Mössbauer Study of the *cis–trans* Isomers of Tin(IV) Complexes. Some Considerations about the Sign of the Electric-field Gradient

David Tudela* and Vicente Fernández
Departamento de Química Inorgánica, Facultad de Ciencias, Universidad Autónoma de Madrid, Spain
Jesus D. Tornero
Departamento de Electroquímica, Facultad de Ciencias, Universidad Autónoma de Madrid, Spain

Mössbauer spectra are reported for the *cis–trans* isomers of $SnCl_4L_2$ [L = *NN*-dimethylacetamide (dma), *NN*-dimethylformamide (dmf), dimethyl sulphoxide (dmso), or tetrahydrothiophen (tht)] and $SnBr_4(dmf)_2$. The following octahedral partial quadrupole splitting values were obtained: tht = +0.09, dmso = +0.14, dmf = +0.18, and dma = +0.20 mm s^{-1}. A correlation has been found between the quadrupole splitting and the values for ν(Sn–Cl) (from i.r. and Raman spectra) for *trans*-$SnCl_4L_2$.

Mössbauer spectroscopy has been widely used in studies on the stereochemistry of tin tetrahalide complexes.[1-4] In one case, $SnCl_4[(n\text{-}C_3H_7)_2SO_2]$, despite the fact that conditions regarding its formation and structure are not well defined, two forms have been isolated with quadrupole splittings approximating to a 2:1 ratio[4] as expected for a *cis–trans* pair.[5] Ruzicka and Merbach[6] reported the synthesis of $SnCl_4(tht)_2$ (tht = tetrahydrothiophen) with a *trans* geometry in dichloromethane and a *cis* geometry in n-pentane; however, ^{35}Cl n.q.r. studies have only provided evidence of the *trans* isomer.[7,8] In this paper we report our studies, using Mössbauer spectroscopy, on the *cis* and *trans* isomers of $SnCl_4(tht)_2$, in which we found small but perceptible differences between the two. We also report a Mössbauer study of the *cis–trans* isomer pairs of $SnCl_4L_2$ [L = *NN*-dimethylformamide (dmf), *NN*-dimethylacetamide (dma), or dimethyl sulphoxide (dmso)] and $SnBr_4(dmf)_2$.[9]

Experimental

cis-$SnCl_4(tht)_2$ was prepared by dropwise addition, with constant stirring, of a 10% solution of tht (10% excess) in n-pentane to a 10% solution of $SnCl_4$ in the same solvent cooled to −5 °C. The precipitated white complex was washed with n-pentane and dried *in vacuo*. Constant and thorough stirring is essential because any local excess of ligand during the addition could lead to mixing of the *cis* and *trans* isomers. If a solution of $SnCl_4$ is added to a solution of tht, the final product is the *trans* isomer. Both isomers were characterized by i.r. and Raman spectroscopy.[6] When $SnCl_4$ was added to a solution of dma in $CHCl_3$ a mixture of *cis*- and *trans*-$SnCl_4(dma)_2$ was formed. The *cis* isomer was isolated by vacuum sublimation.

trans-$SnCl_4(dmso)_2$ was obtained by keeping a freshly-prepared sample of its *cis* isomer for 17 d at 22 °C,[10] and subsequently heating it to 135 °C for 20 h. The remaining compounds were prepared by previously reported methods and were characterized by i.r. and Raman spectroscopy.[9] In all preparations the usual precautions were taken to avoid moisture.

The i.r. spectra were recorded on a Nicolet 5DX FT-IR spectrometer in the range 4 000—200 cm^{-1}, using Nujol mulls between CsI windows. The Raman spectra were recorded in a Jarrell-Ash spectrophotometer, model 25—300, using an Ar^+ laser (4 880 Å). The Mössbauer spectra were obtained with polycrystalline samples at liquid N_2 temperature. The constant acceleration spectrometer, velocity calibration, temperature control, and computation procedures have been described previously.[11] A standard source of $Ca^{119}SnO_3$ was used in transmission geometry, filtering the γ-radiation with a Pd (50 μm) foil filter. The isomer shifts are referred to $BaSnO_3$ at room temperature. The sample thickness in every case was 11 mg of natural tin per cm^2 and the maximum statistical error in the experimental points was 0.2%. The reproducibility of the parameters was ± 0.02 mm s^{-1} for δ and Δ and ±0.03 mm s^{-1} for Γ. After recording the Mössbauer spectra, samples were collected and checked by Raman spectroscopy to ensure that they had not undergone any changes.

