cis–trans Isomerism in some Octahedral Diaryltin(IV) Dichloride Complexes with Bidentate Ligands

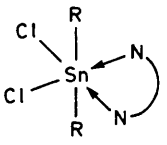
Brian N. Biddle and John S. Gray*
Faculty of Applied Sciences, Luton College of Higher Education, Park Square, Luton, Bedfordshire LU1 3JU
Alan J. Crowe
International Tin Research Institute, Kingston Lane, Uxbridge, Middlesex UB8 3PJ

A series of 24 octahedral organotin complexes (including 16 new compounds) of general formula $Sn(C_6H_4Z\text{-}4)_2Cl_2{\cdot}L_2$ (Z = OMe, Me, Bu^t, H, F, or CF_3; L = dimethyl sulphoxide or L_2 = 2,2′-bipyridyl, 4,4′-dimethyl-2,2′-bipyridyl, 1,10-phenanthroline, or 3,4,7,8-tetramethylphenanthroline) has been prepared under a variety of experimental conditions. The optimum conditions for obtaining either *cis* or *trans* isomeric forms are indicated. The ^{119}Sn Mössbauer parameters for all the complexes have been determined and used in each case to assign either *cis* or *trans* configurations. The isolation of pure *cis* and *trans* isomeric pairs has been achieved in four cases where Z = OMe, CF_3, or H and L_2 = 4,4′-dimethyl-2,2′-bipyridyl and Z = OMe and L_2 = 2,2′-bipyridyl. The effects of both structure and solvent on relative *cis–trans* stabilities are discussed. Infrared spectra have been recorded for the *cis–trans* isomeric pairs and substantial differences in the aromatic substitution pattern are indicated.

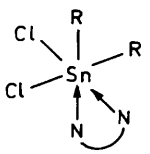
Octahedral tin(IV) complexes have potential as anti-tumour and -viral agents[1] and a number has been shown to be active. The mechanism of activity of these complexes requires an understanding of their structure and isomerism. A dialkyl- or diaryl-tin(IV) dihalide complex with a bidentate ligand of general formula $SnR_2Cl_2{\cdot}L_2$ can exist in three ideal stereoisomeric forms (**1**)—(**3**). A study of the Mössbauer spectroscopic data[2] of 114 complexes has already revealed a distinct preference for the *trans* geometry (**1**) although the R–Sn–R angle sometimes deviates substantially from the ideal 180°. In the case of dialkyl complexes the ideal structure (**1**) is generally encountered. In some cases, however, an alternative *cis* configuration [structures (**2**) or (**3**)] is energetically favoured. All of these *cis* examples have either aryl or heterocyclic groups[3] attached to the tin atom in place of alkyl groups, although not all reported diaryl complexes have the *cis* configuration. Other structural features are necessary and both the bidentate ligand and the halide or pseudohalide may play an important steric or electronic role in allowing the isolation of a *cis* configuration. This is exemplified by the fact that all 2-aminomethylpyridine complexes show a *cis* configuration when R is aryl[4] as do all the reported isothiocyanates.[5]

Mössbauer data have been used extensively to distinguish the *trans* configuration (**1**) from the alternative *cis* configurations (**2**) and (**3**). However, *X*-ray diffraction studies are necessary for complete stereochemical analysis and for a distinction to be made between the *cis*SnR_2 configurations (**2**) and (**3**). *X*-Ray data have been used extensively to confirm the *trans*-SnR_2 geometry for many isomers[2,6] and to assign the distorted *cis* configuration (**3**) to $Sn(C_6H_4Me\text{-}4)_2Cl_2{\cdot}(bipy)$[2,6] (bipy = 2,2′-bipyridyl).

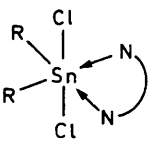
More recently the successful isolation and characterisation by *X*-ray analysis of the 1:1 complex of $Sn(C_6H_4Cl\text{-}4)_2Cl_2$ with 4,4′-dimethyl-2,2′-bipyridyl(dmbipy) has been reported.[6,7] Again, the *cis* isomer is shown to have the distorted configuration (**3**). This work has prompted us to examine further the *cis–trans* isomerism of a range of related compounds which we have prepared for anti-tumour testing and our findings are published here.



