

The First Authenticated Example of Geometrical Isomers in Organotin(IV) Co-ordination Chemistry. The Crystal and Molecular Structures of Octahedral *cis*- and *trans*-SnR₂ Isomeric Adducts of Dichlorobis(4-chlorophenyl)tin(IV) with 4,4'-Dimethyl-2,2'-Bipyridyl†

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The crystal structures of the *cis*- and *trans*-SnR₂ skeletal isomers of the octahedral complex, Sn(C₆H₄Cl-4)₂Cl₂·(4,4'-Me₂bipy) (4,4'-Me₂bipy = 4,4'-dimethyl-2,2'-bipyridyl), solved by X-ray analysis, are reported together with some preliminary observations on their solution structures as studied by ¹H and ¹¹⁹Sn Fourier-transform n.m.r. The complex is isolated exclusively as the *cis* isomer (**2**) upon mixing the Lewis-acid and -base components in ethanol medium. Recrystallization from hot methanol or dimethylformamide generates the *trans* isomer (**1**), which is readily reconverted to the *cis* form in toluene. Two crystalline modifications of the *cis* form, containing toluene molecules included in different host lattices, have been characterized as (**2a**) [C₂₄H₂₀Cl₄N₂Sn₂C₇H₈, space group *Pccn*, *a* = 12.221(8), *b* = 28.10(2), *c* = 20.548(6) Å, *Z* = 8] and (**2b**) [C₂₄H₂₀Cl₄N₂Sn₂C₇H₈, space group *P2₁/n*, *a* = 15.231(7), *b* = 12.422(6), *c* = 16.844(5) Å, β = 96.22(3)°, *Z* = 4]. Compound (**2**) exists as a discrete octahedral molecule in both (**2a**) and (**2b**) with the following respective molecular dimensions: C(1)–Sn–C(7) 106.2(6), 106.3(3); Cl(1)–Sn–Cl(2) 163.5(1), 163.0(1); N(1)–Sn–N(2) 69.8(4), 69.4(2)°; Sn–C(1) 2.139(18), 2.158(7); Sn–C(7) 2.170(13), 2.183(8) Å; Sn–N(1) 2.311(12), 2.322(6); Sn–N(2) 2.327(12), 2.294(6); Sn–Cl(1) 2.459(4), 2.509(2); Sn–Cl(2) 2.491(4), 2.475(2) Å. Compound (**1**) crystallizes from dimethylformamide in space group *P4₂* with *a* = 10.884(4), *c* = 10.204(2) Å, and *Z* = 2. The lattice of (**1**) contains discrete octahedral molecules [C(1)–Sn–C(1') 177.4(7), N(1)–Sn–N(1') 68.3(4), Cl(1)–Sn–Cl(1') 104.2(2)°; Sn–C 2.156(9); Sn–Cl 2.482(5); Sn–N 2.402(8) Å], with a crystallographic C₂ axis passing through Sn and the mid-point of the C–C bond joining the two halves of the bidentate ligand.

Six-co-ordination in organotin(IV) chemistry is widely observed for mono- and di-organotin(IV) compounds,^{1–7} and less so for triorganotin(IV) derivatives,^{8–10} which possess diminished acceptor strengths.³ Dialkyl- and diaryl-tin(IV) dihalides and dipseudohalides, in particular, afford a large number of octahedral tin structures of the type SnR₂X₂L₂ (L = neutral unidentate or ½ bidentate ligand) and SnR₂L'₂ (HL' = bidentate ligand). Furthermore, the stoichiometric 1:1 adducts formed by diorganotin dihalides with non-sterically demanding 'pointed' ligands containing the >C=O, >C=S, >S=O, >N→O, or >P=O grouping appear in most cases to be actually six-co-ordinated oligomeric structures as a result of intermolecular halogen bridging.^{11,12} The latter feature has also been evidenced in the associated solid-state structures of several diorganotin Lewis acids, for example, SnMe₂X₂ (X = F,¹³ Cl,¹⁴ CN,¹⁵ or NCS¹⁶).

Accumulated X-ray results on six-co-ordinated diorganotin(IV) structures^{1,2} indicate that the stereochemistry of the SnR₂ skeleton in the octahedral geometries is generally *trans* or distorted *trans* for dialkyltin(IV) complexes, the only exceptions recorded being for SnMe₂(quin)₂^{17a} (Hquin = quinolin-8-ol) and SnMe₂(ONHCOMe)₂.^{17b} These complexes have *cis*-SnR₂ structures (with C–Sn–C bond angles of 110.7 and 109.1° respectively) compared, for example, to the *trans*

skeleton in SnMe₂(acac)₂¹⁸ (Hacac = acetylacetonate; C–Sn–C bond angle 180°). The bis-acetylacetonate complex has, however, been shown from an i.r. study¹⁹ to coexist as *cis* and *trans* isomers in carbon disulphide solution. Semi-theoretical treatments^{20–22} of the bis-chelates on the ligand–ligand repulsion model have suggested a steric preference for the *cis* geometry over the *trans*, particularly when the 'bite' size of the chelating ligand is small. In conflict with these models, however, is the *trans*-SnR₂ structure recently observed for SnEtPr^m(mqin)₂²³ (Hmqin = 2-methylquinolin-8-ol), which reveals a smaller bite angle for the ligand than in SnMe₂(quin)₂ (70.9 vs. 73.5°). Although X-ray documentation of diphenyltin bis-chelate structures is sparse,^{1,2,24–26} support for the predicted *cis*-SnR₂ configuration nevertheless comes from a large body of Mössbauer information.^{7,27–29} To the best of our knowledge, only in one case has the influence of packing forces on SnR₂ skeletal geometry been clearly demonstrated, namely in the octahedral complex *trans*-SnPh₂[SP(=S)(OPr')₂]₂,²⁶ which differs from the *cis* diethyl ester analogue in having the SPS chelate rings shifted by half a cell dimension to lie between, instead of about, the tin atoms so as to yield a structure with a tightened lattice that has been described as a 'virtual polymer.'

Comparison of diphenyltin(IV) and dichlorotin(IV) bis-chelates with dialkyltin(IV) analogues has prompted the suggestion³⁰ that the poor σ-donor characteristics of the Ph and Cl groups permit realization of the predicted *cis* structures in these systems more readily than in the latter, where electronic

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.