Results and Discussion

The Mössbauer spectra of the *cis* and *trans* isomers are shown in Figure 1 whilst their corresponding parameters are given in Table 1. Those spectra that do not display a resolved quadrupole doublet were first fitted as a single line. From the results for χ^2 and Γ (see Table 1), the spectra were taken to be quadrupole doublets. On the other hand, reasonable parameters for *cis*-$SnCl_4(tht)_2$ were obtained from a single-line fitting (see Table 1). The possible existence of a quadrupole doublet was also considered because the quadrupole splitting of its *trans* isomer shows that the partial quadrupole splitting (p.q.s.)[12] of tht does not equal zero. An abnormal line asymmetry appeared during the fitting process which made us consider a symmetrical quadrupole splitting (Table 1). In this case, the error for Δ is possibly larger than ± 0.02 mm s^{-1}.

The Mössbauer spectra of *cis*-$SnCl_4L_2$ (L = dmf, dmso, or dma) and *trans*-$SnCl_4(tht)_2$ have been previously reported,[1,3,4,13-17] and they present an isomer shift that is in good agreement with that measured in our study. For the quadrupole splitting, spectra were mainly fitted as a single line. Values for Δ other than zero have been reported for $SnCl_4L_2$ (L = dmso or dma)[13,15] and agree reasonably with our measurements. From our results, however, (see Table 1) it would appear evident, in the case of $SnCl_4(dmf)_2$, that the values of 0.73—0.75 mm s^{-1} attributed to the quadrupole splitting[13,15] are for the *trans* isomer.

Although Davanzo and Gushikem[9] have found that *cis*-$SnCl_4L_2$ (L = dmf or dmso) complexes undergo a spontaneous isomerization at room temperature, in 15 and 30 d respectively, we have been unable to confirm the fact by i.r. and Raman spectroscopy. We have recorded the Mössbauer spectra of samples of *cis*-$SnCl_4(dmf)_2$ which had been kept at 22 °C for 19 d and 11 weeks respectively, and in both cases we obtained parameters corresponding to the *cis* isomer. From these data, certain details in the Experimental section, and the existing controversy regarding *cis*-$SnCl_4(tht)_2$,[7,8] we believe that some factors, as yet not fully understood, govern the formation of

