

## Structure of Tetrachlorobis(dimethyl sulphoxide)tin(IV), $[\text{SnCl}_4(\text{C}_2\text{H}_6\text{OS})_2]$

BY JONATHAN M. KISENYI AND GERALD R. WILLEY

*Department of Chemistry, University of Warwick, Coventry CV4 7AL, England*

AND MICHAEL G. B. DREW

*Department of Chemistry, University of Reading, Whiteknights, Reading RG6 2AD, England*

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**Abstract.**  $M_r = 416.8$ , monoclinic,  $P2_1/n$ ,  $a = 7.417$  (8),  $b = 14.414$  (8),  $c = 13.346$  (8) Å,  $\beta = 91.0$  (1)°,  $V = 1426.6$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.94$ ,  $D_m = 1.91$  (1) g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 27.9$  cm<sup>-1</sup>,  $F(000) = 808$ , room temperature,  $R = 0.065$  for 2401 independent observed reflections. The Sn atom is six-coordinate with *cis* octahedral geometry. The two molecules of dimethyl sulphoxide are bonded through O [Sn—O 2.110 (7), 2.110 (8) Å]. The Sn—Cl bond lengths vary between 2.369 (3) and 2.406 (3) Å. The S—O bond lengths, 1.538 (8) and 1.578 (8) Å, are longer than the S=O bond, 1.471 Å, in the uncomplexed ligand. S—C distances are essentially the same as those in the free ligand.

**Introduction.** Recent structural studies of  $N,N'$ -disubstituted oxamide and dithiooxamide complexes with  $\text{MX}_3$  ( $M = \text{As, Sb, Bi}$ ;  $X = \text{Cl, Br, I}$ ) and  $\text{MX}_4$  ( $M = \text{Ti, Sn}$ ;  $X = \text{Cl, Br}$ ) have shown that ligand attachment can feature either bidentate (OO/SS) bridging or chelation but never direct N-donor involvement (Drew, Kisenyi & Willey, 1982, 1984*a,b*; Drew, Kisenyi, Willey & Wandiga, 1984). From attempts to recrystallize the product of the reaction between  $\text{SnCl}_4$  and  $\text{EtNH.CO.CH}_2\text{CO.NHEt}$  we obtained colourless crystals which were assumed to be the *cis* octahedral (OO)-chelated 1:1 adduct.

The structure determination, however, revealed the product as  $[\text{SnCl}_4(\text{Me}_2\text{SO})_2]$  (1); evidently ligand substitution has occurred with the 'hard'  $\text{Sn}^{\text{IV}}$  showing a preference for the O-donor solvent ( $\text{Me}_2\text{SO}$ ) molecules used. Since the structural parameters of (1) obtained in this present study differ significantly from those reported very briefly in an earlier less precise determination (Lindqvist, 1963), we report here the structure of this typical *cis* octahedral  $\text{SnCl}_4L_2$  molecule.

**Experimental.** Crystal of (1),  $0.3 \times 0.3 \times 0.3$  mm, obtained as described above and placed in Lindemann tube,  $D_m$  measured by flotation; precession photographs established preliminary cell constants and space group, systematic absences  $0k0$ ,  $k = 2n + 1$ ,  $h0l$ ,  $h+l = 2n+1$ ; crystal mounted on a Stoe STADI2

diffractometer to rotate about **a**. Cell dimensions obtained by measurement of *ca* 20 high-angle axial reflections; intensity data collected by variable-width  $\omega$  scan, background counts 20 s, step-scan rate  $0.033^\circ\text{s}^{-1}$ , scan width  $(1.5 + \sin\mu/\tan\theta)^\circ$ . Absorption and extinction corrections not applied.  $h22$  standard reflections measured every 20 measurements for each layer; no significant change in intensity. 4152 independent data measured with  $2\theta_{\text{max}} \leq 60^\circ$ , 2401 with  $I > 4\sigma(I)$  used in analysis; index range  $h \pm 10$ ,  $k 0/20$ ,  $l 0/18$ . Position of Sn obtained from the Patterson function; remaining heavy atoms by Fourier methods. H atoms bonded to C included as rigid groups with a common refined thermal parameter. Non-H atoms refined anisotropically by full-matrix least squares,  $F$  magnitudes; scattering factors and dispersion corrections from *International Tables for X-ray Crystallography* (1974).  $R = 0.065$ ,  $wR = 0.068$ ;  $w = 1/[\sigma^2(F) + 0.003F^2]$ . Final difference-Fourier map showed max. and min. heights of 0.65 and  $-0.56 \text{ e \AA}^{-3}$ . In final cycle of refinement all shifts  $< 0.1\sigma$ . Calculations carried out using *SHELX76* (Sheldrick, 1976) at the University of Manchester Regional Computer Centre.

