Outer-sphere Coordination in the Phenanthroline and Bipyridine Complexes of Triphenyltin Chloride

E. J. GABE, F. L. LEE

Chemistry Division, National Research Council of Canada, Ottawa, Ont., K1A OR6 Canada

and F. E. SMITH*

Chemistry Department, Laurentian University, Sudbury, Ont. P3E 2C6, Canada

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The indirect binding of ligands to metal ions via hydrogen bonding to coordinated water molecules is well known in the study of biochemical systems, particularly in the binding of cations to nucleic acids and their components [1–3]. However, very few low molecular weight metal complexes displaying this type of outer-sphere coordination have been described [4–7]. We now report the synthesis and characterisation of the 1,10-phenanthroline and 2,2′-bipyridine complexes of triphenyltin chloride, and the crystal structure of the former complex. Both are outer-sphere complexes in which the potentially bidentate ligands are not directly coordinated to the tin atom at all, but are held in position by hydrogen bonding between coordinated water molecules and the nitrogen atoms of the heterocyclic bases.

Experimental

Preparation of Complexes

The reagents triphenyltin chloride (a gift from M and T chemicals), 1,10-phenanthroline and 2,2′-bipyridine (purchased from Aldrich) were all used without further purification.

The complexes were obtained as white crystals in good yield by mixing hot toluene solutions containing the stoichiometric quantities of triphenyltin chloride and the appropriate ligand. The complexes separated overnight, were filtered off, washed with cold toluene, and recrystallised from toluene. Microanalyses were carried out by the CSIRO (Melbourne, Australia). *Anal.* (i) $Ph_3SnCl \cdot phen \cdot H_2O$ (M.Pt. 124 °C): Calculated for $C_{30}H_{25}N_2ClOSn$ (%): C, 61.73; H, 4.32; N, 4.80; Sn, 20.33. Found (%): C, 61.74; H, 4.44; N, 4.85; Sn, 20.1. (ii) $Ph_3SnCl \cdot bipy \cdot H_2O$ (M.Pt. 90 °C): Calculated for $C_{28}H_{25}N_2ClOSn$ (%): C, 60.09; H, 4.50; N, 5.00; Sn, 21.2. Found (%): C, 59.82; H, 4.54; N, 4.94; Sn, 21.9.

Crystal Structure Determination of $Ph_3SnCl \cdot phen \cdot H_2O$

Crystal Data

Space group $P2_1/c$; $a = 11.9602(7)$ Å, $b = 12.2196(7)$ Å, $c = 17.8539(14)$ Å, $\beta = 92.409(6)°$, derived from 40 reflections with $2\theta > 40°$ ($\lambda(\text{MoK}\alpha_1) = 0.70932$ Å).

Intensity Data

Measurements were made at room temperature (295 K) with graphite monochromatized MoKα radiation. The data were collected from 1 of 4 crystals examined, each of which had an inseparable twin component which gave intensities of about 4% of the main fragment. A total of 5749 reflections were measured, of which 4607 were unique and 2953 had $I_{\text{net}} \geqslant 2.5\sigma(I_{\text{net}})$ based on counting statistics. Agreement between symmetry related reflections $(\Sigma\Delta I/\Sigma I)$ was 0.011.

Structure Solution and Refinement

The structure was solved with MULTAN [8] and refined by full matrix least squares methods to $R_1(\Sigma|\Delta F|/\Sigma F_o) = 0.128$ and $R_2(\Sigma w\Delta F^2/\Sigma F_o^2) = 0.140$ for the observed data. The effect of the small twin component is to degrade the quality of the intensity data and this is probably the reason for the high residuals. All computations were performed with the NRC PDP-8e program system [9] adapted for the VAX computer.

Results and Discussion

The dimeric unit of the 1,10-phenanthroline/triphenyltin chloride complex is shown in Fig. 1 and a stereo view of the same unit in Fig. 2. Each Sn atom is positioned at the centre of a trigonal bipyramid, with phenyl groups in the three equatorial positions, a water molecule at one apex and a chlorine atom at the other apex. The water molecule is hydrogen-bonded to the N atoms of the phenanthroline molecule. These units form centrosymmetric hydrogen-bonded dimers. The two bipyramidally-coordinated tin atoms are positioned co-axially, with the water molecules adjacent and the chlorines furthest apart. The two phenanthroline molecules are held mid-way between the two tin atoms, in a plane

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*Author to whom correspondence should be addressed.

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TABLE I. ^{119}Sn Mössbauer Data for the Complexes.

Complex	Isomer Shift[a] δ (mm/sec ± 0.05)	Quadrupole Splitting Δ (mm/sec ± 0.05)
$Ph_3SnCl \cdot phen \cdot H_2O$	1.29	3.25
$Ph_3SnCl \cdot bipy \cdot H_2O$	1.31	3.32

[a] Relative to $BaSnO_3$.

