# Isomerism in Adducts of Tin(IV) Tetrahalides with *NN*-Dimethylacetamide, *NN*-Dimethylformamide, and Dimethyl Sulphoxide in the Solid State

By **Celso U. Davanzo** and **Yoshitaka Gushikem**,* Instituto de Quimica, Universidade Estadual de Campinas CP 1170, 13100 Campinas, S.P., Brasil

The adducts $SnCl_4L_2$ (L = dimethylformamide, dmf, dimethylacetamide, dma, or dimethyl sulphoxide, dmso) and $SnBr_4(dmf)_2$ were isolated as *cis* isomers from different solvents. The compounds underwent transformations in the solid state and the *trans* isomers could also be obtained. The transitions in the solid state were studied by vibrational spectroscopy, thermal analysis, and *X*-ray powder diffraction. The adduct *cis*-$SnBr_4(dma)_2$ showed a transition in the solid state which could not be unequivocally characterized as an isomerization.

THE $^1H$ n.m.r. and the vibrational spectra of several $SnX_4L_2$ adducts (X = Cl or Br; L = Lewis base) in solution have shown the existence of *cis* and *trans* isomers in an equilibrium which is dependent on the solvent polarity.[1] Ruzicka and Merbach [1] were able to synthesize $SnCl_4(tht)_2$ (tht = tetrahydrothiophen) with the *cis* geometry in dichloromethane and the *trans* geometry in n-pentane.

In our laboratory we have observed that some of the $SnX_4$ adducts when stored at 293 K underwent isomerization in the solid state. Apparently these transformations do not occur at lower temperatures, such as 253 K. This fact led us to investigate the adducts $SnCl_4L_2$ [L = dimethylformamide (dmf), dimethylacetamide (dma), or dimethyl sulphoxide (dmso)] and $SnBr_4L_2$ (L = dmf or dma), the effect of the solvent on their preparation, and the temperature of the isomerization in the solid state.

TABLE 1

Temperature and enthalpy of transition observed with d.s.c. and analytical data for $SnX_4L_2$ adducts

| Adduct | $T$/K | $\Delta H$(transition)/ kJ mol$^{-1}$ | Analysis (%) [a] C | H | N | X |
|---|---|---|---|---|---|---|
| $SnCl_4(dmf)_2$ | 429 | $-0.24 \pm 0.03$ | 17.6 (17.7) | 3.15 (3.45) | 6.65 (6.90) | 34.8 (34.85) |
| $SnCl_4(dma)_2$ | 412, 420 | small [b] | 21.65 (22.1) | 3.60 (4.15) | 6.25 (6.45) | 32.2 (32.6) |
| $SnCl_4(dmso)_2$ | 393 [c] | | 11.75 (11.55) | 2.55 (2.90) | | 34.4 (34.05) |
| $SnBr_4(dmf)_2$ | 367 [c] | | 12.35 (12.35) | 2.05 (2.40) | 4.55 (4.80) | 55.0 (54.7) |
| $SnBr_4(dma)_2$ | 363 | $7.6 \pm 0.2$ | 15.5 (15.7) | 2.35 (2.95) | 4.45 (4.55) | 52.5 (52.2) |

[a] Found (calc.). [b] Determination of the area under the d.s.c. peak is very difficult because of the proximity of the two transitions. [c] See Experimental section.

## EXPERIMENTAL

All manipulations of the substances were made using a conventional vacuum line and a Schlenk apparatus. Reactions were carried out using $SnX_4$ stored over metallic tin, which was distilled into a calibrated ' break-seal ' tube and sealed off. All the solvents and ligands were purified and dried before use.

In a typical preparation of the adduct, $SnX_4$ (8 mmol), dissolved in $CHCl_3$ (10 cm$^3$), and a stoicheiometric amount of the ligand in the same solvent (10 cm$^3$) were allowed to react in a nitrogen atmosphere. The solid product was left for 3 h, with stirring, and then filtered off, washed with solvent (5 cm$^3$), and dried *in vacuo*. Although the compounds are not hygroscopic, they were stored *in vacuo*. Other solvents used to prepare the complexes were dichloromethane, acetonitrile, diethyl ether, ethanol, and diethyl carbonate in order to check the influence of solvent polarity on the structure of the final product.[1] The microanalysis of the compounds indicated in every case formation of the 1 : 2 adducts; analytical data are given in Table 1.

