# Crystal and Molecular Structure of [NN'-ethylenebis(salicylideneiminato)]dimethyltin(IV)

By M. Calligaris, G. Nardin, and L. Randaccio, Istituto di Chimica, Università di Trieste, 34127 Trieste, Italy

The crystal and molecular structure of the title compound has been determined from three-dimensional photographic X-ray data by the heavy-atom method. The crystals are orthorhombic, space group $Pca2_1$, with $a$ = 12·19, $b$ = 6·91, $c$ = 40·41 Å, $Z$ = 8. The structure was refined by least-squares methods to $R$ 0·098 for 1636 reflexions. The crystals are built up of discrete molecules [Me$_2$Sn(salen)] with the salen ligand occupying the four equatorial positions of a distorted octahedron around the tin atom, the methyl groups being in the *trans*-positions. The co-ordination polyhedron distortions and the conformation of the molecule are compared with those of similar compounds.

BARBIERI and his co-workers [1] reported the preparation of some new organotin(IV) chelates of quadridentate Schiff bases such as bis(salicylaldehyde)ethylenedi-imine (salenH$_2$) of the type R$_2$Sn(salen) (R = Me or Ph), and recently suggested [2] a *trans*-diorgano structure (I) in such six-co-ordinate compounds on the basis of Mössbauer spectroscopy results.

However, the n.m.r. results obtained by Murray et al.[3] were interpreted as being in agreement with a *cis*-di-organo-arrangement and a non-planar quadridentate salen ligand resulting in the *cis*-β-configuration (II) already found in some cobalt–salen compounds.[4]
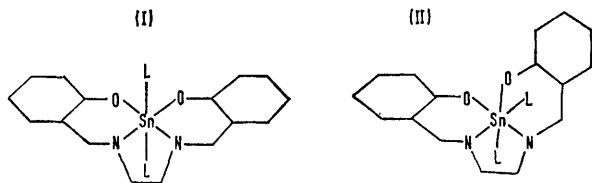


In order to solve the disagreement between the interpretation of Mössbauer and n.m.r. results, and to provide further insight into the steric requirements determining the co-ordination of salen-type ligands with different metals, we have undertaken the crystal structure determination of the [Me$_2$Sn$^{IV}$(salen)] compound.

## EXPERIMENTAL

*Crystal Data.*—C$_{18}$H$_{20}$N$_2$O$_2$Sn, $M$ = 414·8, Orthorhombic, $a$ = 12·19 ± 0·03, $b$ = 6·91 ± 0·03, $c$ = 40·41 ± 0·05 Å,

$U$ = 3404 Å$^3$, $D_m$ = 1·59 (by flotation), $Z$ = 8, $D_c$ = 1·60. Co-$K_\alpha$ radiation, $\lambda$ = 1·7902 Å; $\mu$(Co-$K_\alpha$) = 182·2 cm$^{-1}$. Absent reflexions: $0kl$ with $l = 2n + 1$ and $h0l$ with $h = 2n + 1$ indicate space group $Pca2_1$ ($C_{2v}^5$) or $Pcam$ ($D_{2h}^{11}$), $Pca2_1$ from structure determination.

Unit-cell parameters were obtained from Weissenberg photographs taken with Co-$K_\alpha$ radiation.

*Intensity Measurements.*—Intensity data were collected by the equi-inclination Weissenberg method by use of Co-$K_\alpha$ radiation. Although the absorption coefficient was rather high, this radiation was used to allow a better separation of the reflexions along the $c$ axis.

Intensity data were recorded for the reciprocal lattice levels $h0$—$5l$ and $0kl$, $1kl$ by the multiple-film equi-inclination Weissenberg technique. A crystal, 0·13 × 0·10 × 0·03 mm$^3$ was used for the collection of 1636 independent reflexions. Intensities were estimated visually by comparison with a calibrated scale.

Corrections for Lorentz and polarization factors, spot-shape,[5] and absorption were applied. A cylindrical absorption correction was applied to the data using $r$ 0·005 cm.