(**1**)



(**2**)



(**3**)

Results and Discussion

Complexes with Dimethyl Sulphoxide.—The Mössbauer parameters for the series of dimethyl sulphoxide (dmso) complexes (Table 1) indicate a *trans*-SnR_2 geometry in every case. This is in agreement with all previous observations.[2,5] The *trans* configuration is preferred for all complexes with monodentate ligands where the steric restraint imposed by bidentate ligands is absent. This observation is in agreement with Bent's rule[8] which predicts a R–Sn–R bond angle of 180°, to allow the maximum 5*s* electron contribution in the Sn–C bond. It is noteworthy that, whereas complexes with electron-donating aryl groups, $C_6H_4Z\text{-}4$ (Z = OMe, Me, or Bu^t), have a Mössbauer quadrupole splitting (q.s.) parameter close to that required (q.s. = 4.00 mm s^{-1}) for a C–Sn–C angle of 180° in line with Bent's rule, electron-withdrawing groups (Z = F, Cl, or CF_3) distort the ideal *trans* geometry. This can be explained by the increased electronegativity of the aryl ring carbon attached to tin which presumably decreases the *s* character in the bond and decreases the bond angle.

Complexes with Bidentate Nitrogen Ligands.—It is clear from previously published work[4,5,9] that bidentate ligands play an important role in determining the *cis* or *trans* geometry and presumably this is due to several factors including changing steric requirements and variation in the N–Sn–N bite angle. The effect of a bidentate ligand on the geometry of the complex can be seen by comparison of the Mössbauer parameters of the dmso, bipy, and dmbipy complexes (Table 1 and 2). When the small monodentate ligand with no angle restriction is replaced by bidentate ligands with larger steric

Table 1. ^{119}Sn Mössbauer data (mm s^{-1}) for diaryltindichloride complexes, with dmso

$Sn(C_6H_4Z\text{-}4)_2Cl_2\cdot 2dmso$ Z	δ	q.s.	Γ_1	Γ_2	Inferred structure
OMe	1.30	3.89	0.89	0.87	*trans*
Me	1.31	3.93	0.97	1.02	*trans*
Bu^t	1.34	3.97	0.91	0.93	*trans*
H	1.27	3.95			*trans*[a]
Cl	1.14	3.64	1.14	1.10	*trans*[b]
F	1.22	3.65	0.86	0.81	*trans*
CF_3	1.15	3.60	1.15	1.12	*trans*

[a] Ref. 2. [b] Ref. 5.

Table 2. ^{119}Sn Mössbauer data (mm s^{-1}) for complexes of diaryltin dichloride with nitrogen-donor ligands