The Raman spectra were obtained with the samples in a vacuum-sealed glass tube of 2 mm internal diameter. A rotating cell (2 000 r.p.m.) was used to record the spectra at room temperature. Using a static cell, no transformation induced by the laser beam was observed, when the maximum incident radiation power of 100 mW on the sample surface was used. Above room temperature a cell similar to that described by Miller and Harney [2] was used and the temperature was controlled with a flux of hot air. A Cary 82 spectrophotometer with an Ar ion laser of Spectra Physics model 165-08 was used to record the Raman spectra.

The i.r. spectra were obtained with a Perkin-Elmer model 180 spectrophotometer. Dried paraffin and fluorocarbon oils were used to prepare the mulls and CsI and polyethylene windows were used to record the spectra. The results of the vibrational spectra are presented in Table 2.

*X*-Ray powder-diffraction data (Table 3) were obtained with a Rigaku diffractometer using Cu-$K_\alpha$ radiation ($\lambda$ = 154.2 pm) and a Ni filter.

The differential scanning calorimetry (d.s.c.) data (Table 1) were obtained with a Perkin-Elmer model DSC-2. In a typical experiment $5.00 \pm 0.02$ mg of the sample in a sealed aluminium pan were heated at 5 K min$^{-1}$ and over a range of 2 mcal s$^{-1}$.[†] The enthalpy and transition temperature were calibrated against standard In. Thermogravimetric analyses (t.g.a.) were recorded on a Perkin-Elmer TGS-1 equipped with a Cahn-RG electrobalance and the temperature scale was calibrated with suitable standards. All the measurements (d.s.c. and t.g.a.) were made under a flux of dry nitrogen.

It is important to observe that $SnCl_4(dmf)_2$, $SnCl_4(dmso)_2$, and $SnBr_4(dmf)_2$ undergo complete transformation

[†] Throughout this paper: 1 cal = 4.184 J; 1 mmHg ≈ 13.6 × 9.8 Pa.

TABLE 2

Infrared and Raman frequencies in the region 180—350 cm$^{-1}$ for $SnCl_4L_2$ and 150—250 cm$^{-1}$ for $SnBr_4L_2$

| Compound |  | $\nu$(SnX) $^a$ $B_2$ | $A_1$ | $B_1$ | $A_1$ | Other bands |
|---|---|---|---|---|---|---|
| (1) *cis*-$SnCl_4(dmf)_2$ | i.r. | 340vs | 328s | 314s | 287w | 206w, 183s |
|  | R |  | 328vvs | 282s |  | 267vw, 197vw, 180w |
| (2) *cis*-$SnCl_4(dma)_2$ | i.r. | 333vs | 324s | 308s | 280m | 250w |
|  | R |  | 322vvs | 310 (sh) | 284m | 250vvw |
| (3) *cis*-$SnCl_4(dmso)_2$ | i.r. | 334vs,br | 321vs,br | 303m | 272m | 329vs,br, 278 (sh), 227w, 195vw |
|  | R | 335 (sh) | 321vvs | 303w | 275m | 222w, 193w, 180w |
| (4) *cis*-$SnCl_4([^2H_6]dmso)_2$ | i.r. | 333s | 323vs | 313s | 283m | 274 (sh), 256vvw, 214m |
|  | R | 334 (sh) | 322vvs | 311 (sh) | 284s | 267w, 212vvw, 191w |
| (5) *cis*-$SnBr_4(dmf)_2$ | i.r. | 235vs, br | 201 (sh) |  | 181w |  |
|  | R | 234m | 201vs | 222m | 182 (sh) |  |
| (6) *cis*-$SnBr_4(dma)_2$ | i.r. | 244vs,br |  | 215vs |  |  |
|  | R |  | 209vvs |  | 186s | 158m |
|  |  | $E_u$ | $A_{1g}$ | $B_{1g}$ |  |  |
| (7) *trans*-$SnCl_4(dmf)_2$ | i.r. | 335vvs |  |  |  | 252m, 205w, 185m |
|  | R | 313vvs | 249m | 256 (sh) |  |  |
| (8) *trans*-$SnCl_4(dma)_2$ | i.r. | 340vvs |  |  |  | 319vs, 248w, 192w |
|  | R |  | 310vvs | 248s |  | 340m, 218w |
| (9) *trans*-$SnCl_4(dmso)_2$ | i.r. | 328vvs |  |  |  | 248w, 231vw, 206w |
|  | R |  | 304vvs | 248s |  | 332m, 325vs, 218w |
| (10) *trans*-$SnCl_4([^2H_6]dmso)_2$ | i.r. | 329vvs |  |  |  | 315 (sh), 278vw, 221m, 206m |
|  | R |  | 309vvs | 250m |  | 273w, 212w |
| (11) *trans*-$SnBr_4(dmf)_2$ | i.r. | 243vs |  |  |  |  |
|  | R |  | 198vvs | 150m |  |  |
| (12) *trans*-$SnBr_4(dma)_2$ $^b$ | R |  | 200vvs | 150w |  | 245vvw, 235w, 187 (sh) |

