Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Dichloro[1,1′-(5,9-dithia-2,12-diazoniatrideca-1,12-diene-1,13-diyl)-dinaphthalen-2-olato-κ^2O,O']dimethyltin(IV) acetonitrile solvate

Stanley A. Bajue,[a] Shellie Gumbs,[a] Lauren Jones,[a] Fitzgerald B. Bramwell,[b] Brian O. Patrick,[b] John P. Selegue[b] and Carolyn Pratt Brock[b]*

[a]Department of Physical Sciences and Computer Science, Medgar Evers College, City University of New York, Brooklyn, NY 11225-2298, USA, and [b]Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055, USA
Correspondence e-mail: cpbrock@uky.edu

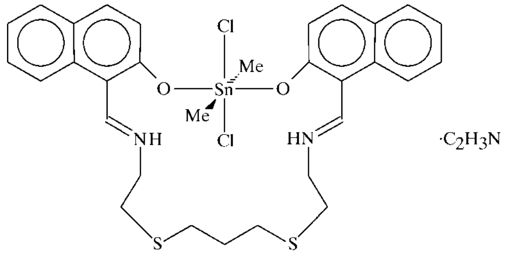
Received 21 October 2002
Accepted 18 November 2002
Online 10 December 2002

Reaction of the potentially hexadentate ligand 1,9-bis(2-hydroxy-1-naphthalenemethylimino)-3,7-dithianonane with dimethyltin chloride gave the title 1:1 adduct, in which the long ligand wraps around the $SnCl_2Me_2$ unit and in which the stereochemistry is fully *trans*. This compound crystallizes from acetonitrile as the 1:1 solvate $[Sn(CH_3)_2(C_{29}H_{30}N_2O_2S_2)Cl_2]\cdot C_2H_3N$. During the reaction, the hydroxyl protons move to the N atoms. Most of the chemically equivalent bond lengths agree to within experimental uncertainty, but the Sn—Cl bond that is inside the ligand pocket is substantially longer than the Sn—Cl bond that points away from the long ligand [2.668 (1) *versus* 2.528 (1) Å]. The O—Sn—O angle is 166.0 (1)°. Comparison of the Sn—O, C—O and aryl C—C bond lengths with those of related compounds shows that the most important resonance forms for the Schiff base aryloxide ligand are double zwitterions, but that the uncharged resonance forms having carbonyl groups also contribute significantly.

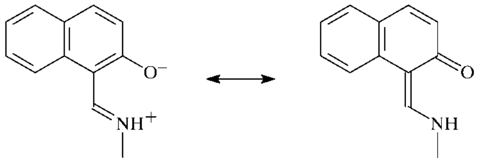
Comment

The structure of the title complex, (I), was determined as part of a continuing study (Bajue *et al.*, 1998) of organotin adducts of potentially hexadentate Schiff base ligands. In most of the known structures of this type, there are two (or more) metal centers per ligand (*e.g.* Bajue *et al.*, 1998; Degaonkar *et al.*, 1994; Wang *et al.*, 1994), but in (I) there is only one. The number of donor atoms bonded to the Sn atom varies from two to six in the comparison structures, but in (I) the ligand is bidentate. In this structure, the two ends of the long ligand wrap around the *trans*-$SnCl_2Me_2$ fragment so that the most basic ligand donors, the O atoms, coordinate in a *trans* arrangement.

The refined structure of (I) shows that the hydroxyl protons of the dinaphthol ligand migrate during the coordination reaction to the N atoms; a double zwitterion is formed if there is no rearrangement of the double bonds. The distances (Table 1) suggest, however, that the naphthoxy resonance forms (see *Scheme* below) without local charges, and in which O1—C1, O2—C20, C10—C11 and C29—C19 are all double bonds, may also be important. Resonance forms in which one side of the ligand is zwitterionic and the other uncharged must also be considered. The transfer of the protons from the O to the N atoms upon coordination can be attributed to an increase in the acidity of the naphthols upon coordination to the Lewis-acidic Sn^{IV} center. The coordinated O atoms are weaker bases than are the uncoordinated N atoms.



(I)



In the Cambridge Structural Database (CSD, Version 5.23; Allen, 2002), there are five structures, with *R* factors of 0.05 or less, of six-coordinate Sn complexes that have two halo ligands, two C ligands and one or two Schiff base aryloxide ligands: DAHVEN (Kamwaya & Khoo, 1985), KUDKID (Teoh *et al.*, 1991), LAZXEP (Hazell *et al.*, 1994), NOZMEU (Yeap & Ishizawa, 1998) and SODBUI (Fun *et al.*, 1991). In all five structures, the C1—C10 bond (numbering as in Fig. 1) is at least 0.048 Å longer than the C2—C3 bond; the maximum difference is 0.076 Å. These differences suggest that the uncharged resonance form having a carbonyl group is important. The two bond-length differences in this study [both 0.075 (6) Å] are among the largest found.