Table 1. Crystal data and experimental conditions for (1), (2a), and (2b)

	(1)	(2a)	(2b)
Formula	C ₂₄ H ₂₀ Cl ₄ N ₂ Sn	C ₂₄ H ₂₀ Cl ₄ N ₂ Sn· $\frac{3}{2}$ C ₇ H ₈	C ₂₄ H ₂₀ Cl ₄ N ₂ Sn·C ₇ H ₈
<i>M</i>	596.94	735.15	689.08
System	Tetragonal	Orthorhombic	Monoclinic
<i>a</i> /Å	10.884(4)	12.221(8)	15.231(7)
<i>b</i> /Å		28.10(2)	12.422(6)
<i>c</i> /Å	10.204(2)	20.548(6)	16.844(5)
β /°			96.22(3) ^a
<i>U</i> /Å ³	1 208.8(9)	7 056(7)	3 168(2)
Space group	<i>P</i> 4 ₂	<i>Pccn</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i>	2	8	4
<i>D_c</i> /Mg m ⁻³	1.640	1.384	1.445
<i>D_m</i> /Mg m ⁻³ (KI H ₂ O)	1.638	1.385	1.441
μ /cm ⁻¹ (Mo- <i>K</i> _α)	15.21	10.56	11.71
Crystal size (mm)	0.40 × 0.38 × 0.35	0.38 × 0.34 × 0.18	0.38 × 0.32 × 0.20
Mean μ_r	0.25	0.11	0.16
Transmission factors	0.468—0.551	0.722—0.877	0.590—0.710
Collection range; 2 θ _{max}	<i>h, k, l</i> ; 65°	<i>h, k, l</i> ; 45°	<i>h, k, ±l</i> ; 50°
Unique data measured	1 961	2 701	4 614
Observed data with $ F_o > 3\sigma(F_o)$, <i>n</i>	1 624	1 984	3 846
No. of variables, <i>p</i>	140	267	296
$R = \Sigma F_o - F_c /\Sigma F_o $	0.085	0.073	0.057
Weighting scheme: x in $w = [\sigma^2(F_o) + x F_o ^2]^{-1}$	0.002	0.0012	0.001
$R' = [\Sigma w(F_o - F_c)^2/\Sigma w F_o ^2]^{1/2}$	0.098	0.083	0.077
$S = [\Sigma w(F_o - F_c)^2/(n - p)]^{1/2}$	1.722	1.627	1.699
Residual extrema in final difference map (e Å ⁻³)	+7.90 to -0.59	+0.63 to -0.73	+0.84 to -0.53

effects of the alkyl groups, in accordance with Bent's rule,³¹ tend to favour the *trans* or distorted *trans* structure. However, in cases where the structural distortion of the octahedron is severe, *cis-trans* designations would be of questionable validity and a description of the geometry as skewed or trapezoidal bipyramidal would probably be more appropriate.^{21,32}

We were especially intrigued by the observation¹⁻³ in SnPh₂X₂L₂ complexes that *trans*-SnR₂ geometries were exclusively obtained with unidentate ligands when X = halide or pseudohalide, but not so with bidentate ligands. Thus, with α -diimine ligands, in particular, diphenyltin dipseudohalides yield, presumably on steric grounds,³³ *cis*-SnR₂ octahedral adducts, while with the dihalides only *trans* geometries have thus far been reported. We reasoned that if *cis-trans* energy differences were small in these systems, it might be conceivable, by a suitable choice of substituents on the aryl groups and/or the chelating ligand, to favour one geometrical isomer over the other and, perhaps, even to allow the isolation of both forms, a goal hitherto unaccomplished in organotin co-ordination chemistry.* We succeeded in this when we isolated and crystallographically characterized the complex *cis*-Sn(C₆H₄-Me-4)₂Cl₂-bipy³⁶ (bipy = 2,2'-bipyridyl, C-Sn-C bond angle 108.7°). This was soon followed by the isolation of both the *cis* and *trans* isomers, as characterized by Mössbauer spectroscopy, of the 4,4'-dimethyl-2,2'-bipyridyl adduct Sn(C₆H₄Cl-4)-Cl₂·(4,4'-Me₂bipy).³⁷ In this paper we present *X*-ray evidence which confirms the geometrical assignments for this pair of isomeric adducts.

Experimental

The synthesis of *cis*-Sn(C₆H₄Cl-4)₂Cl₂·(4,4'-Me₂bipy) (2), and

its conversion to the *trans* isomer (1), have been reported previously.³⁷ Single crystals of (1), which exhibit a pink tinge, were obtained by slow evaporation of a dimethylformamide solution of the adduct. The use of toluene as the recrystallizing medium, however, gave colourless crystals which proved to be a toluene solvate of the *cis* adduct, (2a), with molecular formulation C₂₄H₂₀Cl₄N₂Sn· $\frac{3}{2}$ C₇H₈. Interestingly, recrystallization of the *cis* isomer (2) from toluene afforded (2a) and another crystalline form (2b) of higher density. Crystallographic investigation of the latter showed it to be a different toluene solvate of the *cis* isomer, having the molecular formulation C₂₄H₂₀Cl₄N₂Sn·C₇H₈.

Data Collection and Structure Refinement.—A single crystal of each of (2a) and (2b) was respectively enclosed in its solvent atmosphere inside a thin-walled capillary (Lindemann glass; 0.5 mm) to guard against the loss of crystallinity in air. This precaution, however, was not required for (1). All *X*-ray crystallographic measurements were carried out using a Nicolet R3m automated four-circle diffractometer and graphite-monochromated Mo-*K*_α radiation ($\lambda = 0.71069$ Å) at an ambient laboratory temperature of 22 °C. The $\omega/2\theta$ scan technique was used with scan range 1° below *K*_{α1} to 1° above *K*_{α2} and scan speeds between 2.02 and 8.37° min⁻¹. Crystal data and specific parameters relating to the collection of the three data sets are listed in Table 1. Backgrounds were measured at each end of the scan range for one-half of the scan time. Two standard reflections were used to monitor every 125 reflections. Empirical absorption corrections were applied by pseudo-ellipsoidal treatment of the intensities of selected strong reflections measured at different azimuthal (ψ) angles.^{38,39} Redundant and equivalent reflections were averaged and converted into unscaled $|F_o|$ values after corrections for Lorentz and polarization factors. Direct phase determination revealed the positions of the tin atoms; the remaining non-hydrogen atoms were located from subsequent difference-Fourier maps. All non-hydrogen atoms in the tin(IV) complex, except the carbon atoms of the bidentate ligand in (2a), were refined anisotropically. The hydrogen atoms of the aryl or heteroaryl