$^a$ v = Very, s = strong, m = medium, w = weak, sh = shoulder, br = broad. $^b$ See text.

at 293 K in approximately 15, 30, and 150 d respectively. At higher temperatures such as those specified in Table 2, the process of isomerization can be followed by Raman spectroscopy and is complete in all cases in nearly 30 min. The transition temperatures for $SnCl_4(dmso)_2$ and $SnBr_4(dmf)_2$ were determined by following the changes in the Raman spectra with temperature, since the d.s.c. in both cases did not show any detectable peak. The adduct $SnCl_4(dma)_2$ does not isomerize at room temperature, but at 412 K isomerizes in 30 min; $SnBr_4(dma)_2$ shows a transition at 363 K but the resulting Raman spectrum shows an additional complication (see the Discussion). Finally, every compound when sublimed in high vacuum (*ca.* $10^{-4}$ mmHg) between 373 and 403 K forms condensed crystals with the *cis* configuration, independent of the configuration of the starting compound (*i.e.*, whether *cis* or *trans*).

## RESULTS AND DISCUSSION

In the complexes of general formula $SnX_4L_2$, the skeleton $Y_2SnX_4$ (Y = donor atom of the ligand) shows the Sn–X stretching modes [$\nu$(SnX)] which are easily assignable.[1,3–5] The localization as well as the number of these modes depends on the configuration of the skeleton *i.e.*, *cis* ($C_{2v}$) or *trans* ($D_{4h}$).

For the skeleton *cis*-$Y_2SnCl_4$ the four $\nu$(SnCl) modes ($2A_1 + B_1 + B_2$) are active in both the i.r. and Raman spectra. The $A_1$ bands are better assigned in the Raman spectrum, one at *ca.* 323vs cm$^{-1}$ and the other at *ca.* 280mw cm$^{-1}$. In the i.r. spectrum, the $B_2$ mode appears as a strong absorption band and always occurs at higher energy than the $A_1$ modes. The $B_1$ mode is not assigned easily in some compounds [1] but in our case the band at *ca.* 300 cm$^{-1}$ was confirmed as belonging to this mode by carrying out an approximate normal coordinate analysis. The corresponding *trans* skeleton presents three $\nu$(SnCl) bands [$A_{1g}$(Raman) + $B_{1g}$(Raman) + $E_u$(i.r.)]. The Raman spectrum normally shows one strong band at *ca.* 310 cm$^{-1}$ ($A_{1g}$) and one medium band at *ca.* 250 cm$^{-1}$ ($B_{1g}$) while the i.r. spectrum shows one strong absorption at *ca.* 330 cm$^{-1}$ ($E_u$).

In the $SnBr_4$ complexes, the $\nu$(SnBr) bands occur at lower frequencies but the observed intensities in both spectra are very similar with those observed for $SnCl_4$ compounds. For the *cis* skeleton, the $A_1$ modes are observed at *ca.* 205 cm$^{-1}$ and at *ca.* 180 cm$^{-1}$. The $B_2$ and $B_1$ modes are observed respectively at *ca.* 240 cm$^{-1}$

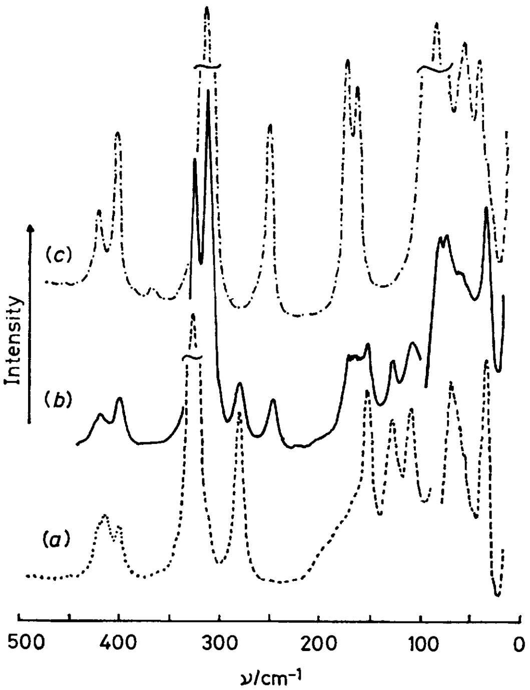

FIGURE 1 Raman spectra of $SnCl_4(dmf)_2$: (*a*) *cis* isomer, (*b*) mixture of *cis* and *trans* isomers, (*c*) *trans* isomer