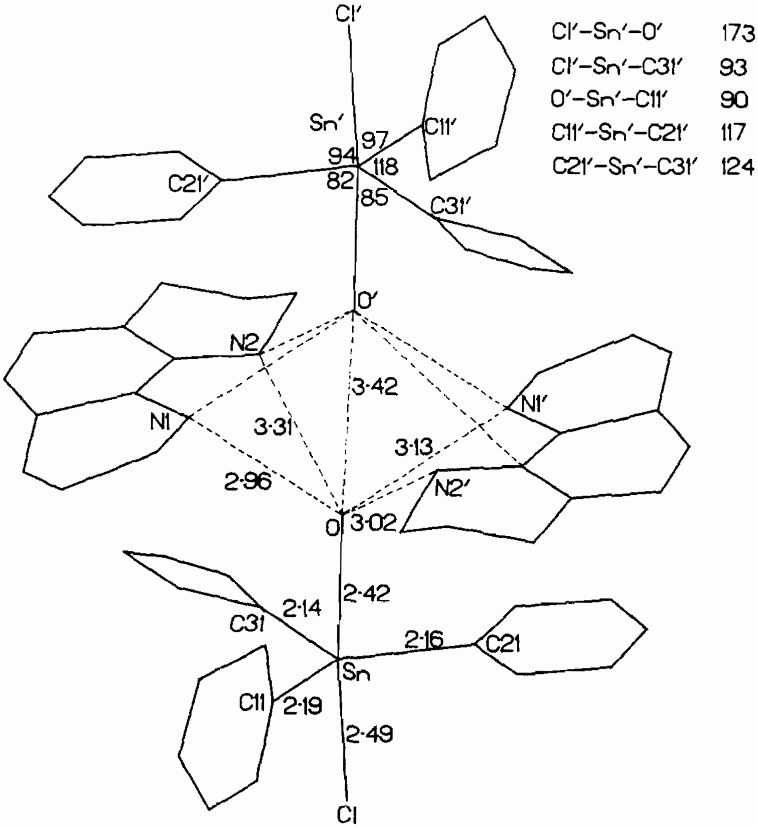

Fig. 1. The structure of 1,10-phenanthroline-aquachlorotriphenyltin(IV) (2:2). Legend: Bond distances (Å) are uncorrected for thermal motion. The e.s.d.s on bond distances involving Sn are 0.002–0.003 Å, the others range from 0.003–0.006 Å. Bond angles (°). The e.s.d.s in angles involving Sn are 0.1° and the others range from 0.2–0.3°.

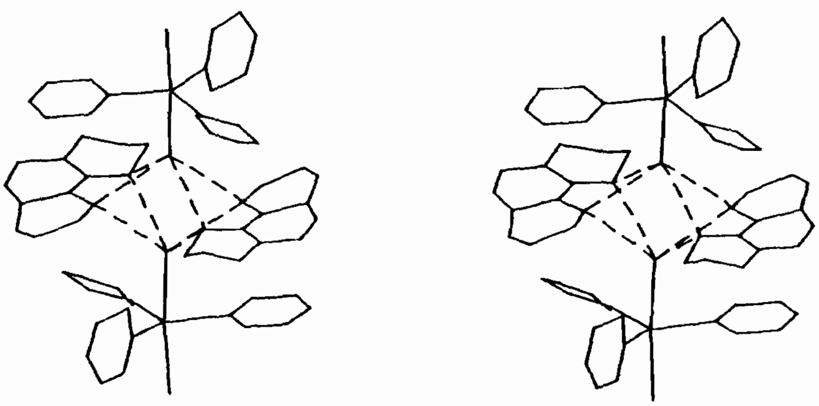

Fig. 2. A stereoscopic view of the molecule.

perpendicular to the Sn–S axis, with both sets of N atoms directed towards that axis. Hydrogen bonding between the coordinated water molecules and the N atoms of the phenanthroline molecules binds the two bipyramidally-coordinated units together into a discrete dimeric molecule. There are four distinct N–O distances (2.96–3.31 Å) to each O atom, above and below the plane of the two phenanthrolines. The O-----O distance is 3.42 Å. In each of the bipyramidally-coordinated units, two of the equatorial phenyl rings are parallel to the plane of the phenanthrolines and the third phenyl ring is set at right angles to this plane. The Mössbauer data (Table I) for the bipyridine complex are similar to those for the phenanthroline complex, and are consistent with five-coordination around the Sn atom [10–12]. Also, the infrared spectra for the two complexes in the ν(N–H) and ν(O–H) region above 3000 cm^{-1} are virtually identical (3040(m), 3060(m), 3350(br)). The similarity of these data, coupled with the similarity in stoichiometry, suggest very strongly that the bipyridine complex has a similar structure to that of the phenanthroline complex.

Although this type of bridging behaviour by coordinated water molecules has so far been reported for only very few simple systems, it is likely to prove to be of fairly common occurrence in the coordination chemistry of both main group and transition metals.

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References

1 A. Jack, J. E. Ladner, D. Rhodes, R. S. Brown and A. Kly, *J. Mol. Biol., 111,* 315 (1977).

2 J. D. Robertus, J. E. Ladner, J. T. Finch, T. Rhodes, R. S. Brown, B. F. C. Clark and A. Klug, *Nature, 250,* 546 (1974).

3 C. Stout, J. Mizano, J. Rubin, T. Brennan, S. Rao and M. Sundaralingham, *Nucleic Acids Res., 4,* 2811 (1976).

4 L. Prasad, F. L. Lee, Y. LePage and F. E. Smith, *Acta Cryst., B38,* 59 (1982).

5 L. Prasad and F. E. Smith, *Acta Cryst., B38,* 1815 (1982).

6 F. Smith, L. Prasad, D. Povey and M. Ladd, *Experientia, 39,* 719 (1983).

7 D. Povey, M. Ladd and F. E. Smith, *J. Cryst. Spect. Res.,* in press.

8 G. Germain, P. Main and M. M. Woolfson, *Acta Cryst., A27,* 368 (1971).

9 A. C. Larson and E. J. Gabe, in H. Schenk, R. Olthof-Hazekamp, H. vanKoningsveld and G. C. Bassi (Eds.), 'Computing in Crystallography'.Delft University Press, 1978, p. 81.

10 P. G. Harrison, *Adv. Chem. Ser., 157,* 258 (1976).

11 P. J. Smith, *Organomet. Chem. Rev. (A), 5,* 373 (1970).

12 A. G. Davies and P. J. Smith, in 'Comprehensive Organometallic Chemistry', Pergamon, Oxford, 1982, pp. 523–7.