The observed structure amplitudes were correlated by the method of Hamilton et al.[6]

*Structure Determination and Refinement.*—The choice of the non-centrosymmetric space group $Pca2_1$ was suggested by the Sn · · · Sn vector distribution on the three-dimensional

[1] F. Maggio, R. Cefafù, R. Pellerito, and R. Barbieri, Abstracts Ann. Meeting Inorg. Chem., Univ. Padova, 1967, p. 5.

[2] R. Barbieri, R. H. Herber, and S. C. Chandra, Abstracts 5th Internat. Conf. Organometallic Chem., Moscow, 1972, vol. I, Paper 103, p. 278.

[3] A. van der Bergen, R. J. Cozens, and K. S. Murray, *J. Chem. Soc.* (*A*), 1970, 3060.

[4] M. Calligaris, G. Nardin, and L. Randaccio, *Chem. Comm.*, 1969, 1240; M. Calligaris, G. Manzini, G. Nardin, and L. Randaccio, *J.C.S. Dalton*, 1972, 543; M. Calligaris, G. Nardin, and L. Randaccio, *Chem. Comm.*, 1970, 1079; N. A. Bailey, B. M. Higson, and E. D. McKenzie, *J.C.S. Dalton*, 1972, 503.

[5] D. C. Phillips, *Acta Cryst.*, 1954, 7, 746.

[6] W. C. Hamilton, J. S. Rollet, and A. Sparks, *Acta Cryst.*, 1965, 18, 129.

Patterson map and confirmed by the successful refinement of the structure. The approximate position of the two crystallographically independent tin atoms was readily determined from peak locations on the three-dimensional Patterson map. The remaining non-hydrogen atoms were located from Fourier syntheses. Three cycles of isotropic block-diagonal least-squares refinement reduced $R$ to $0\cdot12$.

Two more cycles with anisotropic temperature factors assigned to the tin atoms only reduced $R$ to $0\cdot098$. No attempt was made to locate the hydrogen atoms. The weighting scheme used was $w = 1/(A + B\,.\,|F_o| + C\,.\,|F_o|^2)$, where $A = 10$, $B = 1$, and $C = 0\cdot003$ chosen so that the value of $w\,.\,(|F_o| - |F_c|)^2$ was essentially constant over all ranges of $|F_o|$ and $(\sin\theta/\lambda)$.

The final parameters of all the non-hydrogen atoms are listed in Table 1 together with their estimated standard deviations, which were derived from the residuals and the diagonal elements of the inverse matrix of the last least-squares cycle. The numbering scheme for the atoms is shown in Figure 1. Co-ordination bond lengths and angles are listed in Table 2 together with their estimated standard