**Discussion.** Final coordinates are given in Table 1\* and molecular dimensions in Table 2.

A perspective view of the molecule with labelled atoms is given in Fig. 1. Sn is six-coordinate bonded to four Cl and two mutually *cis* O atoms of  $\text{Me}_2\text{SO}$  ligands. Although interbond angles are close to ideal there are some slight distortions from the ideal octahedron. The smallest angle is that between the *cis* ligands [O(1)—Sn—O(2)  $83.3$  (3)°] and the largest that between *cis* Cl atoms [Cl(3)—Sn—Cl(4)  $97.5$  (1)°]. The two mutually *trans* Cl atoms, Cl(1) and Cl(2) [Cl(1)—Sn—Cl(2)  $173.0$  (1)°], show a definite 'tilt' towards the

\* Lists of structure factors, anisotropic thermal parameters and H positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42004 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Me<sub>2</sub>SO ligands and away from the remaining two Cl atoms. In the absence of crystal-field effects the most likely cause of these deviations is the size inequality of the surrounding atoms, O < S. As is clear from Fig. 1, the flexibility of the Me<sub>2</sub>SO ligand ensures that the SMe<sub>2</sub> groups are kept well away from the coordination sphere.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ ) with e.s.d.'s in parentheses

	x	y	z	$U_{\text{eq}}^\dagger$
Sn(1)	4974 (1)	3431.2 (4)	7701 (1)	47 (1)
Cl(1)	2850 (4)	3395 (3)	9006 (3)	82 (4)
Cl(2)	7070 (4)	3267 (3)	6367 (3)	80 (4)
Cl(3)	6645 (4)	4684 (2)	8409 (3)	63 (3)
Cl(4)	2955 (4)	4338 (2)	6665 (3)	76 (3)
S(1)	7211 (4)	1580 (2)	8234 (2)	60 (3)
S(2)	3256 (4)	2012 (2)	6078 (2)	52 (2)
O(1)	3765 (11)	2180 (5)	7217 (6)	52 (7)
O(2)	6574 (12)	2536 (6)	8596 (7)	63 (9)
C(3)	9384 (23)	1489 (12)	8841 (14)	89 (19)
C(4)	5954 (23)	773 (11)	8935 (17)	86 (20)
C(5)	4325 (25)	946 (13)	5817 (15)	91 (21)
C(6)	986 (21)	1694 (17)	6118 (14)	97 (22)

$$\dagger U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j \cdot a_j$$

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

Sn(1)—Cl(1)	2.369 (3)	S(1)—O(2)	1.538 (8)
Sn(1)—Cl(2)	2.396 (3)	S(1)—C(3)	1.796 (16)
Sn(1)—Cl(3)	2.377 (3)	S(1)—C(4)	1.768 (17)
Sn(1)—Cl(4)	2.406 (3)	S(2)—O(1)	1.578 (8)
Sn(1)—O(1)	2.110 (7)	S(2)—C(5)	1.766 (15)
Sn(1)—O(2)	2.110 (8)	S(2)—C(6)	1.747 (16)
Cl(1)—Sn(1)—Cl(2)	173.01 (15)	Cl(3)—Sn(1)—O(2)	87.45 (25)
Cl(1)—Sn(1)—Cl(3)	94.22 (14)	Cl(4)—Sn(1)—O(2)	174.77 (25)
Cl(2)—Sn(1)—Cl(3)	91.68 (13)	O(1)—Sn(1)—O(2)	83.26 (30)
Cl(1)—Sn(1)—Cl(4)	91.10 (14)	O(2)—S(1)—C(3)	101.6 (6)
Cl(2)—Sn(1)—Cl(4)	91.84 (13)	O(2)—S(1)—C(4)	104.8 (7)
Cl(3)—Sn(1)—Cl(4)	97.51 (12)	C(3)—S(1)—C(4)	101.0 (8)
Cl(1)—Sn(1)—O(1)	85.53 (24)	O(1)—S(2)—C(5)	102.9 (7)
Cl(2)—Sn(1)—O(1)	88.05 (24)	O(1)—S(2)—C(6)	103.0 (6)
Cl(3)—Sn(1)—O(1)	170.71 (23)	C(5)—S(2)—C(6)	102.3 (10)
Cl(4)—Sn(1)—O(1)	91.78 (22)	Sn(1)—O(1)—S(2)	121.3 (4)
Cl(1)—Sn(1)—O(2)	86.85 (28)	Sn(1)—O(2)—S(1)	122.9 (5)
Cl(2)—Sn(1)—O(2)	89.68 (28)		