and at *ca.* 220 cm$^{-1}$. The ***trans*** skeleton presents the $A_{1g}$ mode at *ca.* 200 cm$^{-1}$ and the $B_{1g}$ mode at *ca.* 150 cm$^{-1}$ in the Raman spectrum while the i.r. shows the $E_u$ mode at *ca.* 240 cm$^{-1}$.

Considering the vibrational spectra of each configuration, it is not difficult to assign any spectral change due to isomerization even when a mixture of both configurations is present in the solid complex. As a first example we will consider the Raman spectra of $SnCl_4(dmf)_2$ (0—500 cm$^{-1}$) shown in Figure 1. Figure 1(*a*) shows two bands at 328 and 282 cm$^{-1}$ which are very characteristic of the *cis* isomer and they are also active in the i.r. spectrum [(1), Table 2]. The i.r. spectrum of the *cis* isomer is perfectly in accordance with that reported previously by Farona and Grasselli.[6] At 429 K a transition occurs (see Table 1) and two new additional bands at 313 and 249 cm$^{-1}$ are observed [Figure 1(*b*)], which clearly indicates the formation of a new isomer. After 30 min the bands at 328 and 282 cm$^{-1}$ disappeared completely and the resulting spectrum is clearly that of the *trans* isomer [Figure 1(*c*)].

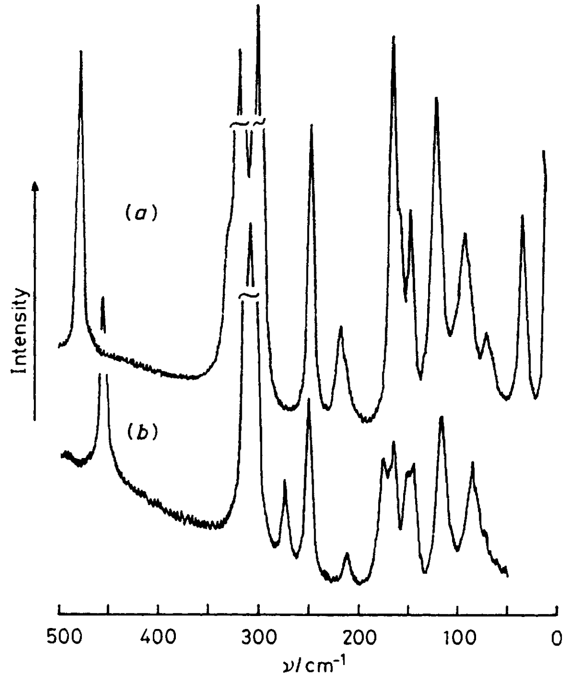

FIGURE 2 Raman spectra of *trans*-$SnCl_4(dmso)_2$: (*a*) $SnCl_4[(CH_3)_2SO]_2$, (*b*) $SnCl_4[(CD_3)_2SO]_2$

As a second example, $SnCl_4(dmso)_2$ deserves special comments because the freshly prepared compound has the vibrational spectrum characteristic of the *cis* form (3) (Table 2) as previously observed by Tanaka[7] and in accord with the *X*-ray structure of this compound.[8] The Raman spectrum of the transformed solid shows some complexity because it exhibits very strong bands at 325 and 304 cm$^{-1}$ [Figure 2(*a*)] although only one should be expected in this region for a *trans* configuration. In the corresponding hexadeuteriated compound [Figure 2(*b*)] the band at 325 cm$^{-1}$ is replaced by a weak one at 273 cm$^{-1}$. This isotopic shift has a correspondent in free dmso for the δ(CSC) bands which are observed at 308 and 262 cm$^{-1}$ respectively, for non-deuteriated and hexadeuteriated molecules.[9] The i.r. spectra of both transformed isotopic species show a strong absorption near 330 cm$^{-1}$ [(9) and (10), Table 2] and this supports the conclusion that the spectra in Figure 2 are due to a ***trans*** configuration.