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystals consist of discrete molecules, [Me$_2$Sn-(salen)], in which the salen ligand occupies the four equatorial positions of a distorted octahedron around the tin atom, whereas the methyl groups occupy the *trans*-positions. The two crystallographically independent molecules of the asymmetric unit are quite similar, being related by a pseudosymmetry centre at about $x = 0\cdot14$, $y = 0\cdot26$, and $z = 0\cdot12$. The Sn–O distances range from $2\cdot19$—$2\cdot25(2)$ Å and compare well with the values found in other octahedral tin compounds.[13] The Sn–N bond lengths vary from $2\cdot24$—$2\cdot27(3)$ Å and do not differ significantly from each other or from the values observed in other octahedral compounds {$2\cdot35(4)$ Å in [Me$_2$Sn(C$_9$H$_6$NO)$_2$][14] and $2\cdot36(4)$ Å in [MeSn$^{IV}$Cl,ter-pyridyl][Me$_2$Sn$^{IV}$Cl$_3$]}.[15] The Sn–C($sp^3$) bond lengths [$2\cdot07$—$2\cdot16(4)$ Å] fall in the range ($2\cdot08$—$2\cdot22$ Å) reported for octahedral tin compounds.[13] The co-ordination polyhedron around the tin atoms in both molecules
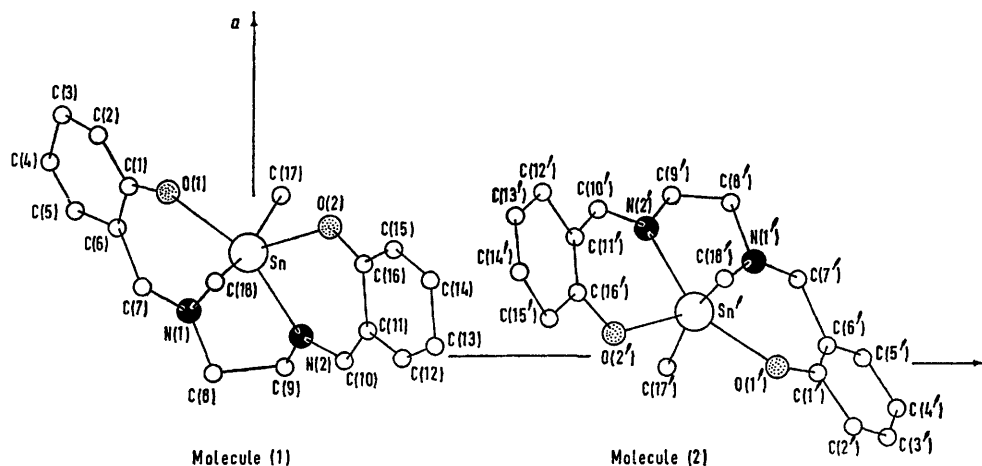


FIGURE 1 The numbering scheme of the atoms of the two crystallographically independent molecules

deviations. Some least-squares planes of interest, calculated according to Schomaker *et al.*[7] with unit weights for all the atoms, are reported in Table 3 together with the distances of the individual atoms from these planes. The final observed and calculated structure factors are listed in Supplementary Publication No. 20432 (9 pp., 1 microfiche).*

The atomic scattering factors used were taken from ref. 8 for tin, from ref. 9 for nitrogen, and from ref. 10 for oxygen and carbon atoms.

*Calculations.*—All calculations were performed on an IBM 7044 computer, using programmes written by Immirzi[11] and by Albano *et al.*[12] A programme of our own design (unpublished) was used to calculate best molecular planes.

deviates from the idealized octahedron. The main deviations take place without altering the ortho-normality (*ca.* 89°) between the co-ordination plane and the plane passing through the Sn, C(17), and C(18) atoms. The equatorial co-ordination atoms are nearly coplanar as shown by the deviations of these atoms from their least-squares planes, and from the sum of the equatorial angles around the Sn atoms of *ca.* 360°.

In the equatorial plane, the large opening of the O–Sn–O angle (125 and 128° in the two molecules) corresponds to a closing of the N–Sn–N angles (73° in both molecules) and to a strong deviation of the O–Sn–N angles from 180°. Such a distortion can easily be

* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

7 V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Cryst.*, 1959, 12, 600.

8 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

9 J. Berghuis, I. J. M. Haanappell, M. Potters, B. O. Loopstra, C. M. MacGillavry, and A. L. Veenedaal, *Acta Cryst.*, 1955, 8, 478.

10 H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, 17, 1040.

11 A. Immirzi, *Ricerca sci.*, 1967, 10, 846.

12 V. Albano, A. Domenicano, and A. Vaciago, *Gazzetta*, 1966, 96, 922.

13 W. W. Isaacs and C. H. L. Kennard, *J. Chem. Soc.* (*A*), 1970, 1257, and references therein.

14 E. O. Schlemper, *Inorg. Chem.*, 1967, 11, 2012.

15 F. W. B. Einstein and B. R. Penfold, *J. Chem. Soc.* (*A*), 1968, 3019.

rationalized in terms of the strains imposed by the tetradentate ligand, because the formation of the chelate rings requires the bites $\overline{ON}$ and $\overline{NN}$ to be constant. Similar geometry has been found in a compound of $UO_2$ with an analogous quadridentate