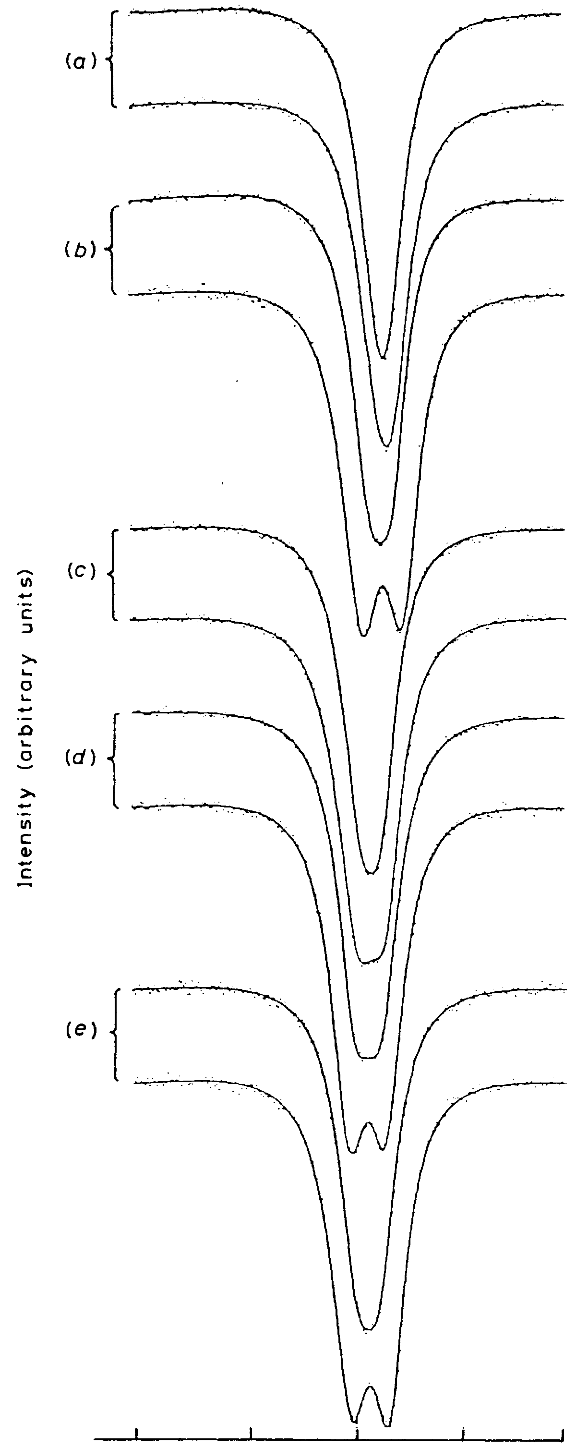

Figure 1. Mössbauer spectra of (*a*) $SnCl_4(tht)_2$, (*b*) $SnBr_4(dmf)_2$, (*c*) $SnCl_4(dmso)_2$, (*d*) $SnCl_4(dmf)_2$, and (*e*) $SnCl_4(dma)_2$. The upper spectrum of each pair corresponds to the *cis* isomer

either isomer and the transformation from one to the other. Studies of these compounds should always include verification of the compound's stereochemistry. Raman spectroscopy is useful for this purpose.[6,9]

From Table 1 it is evident that values for the isomer shift of the *cis* and *trans* compounds of each species are the same within the margin of experimental error. Such behaviour differs from that generally observed for Sn^{IV} organometallic compounds; the isomer shift of the *cis* compounds is usually lower than that of the *trans* compounds.[18,19] We have also observed that the *trans* isomers present a greater resonance area than their corresponding *cis* isomers (see Table 1). This may be due to the greater symmetry in the *trans* isomers which permits a more compact lattice.