* Complexation of the quadridentate ligand, *N,N'*-ethylenebis(salicylideneimine) with dimethyltin dichloride has been claimed in an earlier report³⁴ to yield *cis* and *trans* isomeric products, but the isomers were not characterized. Interestingly, *cis-trans* isomerism in complexes of tin(IV) chloride has been observed with some unidentate oxygen-donor ligands such as tetrahydrofuran.³⁵

Table 2. Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for (1)

Atom	x	y	z	Atom	x	y	z
Sn	0	5 000	0	C(6)	-964(12)	2 515(10)	1 214(13)
Cl(1)	1 674(4)	4 341(3)	-1 494(5)	N(1)	1 153(8)	4 548(8)	1 948(9)
Cl(2)	-2 049(3)	-791(2)	-39(7)	C(7)	655(10)	4 801(8)	3 127(11)
C(1)	-717(8)	3 154(8)	48(14)	C(8)	1 357(10)	4 688(9)	4 287(11)
C(2)	-880(12)	2 572(15)	-1 116(18)	C(9)	2 544(11)	4 342(11)	4 220(14)
C(3)	-1 310(12)	1 321(10)	-1 162(14)	C(10)	3 064(11)	4 049(11)	3 023(16)
C(4)	-1 551(7)	727(7)	8(18)	C(11)	2 290(10)	4 147(12)	1 894(14)
C(5)	-1 384(12)	1 332(13)	1 212(15)	C(12)	3 372(13)	4 262(16)	5 434(18)

Table 3. Atomic co-ordinates ($\times 10^5$ for Sn; $\times 10^4$ for other atoms in the ligands; $\times 10^3$ for atoms in the toluene molecules) with estimated standard deviations in parentheses for (2a)

Atom	x	y	z	Atom	x	y	z
Sn	42 314(9)	5 035(4)	19 046(5)	C(10)	4 152(14)	-460(6)	3 917(7)
Cl(1)	5 797(3)	997(2)	2 234(2)	C(11)	4 945(13)	-116(6)	3 826(7)
Cl(2)	2 958(3)	-16(2)	1 278(2)	C(12)	4 961(12)	139(5)	3 277(7)
Cl(3)	444(5)	2 140(2)	2 635(3)	C(13)	4 156(14)	1 212(6)	675(8)
Cl(4)	4 051(4)	-787(2)	4 647(2)	C(14)	4 435(13)	1 417(6)	69(8)
N(1)	4 640(9)	815(4)	892(6)	C(15)	5 272(14)	1 216(6)	-309(8)
N(2)	5 567(9)	45(4)	1 396(5)	C(16)	5 722(14)	805(5)	-61(7)
C(1)	3 044(14)	1 046(7)	2 089(8)	C(17)	5 424(11)	606(5)	522(7)
C(2)	1 991(19)	1 003(6)	1 903(8)	C(18)	5 919(11)	182(5)	806(7)
C(3)	1 141(14)	1 348(7)	2 083(9)	C(19)	6 696(11)	-92(5)	495(7)
C(4)	1 445(17)	1 733(6)	2 435(9)	C(20)	7 147(12)	-488(5)	769(7)
C(5)	2 511(18)	1 795(7)	2 621(9)	C(21)	6 782(12)	-614(5)	1 369(7)
C(6)	3 297(13)	1 447(6)	2 426(9)	C(22)	5 957(13)	-338(6)	1 656(8)
C(7)	4 258(11)	55(5)	2 764(6)	C(23)	5 581(15)	1 437(6)	-981(9)
C(8)	3 461(11)	-291(5)	2 849(7)	C(24)	8 014(14)	-784(6)	427(8)
C(9)	3 400(13)	-550(6)	3 423(8)				
Toluene molecule I							
C(25)	250	250	439(2)	C(28)	250	250	579(2)
C(26)	324(3)	227(1)	473(2)	C(29)*	416(5)	206(3)	440(3)
C(27)	328(2)	223(1)	542(1)				
Toluene molecule II							
C(30)	750	250	424(2)	C(33)	750	250	308(2)
C(31)	681(4)	210(1)	399(2)	C(34)*	618(5)	170(2)	390(3)
C(32)	690(3)	211(1)	326(2)				
Toluene molecule III							
C(35)	655(3)	232(2)	115(1)	C(37)	835(3)	215(2)	115(1)
C(36)	735(4)	196(1)	115(1)	C(38)*	556(5)	215(3)	115(1)

* Disordered methyl C atom of site occupancy 0.5.

rings in the tin(IV) adduct were generated geometrically (C-H 0.96 Å), assigned fixed isotropic thermal factors, and allowed to ride on their respective parent carbon atoms. The aromatic ring of the included toluene molecule in (2b) was treated as a rigid group (hexagon of edge 1.395 Å). The C atoms of the three toluene molecules in (2a), on the other hand, were individually refined. For all three toluene molecules two-fold disorder was observed in their methyl carbon atoms, which were refined with half site occupancy.

All computations were performed on a Data General Corporation Nova 3/12 minicomputer with the SHELXTL program package.³⁸ Analytical expressions⁴⁰ of neutral-atom scattering factors⁴¹ were employed, and anomalous dispersion corrections⁴² were applied. Blocked-cascade least-squares refinement^{38,43} of the variables (p) in each set converged to the R indices indicated in Table 1. A slightly lower order of accuracy was obtained for the *trans* isomer (1) whose final difference map revealed two residual peaks ($7.90 \text{ e } \text{Å}^{-3}$) lying 0.68 Å on either side of Sn along the c axis.

The final atomic co-ordinates for (1), (2a), and (2b) are

reported respectively in Tables 2–4, the bond distances and angles in Tables 5 [for (1)] and 6 [for (2a) and (2b)]; least-squares mean planes and dihedral angles are in Table 7.

N.M.R. Measurements.—Proton n.m.r. spectra were measured on a Fourier-transform JEOL JNM-FX 100 spectrometer operating at 99.55 MHz; the ambient probe temperature was typically 28 °C. Tin-119 n.m.r. spectra were measured using 10-mm tubes at 30 °C on a JEOL-FX60Q spectrometer, operating at 22.24 MHz under nuclear Overhauser suppressed conditions;⁴⁴ the field frequency lock was to external D_2O . Owing to the poor solubility of the compounds in CDCl_3 , accumulations were carried out over at least 2 d and each sample was recorded twice to check the accuracy of the chemical shift ($\pm 0.5 \text{ p.p.m.}$, relative to SnMe_4).