$Sn(C_6H_4Z\text{-}4)_2Cl_2\cdot L_2$ L_2	Z	δ	q.s.	Γ_1	Γ_2	Inferred structure	Preparation[a]
dmbipy	OMe	1.28	3.63	0.87	0.87	*trans*	(*i*)
		1.01	2.27	0.91	0.90	*cis*	(*ii*)
		0.90	2.10	1.18	1.18	*cis*	(*iii*)
	Me	1.34	3.40	0.87	1.14	*trans*	(*i*)
		0.85	2.41	0.84	1.14	*cis*	
		1.35	3.40	0.80	1.11	*trans*	(*ii*)
		0.86	2.42	1.02	1.11	*cis*	
		0.99	2.23	0.94	1.00	*cis*	(*iii*)
		1.34	3.49	1.58	1.13	*trans*	(*iv*)
		0.75	2.35	1.58	1.76	*cis*	
	Bu^t	1.29	3.54	0.88	0.88	*trans*	(*i*)
		1.24	3.47	1.16	1.13	*trans*	(*iii*)
	H	1.20	3.41	1.07	1.07	*trans*	(*i*)[b]
		0.91	2.07	1.04	1.36	*cis*	(*iii*)
	F	0.93	1.93	0.84	0.88	*cis*	(*i*)
		0.92	1.93	0.91	0.87	*cis*	(*ii*)
		0.87	1.91	0.99	1.22	*cis*	(*iii*)
		0.84	1.96	1.04	0.96	*cis*	(*iv*)
		0.90	1.98	1.07	1.14	*cis*	(*v*)
	CF_3	1.12	3.32	1.02	0.97	*trans*	(*i*)
		0.86	1.86	0.97	1.14	*cis*	(*ii*)
		1.11	3.34	0.97	0.97	*trans*	(*iv*)
bipy	OMe	0.88	1.95	1.17	1.52	*cis*	(*iii*)
		1.26	3.54	0.91	0.91	*trans*	(*vi*)[c]
	Me	0.93	2.21	1.05	1.13	*cis*	(*iv*)
		1.01	2.26	0.87	0.85	*cis*	(*vi*)[c]
	Bu^t	1.27	3.56	1.18	1.12	*trans*	(*iii*)
		1.29	3.54	0.88	0.88	*trans*	(*vi*)
	H	1.25	3.52			*trans*	(*vi*)[c]
		1.21	3.44	1.11	1.16	*trans*	(*iii*)
	F	1.20	3.38	0.94	1.05	*trans*	(*iii*)
		1.21	3.43	1.19	1.19	*trans*	(*iv*)
		1.22	3.44	0.93	0.89	*trans*	(*vi*)[c]
	CF_3	1.19	3.31	0.95	0.91	*trans*	(*vi*)[c]
		1.13	3.31	1.04	1.03	*trans*	(*iii*)
	Bu^t	1.26	3.52	0.87	0.84	*trans*	(*vi*)
	Bu^t	1.30	3.52	1.25	1.05	*trans*	(*vi*)

[a] See Experimental section for details. [b] Low temperature method (below 0 °C). [c] Ref. 4.

requirements the *trans* geometry is distorted in all cases with a decrease in the R–Sn–R angle as indicated by reduction of the Mössbauer q.s. value from 4.00 mm s^{-1}.[10] It is also interesting that the non-planar 2-aminomethylpyridine ligand shows an exclusive preference for the *cis* geometry when chelated to a diaryltin dichloride[4] and distorts the C–Sn–C angle in the complexes of the alkyltin dihalides.[2] These observations have prompted us to investigate the *cis–trans* isomerism of a range of 4-substituted phenyltin dichlorides with different bidentate ligands.

The tendency of dmbipy towards the formation of *cis* isomers has already been reported in the case of $Sn(C_6H_4Cl\text{-}4)_2Cl_2$,[6] where for the first time both *cis* and *trans* isomers of octahedral tin were successfully isolated and characterised. It has also been reported that $Sn(C_6H_4Me\text{-}4)_2Cl_2$ reacts with dmbipy to give a mixture of the *cis* and *trans* isomers, which could not be separated.[5] Table 2 gives the Mössbauer data for a series of *cis* and *trans* isomers of $Sn(C_6H_4Z\text{-}4)_2Cl_2$ where the group Z varies appreciably in both electronic effect and size.

When examining Mössbauer spectra the full width at half height (f.w.h.h.) parameters (Γ) are often an indication of the validity of the results provided by the data-fitting program. Typically Γ values of 1.00 ± 0.2 mm s^{-1} are acceptable. In a few of our spectra (L_2 = dmbipy, Z = Me or H) Γ values outside this range were given. We have included these results in Table 2 since the q.s. values obtained clearly indicate the presence of *cis*

and/or *trans* isomers. In addition the i.r. spectra of these complexes further support our claim that certain isomers were present. It is believed that the large Γ values obtained for two of the samples where Z = Me arose from a limitation in the fitting program. The *cis* isomer, where Z = H, repeatedly gave the same result: $\Gamma_1 = 1.04$ and; $\Gamma_2 = 1.36$ mm s^{-1}. Such inequalities in the Γ values can arise due to the effects of partial orientation of crystallites. Since all our samples were thoroughly ground to prevent this effect and the spectrum of this complex was recorded several times using different samples of the same material we believe that this derivative may be exhibiting the Goldanskii–Karyagin effect, which arises from vibrational anisotropy in polycrystalline materials.[11]