The structures in the literature have all been formulated as zwitterions; the precedent for this description seems to be Bullock *et al.* (1979). Further justification for the conclusion that the resonance forms with charge separation are more important than the uncharged forms comes from the comparison of the Sn—O and C—O bond lengths in the six Schiff base aryloxide complexes [the five literature structures plus (I)] with the corresponding Sn—O and C—O bonds in the three true Sn–ketone structures found in the CSD using search criteria analogous to those listed above. The Sn–ketone structures are BENFOP10 (Ng *et al.*, 1982), MASYUA (Howie & Wardell, 2000) and SUZWOZ (Howie & Wardell, 2001). The average Sn—O distance in the true ketone complexes

© 2003 International Union of Crystallography DOI: 10.1107/S0108270102021091

[2.444 (7) Å from four contributing values] is 0.206 (7) Å longer than in the Schiff base aryloxide complexes [2.238 (2) Å from seven contributing values]. The average C—O distance in the ketone complexes [1.227 (1) Å] is 0.077 (2) Å shorter than in the Schiff base aryloxide complexes [1.304 (2) Å].

We conclude that there is charge separation in the most important resonance forms of the Schiff base aryloxide ligand in six-coordinate Sn complexes. The non-zwitterionic resonance forms, however, are also important.

Formulating a name for the compound proved difficult. The oxidation state of the Sn atom is IV, but if the ligand is a double zwitterion then the formal charge on the Sn is −2.

The O—Sn—O bond in (I) is non-linear (Table 1 and Fig. 1), because the $SnCl_2Me_2$ fragment cannot fit further down into the ligand pocket. The determining contacts appear to be between Cl2 and the (calculated) H atoms on C12 (2.99 Å) and C17 (3.11 Å). The exact rotation of the $SnCl_2Me_2$ unit around the O1···O2 vector and the overall distortions of the molecule from potential mirror symmetry are almost certainly determined by both intra- and intermolecular contacts. There might be room in the ligand pocket for the $SnCl_2Me_2$ unit to make 180° jumps, but there is no evidence of the Cl/Me disorder that would result from 90° jumps.

The difference in lengths of the Sn—Cl bonds [0.140 (1) Å] is noteworthy, because all other pairs of chemically equivalent bonds are essentially equal in length. The longer Sn—Cl bond, which is inside the ligand pocket, may be the result of steric crowding. The distances of Cl2 to H10 and H20 (the H atoms attached to N1 and N2) are 2.75 and 2.77 Å, respectively, while the sum of the van der Waals radii for Cl and H (Bondi, 1964) is 2.95 Å. These Cl2···H distances would be even shorter if the Sn—Cl2 bond were as short as the Sn—Cl1 bond.

The packing diagram for (I) (Fig. 2) is surprisingly simple. The widths of the naphthyl and $S(CH_2)_3S$ units are similar, so that 2:1 stacks are formed. There is no evidence, however, of strong π–π-stacking interactions; distances between corresponding C atoms in overlapping naphthyl fragments vary from 3.65 to 4.16 Å. The $SnCl_2Me_2$ units are substantially thinner than the repeat unit of the 2:1 stack, so acetonitrile molecules are included in the unit cell. The shortest S···S contact [3.646 (1) Å] is between two S1 atoms related by an inversion center; the shortest contacts involving S2 are to the disordered solvent molecule.

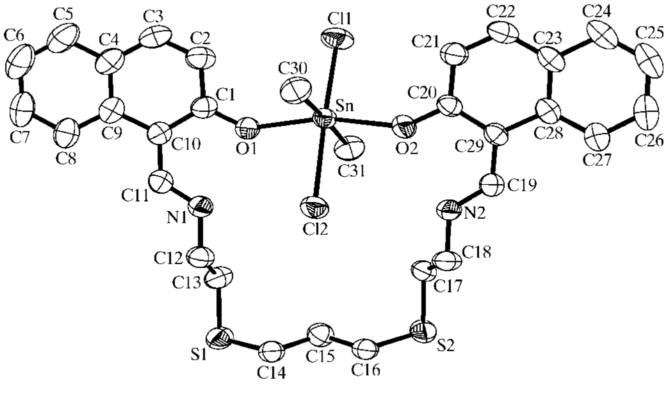


Figure 1
A perspective drawing of the molecule of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for the sake of clarity.