Results and Discussion

Description of the Structures.—A stereoview, with atom labelling, of the molecular structure of isomer (1) is shown in

Table 4. Atomic co-ordinates ($\times 10^5$ for Sn; $\times 10^4$ for other atoms) with estimated standard deviations in parentheses for (2b)

Atom	x	y	z	Atom	x	y	z
Sn	26 010(3)	4 903(4)	12 541(3)	C(10)	4 914(6)	3 054(7)	655(4)
Cl(1)	1 365(1)	1 834(2)	1 190(1)	C(11)	4 120(6)	3 432(7)	853(4)
Cl(2)	3 500(1)	-1 122(2)	1 039(1)	C(12)	3 466(5)	2 716(6)	977(4)
Cl(3)	3 260(3)	549(2)	5 233(1)	C(13)	1 344(5)	-1 378(6)	1 844(5)
Cl(4)	5 770(2)	3 947(2)	490(2)	C(14)	719(5)	-2 225(6)	1 799(5)
N(1)	1 500(4)	-809(4)	1 201(3)	C(15)	279(5)	-2 486(6)	1 099(5)
N(2)	1 996(4)	222(5)	-38(3)	C(16)	451(5)	-1 891(5)	435(5)
C(1)	2 748(4)	450(5)	2 543(4)	C(17)	1 075(4)	-1 065(5)	500(4)
C(2)	3 349(5)	-243(6)	2 950(5)	C(18)	1 297(4)	-441(5)	-188(4)
C(3)	3 506(6)	-230(6)	3 784(5)	C(19)	830(5)	-504(6)	-934(4)
C(4)	3 039(6)	496(6)	4 191(5)	C(20)	1 070(5)	118(7)	-1 575(5)
C(5)	2 445(5)	1 177(6)	3 813(4)	C(21)	1 783(6)	767(7)	-1 414(5)
C(6)	2 294(5)	1 154(6)	2 982(4)	C(22)	2 244(6)	822(7)	-644(5)
C(7)	3 582(5)	1 633(6)	912(4)	C(23)	-396(6)	-3 371(7)	1 043(6)
C(8)	4 385(5)	1 275(7)	706(5)	C(24)	578(6)	41(8)	-2 382(5)
C(9)	5 056(6)	1 983(7)	570(5)				
Toluene molecule							
C(25)	8 727(6)	2 911(7)	2 559(7)	C(29)	7 424(6)	1 798(7)	2 315(7)
C(26)	8 864(6)	2 525(7)	3 340(7)	C(30)	8 007(6)	2 548(7)	2 046(7)
C(27)	8 282(6)	1 775(7)	3 608(7)	C(31)	9 452(16)	3 555(23)	2 508(18)
C(28)	7 562(6)	1 412(7)	3 096(7)				

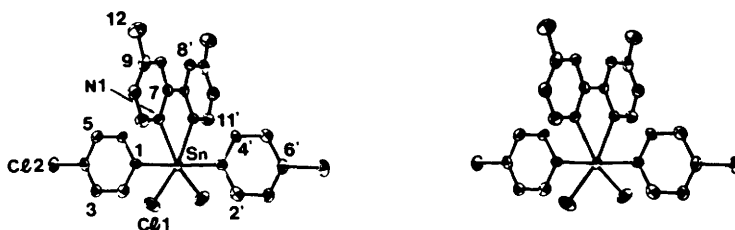
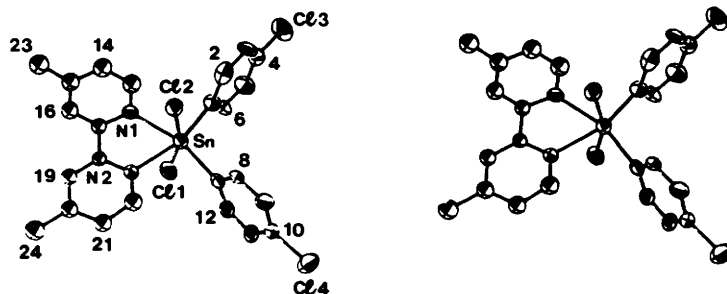
**Figure 1.** The molecular structure of *trans*-Sn(C₆H₄Cl-4)₂Cl₂·(4,4'-Me₂bipy) (1) with the atom numbering scheme**Figure 2.** The molecular structure of *cis*-Sn(C₆H₄Cl-4)₂Cl₂·(4,4'-Me₂bipy) (2) as observed in the toluene solvates (2a) and (2b), for which the same atom numbering scheme was used

Figure 1, and the corresponding diagram for isomer (2), as occurring in the crystalline solvates (2a) and (2b), is shown in Figure 2. Compounds (2a) and (2b) constitute a rare example of polymorphism featuring the inclusion of toluene molecules in two different crystalline lattices constructed from organometallic host molecules of the same kind.

Crystal structure of (1). The title isomer (1) exists as a six-co-ordinated, monomeric species with a crystallographic C_2 axis passing through the tin atom and the mid-point of the C(7)–C(7') bond. The molecules have normal van der Waals separations and are related in the unit cell by 4_2 screw spirals in the c direction [Figure 3(a) and (b)]. The orientation of the 4-chlorophenyl groups in the octahedral tin(IV) complex is unambiguously *trans*: the observed C–Sn–C bond angle is

$177.4(7)^\circ$ (Table 5) and the aryl rings have an incipient twist between them of *ca.* 4° . This contrasts with the structurally analogous *trans*-SnPh₂Cl₂·bipy⁴⁵ (3) (bipy = 2,2'-bipyridyl), which has a C–Sn–C bond angle of 173.5° and a dihedral angle of 79.5° between the phenyl rings. However, the 'bite' angles of the chelating ligands in both complexes are similar (*ca.* 69°).

The ligand 4,4'-Me₂bipy is known to be a stronger base than bipy,⁴⁶ but would be expected⁴⁷ to present steric inhibition to the *trans*-SnR₂ octahedral geometry, and especially in this instance where the acceptor moiety is bulkier than that present in (3). This is evidenced in the somewhat longer Sn–N bonds in (1) (Table 5) than in (3) (2.344, 2.375 Å)⁴⁵ and the presence of a higher degree of torsion along the bipyridyl axis. Thus the dihedral angle between the 4-MeC₅H₃N rings of 4,4'-Me₂bipy

in (1) is 13° relative to the dihedral angle of 4.2° between the C_5H_4N rings of bipy in (3). Attendant variations in the intraring ligand bond lengths and angles are also evident. Noteworthy is the inequivalence observed in the bonds linking the nitrogen and α -carbon atoms in the $4-MeC_5H_3N$ unit: N(1)-C(7) 1.35(1), N(1)-C(11) 1.31(1) Å [cf. 1.35 Å for the near-equivalent N-C $_{\alpha}$ bonds in the C_5H_4N units of bipy in (3)].