TABLE 3

*X*-Ray powder-diffraction data. Only $I/I_1 > 50$ are listed

| | | | |
|---|---|---|---|
| $SnCl_4(dmf)_2$ | | | |
| *cis* | | *trans* | |
| *d*/Å | $I/I_1$ | *d*/Å | $I/I_1$ |
| 7.168 | 100 | 6.944 | 93 |
| 7.026 | 70 | 6.326 | 100 |
| 4.997 | 58 | 4.312 | 53 |
| 4.530 | 50 | 3.297 | 50 |
| 3.339 | 56 | | |
| $SnCl_4(dmso)_2$ | | | |
| *cis* | | *trans* | |
| 6.560 | 100 | 6.759 | 69 |
| 5.986 | 50 | 6.006 | 98 |
| | | 3.460 | 100 |
| $SnCl_4(dma)_2$ | | | |
| *cis* | | *trans* | |
| 7.501 | 66 | 6.535 | 100 |
| 6.535 | 59 | 4.647 | 63 |
| 5.927 | 100 | | |
| 3.634 | 76 | | |
| 2.589 | 62 | | |
| $SnBr_4(dmf)_2$ | | | |
| *cis* | | *trans* | |
| 7.054 | 78 | 7.110 | 82 |
| 6.811 | 100 | 6.998 | 100 |
| | | 4.134 | 96 |
| | | 2.731 | 68 |

Finally we need to observe that $SnBr_4(dma)_2$ presents a transition detected by d.s.c. (Table 2) at 363 K, which can be followed by the changes in the Raman spectrum. Two bands are observed, one strong at 200 cm$^{-1}$ and one weak at 150 cm$^{-1}$ [(12), Table 2], which are characteristic of the ***trans*** configuration, but a shoulder at 187 cm$^{-1}$ persisted even with prolonged heating at the above temperature. However, it is interesting that, nearly 60 min after cooling the compound to room temperature, the original Raman spectrum of *cis*-$SnBr_4(dma)_2$ is obtained [(6), Table 2].

The *X*-ray diffraction pattern showed that the freshly prepared compound and the transformed one have different structures in every case. However, the observed transformations cannot be interpreted as decomposition or polymerization of the samples. In every case the thermal analysis did not show any loss of ligand in the temperature range of isomerization and the vibrational spectra did not present any complications in the spectra of the ligands or in the ν(SnX) absorptions due to polymerization.

*Conclusion*.—It is known that in solution the adduct

$SnX_4L_2$ exists in equilibrium between *cis* and *trans* configurations.[1] The solid when isolated from this solution had in every case a *cis* configuration, although solvents of different polarities were used to prepare the complex. The existing models,[10-14] especially those referring to non-ligand interactions, predict for $SnCl_4L_2$ adducts a higher stability of the *cis* isomer when L is an oxygen-donor ligand. However, it should be pointed out that in the existing models, interactions which exist in the solid state are not considered and are very important in the process of isomerization in the solid state.

[0/713 *Received*, 14*th May*, 1980]

REFERENCES

[1] S. J. Ruzicka and A. E. Merbach, *Inorg. Chim. Acta*, 1976, **20**, 221; 1977, **22**, 191.

[2] F. A. Miller and B. M. Harney, *Appl. Spectrosc.*, 1970, **24**, 1970.

[3] I. R. Beattie and L. Rule, *J. Chem. Soc.*, 1964, 3267; 1965, 2995.

[4] N. Ohkaku and K. Nakamoto, *Inorg. Chem.*, 1973, **12**, 2440, 2446.

[5] A. J. Carty, T. Hinsperger, L. Mihichuk, and H. D. Sharma, *Inorg. Chem.*, 1970, **9**, 2573.

[6] M. Farona and J. G. Grasselli, *Inorg. Chem.*, 1967, **6**, 1675.

[7] T. Tanaka, *Inorg. Chim. Acta*, 1967, **1**, 217.

[8] A. Hansson and O. Brunge, personal communication.

[9] W. D. Horrocks and F. A. Cotton, *Spectrochim. Acta, Part A*, 1961, **17**, 134.

[10] I. R. Beattie, *Q. Rev., Chem. Soc.*, 1963, **17**, 382.

[11] R. T. Zahrobsky, *J. Am. Chem. Soc.*, 1971, **93**, 3313.

[12] J. A. S. Smith and E. J. Wilkins, *Chem. Commun.*, 1965, 381.

[13] J. C. Hill, R. S. Drago, and R. H. Herber, *J. Am. Chem. Soc.*, 1968, **91**, 1644.

[14] L. A. Aslanov, V. M. Ionov, V. M. Attiya, A. B. Permin, and V. S. Petrosyan, *J. Struct. Chem.* (*Engl. Transl.*), 1977, **18**, 876.