TABLE 1

Final atomic parameters of the non-hydrogen atoms, with estimated standard deviations in parentheses

|       | $x/a$ | $y/b$ | $z/c$ | $B$ |
|-------|-------|-------|-------|-----|
| Sn    | 0·1870(2) | −0·0672(3) | −0·0032(1) | * |
| O(1)  | 0·281(2) | 0·073(3) | −0·0504(5) | 3·7(5) |
| O(2)  | 0·232(2) | 0·083(3) | 0·0442(6) | 4·0(5) |
| N(1)  | 0·080(3) | −0·262(5) | −0·0340(7) | 3·6(7) |
| N(2)  | 0·038(2) | −0·141(4) | 0·0278(6) | 2·8(5) |
| C(1)  | 0·304(3) | −0·224(6) | −0·0680(9) | 4·1(8) |
| C(2)  | 0·393(3) | −0·220(6) | −0·0882(9) | 4·5(8) |
| C(3)  | 0·420(3) | −0·373(6) | −0·1078(10) | 4·7(8) |
| C(4)  | 0·347(4) | −0·523(7) | −0·1113(11) | 5·8(9) |
| C(5)  | 0·250(3) | −0·525(6) | −0·0934(9) | 4·2(8) |
| C(6)  | 0·224(3) | −0·374(5) | −0·0722(8) | 3·4(7) |
| C(7)  | 0·114(3) | −0·380(6) | −0·0569(10) | 4·8(8) |
| C(8)  | −0·029(3) | −0·277(6) | −0·0209(9) | 4·1(8) |
| C(9)  | −0·022(3) | −0·313(6) | 0·0164(9) | 4·4(8) |
| C(10) | −0·003(3) | −0·019(5) | 0·0000(7) | 3·0(6) |
| C(11) | 0·046(3) | 0·139(5) | 0·0645(8) | 3·7(7) |
| C(12) | −0·015(3) | 0·262(6) | 0·0840(8) | 3·7(8) |
| C(13) | 0·021(4) | 0·437(6) | 0·0996(10) | 4·8(9) |
| C(14) | 0·140(5) | 0·465(8) | 0·0957(13) | 6·7(2) |
| C(15) | 0·202(3) | 0·355(5) | 0·0773(8) | 3·4(7) |
| C(16) | 0·167(2) | 0·194(5) | 0·0612(7) | 2·7(6) |
| C(17) | 0·295(3) | −0·290(6) | 0·0151(10) | 4·8(8) |
| C(18) | 0·135(2) | 0·199(5) | −0·0209(7) | 3·0(5) |
| Sn′   | 0·0882(2) | 0·4494(3) | 0·2432(1) | * |
| O(1′) | −0·002(2) | 0·481(4) | 0·2898(6) | 4·4(5) |
| O(2′) | 0·044(2) | 0·591(4) | 0·1966(6) | 3·9(5) |
| N(1′) | 0·189(2) | 0·258(5) | 0·2763(7) | 4·1(6) |
| N(2′) | 0·237(2) | 0·360(4) | 0·2143(6) | 3·1(6) |
| C(1′) | −0·026(3) | 0·318(6) | 0·3103(8) | 3·3(7) |
| C(2′) | −0·127(3) | 0·327(6) | 0·3280(9) | 4·6(8) |
| C(3′) | −0·151(4) | 0·191(7) | 0·3502(11) | 6·0(10) |
| C(4′) | −0·085(4) | 0·028(8) | 0·3544(12) | 6·2(10) |
| C(5′) | 0·016(4) | 0·016(7) | 0·3356(10) | 4·9(9) |
| C(6′) | 0·038(4) | 0·156(7) | 0·3147(11) | 5·2(10) |
| C(7′) | 0·156(3) | 0·146(5) | 0·3005(8) | 3·4(7) |
| C(8′) | 0·302(3) | 0·209(6) | 0·2646(10) | 4·6(9) |
| C(9′) | 0·296(3) | 0·201(5) | 0·2270(8) | 3·5(6) |
| C(10′)| 0·277(3) | 0·465(6) | 0·1884(9) | 4·3(7) |
| C(11′)| 0·222(3) | 0·641(5) | 0·1751(8) | 3·2(6) |
| C(12′)| 0·299(3) | 0·763(6) | 0·1569(10) | 4·7(8) |
| C(13′)| 0·258(4) | 0·921(6) | 0·1420(11) | 5·3(10) |
| C(14′)| 0·157(4) | 0·975(7) | 0·1447(11) | 4·9(9) |
| C(15′)| 0·068(3) | 0·861(5) | 0·1633(9) | 3·8(7) |
| C(16′)| 0·117(3) | 0·698(6) | 0·1787(10) | 4·5(9) |
| C(17′)| −0·021(4) | 0·224(7) | 0·2292(11) | 4·7(10) |
| C(18′)| 0·144(3) | 0·715(5) | 0·2595(8) | 3·5(6) |