Table 5. Bond lengths (Å) and angles ($^\circ$) with estimated standard deviations in parentheses for (1)

Sn-Cl(1)	2.482(5)	Sn-C(1)	2.156(9)
Sn-N(1)	2.402(8)	Cl(2)-C(4)	1.749(8)
C(1)-C(2)	1.36(2)	C(1)-C(6)	1.40(2)
C(2)-C(3)	1.44(2)	C(3)-C(4)	1.38(2)
C(4)-C(5)	1.41(2)	C(5)-C(6)	1.37(2)
N(1)-C(7)	1.35(1)	N(1)-C(11)	1.31(1)
C(7)-C(18)	1.41(2)	C(7)-C(7')	1.49(2)
C(8)-C(9)	1.35(2)	C(9)-C(10)	1.38(2)
C(9)-C(12)	1.53(2)	C(10)-C(11)	1.43(2)
Cl(1)-Sn-C(1)	90.6(3)	Cl(1)-Sn-N(1)	93.8(2)
C(1)-Sn-N(1)	88.8(4)	Cl(1)-Sn-Cl(1')	104.2(2)
C(1)-Sn-Cl(1')	91.0(3)	N(1)-Sn-Cl(1')	162.0(2)
C(1)-Sn-C(1')	177.4(7)	N(1)-Sn-C(1')	89.0(4)
N(1)-Sn-N(1')	68.3(4)	Sn-C(1)-C(2)	117.5(10)
Sn-C(1)-C(6)	123.4(9)	C(2)-C(1)-C(6)	119.0(10)
C(1)-C(2)-C(3)	120.8(14)	C(2)-C(3)-C(4)	118.3(13)
Cl(2)-C(4)-C(3)	118.6(12)	Cl(2)-C(4)-C(5)	120.6(12)
C(3)-C(4)-C(5)	120.8(9)	C(4)-C(5)-C(6)	119.1(13)
C(1)-C(6)-C(5)	122.0(12)	Sn-N(1)-C(7)	119.1(7)
Sn-N(1)-C(11)	121.7(8)	C(7)-N(1)-C(11)	119.0(10)
N(1)-C(7)-C(8)	120.8(9)	N(1)-C(7)-C(7')	116.4(6)
C(8)-C(7)-C(7')	122.8(6)	C(7)-C(8)-C(9)	120.0(11)
C(8)-C(9)-C(10)	120.1(12)	C(8)-C(9)-C(12)	122.6(13)
C(10)-C(9)-C(12)	117.3(11)	C(9)-C(10)-C(11)	116.9(11)
N(1)-C(11)-C(10)	123.0(12)		

The octahedral geometry at tin(IV) in (1) is more regular than in (3): the two pairs of chlorine and nitrogen ligand atoms lie in an equatorial plane though not so constrained by the molecular symmetry. The observed C-Sn-C bond angle in (1) closely agrees with the predicted value of 178° based on Mössbauer data³⁷ [isomer shift (i.s.) 1.14 mm s⁻¹, quadrupole splitting (q.s.) 3.49 mm s⁻¹] and the point-charge approach given by the equation $[q.s.] = 4[R](1 - 3\sin^2\theta\cos^2\theta)^{\frac{1}{2}}$,³⁰ where $(180 - 2\theta)$ is the R-Sn-R bond angle, and partial q.s. contributions from ligands other than R groups ($[aryl] = -0.95$ mm s⁻¹) are considered to be negligible. The correlation expressed by the above equation is reasonably well supported by data from compounds for which both Mössbauer and diaryltin C-Sn-C angles are available.^{30,48}

Crystal structures of (2a) and (2b). Of the three independent toluene molecules in (2a), I and II each has a crystallographic diad passing through two opposite corners of its aromatic ring, while III lies normal to the diad associated with II; all have two-fold disordered methyl groups. As illustrated in Figure 4, types II and III molecules stack alternately and regularly (centres of adjacent molecules separated by $c/4$) in columns along C_2 axes parallel to c , and the linear array of type I molecules (related by the c glide normal to b) is partitioned by the protruding chlorophenyl groups of neighbouring tin(IV) complexes. The crystal structure of (2a) may be regarded as being composed of alternate layers of host tin complexes and guest toluene molecules normal to the b axis. In the unit cell of (2b) (Figure 5), the toluene molecules stack about the periphery of the chelating ligands. In both (2a) and (2b), a closer approach of the chelating ligand to tin appears sterically favoured relative to (1). This is indicated by the somewhat lesser torsional twist between the $4-MeC_5H_3N$ rings of the chelating ligands [2° for (2a) and 9° for (2b)].

For isomer (2), examined in the solvent-free amorphous state, the measured q.s. has a value almost half that of the *trans* isomer

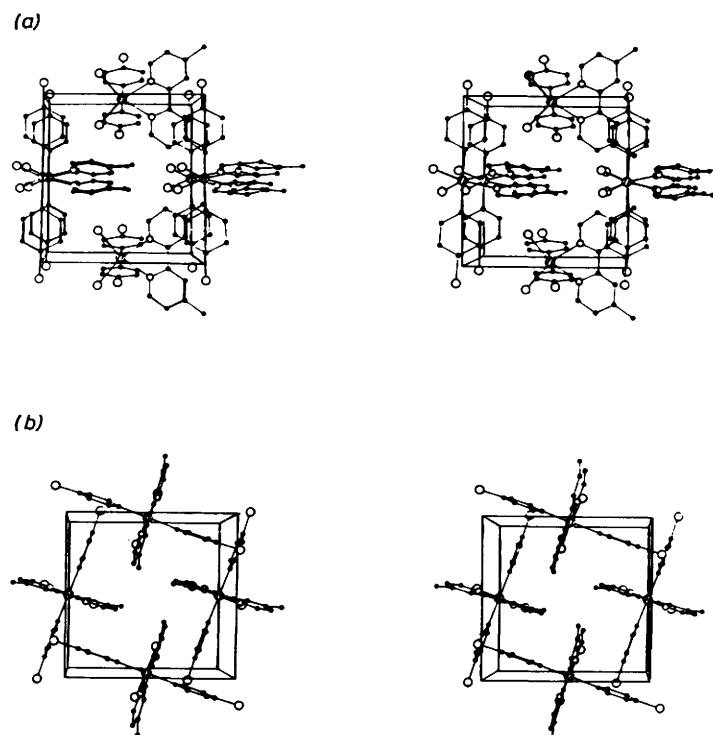


Figure 3. Stereoscopic views of the molecular packing in compound (1) along (a) the a axis and (b) the c axis