It can be seen that when Z = F the complex obtained is the *cis* isomer. All attempts to prepare the *trans* isomer or to convert the *cis* into the *trans* isomer failed. The stability of the *cis* isomer may be attributed to the electron-withdrawing effect of the fluorine atom, already discussed in the previous section. The reverse is true, however, for the weakly electron-donating tertiary butyl group (Z = Bu^t) where only the *trans* isomer is formed and all attempts to prepare the *cis* isomer failed. This preference for the *trans* configuration by the tertiary butyl compound is supported by the preparation of complexes with other ligands [1,10-phenanthroline(phen) and 3,4,7,8-tetramethylphenanthroline(tmphen) (Table 2)] and the failure to prepare a stable 2-aminomethylpyridine (ampy) complex of $Sn(C_6H_4Bu^t\text{-}4)_2Cl_2$. This latter observation is not unexpected since ampy requires a *cis*-SnC_2 geometry

make a large contribution to the overall dipole moment of the complex. On the other hand less polar solvents, which may be accommodated in the crystal lattice, favour the formation of the alternative *cis* isomer and may bring about a *trans–cis* isomerisation. In these complexes the two chlorines may be *trans*[7] thus making little contribution to the overall dipole moment of the complex. The important role of solvent polarity has also been observed by White and co-workers[12] in the isomerism of some Lewis base adducts of copper(I) halides.

The overall effect of the 4 substituent on the relative stability of *cis* and *trans* isomers is difficult to explain. A correlation with electronic effects of the substituents Z might be expected. Inspection of the Mössbauer q.s. parameters for the dmso complexes (already referred to in the previous section) and for the *trans* isomers recorded in Table 2 gives an indication of the distortion from the ideal *trans* form (**1**). This distortion is greatest when Z = CF_3 (q.s. = 3.32 mm s^{-1}) which is powerfully electron withdrawing and least when Z = OMe (q.s. = 3.63 mm s^{-1}) which is powerfully electron donating. Thus according to Bent's rule 4-OMe should favour a stable *trans* isomer, whereas 4-CF_3 should favour a stable *cis* isomer in the absence of other effects. In fact both of these substituents, with opposing effects, behave similarly, forming stable *cis* isomeric forms. The other substituents investigated fall between these two extremes in electronic effects and, as already stated, 4-F and 4-Bu^t allow the isolation of one isomer only. An explanation in simple electronic terms cannot be seen. Although steric effects would be expected to make little contribution to the relative

Table 3. Infrared data (cm^{-1}) for *cis* and *trans* isomers of $Sn(C_6H_4$-Z-4)$_2Cl_2$·dmbipy

Z		Ligand C–H deformation > 900 cm^{-1}	Ligand and disubstituted aryl C–H deformation < 900 cm^{-1}
CF_3	(*trans*)	923s, 901vw	830s, 816s
	(*cis*)	924m, 909w	836s
OMe	(*trans*)	924s	852s, 805vs

obtained commercially. Dimethyl sulphoxide and 4,4′-dimethyl-2,2′-bipyridyl were used without further purification. Commercial 2,2′-bipyridyl was crystallised from light petroleum (b.p. 60—80 °C). Elemental microanalyses of the complexes were performed by the Microanalytical Service of University College, London. The melting points listed are uncorrected.

Preparation of Dimethyl Sulphoxide Complexes.—The complexes were formed by mixing the appropriate diaryltin

Table 5. Analytical data for complexes of diaryltin dichlorides with nitrogen-donor ligands