* Anisotropic temperature factors ($\times 10^5$) of the tin atoms in the form

$$\exp -(b_{11}h^2 + b_{12}hk + b_{13}hl + b_{22}k^2 + b_{23}kl + b_{33}l^2).$$

|     | | | | | | |
|-----|------|--------|------|---------|--------|-------|
| Sn  | 478(12) | 64(8) | 7(8) | 1645(47) | −22(20) | 54(1) |
| Sn′ | 507(12) | 223(53) | 15(8) | 1544(52) | 10(19) | 58(1) |

TABLE 2

Molecular geometry

(a) Co-ordination bond lengths and angles; estimated standard deviations in parentheses

(i) Bond lengths (Å)

| Sn−O(1) | 2·22(2) | Sn′−O(1′) | 2·19(2) |
|---------|---------|-----------|---------|
| Sn−O(2) | 2·25(2) | Sn′−O(2′) | 2·19(2) |
| Sn−N(1) | 2·25(3) | Sn′−N(1′) | 2·24(3) |
| Sn−N(2) | 2·27(3) | Sn′−N(2′) | 2·24(3) |
| Sn−C(17) | 2·16(4) | Sn′−C(17′) | 2·13(5) |
| Sn−C(18) | 2·07(3) | Sn′−C(18′) | 2·07(4) |

TABLE 2 (Continued)

(ii) Bond angles (°)

| O(1)−Sn−O(2) | 128(1) | O(1′)−Sn′−O(2′) | 125(1) |
|--------------|--------|-----------------|--------|
| O(1)−Sn−N(1) | 79(1) | O(1′)−Sn′−N(1′) | 80(1) |
| O(1)−Sn−N(2) | 152(1) | O(1′)−Sn′−N(2′) | 152(1) |
| O(1)−Sn−C(17) | 88(1) | O(1′)−Sn′−C(17′) | 89(1) |
| O(1)−Sn−C(18) | 83(1) | O(1′)−Sn′−C(18′) | 79(1) |
| O(2)−Sn−N(1) | 153(1) | O(2′)−Sn′−N(1′) | 156(1) |
| O(2)−Sn−N(2) | 80(1) | O(2′)−Sn′−N(2′) | 83(1) |
| O(2)−Sn−C(17) | 84(1) | O(2′)−Sn′−C(17′) | 84(1) |
| O(2)−Sn−C(18) | 88(1) | O(2′)−Sn′−C(18′) | 88(1) |
| N(1)−Sn−N(2) | 73(1) | N(1′)−Sn′−N(2′) | 73(1) |
| N(1)−Sn−C(17) | 97(1) | N(1′)−Sn′−C(17′) | 94(1) |
| N(1)−Sn−C(18) | 99(1) | N(1′)−Sn′−C(18′) | 99(1) |
| N(2)−Sn−C(17) | 98(1) | N(2′)−Sn′−C(17′) | 100(1) |
| N(2)−Sn−C(18) | 98(1) | N(2′)−Sn′−C(18′) | 98(1) |
| C(17)−Sn−C(18) | 160(1) | C(17′)−Sn′−C(18′) | 161(1) |