Table 6. Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for (2a) and (2b)

Bond lengths	(2a)	(2b)	Bond lengths	(2a)	(2b)
Sn-Cl(1)	2.459(4)	2.509(2)	C(7)-C(8)	1.39(2)	1.38(1)
Sn-Cl(2)	2.491(4)	2.475(2)	C(7)-C(12)	1.38(2)	1.36(1)
Sn-N(1)	2.311(12)	2.322(6)	C(8)-C(9)	1.39(2)	1.39(1)
Sn-N(2)	2.327(12)	2.294(6)	C(9)-C(10)	1.39(2)	1.36(1)
Sn-C(1)	2.139(18)	2.158(7)	C(10)-C(11)	1.38(2)	1.37(1)
Sn-C(7)	2.170(13)	2.183(8)	C(11)-C(12)	1.34(2)	1.37(1)
Cl(3)-C(4)	1.72(2)	1.753(8)	C(13)-C(14)	1.41(2)	1.42(1)
Cl(4)-C(10)	1.76(2)	1.756(9)	C(14)-C(15)	1.40(2)	1.33(1)
N(1)-C(13)	1.34(2)	1.34(1)	C(15)-C(16)	1.38(2)	1.39(1)
N(1)-C(17)	1.36(2)	1.32(1)	C(15)-C(23)	1.56(2)	1.50(1)
N(2)-C(18)	1.34(2)	1.35(1)	C(16)-C(17)	1.37(2)	1.39(1)
N(2)-C(22)	1.29(2)	1.35(1)	C(17)-C(18)	1.46(2)	1.47(1)
C(1)-C(2)	1.35(3)	1.38(1)	C(18)-C(19)	1.38(2)	1.38(1)
C(1)-C(6)	1.36(3)	1.38(1)	C(19)-C(20)	1.36(2)	1.41(1)
C(2)-C(3)	1.47(3)	1.40(1)	C(20)-C(21)	1.36(2)	1.36(1)
C(3)-C(4)	1.35(3)	1.38(1)	C(20)-C(24)	1.52(2)	1.48(1)
C(4)-C(5)	1.37(3)	1.35(1)	C(21)-C(22)	1.40(2)	1.41(1)
C(5)-C(6)	1.43(3)	1.39(1)			
Bond angles			Bond angles		
Cl(1)-Sn-Cl(2)	163.5(1)	163.0(1)	C(1)-C(6)-C(5)	124(2)	121.0(7)
Cl(1)-Sn-N(1)	82.3(3)	85.7(1)	Sn-C(7)-C(8)	120(1)	120.5(6)
Cl(2)-Sn-N(1)	83.8(3)	80.8(1)	Sn-C(7)-C(12)	122(1)	121.5(6)
Cl(1)-Sn-N(2)	83.7(3)	80.4(2)	C(8)-C(7)-C(12)	118(1)	117.6(7)
Cl(2)-Sn-N(2)	83.2(3)	85.2(2)	C(7)-C(8)-C(9)	121(1)	121.7(8)
N(1)-Sn-N(2)	69.8(4)	69.4(2)	C(8)-C(9)-C(10)	119(2)	118.4(8)
Cl(1)-Sn-C(1)	94.4(5)	93.1(2)	Cl(4)-C(10)-C(9)	119(1)	118.2(7)
Cl(2)-Sn-C(1)	94.9(5)	97.5(2)	Cl(4)-C(10)-C(11)	122(1)	120.7(7)
N(1)-Sn-C(1)	92.1(5)	91.0(2)	C(9)-C(10)-C(11)	120(1)	121.0(8)
N(2)-Sn-C(1)	161.8(5)	159.7(2)	C(10)-C(11)-C(12)	120(1)	119.3(8)
Cl(1)-Sn-C(7)	95.3(4)	95.0(2)	C(7)-C(12)-C(11)	123(1)	121.8(7)
Cl(2)-Sn-C(7)	95.2(4)	94.7(2)	N(1)-C(13)-C(14)	122(2)	121.9(7)
N(1)-Sn-C(7)	161.7(5)	162.5(2)	C(13)-C(14)-C(15)	120(2)	119.9(7)
N(2)-Sn-C(7)	91.9(5)	93.4(2)	C(14)-C(15)-C(16)	115(2)	117.5(7)
C(1)-Sn-C(7)	106.2(6)	106.3(3)	C(14)-C(15)-C(23)	120(2)	120.7(7)
Sn-N(1)-C(13)	121(1)	121.9(4)	C(16)-C(15)-C(23)	124(2)	121.8(7)
Sn-N(1)-C(17)	120(1)	118.9(4)	C(15)-C(16)-C(17)	124(2)	121.0(7)
C(13)-N(1)-C(17)	119(1)	118.9(6)	N(1)-C(17)-C(16)	120(1)	120.7(6)
Sn-N(2)-C(18)	118(1)	119.6(5)	N(1)-C(17)-C(18)	115(1)	116.5(6)
Sn-N(2)-C(22)	122(1)	121.3(5)	C(16)-C(17)-C(18)	125(1)	122.8(6)
C(18)-N(2)-C(22)	120(1)	118.4(6)	N(2)-C(18)-C(17)	118(1)	114.9(6)
Sn-C(1)-C(2)	122(1)	120.2(5)	N(2)-C(18)-C(19)	119(1)	121.7(6)
Sn-C(1)-C(6)	122(1)	121.5(5)	C(17)-C(18)-C(19)	124(1)	123.4(6)
C(2)-C(1)-C(6)	116(2)	118.1(7)	C(18)-C(19)-C(20)	123(1)	121.1(7)
C(1)-C(2)-C(3)	123(2)	121.5(7)	C(19)-C(20)-C(21)	117(1)	116.2(7)
C(2)-C(3)-C(4)	118(2)	117.8(7)	C(19)-C(20)-C(24)	122(1)	121.4(7)
Cl(3)-C(4)-C(3)	118(2)	118.0(6)	C(21)-C(20)-C(24)	121(1)	122.4(8)
Cl(3)-C(4)-C(5)	122(1)	119.8(6)	C(20)-C(21)-C(22)	118(1)	121.4(8)
C(3)-C(4)-C(5)	121(2)	122.2(7)	N(2)-C(22)-C(21)	124(2)	121.1(8)
C(4)-C(5)-C(6)	118(2)	119.4(7)			

