*
C(42)	1406 (10)	5514 (8)	5472 (8)	42 (6)*
C(43)	502 (10)	6235 (8)	4797 (7)	37 (5)*
O(44)	-15 (6)	7224 (5)	4893 (4)	32 (3)*
C(45)	-1000 (10)	7901 (9)	4365 (8)	42 (6)*
O(46)	-1418 (10)	8920 (9)	4470 (7)	38 (6)*
C(47)	-509 (6)	9420 (5)	4111 (5)	33 (3)*
C(48)	-807 (10)	10462 (8)	3924 (6)	32 (5)*
C(49)	-1950 (10)	11090 (8)	4028 (7)	36 (5)*
C(50)	-2197 (11)	12165 (8)	3777 (7)	39 (6)*
C(51)	-1276 (11)	12585 (9)	3468 (7)	42 (6)*
C(52)	-84 (10)	11952 (8)	3381 (6)	33 (5)*
C(53)	127 (9)	10896 (7)	3611 (6)	28 (5)*
O(54)	1223 (7)	10216 (5)	3524 (5)	37 (4)*
C(55)	2212 (10)	10629 (8)	3153 (7)	37 (5)*
C(56)	3271 (11)	9814 (8)	2950 (7)	38 (6)*
O(57)	3680 (6)	8931 (5)	3748 (4)	32 (3)*
C(58)	4680 (10)	8143 (8)	3591 (8)	40 (6)*
C(59)	5032 (10)	7224 (9)	4453 (8)	41 (6)*
O(60)	4103 (6)	6752 (5)	4760 (4)	32 (3)*
C(61)	4284 (9)	5836 (8)	5515 (7)	31 (5)*
C(62)	5284 (11)	5327 (8)	5977 (7)	44 (6)*
C(63)	5377 (14)	4419 (9)	6734 (8)	53 (7)*
C(64)	4422 (12)	4036 (8)	7044 (7)	44 (6)*
C(65)	3387 (11)	4530 (8)	6574 (7)	42 (6)*
C(66)	3318 (10)	5436 (8)	5793 (7)	37 (5)*
C(1)	4660 (34)	-45 (31)	9239 (27)	95 (11)
C(2)	4991 (29)	662 (25)	9354 (21)	74 (9)
C(3)	5637 (42)	560 (37)	10039 (31)	130 (16)

*Equivalent isotropic U defined as one third of the trace of the orthogonalized U_j tensor.

range $102.6(1)$ – $121.3(1)^\circ$ with an average of $109.6(3)^\circ$. It is interesting to note that in the series $[\text{DB18C6-K}]_2[\text{HgX}_4]$ ($X = \text{CN}$, I and SCN), the $X\text{—Hg—X}$ angle has the narrowest range from 106 to 115° in the tetracyano anion in which one CN forms a bridging group between Hg and K atoms (Mok, McKee & Robinson, 1987) and the widest range from 98 to 127° in the tetrathiocyanato anion in which three SCN groups are bridging (Mok, McKee & Robinson, 1989). The tetraiodo anion has

Table 2. Selected bond lengths (Å) and angles (°)