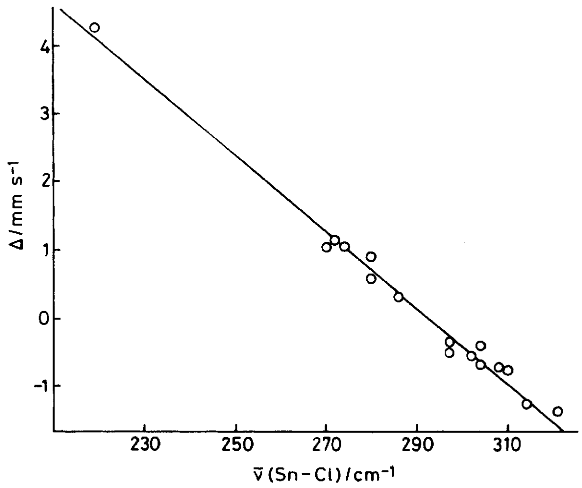

Figure 2. Relationship between ν̄(Sn–Cl) and Δ

Although *trans* compounds have larger quadrupole splittings than their *cis* isomers, the $\Delta_{trans}/\Delta_{cis}$ quotients deviate from the expected value of 2 (Table 1). Two main contributions can explain such behaviour. (*i*) The vibrational spectra of *cis*- and *trans*-$SnCl_4L_2$ (L = dmf, dmso, or dma) and $SnBr_4(dmf)_2$[9,20] show an increase in the average values for ν(Sn–L) and a decrease in the average values for ν(Sn–X) (X = Cl or Br) when going from the *cis* to the *trans* isomers. This is in agreement[21] with a stronger Sn–L bond in *trans* isomers and implies a greater donor strength for the ligands, and hence a more negative p.q.s. value[12] when these co-ordinate in the *trans* position. Bearing in mind that these ligands have a positive p.q.s. value,[22] $(L)^{oct}$ (the octahedral partial quadrupole splitting of L) would no longer be constant and would be greater in the *cis* than in the *trans* isomers, so that the $\Delta_{trans}/\Delta_{cis}$ quotient would be less than 2. (*ii*) Important distortions are not foreseen for the configuration of the *trans* compounds as predicted by Zahrobsky's stereochemical model[23] and observed in single-crystal diffraction studies.[24–26] However, *cis* compounds usually present distortions from regular geometry[27,28] which could contribute to the disagreement between experimental and calculated quadrupole splittings.[12] In this respect, the value obtained for $\Delta_{trans}/\Delta_{cis}$ (Table 1) would indicate considerable distortion for *cis*-$SnCl_4(dmso)_2$, which is confirmed by a *X*-ray single-crystal study.[29]

Both contributions could be related because distortions from regular geometry modify the hybrid orbitals at the tin atom and hence affect the bonding properties.

From a previous study by Bancroft *et al.*,[22] a positive sign for V_{zz} can be deduced for *trans*-$SnCl_4L_2$ (L = dmso, dmf, or dma). Likewise, for *trans*-$SnCl_4(tht)_2$, we predict a positive value for V_{zz} (see Table 2). From these statements and the quadrupole splitting values shown in Table 1 for *trans*-$SnCl_4L_2$ (where minimum distortions from regular geometry are assumed), we can calculate the following p.q.s. values: tht = +0.09, dmso = +0.14, dmf = +0.18, and dma = +0.20 mm s^{-1}. These values indicate donor strengths, against $SnCl_4$, increasing in the order dma < dmf < dmso < tht,[12] and are in agreement with

Table 1. Mössbauer parameters

Compound	δ/mm s^{-1}	Δ/mm s^{-1}	Γ_1/mm s$^{-1\,a,b}$	Γ_2/mm s$^{-1\,a}$	$\Delta_{trans}/\Delta_{cis}$	Area *trans*/ Area *cis*	$\chi^{2\,c}$
trans-$SnCl_4(tht)_2$	0.72	0.35	0.90 (1.10)	0.91	1.5	1.2	284 (776)
cis-$SnCl_4(tht)_2$	0.70	0.24	0.89^d (0.98)	0.89^d			256^e (356)
trans-$SnCl_4(dmso)_2$	0.41	0.57	0.92 (1.46)	0.93	1.4	1.2	216 (3 376)
cis-$SnCl_4(dmso)_2$	0.40	0.41	0.90 (1.15)	0.85			301 (1 333)
trans-$SnCl_4(dmf)_2$	0.38	0.73	0.87	0.85	1.4	1.2	316
cis-$SnCl_4(dmf)_2$	0.39	0.53	0.90 (1.35)	0.87			228 (3 812)
trans-$SnBr_4(dmf)_2$	0.66	0.83	0.88	0.89	1.9	1.3	255
cis-$SnBr_4(dmf)_2$	0.66	0.44	0.80 (1.16)	0.88			219 (1 703)
trans-$SnCl_4(dma)_2$	0.38	0.78	0.87	0.90	1.7	1.2	277
cis-$SnCl_4(dma)_2$	0.38	0.45	0.92 (1.23)	0.87			265 (1 069)

[a] Γ_1 and Γ_2 are computed full widths at half height at higher and lower energy respectively. [b] Γ are given in parentheses for the single-line fitting. For the cubic compound $[NH_4]_2[SnCl_6]$, Γ was 0.82 mm s^{-1} at room temperature, under the same conditions of geometry and sample thickness. [c] With 191 degrees of freedom unless specifically indicated; χ^2 are given in parentheses (with 194 degrees of freedom) for the single-line fitting. [d] Constrained parameter (see text). [e] With 193 degrees of freedom.

