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68. Structural and Dynamic Study of $SnCl_4 . 2 Me_2O$ and $SnCl_4 . 2 Me_2Se$

Preliminary communication

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(23. XII. 74)

Summary. The solid *cis*-$SnCl_4 \cdot 2Me_2O$ and *trans*-$SnCl_4 \cdot 2Me_2Se$ adducts have been synthesised and characterised by IR. and *Raman* spectroscopy. NMR. and vibrational spectroscopy show a fast *cis-trans* equilibrium for both complexes in solution in an inert solvent.

Numerous 1:2 adducts of tin tetrahalides with unidentate ligands, $SnX_4 \cdot 2L$, have already been prepared and characterised in the solid state as *cis* or *trans* isomers. In solution, little has been done, and possible *cis-trans* equilibria were not observed [1]. We have undertaken a systematic study of this type of adduct in order to determine the nature and the structure of the different species present in solution, the equilibrium constants and the dynamics involved. Structural information shall mainly be deduced by vibrational spectroscopy and the dynamic aspect by NMR. In this communication, we discuss a *cis* and a *trans* compound, both presenting *cis-trans* equilibria in solution.

A simple comparison between the *Raman* and the IR. spectra (Fig. 1) of $SnCl_4 \cdot 2Me_2O$1), and $SnCl_4 \cdot 2Me_2Se$1), allows the distinction between both isomeric forms; for the stretching modes of a *trans* compound, no common band occurs in

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1) The adducts were prepared in a dry atmosphere, and gave satisfactory elemental analysis.

both spectra, while for the *cis* compound all the bands are common to both [2]. In a *trans*-$SnCl_4 \cdot 2L$ (D_{4h}) the vibrations are classified in 3ν(Sn–X) stretching modes (A_{1g}(R.) + B_{1g}(R.) + E_u(IR.)) and 2ν(Sn–L) (A_{1g}(R.) + A_{2u}(IR.)). A *cis*-$SnX_4 \cdot 2L$ (C_{2v}) has 4ν(Sn–X) ($2A_1$(IR., R.) + B_1(IR., R.) + B_2(IR., R.)) and 2ν(Sn–L) (A_1(IR., R.) + B_2(IR., R.)).

For solid *$SnCl_4 \cdot 2Me_2Se$*, none of the Sn–Cl stretching modes coincide in the IR. and Raman spectra, and we thus conclude a *trans* configuration. In the IR. the two bands at 310 and 210 cm^{-1} are assigned to ν(Sn–Cl) (E_u) and ν(Sn–Se) (A_{2u}). The *Raman* spectrum shows also two bands in this region, at 281 and 239 cm^{-1}, which are the ν(Sn–Cl) (A_{1g}) and ν(Sn–Cl) (B_{1g}). The vibration at 245(IR.) and 249(R.) cm^{-1} is due to the bending mode of the coordinated Me_2Se. The A_{1g} and B_{1g} assignment is reconfirmed in solution by depolarisation measurements.

The solid *$SnCl_4 \cdot 2Me_2O$* spectra show a complete correspondence of frequencies, so a *cis* configuration is attributed. The 357(IR.) and 359(R.) cm^{-1} vibration is assigned to a ν(Sn–Cl) (B)2), the 338(IR.) and 336(R.) cm^{-1} as a ν(Sn–Cl) (A_1), the 298(IR.) and 299(R.) cm^{-1} as ν(Sn–Cl) (A_1). The remaining IR. band at 260 cm^{-1} is probably a Sn–O stretching mode. The other ν(Sn–Cl) (B)2) vibration is not observed, probably hidden under the 336 cm^{-1} band. The IR. band at 464 cm^{-1} is also found in the *Raman* spectrum at the same frequency, and is due to the bending mode of coordinated Me_2O. The differentiation between A and B modes is also based on depolarisation measurements in solution.

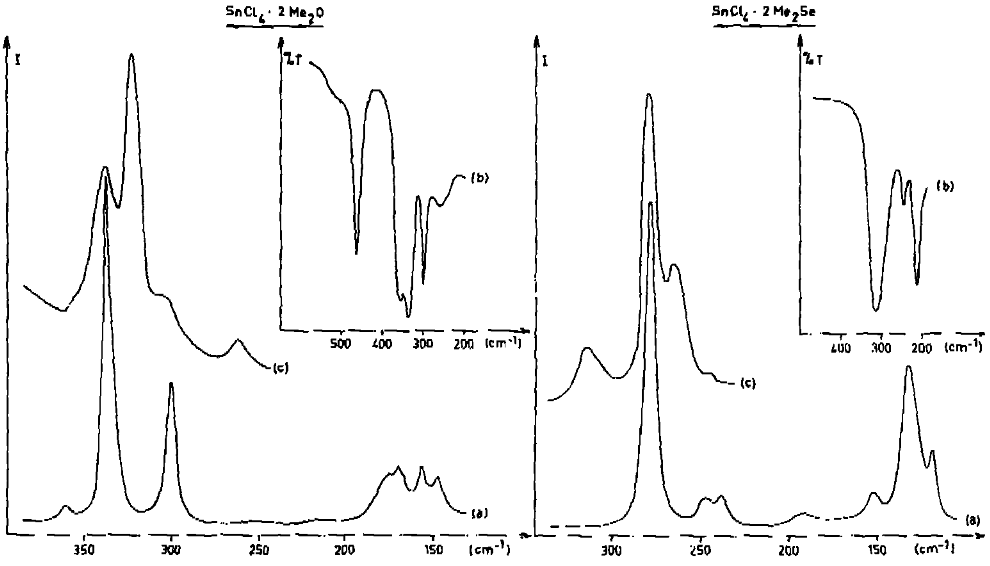

Fig. 1. *Vibrational spectra of $SnCl_4 \cdot 2Me_2O$ and $SnCl_4 \cdot 2Me_2Se$*. (a) *Raman* and (b) IR. spectra of the solid; (c) *Raman* spectra in CH_2Br_2 ($SnCl_4$/Ligand = 1/4)