Hg—I(1)	2.783 (1)	Hg—I(2)	2.825 (1)
Hg—I(3)	2.797 (1)	Hg—I(4)	2.799 (1)
I(1)—K(1)	3.520 (3)	I(2)—K(2)	3.474 (3)
K(1)—O(11)	2.743 (8)	K(1)—O(14)	2.744 (8)
K(1)—O(17)	2.728 (10)	K(1)—O(24)	2.765 (9)
K(1)—O(27)	2.699 (9)	K(1)—O(30)	2.780 (10)
K(2)—O(41)	2.705 (7)	K(2)—O(44)	2.717 (9)
K(2)—O(47)	2.755 (7)	K(2)—O(54)	2.744 (7)
K(2)—O(57)	2.783 (9)	K(2)—O(60)	2.755 (7)
O(11)—C(12)	1.442 (14)	O(11)—C(36)	1.374 (14)
C(13)—O(14)	1.419 (17)	O(14)—C(15)	1.419 (15)
C(16)—O(17)	1.455 (15)	O(17)—C(18)	1.351 (15)
C(23)—O(24)	1.372 (20)	O(24)—C(25)	1.440 (16)
C(26)—O(27)	1.439 (13)	O(27)—C(28)	1.440 (20)
C(29)—O(30)	1.453 (14)	O(30)—C(31)	1.368 (13)
O(41)—C(42)	1.450 (17)	O(41)—C(66)	1.363 (13)
C(43)—O(44)	1.454 (15)	O(44)—C(45)	1.407 (13)
C(46)—O(47)	1.427 (15)	O(47)—C(48)	1.365 (13)
C(53)—O(54)	1.364 (11)	O(54)—C(55)	1.437 (15)
C(56)—O(57)	1.427 (11)	O(57)—C(58)	1.419 (13)
C(59)—O(60)	1.422 (16)	O(60)—C(61)	1.382 (10)
I(1)—Hg—I(2)	102.6 (1)	I(1)—Hg—I(3)	121.3 (1)
I(2)—Hg—I(3)	104.8 (1)	I(1)—Hg—I(4)	105.9 (1)
I(2)—Hg—I(4)	116.9 (1)	I(3)—Hg—I(4)	106.1 (1)
Hg—I(1)—K(1)	123.6 (1)	Hg—I(2)—K(2)	121.7 (1)
I(1)—K(1)—O(11)	82.9 (2)	I(1)—K(1)—O(14)	92.4 (2)
I(1)—K(1)—O(17)	99.8 (2)	I(1)—K(1)—O(24)	89.0 (2)
I(1)—K(1)—O(27)	80.8 (2)	I(1)—K(1)—O(30)	81.0 (2)
I(2)—K(2)—O(41)	99.8 (2)	I(2)—K(2)—O(44)	89.4 (2)
I(2)—K(2)—O(47)	87.8 (2)	I(2)—K(2)—O(54)	86.8 (2)
I(2)—K(2)—O(57)	91.2 (2)	I(2)—K(2)—O(60)	100.9 (2)
O(11)—K(1)—O(14)	62.5 (3)	O(11)—K(1)—O(17)	124.4 (3)
O(14)—K(1)—O(17)	61.9 (3)	O(11)—K(1)—O(24)	171.9 (3)
O(14)—K(1)—O(24)	117.4 (3)	O(17)—K(1)—O(24)	56.3 (3)
O(11)—K(1)—O(27)	117.1 (3)	O(14)—K(1)—O(27)	173.1 (3)
O(17)—K(1)—O(27)	118.1 (3)	O(24)—K(1)—O(27)	61.9 (3)
O(11)—K(1)—O(30)	56.1 (2)	O(14)—K(1)—O(30)	118.5 (3)
O(17)—K(1)—O(30)	179.0 (2)	O(24)—K(1)—O(30)	123.4 (3)
O(27)—K(1)—O(30)	61.6 (3)	O(41)—K(2)—O(44)	62.0 (2)
O(41)—K(2)—O(47)	123.3 (2)	O(44)—K(2)—O(47)	62.0 (2)
O(41)—K(2)—O(54)	173.4 (3)	O(44)—K(2)—O(54)	117.8 (2)
O(47)—K(2)—O(54)	55.8 (2)	O(41)—K(2)—O(57)	117.7 (2)
O(44)—K(2)—O(57)	179.3 (3)	O(47)—K(2)—O(57)	118.1 (2)
O(54)—K(2)—O(57)	62.4 (2)	O(41)—K(2)—O(60)	56.2 (2)
O(44)—K(2)—O(60)	118.3 (2)	O(47)—K(2)—O(60)	171.2 (3)
O(54)—K(2)—O(60)	123.4 (3)	O(57)—K(2)—O(60)	61.5 (2)