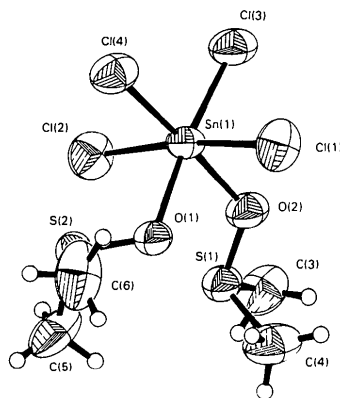


Fig. 1. The structure of  $[\text{SnCl}_4(\text{Me}_2\text{SO})_2]$ . 50% probability ellipsoids are shown.

Bond distances for Sn—Cl are listed in Table 2. There is no obvious pattern between Cl atoms which are *trans* to an Me<sub>2</sub>SO ligand and those *trans* to another Cl atom. The range of Sn—Cl bond lengths, *viz* 2.369 (3)–2.406 (3)  $\text{\AA}$  is similar to that in *cis*-SnCl<sub>4</sub>L<sub>2</sub> complexes in general (Zubieta & Zuckerman, 1978) and in particular where L = monodentate O donor {*cf.* [SnBr<sub>4</sub>(OH<sub>2</sub>)<sub>2</sub>].(C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>)<sub>2</sub> (Barnes & Weakley, 1976), [SnCl<sub>4</sub>(OH<sub>2</sub>)<sub>2</sub>].3H<sub>2</sub>O (Barnes, Sampson & Weakley, 1980), and [SnCl<sub>4</sub>(OH<sub>2</sub>)<sub>2</sub>].(18-crown-6).2H<sub>2</sub>O.CHCl<sub>3</sub> (Cusack, Patel, Smith, Allen & Nowell, 1984)}.

The Sn—O distances are identical at 2.110 (7) and 2.110 (8)  $\text{\AA}$ . There is approximate trigonal geometry (*sp*<sup>2</sup>) about the O centres, 122.9 (5) and 121.3 (4) $^\circ$ , leaving space for a formal lone pair on each. The S—O bond lengths are 1.538 (8) and 1.578 (8)  $\text{\AA}$  which represents a decrease of multiplicity of the S=O bond following O-donation to the metal; uncomplexed Me<sub>2</sub>SO has S=O 1.471  $\text{\AA}$  (Viswamitra & Kannan, 1966). The S—C distances vary between 1.747 (16) and 1.796 (16)  $\text{\AA}$  and are essentially unchanged from those of the free ligand. There is approximate tetrahedral geometry about the S atoms, angles varying between 101.0 (8) and 104.8 (7) $^\circ$  with an incipient lone pair occupying the remaining tetrahedral position.

This structural characterization of *cis*-[SnCl<sub>4</sub>-(Me<sub>2</sub>SO)<sub>2</sub>] is of interest *vis-à-vis* the observed isomerism of SnX<sub>4</sub>L<sub>2</sub> compounds in general (X=Cl, Br, I; L=O-, S-, Se-, N-donor systems) (Ruzicka & Merbach, 1977). In particular, Zahrobsky (1971) argues that theoretical arguments point to the preferential stability of the *cis*-isomer especially for O-donor ligands. *cis-trans*-Isomerism of (1) in the solid state has been reported by Davanzo & Gushikem (1981).

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## Structure du Chlorure de *trans*-Diamminechloro(diméthylsulfoxyde)platine(II), $[\text{PtCl}(\text{NH}_3)_2(\text{C}_2\text{H}_5\text{OS})]\text{Cl}$

PAR J.-M. DELAFONTAINE, P. KHODADAD, P. TOFFOLI ET N. RODIER

Laboratoire de Chimie Minérale, Faculté des Sciences Pharmaceutiques et Biologiques, rue J.-B. Clément,  
 92290 Châtenay-Malabry, France

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**Abstract.**  $M_r = 378.2$ , monoclinic,  $P2_1/c$ ,  $a = 6.718$  (1),  $b = 15.108$  (3),  $c = 9.426$  (2) Å,  $\beta = 104.31$  (2)°,  $V = 927.0$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 2.64$  (4),  $D_x = 2.71$  Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 16.03$  mm<sup>-1</sup>,  $F(000) = 696$ ,  $T = 294$  (1) K,  $R = 0.023$  for 1271 independent reflections [ $I > 3\sigma(I)$ ]. The coordination around the Pt atom is 'square planar'. The Pt atoms are almost situated in the  $x = \frac{1}{2}$  plane. The  $[\text{Pt}(\text{NH}_3)_2\text{Cl}\{(\text{CH}_3)_2\text{SO}\}]^+$  cations form columns parallel to the  $a$  axis; they are linked within each column by  $\text{NH}\cdots\text{O}$  hydrogen bonds and between columns by  $\text{NH}\cdots\text{Cl}$  hydrogen bonds.