(i.s. 0.84 mm s^{-1} , q.s. 1.99 mm s^{-1}),³⁷ which is in accord with the *cis*- SnR_2 assignment on the point-charge model.^{27,28} The predicted value of 100° for the C-Sn-C bond angle in (2) compares favourably to the values observed crystallographically in both (2a) and (2b), ca. 106° (Table 6). Seemingly, the toluene molecules in the crystalline solvates cause little perturbation of the octahedral geometry at tin and serve to consolidate the crystal lattice *via* interactions of the van der Waals type.

A comparison with the isostructural complex *cis*- $\text{Sn}(\text{C}_6\text{H}_4\text{-Me-4})_2\text{Cl}_2\cdot\text{bipy}$ ³⁶ (4) reveals (Table 7) for the latter a larger C-Sn-C angular opening. This is accompanied by a reduced twist of the aryl rings and a value for the dihedral angle between the pyridyl rings of the ligand that is intermediate between those of (2a) and (2b). The inequivalence of the two Sn-N bonds which is slight in (4) is now more conspicuous in (2a) and (2b). We consider these differences to be the artefacts of structural

distortions in the aforesaid complexes. All the co-ordination bond lengths tabulated for the isomers (1) and (2) are normal, and well within the range of values commonly encountered in six-co-ordinate diorganotin(IV) dichloride complexes.

A noteworthy feature in comparing the complexes (2), (4), and $\text{SnPh}_2(\text{NCS})_2\cdot\text{bipy}$ ⁴⁹ [C-Sn-C bond angle (*X*-ray) 106.3°] is the *trans* array, presumably preferred on steric grounds, of the halide or pseudohalide groups relative to other alternative *cis* arrangements. This steric circumstance may also be responsible for the observed Cl-Sn-Cl bond angle opening in (1) relative to the ideal *cis* angle.

Solution Structures.—Although complexes (1) and (2) are poorly soluble in most common non-polar solvents, an attempt was made to probe their structures in CDCl_3 by ^1H and ^{119}Sn n.m.r. measurements in pulse mode with Fourier transform.

The data are summarized in Table 8. One of the most notable features of ^{119}Sn n.m.r. spectroscopy is the dependence of ^{119}Sn chemical shifts on the co-ordination number of tin,^{50–52} and the chemical shift values for (1) and (2) argue for the presence of only six-co-ordinated tin species in solution.^{52–54} However, the observation of a single ^{119}Sn resonance for both these cases implies either the preferential formation of only one isomer in solution or the co-existence of both isomers with virtually identical chemical shifts. Some indications tentatively favouring the latter possibility come from the ^1H n.m.r. spectra.

Thus, in contrast to the free ligand which shows a singlet

Table 7. Comparison of selected molecular dimensions of (2a) and (2b) with those of $\text{Sn}(\text{C}_6\text{H}_4\text{Me-4})_2\text{Cl}_2\cdot\text{bipy}$ (4) (ref. 36)

	(2a)	(2b)	(4)
Bond distances (Å)			
Sn–C	2.139(18), 2.170(13)	2.158(7), 2.183(8)	2.159(3), 2.161(3)
Sn–N	2.311(12), 2.327(12)	2.294(6), 2.322(6)	2.306(3), 2.374(3)
Sn–Cl	2.459(4), 2.491(4)	2.475(2), 2.509(2)	2.493(1), 2.507(1)
Bond angles (°)			
Cl–Sn–Cl	163.5(1)	163.0(1)	161.4(1)
N–Sn–N	69.8(4)	69.4(2)	69.1(1)
C–Sn–C	106.2(6)	106.3(3)	108.7(1)
Dihedral angles between planes (°)			
Pyridyl rings	2(1)	9(1)	4.4(8)
Aryl groups	85(1)	85(1)	76.2(8)

methyl resonance at 2.43 p.p.m., complex (2) yields two sharp resonances at 2.56 and 1.56 p.p.m., with an additional third peak at 2.36 p.p.m., attributable to toluene present originally in the

Table 8. Chemical shifts (p.p.m.) of non-aromatic protons^{a,b} and ^{119}Sn nuclei^a

Compound	$\delta(^{119}\text{Sn})^c$	$\delta(^1\text{H})^d$
4,4'-Me ₂ bipy (L)		2.43
$\text{SnPh}_2\text{Cl}_2\cdot\text{L}^e$	–356.5	2.54, 1.55 (1.4:1); 2.54, 1.58 (1:1); ^f 2.58, 1.48 (0.6:1) ^g
$\text{Sn}(\text{C}_6\text{H}_4\text{Me-4})_2\text{Cl}_2\cdot\text{L}^h$	–350.2	2.52, 1.57 (3:1); 2.35 (C ₆ H ₄ -Me)
(1)	–358.5	2.57, 1.55 (0.3:1); 2.63, 1.43 (0.1:1) ^g
(2)	–358.6	2.56, 1.56 (1.9:1), 2.36; ⁱ 2.54, 1.76 (1.5:1); ^j 2.36, ^{i,j} 2.43; ^j 2.59, 1.29 (0.5:1); ^k 2.36 ^{i,k}
$\text{SnMe}_2\text{Cl}_2\cdot\text{L}$		2.58, 1.57 (0.8:1); 1.068, 1.062 (Sn–CH ₃), ² J 101.4 Hz

^a In CDCl_3 (saturated solution), unless otherwise specified, with values in parentheses (for ^1H n.m.r.) depicting the intensity ratios, as per listing order, of the dual methyl resonances of the complexed ligand. ^b Aromatic resonances occur as complex multiplets in the range 7.26–8.30 p.p.m. ^c Relative to SnMe_4 . ^d Relative to SiMe_4 . ^e Exists as the *trans* isomer in the solid state as indicated by Mössbauer data (ref. 37). ^f Under conditions of equilibration of spectral solution overnight. ^g In *ca.* 50% (v/v) mixture of CDCl_3 + CS_2 . ^h Exists as *cis-trans* mixture in the solid state based on Mössbauer evidence (V. G. Kumar Das and Yap Chee Keong, unpublished work). ⁱ Methyl resonance of 'included' toluene (see text). ^j In the presence of added ligand. ^k In *ca.* 30% CDCl_3 + 70% CS_2 (v/v).