(b) Mean bond lengths (Å) and angles (°) in the salen ligands

| O(1)−C(1) | 1·35(3) | Sn−O(1)−C(1) | 124(1) |
|-----------|---------|--------------|--------|
| N(1)−C(7) | 1·33(2) | Sn−N(1)−C(7) | 125(2) |
| N(1)−C(8) | 1·45(2) | Sn−N(1)−C(8) | 115(1) |
| C(8)−C(9) | 1·53(5) | C(7)−N(1)−C(8) | 119(2) |
| C(1)−C(2) | 1·39(2) | O(1)−C(1)−C(2) | 118(2) |
| C(2)−C(3) | 1·38(5) | O(1)−C(1)−C(6) | 122(2) |
| C(3)−C(4) | 1·39(3) | C(2)−C(1)−C(6) | 120(2) |
| C(4)−C(5) | 1·40(2) | C(1)−C(2)−C(3) | 119(3) |
| C(5)−C(6) | 1·38(3) | C(2)−C(3)−C(4) | 122(1) |
| C(6)−C(7) | 1·47(3) | C(3)−C(4)−C(5) | 118(2) |
| C(1)−C(6) | 1·42(4) | C(4)−C(5)−C(6) | 121(2) |
|           |         | C(1)−C(6)−C(5) | 119(2) |
|           |         | C(5)−C(6)−C(7) | 115(2) |
|           |         | C(1)−C(6)−C(7) | 125(2) |
|           |         | C(6)−C(7)−N(1) | 124(1) |
|           |         | C(9)−C(8)−N(1) | 107(2) |

TABLE 3

Equations of least-squares planes in the form $lx + my + nz = p$ where $x$, $y$, and $z$ are fractional co-ordinates and refer to the crystallographic axes. Distances (Å) of relevant atoms from the planes are given in square brackets

Plane (I):

(i) O(1), O(2), N(1),    $-5\cdot880x + 5\cdot619y - 13\cdot158z = -1\cdot440$
    N(2)

   [O(1) 0·040, O(2) −0·039, Sn 0·005, N(1) −0·059, N(2) 0·058]

(ii) O(1′), O(2′),    $6\cdot419x + 5\cdot559y + 11\cdot114z = 5\cdot815$
     N(1′), N(2′)

   [O(1′) 0·067, O(2′) −0·064, Sn′ −0·048, N(1′) −0·097, N(2′) 0·094]

Plane (II):

(i) O(1), N(1),    $-5\cdot424x + 3\cdot354y - 30\cdot412z = -0\cdot251$
    C(1)—(7)

   [O(1) 0·014, N(1) −0·031, C(1) −0·083, C(2) 0·065, C(3) −0·002, C(4) 0·001, C(5) −0·025, C(6) −0·025, C(7) 0·086]

(ii) O(1′), N(1′),    $5\cdot593x + 3\cdot337y + 30\cdot141z = 10\cdot295$
     C(1′)—(7′)

   [O(1′) 0·034, N(1′) −0·050, C(1′) −0·026, C(2′) −0·026, C(3′) 0·054, C(4′) 0·007, C(5′) −0·036, C(6′) −0·077, C(7′) 0·120]

Plane (III):

(i) O(2), N(2),    $-2\cdot401x + 3\cdot891y - 32\cdot427z = -1\cdot631$
    C(10)—(16)

   [O(2) −0·037, N(2) 0·088, C(10) −0·056, C(11) −0·029, C(12) −0·039, C(13) 0·050, C(14) 0·002, C(15) 0·021, C(16) 0·000]

(ii) O(2′), N(2′),    $2\cdot651x + 3\cdot827y + 32\cdot478z = 8\cdot793$
     C(10′)—(16′)
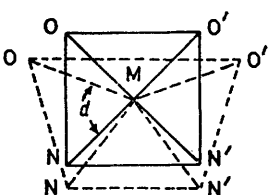
   [O(2′) −0·030, N(2′) 0·176, C(10′) −0·159, C(11′) −0·065, C(12′) 0·017, C(13′) 0·030, C(14′) 0·055, C(15′) −0·014, C(16′) −0·009]

Schiff base [16] where the O · · · O distance increases to allow an alcohol molecule to co-ordinate the uranium atom in the equatorial plane.