Table 2. Quadrupole splitting–ν(Sn–Cl) correlations in *trans*-$SnCl_4L_2$

L	ν(Sn–Cl)(E_u)/cm^{-1}	$\bar{\nu}$(Sn–Cl)/cm^{-1}	Ref.	Δ/mm s$^{-1\,a}$	Ref.
OEt_2	350	321	6	(−)1.37	13
thf	344	314	6	(−)1.26	11
dma	340	310	20	(−)0.78	*b*
dmf	335	308	20	(−)0.73	*b*
$P(O)(NMe_2)_3$	331	304	6	(−)0.69	15
dmso	328	302	20	(−)0.57	*b*
$C(O)(NMe_2)_2$	320	297	20	(−)0.51	15
SMe_2	327	304	6	(−)0.40	13
tht	322	297	6	(−)0.35	*b*
PPh_3	306	286	2	(+)0.31	*c*
$PMePh_2$	302	280	2	(+)0.57	2
$AsEt_3$	307	280	2	+0.90	*d*
PEt_2Ph	289	270	2	(+)1.04	2
PBu_3	292	274	2	(+)1.06	2
PEt_3	290	272	2	+1.15	*d*
Me	235	219	*e,f*	+4.28	*g*

[a] Signs measured experimentally are given without parentheses, the rest are assigned by chemical analogy or a better fit on the straight line. [b] This work. [c] Sh. Bashkirov, I. Ya. Kuramshin, A. S. Khramov, and A. N. Pudovik, *Koord. Khim.*, 1980, **6**, 537. [d] D. Cunningham, M. J. Frazer, and J. D. Donaldson, *J. Chem. Soc., Dalton Trans.*, 1972, 1647. [e] C. W. Hobbs and R. S. Tobias, *Inorg. Chem.*, 1970, **9**, 1037. [f] I. R. Beattie, F. C. Stokes, and L. E. Alexander, *J. Chem. Soc., Dalton Trans.*, 1973, 465. [g] R. V. Parish and R. H. Platt, *Inorg. Chim. Acta*, 1970, **4**, 65.

vibrational spectral data (see later). Our relative order for p.q.s. values for dmso and dmf is contrary to that established previously,[22] but is in agreement with the results found for these same ligands in trigonal-bipyramidal geometry in the apical position.[30] It has also been shown that dmso is a stronger donor than dmf with respect to $SnCl_4$.[31] It must be noted that the above p.q.s. values have been obtained from a *trans* series of compounds with only a small variation in the type of ligands, the same kind of structure, and presumably minimal distortions from regular geometry. For these reasons, they are probably not good 'working values' for the prediction of the quadrupole splittings for a more varied range of compounds, but they do reflect the donor properties of the ligands.

Quadrupole Splitting–Vibrational Frequencies Correlation.— The force constant Sn–Cl for $SnCl_4L_2$ compounds decreases as the Sn–L bond strength[21] increases. Since the p.q.s. value for a ligand becomes more negative as the donor strength of the ligand increases,[12] there must be a relationship between ν(Sn–Cl) and Δ. Table 2 gives Δ values for various *trans*-$SnCl_4L_2$ complexes, together with the average values of the corresponding frequencies for the Sn–Cl stretching vibrations found in the i.r. and Raman spectra [$\bar{\nu}(\text{Sn–Cl}) = \frac{1}{4}(2E_u + A_{1g} + B_{1g})$]. These values are plotted in Figure 2. The sixteen points have been fitted to a least-squares straight line (correlation coefficient 0.993) with a gradient and intercept of -5.56×10^{-2} mm s^{-1} cm and 16.28 mm s^{-1} respectively. This plot could help in the prediction of the sign, and to a certain extent the value, of Δ for *trans*-$SnCl_4L_2$ compounds, from their i.r. and Raman data. Care should be taken regarding the prediction of the sign for Δ from $\bar{\nu}$(Sn–Cl) values around 293 cm^{-1}, by means of the regression line. Although a worse regression (r = 0.985) is obtained, there is also a linear correlation between Δ and the i.r.-active ν(Sn–Cl) (E_u) (see Table 2) with a gradient of -4.79×10^{-2} mm s^{-1} cm and an intercept of 15.18 mm s^{-1}.

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