**Introduction.** L'étude structurale du chlorure de *trans*-diamminechloro(diméthylsulfoxyde)platine(II) a été entreprise dans le but de connaître l'environnement et le rôle de la molécule de diméthylsulfoxyde. Le produit utilisé a été préparé à la température ambiante par action du *trans*-diamminedichloroplatine(II) sur le diméthylsulfoxyde (Khodadad, 1984). Les teneurs en platine, azote, carbone et hydrogène du produit obtenu ont été déterminées par analyse chimique. L'évaporation lente de la solution aqueuse donne des cristaux prismatiques, presque incolores, parmi lesquels a été prélevé le monocristal étudié.

**Partie expérimentale.** Mesure de  $D_m$  sur monocristal, poussée d'Archimède. Cristal parallélépipédique:  $0,035 \times 0,070 \times 0,300$  mm. Diffractomètre Enraf-Nonius CAD-4. Dimensions de la maille déterminées avec 25 réflexions telles que  $4,13 \leq \theta \leq 17,91$ °. Corrections d'absorption empiriques selon Walker & Stuart (1983). Valeurs extrêmes de la correction d'absorption: 0,816 et 1,224.  $0,037 \leq (\sin\theta)/\lambda \leq 0,639$  Å<sup>-1</sup>.  $0 \leq h \leq 8$ ;  $0 \leq k \leq 19$ ;  $-12 \leq l \leq 12$ . Réflexions de contrôle des intensités 120, 040 et 120. Diminution d'intensité: 1%.  $\sigma(I)/I$ : 0,0024. 2023 réflexions indépen-

dantes mesurées, 752 réflexions inobservées [ $I < 3\sigma(I)$ ]. Méthodes directes, programme *MULTAN11/82* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Affinement sur  $F$ , programme à matrice entière. Atomes H non localisés avec certitude. Paramètres affinés:  $x$ ,  $y$ ,  $z$  et  $\beta_{ij}$  de Pt, Cl, S, O, N et C.  $wR = 0,025$ ,\*  $S = 1,08$ ,  $w = 1$  si  $F \leq 0,8 F_{\text{max}}$ ,  $w = (0,8 F_{\text{max}}/F)^2$  si  $F > 0,8 F_{\text{max}}$ .  $(\Delta/\sigma)_{\text{max}} = 0,03$ .  $\Delta\rho_{\text{max}} = 1,0$  (2),  $\Delta\rho_{\text{min}} = -0,9$  (2) e Å<sup>-3</sup>. Facteur de diffusion des *International Tables for X-ray Crystallography* (1974), corrigées des  $f'$  et  $f''$ . Programmes de calcul du système *SDP* de Enraf-Nonius (1979).

**Discussion.** Les noms des atomes sont indiqués sur la Fig. 1. Le Tableau 1 rassemble les coordonnées atomiques et les facteurs de température isotropes équivalents et le Tableau 2 les principales distances interatomiques et les angles des liaisons.

L'atome de platine, tétracoordiné, a un environnement du type 'plan carré'. Il est lié aux atomes d'azote N(1) et N(2) de deux molécules d'ammoniac, à l'atome de chlore Cl(1) et à l'atome de soufre de la molécule de diméthylsulfoxyde. Le quadrilatère N(1)Cl(1)N(2)S est presque plan. Les distances des atomes qui le constituent au plan moyen correspondant sont inférieures à 0,02 Å. Il en est de même pour l'atome de platine. Les côtés du quadrilatère N(1)Cl(1)N(2)S vont de 2,963 (8) à 3,134 (7) Å et les angles de 84,7 (2) à 96,5 (2)°. Les liaisons Pt–N(1) [2,057 (7) Å] et Pt–N(2) [2,066 (8) Å] ont des longueurs comparables à celles de

\* Les listes des facteurs de structure, des paramètres thermiques anisotropes et des distances des atomes du cation au plan moyen ont été déposées au dépôt d'archives de la British Library Lending Division (Supplementary Publication No. SUP 39997: 13 pp.). On peut en obtenir des copies en s'adressant à: The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.