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Preliminary communication

CRYSTAL STRUCTURE OF THE MOLECULAR ADDUCT OF DIMETHYLTIN(IV) CHLORIDE WITH *N,N'*-ETHYLENEBIS(SALICYLIDENEIMINATO)-NICKEL(II)

M. CALLIGARIS* and L. RANDACCIO
Istituto di Chimica, Università di Trieste, 34127 Trieste (Italy)
R. BARBIERI and L. PELLERITO
Istituto di Chimica Generale, Università di Palermo, 90123 Palermo (Italy)

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Summary

N,N'-Ethylenebis(salicylideneiminato)nickel(II) behaves as a neutral bidentate ligand through its oxygen atoms forming binuclear complexes with organotin(IV) chlorides. The crystal structure of the dimethyl derivative is reported.

Metal complexes of tetradentate Schiff bases can act as bidentate ligands coordinating to both transition and alkaline metal atoms [1, 2]. Recently it has been shown that organotin(IV) chlorides form molecular complexes with tetradentate Schiff bases as well as with their metal complexes such as Ni(salen), ($salenH_2$ = bis(salicylaldehyde)ethylenediimine) [3, 4]. In the latter case, 1/1 adducts of formula $[R_nSnCl_{4-n}\cdot Ni(salen)]$. (R = Me, Ph and n = 1, 2) were obtained, whose structure has been studied spectroscopically [4]. In order to obtain direct knowledge of the coordination geometry in such complexes we have performed the crystal structure determination of $[Me_2SnCl_2\cdot Ni(salen)]$. The crystals are monoclinic, space group $P2_1/c$, with a = 9.244, b = 14.214, c = 17.058 Å, β = 115.6°. Observed and calculated densities (Z = 4) are 1.82 and 1.79 g cm^{-3}, respectively. The structure determination was based upon 2807 non-zero independent reflections ($2\theta \leqslant 50°$) collected by the $\theta - 2\theta$ scan technique with Mo-K_α radiation on a Siemens diffractometer. The structure was solved by Patterson and Fourier methods and refined by the block-diagonal matrix least-squares technique to a conventional R factor of 0.075 using anisotropic temperature factors for all the atoms.

The molecular structure in the solid state (Fig. 1) agrees with that proposed on the basis of spectroscopic and magnetic data [4]. It will be seen that upon

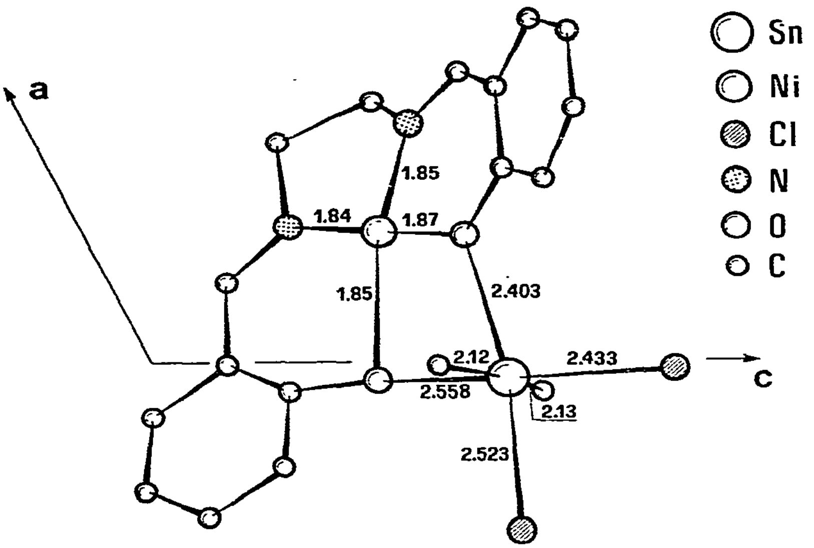

Fig. 1. The molecule projected along the b axis. E.s.d.'s. are 0.004 Å for Sn—Cl, 0.01 Å for Sn—O and Ni—O(N) and 0.02 Å for Sn—C bond lengths.

coordination by the two oxygen atoms of Ni(salen), the tin atom acquires a distorted octahedral geometry with a *trans*-methyl structure. Bond angles around the tin atom are: Cl—Sn—Cl, 97.1(2)°, O—Sn—O, 61.3(3)°; O—Sn—Cl(*cis*), 91.8(3) and 110.0(2)°; C—Sn—C, 161.0(7)°; O—Sn—Cl(*trans*), 152.7(2) and 171.1(3)°. The two *trans*-Sn—C bond lengths are equal within experimental error [2.12(2) and 2.13(1) Å], and rather similar to those in other dimethyltin(IV) complexes [3, 5]. In contrast, the equatorial Sn—Cl and Sn—O bond distances are not equivalent (Fig. 1). At present it is difficult to establish the reasons for this difference.

Coordination bond lengths and angles of nickel are similar to those found in the parent compound Ni(salen) [6]. The four donor atoms are coplanar with the nickel atom (± 0.03 Å), but distortion from planarity of the whole complex is observed. The resulting conformation may be described [7] as an asymmetric umbrella (Fig. 2) with the ethylene bridge in a nearly *gauche* conformation (torsional angle of 38.3°). Furthermore, a slight twisting of the two halves of the

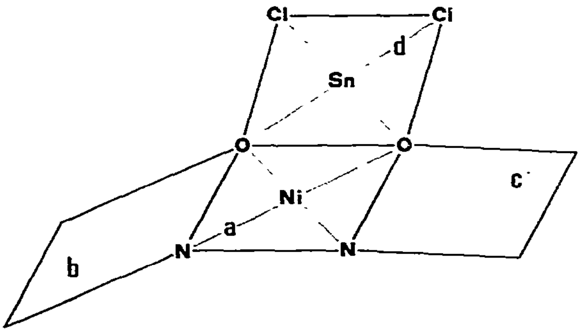

Fig. 2. A sketch of the conformation of the main planes of the molecule. The dihedral angles are: a-b, 25.9°; a-c, 2.4°; a-d, 27.2°; b-c, 28.0°.

salen ligand occurs. Bond lengths and angles in the tetradentate ligand have the expected values [7].

It is noteworthy that the coordinating oxygen atoms have a nearly planar stereochemistry, the sum of the angles around them being 359.4 and 356.0°, so that the equatorial plane of the tin polyhedron makes a dihedral angle of 27.2° with the coordination plane of the nickel atom (Fig. 2). In the other adducts with metal—Schiff base complexes which have been studied by X-ray methods, a slight distortion of the oxygen atoms is observed [2]. On the other hand a more pronounced tetrahedral distortion should be unfavourable in view of steric factors. In the present case a too close approach to the nickel atom one of the axial methyl groups would occur if the oxygen atoms adopted a tetrahedral geometry and the Ni—Sn distance (3.412(2) Å) would decrease, with destabilization of the four-membered ring. On the other hand, the trigonal nature of the salen oxygen atoms is stabilized because of the π-conjugation through the tetradentate ligand [7].

Acknowledgment

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