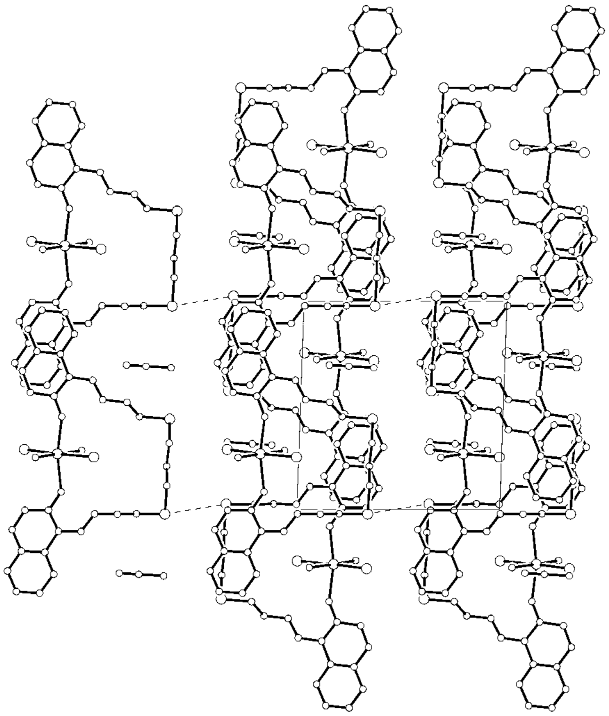


Figure 2
A drawing showing the crystal packing in (I), viewed down the *a* axis; the *c* axis points from left to right and *b* points downwards. Both *c* and *b* point slightly out of the plane of the paper. Molecules have been removed from the leftmost layer so that the overlap of naphthyl units can be seen more clearly.

Experimental

1,9-Diamino-3,7-dithianonane, $H_2N(CH_2)_2S(CH_2)_3S(CH_2)_2NH_2$ or ete, was prepared using the published procedure of Dwyer *et al.* (1952). 1,9-Bis(2-hydroxy-1-naphthalenemethylimino)-3,7-dithianonane or H2*L*, was prepared as follows. Under vigorous stirring, 2-hydroxy-1-naphthaldehyde (10 g) in ethanol (30 ml) was added slowly to ete (5.0 g) in ethanol (20 ml). Stripping off the ethanol from the mixture left a pale-yellow oil, which changed to a green–yellow solid after several days at 276 K. The product was recrystallized several times from ethanol (yield 7.5 g, 57%; m.p. 423–424 K). Analysis found: C 69.22, H 6.11, N 5.62%; calculated: C 69.29, H 6.02, N 5.57%. The title compound was prepared by adding H2*L* (0.344 g, 0.0068 mol) to dichlorodimethyltin(IV) (0.365 g, 0.0017 mol) in ethanol (50 ml). After refluxing for 2 h, the yellow solid that separated from the solution was cooled and filtered. The product was recrystallized from acetonitrile to give a pale-yellow material, (I) (m.p. 481–483 K). Analysis found: C 52.05, H 5.19, N 5.45%; calculated: C 51.92, H 5.15, N 5.50%.

Crystal data

$[Sn(CH_3)_2(C_{29}H_{30}N_2O_2S_2)Cl_2]\cdot$
C_2H_3N
$M_r = 763.38$
Triclinic, $P\bar{1}$
$a = 12.334$ (2) Å
$b = 12.765$ (2) Å
$c = 12.832$ (2) Å
$\alpha = 84.32$ (2)°
$\beta = 66.41$ (2)°
$\gamma = 71.10$ (2)°
$V = 1750.6$ (6) Å^3

$Z = 2$
$D_x = 1.448$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 19 845
reflections
$\theta = 2.9$–25.0°
$\mu = 1.04$ mm^{-1}
$T = 293$ (1) K
Rod, yellow
0.5 × 0.3 × 0.2 mm

Data collection

Nonius KappaCCD area-detector
diffractometer
φ and ω scans with 1.0° steps
Absorption correction: multi-scan
(*SORTAV*; Blessing, 1995, 1997)
$T_{min} = 0.75$, $T_{max} = 0.81$
19 845 measured reflections

6059 independent reflections
5462 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 25°$
$h = -14 \rightarrow 14$
$k = -14 \rightarrow 15$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.077$
$S = 1.06$
6059 reflections
406 parameters

