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Preliminary communication

ISOLATION OF *cis*- AND *trans*-$[SnR_2]$ CONFIGURATIONAL ISOMERS OF THE OCTAHEDRAL COMPLEX, DICHLOROBIS(4-CHLOROPHENYL)-TIN(IV)-4,4′-DIMETHYL-2,2′-BIPYRIDYL

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Summary

The coordinative interaction between dichlorobis(4-chlorophenyl)tin(IV) and the chelating ligand, 4,4′-dimethyl-2-2′-bipyridyl (dmbipy), has allowed the isolation of both *cis*- and *trans*-$[SnR_2]$ configurational isomers of the derived complex, $[Sn(4\text{-}ClC_6H_4)_2Cl_2(dmbipy)]$, constituting the first such case reported for octahedral $[SnR_2X_2L_2]$ systems.

The proclivity of organotin(IV) halides and pseudohalides to form coordination complexes, typically with oxygen and nitrogen donor ligands, has been well documented [1,2]. In particular, diorganotin(IV) dihalides and dipseudohalides are known to form octahedral complexes of the type $[SnR_2X_2L_2]$, where L = monodentate or ½ bidentate ligand. Accumulated X-ray structures [3,4] indicate that the *trans*- or distorted *trans*-$[SnR_2]$ geometry is general for the monodentate case, as well as for dialkyltin(IV) chelates, whereas, for the diaryltin(IV) chelates, the *cis*-$[SnR_2]$ structure is sometimes encountered, particularly when X = NCS [5,6]. However, to date, no report has appeared in the literature of the isolation of both the *cis*- and *trans*-isomers of the six coordinated adducts of diorganotin(IV) dihalides or dipseudohalides with neutral ligands. We report here the first successful isolation of these geometrical isomers for the 1/1 complex of $[Sn(4\text{-}ClC_6H_4)_2Cl_2]$ with dmbipy. The only other documented example in organotin(IV) coordination chemistry of isolable geometrical isomers is that of the dimethyltin(IV) complex of the quadridentate ligand, *N,N′*-ethylenebis(salicylideneimine) [7], but the characterisation of the isomers was not described.

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Mixing ethanolic solutions of the reactants in stoichiometric amounts at room temperature gave an immediate precipitate of the complex $[Sn(4\text{-}ClC_6H_4)_2Cl_2(dmbipy)]$ (1c) (Found: C, 47.91; H, 3.15; N, 4.70; Cl, 23.76; Sn, 19.9. $C_{24}H_{20}Cl_4N_2Sn$ calcd.: C, 48.27; H, 3.35; N, 4.69; Cl, 23.80; Sn, 19.93%; m.p. 241—243°C (decomp.)) in near-quantitative yield. When the complex was recrystallised from hot methanol, the resulting product 1t (Found: C, 47.44; H, 3.46; N, 4.77; Cl, 23.78; Sn, 20.0%; m.p. 250—252°C (decomp.)) showed enhanced values for the isomer shift (δ) and quadrupole splitting (ΔE_Q) parameters in its tin-119m Mössbauer spectrum (Table 1). On the basis of the point-charge model treatment [8—10], which specifies for *trans*-$[SnR_2]$ configurations ΔE_Q values of ca. 4 mm s^{-1} and for *cis*-structures ΔE_Q values only half as large, we label our isomeric title complexes 1c and 1t as *cis* and *trans*, respectively. 1c was also uniquely obtained upon treating *trans*-$[Sn(4\text{-}ClC_6H_4)_2Cl_2(DMSO)_2]$ (δ 1.14, ΔE_Q 3.64 mm s^{-1}) with dmbipy in toluene. The dipseudohalide, $[Sn(4\text{-}ClC_6H_4)_2(NCS)_2]$, not unexpectedly, yielded only the *cis*-complex with dmbipy, unaltered in geometry by recrystallisation from methanol. The C—Sn—C angle in 1c can be calculated from a point charge approach [11] which assumes that the partial ΔE_Q contributions from the ligands are small compared to that from the aryl groups, and the correlation is supported by data from compounds for which Mössbauer and diaryltin(IV) C—Sn—C angles are available [11,12]. On this basis, we predict an angle of 100° for the diaryltin(IV) system in 1c. This is closer to the *cis*-angle of 90° (octahedral geometry) than to the equatorial angle of 120° (trigonal bipyramidal geometry with basal R groups) which might be envisaged if dmbipy was unidentate. That the latter possibility is unlikely for 1c is further indicated by comparison with the following data from the recent literature on the discrete five coordinated complexes, $[SnPh_2Cl_2(benzthiazole)]$ [13] (C—Sn—C (X-ray) 132.5°; δ 1.36, ΔE_Q 2.92 mm s^{-1}) and $[SnPh_2Cl_2(2,6\text{-}lutidine\text{-}N\text{-}oxide)]$ [14] (C—Sn—C (X-ray) 124.1°; δ 1.01, ΔE_Q 2.94 mm s^{-1}). The Mössbauer data for 1c, on the other hand, are rather similar to those of $[Sn(4\text{-}MeC_6H_4)_2Cl_2(bipy)]$ (δ 0.91, ΔE_Q 2.25 mm s^{-1}), for which a