$Sn(C_6H_4Z\text{-}4)_2Cl_2 \cdot L_2$			Analysis (%)				
L_2	Z		C	H	N	M.p. (°C)	Preparation[a]
dmbipy	OMe	(*cis*)	52.85 (53.10)	4.45 (4.45)	4.85 (4.75)	200—201	(*ii*), (*iii*)
		(*trans*)	52.75 (53.10)	4.35 (4.45)	4.70 (4.75)	188—190	(*i*)
	Me	(*cis*)	55.65 (56.15)	4.80 (4.70)	5.10 (5.05)	214[b]	(*iii*)
		(*cis*/*trans*)	55.55 (56.15)	4.60 (4.70)	4.90 (5.05)	218—219[b] (232—235)[c]	(*iv*)
	Bu^t	(*trans*)	59.85 (60.05)	5.95 (6.00)	4.00 (4.35)	262—264	(*i*)
	H	(*cis*)	54.05 (54.60)	4.05 (4.20)	5.20 (5.30)	211—212	(*iii*)
		(*trans*)	54.00 (54.60)	4.15 (4.20)	5.15 (5.30)	215—216 (228—230)[c]	(*i*)
	F	(*cis*)	50.70 (51.10)	3.65 (3.55)	5.10 (4.95)		(*i*)
	CF_3	(*cis*)	47.40 (47.00)	3.10 (3.05)	4.05 (4.20)	230—232	(*ii*)
		(*trans*)	47.05 (47.00)	3.25 (3.05)	4.05 (4.20)	237	(*i*), (*iv*)
bipy	OMe	(*cis*)	51.10 (51.45)	3.95 (3.95)	4.95 (5.00)	168—170	(*iii*)
		(*trans*)	50.75 (51.45)	3.90 (3.95)	4.90 (5.00)	194—195	(*vi*)
	Bu^t	(*trans*)	58.35 (58.85)	5.60 (5.60)	4.60 (4.55)	240—242	(*vi*)
phen	Bu^t	(*trans*)	60.25 (60.40)	5.35 (5.40)	4.55 (4.40)	287—288	(*vi*)
tmphen	Bu^t	(*trans*)	61.45 (62.45)	6.10 (6.10)	3.95 (4.05)	314—315	(*vi*)

[a] See Experimental section for details. [b] Decomposes. [c] Ref. 5.

Infrared Spectra.—Infrared spectra (Table 3) were obtained on a Perkin-Elmer 1330 spectrophotometer as Nujol mulls between NaCl plates and with narrow slit and a 5× chart expansion in the region 650—1 000 cm^{-1}. All spectra were calibrated with polystyrene.

Acknowledgements

The International Tin Research Institute, Uxbridge, London is thanked for permission to publish this paper. The authors acknowledge the support of Bedfordshire County Council for this project and are grateful to Dr. P. J. Smith, International Tin Research Institute, for his helpful comments.

References

1 A. J. Crowe, 'The Chemotherapeutic Properties of Tin Compounds, Drugs of the Future,' 1987, **12**(3), 255—275.
2 A. J. Crowe and P. J. Smith, *J. Organomet. Chem.*, 1982, **224**, 223.
3 D. W. Allen, D. J. Derbyshire, J. S. Brooks, S. J. Blunden, and P. J. Smith, *J. Chem. Soc., Dalton Trans.*, 1984, 1889.
4 B. N. Biddle, J. S. Gray, and A. J. Crowe, *Appl. Organomet. Chem.*, 1987, **1**, 261.
5 V. G. Kumar Das, C. K. Yap, and P. J. Smith, *J. Organomet. Chem.*, 1987, **327**, 311.
6 V. G. Kumar Das, C. K. Yap, and P. J. Smith, *J. Organomet. Chem.*, 1985, **291**, C17.
7 V. G. Kumar Das, C. K. Yap, W. Chen, P. J. Smith, and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1987, 129.
8 H. A. Bent, *J. Inorg. Nucl. Chem.*, 1961, **19**, 43.
9 G. A. Miller and E. O. Schlemper, *Inorg. Chem.*, 1973, **12**, 677.
10 T. K. Sham and G. M. Bancroft, *Inorg. Chem.*, 1975, **14**, 2281.
11 N. N. Greenwood and T. C. Gibb, 'Mössbauer Spectroscopy,' Chapman Hall, London, 1971.
12 J. C. Dyason, P. C. Healy, L. M. Engelhardt, C. Pakawatchai, V. A. Patrick, C. L. Raston, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1985, 831.
13 G. Matsubayashi, H. Koezuka, and T. Tanaka, *Org. Magn. Reson.*, 1973, **5**, 529.

Received 23*rd February* 1989; *Paper* 9/00817I