H atoms treated by a mixture of
independent and constrained
refinement
$w = 1/[\sigma^2(F_o^2) + 0.66P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Sn—Cl1	2.5276 (7)	N1—C12	1.462 (4)
Sn—Cl2	2.6681 (7)	N2—C18	1.452 (3)
Sn—O1	2.223 (2)	N2—C19	1.294 (3)
Sn—O2	2.216 (2)	C1—C10	1.425 (4)
Sn—C30	2.110 (3)	C2—C3	1.350 (4)
Sn—C31	2.113 (3)	C10—C11	1.408 (4)
O1—C1	1.306 (3)	C19—C29	1.410 (4)
O2—C20	1.300 (3)	C20—C29	1.421 (4)
N1—C11	1.299 (3)	C21—C22	1.346 (4)
Cl1—Sn—Cl2	177.06 (3)	Cl2—Sn—C31	86.15 (9)
Cl1—Sn—O1	96.68 (5)	O1—Sn—O2	166.03 (7)
Cl1—Sn—O2	96.95 (5)	O1—Sn—C30	91.72 (11)
Cl2—Sn—O1	84.62 (5)	O1—Sn—C31	87.57 (11)
Cl2—Sn—O2	81.62 (5)	O2—Sn—C30	90.56 (10)
Cl1—Sn—C30	93.13 (9)	O2—Sn—C31	89.10 (11)
Cl1—Sn—C31	91.27 (9)	C30—Sn—C31	175.59 (12)
Cl2—Sn—C30	89.46 (9)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H10$\cdots$O1	0.86 (3)	1.90 (4)	2.601 (3)	138 (3)
N2—H20$\cdots$O2	0.84 (3)	1.92 (3)	2.594 (3)	137 (3)

The acetonitrile solvent molecule is disordered. The two methyl C atoms lie so close together that they are indistinguishable; the displacement parameters for each of the other sets of atoms [C33*A*/C33*B* and N3*A*/N3*B*; occupancy factor of 0.80 (1) for C33*A*] were restrained to be equal. The H atoms for the minor orientation were not included because their positions could not be determined. The rotations of the idealized methyl H atoms around C30—Sn, C31—Sn and C32—C33*A* were varied. All other H atoms on C atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.93–0.97 Å. The H atoms attached to atoms N1 and N2 were initially refined isotropically and without restraints, but the resulting N—H distances [0.78 (4) and 0.67 (2) Å] deviated enough from the standard value that restraints [*DFIX* 0.86 0.01; *SHELXL*97 (Sheldrick, 1997)] were imposed on the two distances. The *U* values for H10 and H20 [0.080 (12) and 0.041 (7) Å^2 in the subsequent restrained refinement] were sufficiently reasonable that the attachment of the H atoms to N1 and N2 (rather than to O1 and O2) was certain. Omitting atoms H10 and H20 from the least-squares refinement, the two highest peaks in the difference Fourier map (0.54 and 0.39 e Å^{-3}) were located *ca* 1 Å from the N atoms and *ca* 2 Å from the O atoms.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97; molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1990).

This work was supported in part by grants provided by the US National Science Foundation HRD 9252789 to Medgar Evers College, and by the Office of the Vice President for Research and Graduate Studies at the University of Kentucky.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1402). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Bajue, S. A., Bramwell, F. B., Brock, C. P. & Bontemps, J. (1998). *Acta Cryst.* C**54**, 1618–1622.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Bullock, J. I., Ladd, M. F. C., Povey, D. C. & Tajmir-Riahi, H.-A. (1979). *Acta Cryst.* B**35**, 2013–2020.
Degaonkar, M. P., Puranik, V. G., Tavale, S. S., Gopinathan, S. & Gopinathan, C. (1994). *Bull. Chem. Soc. Jpn*, **67**, 1797–1801.
Dwyer, F. P., Gill, N. S., Gyarfas, E. C. & Lyons, F. (1952). *J. Am. Chem. Soc.* **52**, 4188–4193.
Fun, H.-K., Teo, S.-B., Teoh, S.-G., Yeap, G.-Y. & Yeoh, T.-S. (1991). *Acta Cryst.* C**47**, 1602–1604.
Hazell, A., Goh, N. K. & Khoo, L. E. (1994). *Acta Cryst.* C**50**, 54–56.
Howie, R. A. & Wardell, J. L. (2000). *Acta Cryst.* C**56**, 806–807.
Howie, R. A. & Wardell, J. L. (2001). *Acta Cryst.* C**57**, 1041–1043.
Kamwaya, M. E. & Khoo, L. E. (1985). *Acta Cryst.* C**41**, 1027–1029.
Ng, S. W., Barnes, C. L., Hossain, M. B., van der Helm, D., Zuckerman, J. J. & Kumar Das, V. G. (1982). *J. Am. Chem. Soc.* **104**, 5359–5364.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1990). *SHELXTL/PC*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Teoh, S. G., Teo, S. B., Yeap, G. Y. & Declercq, J. P. (1991). *Polyhedron*, **10**, 2683–2686.
Wang, J.-T., Gao, S.-H., Zhang, Y.-W., Xu, Y.-M. & Wang, R.-J. (1994). *Chin. J. Struct. Chem.* (*Jiegou Huaxue*), **13**, 91–94. (In Chinese.)
Yeap, G.-Y. & Ishizawa, N. (1998). *Acta Cryst.* C**54**, 720–722.