Conversely in the salen derivatives of cobalt, copper, and iron small deviations of these angles from 90° are observed, so that it seems necessary to ascribe the difference to the values of the co-ordination bond lengths, which in the transition-metal complexes are ca. 1·90 Å, whereas in the tin (or uranium) compounds are ⩾2·20 Å. The geometry of each case is compared in Table 4.

### TABLE 4

Comparison of the co-ordination geometry around the tin and cobalt salen compounds



| | Calc.[a] | Found [b] Molecule (1) | Molecule (2) | Calc.[c] | Found [d] |
|---|---|---|---|---|---|
| O–M–O′ (°) | 140 | 128 | 125 | 90 | 86 |
| O–M–N′ (°) | 147 | 152 | 152 | 180 | 177 |
| N–M–N′ (°) | 73 | 73 | 73 | 90 | 85 |
| O–O′ (Å) | 4·2 | 4·00 | 3·88 | 2·70 | 2·60 |
| N–N′ (Å) | 2·7 | 2·68 | 2·67 | 2·70 | 2·54 |
| O′–N′ (Å) | 2·7 | 2·88 | 2·90 | 2·70 | 2·78 |

[a] $d = 2·20$ Å.   [b] Present work.   [c] $d = 1·90$ Å.   [d] See e.g. M. Calligaris, G. Nardin, L. Randaccio, and A. Ripamonti, J. Chem. Soc. (A), 1970, 1069.

The other significant distortion is shown by the angle C–Sn–C which is 160 and 161° in the two molecules, the methyl groups bending towards the equatorial oxygen atoms.

As far as bond lengths and angles of the salen ligand are concerned, the two chemically equivalent halves in both molecules are similar [Table 2(b)]. Individual values have estimated standard deviations in the range 0·02—0·06 Å (bond lengths) and 2—5° (bond angles), and do not differ from those found for the Co(salen) derivatives.[17]

[16] G. Bandoli, D. A. Clemente, and U. Croatto, Abstracts 4th Symposium Inorg. Chem., Venezia, 1971, Paper C7.

The side view of both molecules is very similar (Figure 2). The molecule exhibits the characteristic ' stepped-shape ' conformation found in other metal–salen octahedral compounds.[17]

The co-ordination equatorial plane makes angles (mean for both molecules) of 32 and 37° with the planes
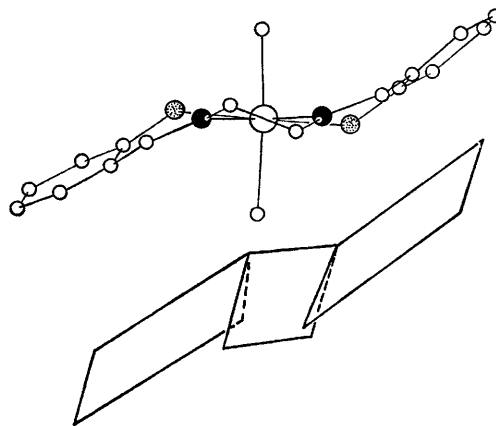


FIGURE 2   A side view of a molecule and a sketch of the relation among the co-ordination plane and the planes of the two salen halves

passing through the two chemically equivalent halves of the salen ligand. However the latter two planes make an angle of 15° indicating a slight mutual twisting. As we already pointed out,[17] the almost symmetrical displacement (0·33 and 0·41, 0·23 and 0·27 Å) of the ethylene carbon atoms above and below the equatorial co-ordination plane confirms a ' stepped ' symmetrical arrangement of the quadridentate ligand.

The ethylene bridges are found in a gauche conformation with torsion angles of 60 and 45° in molecules (1) and (2) as normally found in octahedral complexes of this kind.

Intermolecular distances are quite normal.

[17] M. Calligaris, G. Nardin, and L. Randaccio, Co-ordination Chem. Rev., 1972, 7, 385.