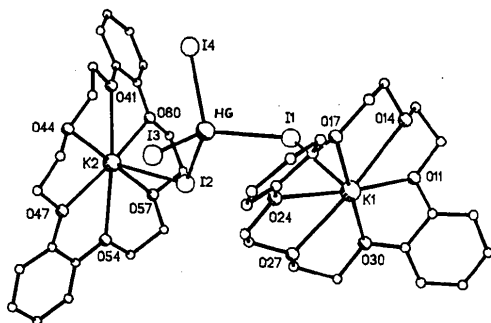


Fig. 1. Diagram showing the molecule with the solvate omitted.

two bidentate iodide ions and the range of angles falls in between the above two. Of the four Hg—I distances with an average of 2.801 (3) Å, two are almost identical at 2.797 (1) and 2.799 (1) Å and these involve non-bridging I atoms. The other two are Hg—I(1) at 2.783 (1) and Hg—I(2) at 2.825 (1) Å, respectively. These are similar to those observed in the [HgI₄]²⁻ ions in other compounds (Fenn, 1966; Van Eck, Wolters & Jaspers, 1956).

As is commonly observed for K ions in crown-ether complexes both K ions are seven coordinated: six O atoms from the crown ether and an I atom from the tetraiodomercurate(II) anion. The K(1)···I(1) and K(2)···I(2) distances are 3.520 (3) and 3.474 (3) Å, respectively, in agreement with those reported for similar compounds (Poonia & Bajaj, 1979; Aldoshin, D'yachenko, Tkachev & Atovmyen, 1981). The Hg—I(1)···K(1) and Hg—I(2)···K(2) angles are 123.6 (1) and 121.7 (1)°, respectively.

In both the [K(C₂₀H₂₄O₆)⁺] ions all the O···K···O angles are close to 60°, ranging from 56.1 (2) to 62.5 (2)° with an average of 60.1 (6)° in one case and from 55.8 (2) to 62.4 (2)° with an average of 60.6° in the other. The K atom is practically coplanar with the six O atoms of the crown ether. Thus K(1) is 0.11 (1) Å from the mean O₆ plane while the O atoms are -0.15 to 0.10 Å from the plane. Similarly K(2) is 0.13 (1) Å and the O atoms are -0.12 to 0.09 (1) Å from the mean O₆ plane. K···O distances vary from 2.699 (9) to 2.780 (10) Å for K(1) and from 2.705 (7) to 2.783 (9) Å for K(2) with an identical average of 2.743 (18) Å. Both the range and the average of the K···O distances are in agreement with corresponding values reported (Hilgenfeld & Saenger, 1981; Rogers & Atwood, 1984; Wink, Fox & Cooper, 1985).

Within the crown-ether molecule the aliphatic and aromatic C—C distances average 1.502 (26) and 1.387 (30) Å, respectively for the K(1) complex ion and the corresponding values are 1.502 (20) and 1.386 (25) Å for the K(2). Average O—C(aliphatic) and O—C(aromatic) distances are 1.438 (25) and 1.366 (20) Å for K(1) and 1.430 (18) and 1.369 (15) Å for the K(2) complex ion respectively, in agreement with corresponding values in other complexes.

The solvent ethanol molecule in the crystal is disordered about a centre of symmetry. The half-occupancy site is probably disordered between O(1)—C(2)—C(3) and C(1)—C(2)—O(3). The presence of the solvent molecule did not significantly affect the refinement of the crystal structure.

References

- ALDOSHIN, S. M., D'YACHENKO, O. A., TKACHEV, V. V. & ATOVMYEN, L. O. (1981). *Koord. Chem.* **7**, 287–296.
- ATWOOD, J. L., HUNTER, W. E., ROGERS, R. D. & WEEKS, J. A. (1985). *J. Inclusion Phenom.* **3**, 113–123.
- DOBLER, M. (1981). *Ionophores and Their Structures*. New York: John Wiley.
- FAN, Y. P., ZHANG, Z. Y., WANG, X. M., ZHANG, J. Z. & HAN, J. F. (1985). *Kexue Tongbao* (foreign language edition), **30**, 910–915.
- FENN, R. H. (1966). *Acta Cryst.* **20**, 24–27.
- HILGENFELD, R. & SAENGER, W. (1981). *Angew. Chem. Int. Ed. Engl.* **20**, 1045–1046.

- 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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