TABLE 1

^{119}Sn MÖSSBAUER DATA AT 80 K (mm s^{-1}) [a]

Complex	δ [b]	ΔE_Q	Γ_1	Γ_2
$[SnPh_2Cl_2(bipy)]$ [c]	1.26	3.51	[d]	[d]
$[SnPh_2(NCS)_2(bipy)]$ [e]	0.82	2.13	[d]	[d]
$[SnPh_2Cl_2(dmbipy)]$	1.10	3.33	0.92	0.91
$[Sn(4\text{-}ClC_6H_4)_2Cl_2(bipy)]$	1.20	3.53	1.10	1.12
$[Sn(4\text{-}ClC_6H_4)_2Cl_2(dmbipy)]$				
(1c)	0.84	1.99	1.04	1.00
(1t)	1.14	3.49	0.91	0.96
$[Sn(4\text{-}ClC_6H_4)_2(NCS)_2(dmbipy)]$	0.72	2.17	0.95	0.91
$[SnMeEtCl_2(bipy)]$	1.51	4.04	1.10	1.03
$[SnMeEtCl_2(dmbipy)]$	1.49	4.07	1.05	0.97
$[SnEtPrCl_2(bipy)]$	1.57	4.07	0.99	1.00
$[SnEtPrCl_2(dmbipy)]$	1.52	4.04	1.08	1.03
$[SnMe_2Cl_2(dmbipy)]$ [f]	1.36	3.96	1.08	1.16

[a] Error ± 0.03 mm s^{-1}. [b] Relative to $Ba^{119}SnO_3$. [c] Ref. 16. [d] Not reported. [e] Ref. 5. [f] Ref. 17.

recent X-ray analysis has revealed [15] a *cis*-[SnR_2] octahedral structure with *trans*-disposition of the chlorine atoms (C—Sn—C 108.7(1)°; Cl—Sn—Cl 161.4(1)°).

Additionally, for both the title complexes **1c** and **1t**, their negligible conductivity in nitrobenzene (Λ_M ca. 10 ohm^{-1} cm^2 mol^{-1} at 25°C) and the absence of higher-than-parent molecular ions in their mass spectra (identical) exclude their formulation as associated ionic structures. The ultraviolet spectrum of either complex **1c** and **1t** in acetonitrile at room temperature shows a split band with peak maxima at 297.5 nm (ϵ 1.33×10^4) and 308 nm (ϵ 1.25×10^4), relative to the free ligand, which shows λ_{max} at 280 nm.

Table 1 also lists some Mössbauer data on the complexes of dmbipy as well as of the unsubstituted ligand, bipy, with diphenyl- and dialkyltin(IV) dichlorides*. In all cases, it is seen that the isolated complexes possess unambiguously the *trans* or distorted-*trans* structures.

X-ray structural investigations on the title complexes **1c** and **1t** are currently being attempted and will be reported at a later date, together with our results on the complexation of dmbipy with a wider range of diaryltin(IV) dihalides.

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Note added in proof. Crystal structure data already obtained [15] for **1c** are in agreement with its *cis*-[SnR_2] geometry: C—Sn—C 106.3(3)°; Cl—Sn—Cl 163.0(1)°; N—Sn—N 69.4(2)°.

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*All new complexes listed gave satisfactory analytical data.