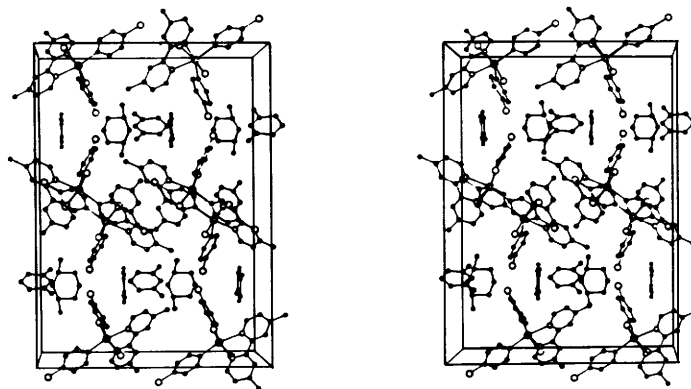


Figure 4. Stereoscopic view of the molecular packing in compound (2a). The origin of the unit cell lies at the upper left corner, with *a* pointing out of the plane of the page, *b* downwards, and *c* from left to right

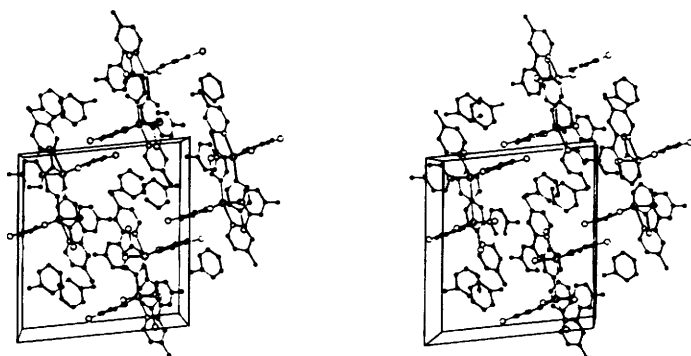


Figure 5. Stereoscopic view of the molecular packing in compound (2b). The origin of the unit cell lies at the upper left corner, with *a* pointing from left to right, *b* out of the plane of the page, and *c* downwards

crystalline matrix of (2) as included solvent. The resonances at 2.56 and 1.56 p.p.m. integrate respectively for peak intensities in the approximate ratio 2:1, and remain distinguishable upon adding free ligand to the spectral solution. The signal at 1.56 p.p.m., however, shifts to lower field in the presence of the added base, and the relative intensities are now in the ratio 3:2. The spectrum of (2) in CS₂ containing 30% CDCl₃ again reveals two sharp ligand methyl resonances at 2.59 and 1.29 p.p.m., which integrate for the ratio 1:2.

The spectrum of (1) in CDCl₃ reveals the ligand methyl resonances at 2.57 and 1.55 p.p.m., almost identical to the situation for (2), but with the intensity ratio in this instance (1:3) favouring the high-field resonance. The relative intensity of the high-field resonance is further enhanced in carbon disulphide.

cis-trans Isomerism appears to be one cogent explanation for these trends in solution, and we suggest that each ligand methyl resonance observed is unique to the respective isomer. Not inconsistent with this view are the data for SnPh₂Cl₂·(4,4'-Me₂bipy)³⁷ (indicated from its Mössbauer spectrum to be the *trans* isomer in the solid state: i.s. 1.10 mm s⁻¹, q.s. 3.33 mm s⁻¹), where the intensity ratio of ca. 1.5:1 for the peaks located at respectively 2.54 and 1.55 p.p.m. becomes ca. 1:1 upon keeping the spectral solution overnight. δ(¹¹⁹Sn) for this complex appears at -356.5 p.p.m. (relative to SnMe₄). While it can only be speculated that the *cis*-SnR₂ isomer in solution adopts a similar *trans* configuration of Cl atoms as in the solid state, we suggest that the combination of closer approach of the chelating ligand to tin and lesser torsional twist of the 4-MeC₅H₃N rings indicated for this isomer from the X-ray data prevails also in the solution state, so that differences in the constraining features of the ligand in the two isomers may lead to the observed non-equivalence in the n.m.r. of the ligand-bound methyl groups for the two isomers. Despite the above, it is also conceivable that the ¹H n.m.r. features may simply be the artefacts of two different configurations presumably adopted by the chelating ligand in the one isomer (*trans* or *cis*), which are fortuitously distinguishable on the n.m.r. time-scale on the basis of attendant differences in the chemical shifts of the ligand methyl groups in the two cases. Clearly, a limiting configuration that may be envisaged as a result of torsional twist between the 4-MeC₅H₃N rings is that which confers a bridging characteristic to the ligand. It is worth recalling here that the unsubstituted bipyridyl ligand shows this dual capacity for chelation and bridging in its complexes to tin.⁵⁵⁻⁵⁷

An appraisal between *cis-trans* isomerism and dichotomous ligand configuration in solution was sought for SnMe₂Cl₂·(4,4'-Me₂bipy)⁴⁷ where it was hoped that direct isomeric identification would be possible on the basis of Sn-Me chemical shifts and ²J(¹¹⁹Sn-C-¹H) coupling constant values.^{52,58} The above complex is known on the basis of its Mössbauer spectrum to exist in the *trans*-SnMe₂ octahedral geometry.⁴⁷ Although its solubility in CDCl₃ was found to be extremely poor, we were able to secure its ¹H Fourier-transform n.m.r. spectrum which revealed two ligand methyl resonances along with two, almost coincident, Me-Sn signals. However, there is only one set of coupling constants, ²J, associated with the Me-Sn resonances of magnitude 101.4 Hz. This strongly suggests a *trans*-SnMe₂ skeletal geometry: *cis*-SnMe₂ configurations as in SnMe₂·(quin)₂¹⁷ are expected to yield ²J values lower than 80 Hz. The implication of this result for SnMe₂Cl₂·(4,4'-Me₂bipy) is that there are two distinct *trans*-octahedral structures in solution engendered either by torsional twist differences in the chelating ligand or by the co-presence of chelate (monomeric) and bridged-ligand (oligomeric) complexes. Variable-temperature n.m.r. investigations in more amenable solvents are currently being attempted to evaluate the structural possibilities raised in this study.

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