The solution *Raman* spectra (Fig. 1) have been run for both compounds with a 1:4 metal to ligand ratio in CH_2Br_2. This solvent does not show any band in the 400–200 cm^{-1} region. For the adduct with Me_2Se, new bands, due to the *cis* isomer, appear at 320(A_1) and 267(A_1) cm^{-1}, in addition to the 281(A_{1g}) and 244(B_{1g}) cm^{-1} of the ***trans*** compound. As expected by this assignment, the 320, 281 and 267 bands are polarised (symmetric stretching) and the 244 cm^{-1} depolarised (asymmetric stretching). The two remaining ν(Sn-Cl) (B_1 and B_2) modes are not observed, due to a low activity (*cf.* solid ***Raman*** spectrum of *cis*-$SnCl_4 \cdot 2Me_2O$).

On the other hand the spectrum of the adduct with Me_2O shows new bands at 322(A_{1g}) and 260(B_{1g}) cm^{-1}, due to the ***trans*** isomer, in addition to the remaining 358(B)[2], 338(A_1) and 302(A_1) cm^{-1} bands of the *cis* compound.

The IR. solution spectra revealed only a broad band, resulting from the overlap of the four Sn-Cl modes of the *cis* compound, and the E_u mode of the ***trans*** compound.

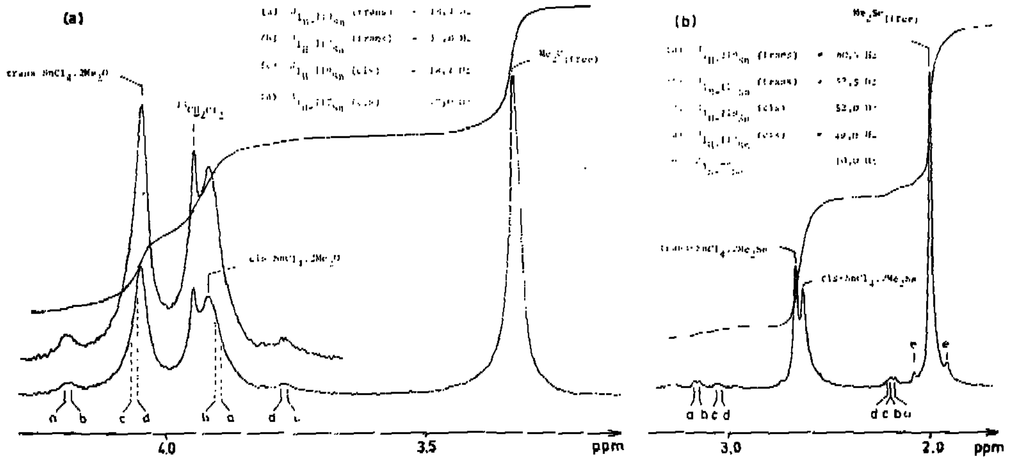

Fig. 2. *^{1}H-NMR. spectra* (60 MHz) *in CH_2Cl_2 at -90° of* (a) *$SnCl_4$* (0,03 molal) ***and Me_2O in a 1:4 ratio*** (b) *$SnCl_4$* (0,16 molal) ***and Me_2Se in a 1:4 ratio***

This *cis-**trans*** equilibrium in solution is demonstrated definitely by ^{1}H-NMR. Both spectra (Fig. 2) show in CH_2Cl_2 at low temperature two signals for coordinated species and one for the free ligand. The integration of free and coordinated ligand shows a 1:2 metal to ligand ratio for coordinated species. The assignment of the two low field resonances to coordinated ligand is confirmed by the coupling of methyl protons with the two spin = $^1/_2$ isotopes of tin. The assignment of the low field signal to the ***trans*** isomer is made upon the observation that this signal increases while the other ligand coordinated signal decreases in changing to a less polar solvent [3].

The chemical shifts at −90° for Me_2Se and Me_2O respectively are: δ (free) = 2.01 and 3.33; δ (*cis*) = 2.63 and 3.92; δ (***trans***) = 2.67 and 4.05 ppm. Increasing the temperature in the $SnCl_4$–Me_2Se system leads to the collapse at −50° of the signals due to the free and *cis* ligand. The two remaining signals collapse at +20°. The first collapse is related to the rate of ligand exchange in the *cis* adduct. The interpretation of the second collapse is not obvious; it may be related to the rate of ligand exchange

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[2] A differentiation between B_1 and B_2 was not possible.

in the *trans* complex and/or to the rate of an hypothetical intramolecular *cis-trans* isomerisation. The same behaviour is found in the $SnCl_4$–Me_2O system, but with faster exchange rates.

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69. The Preparation of *trans*-N-Acyl, N-alkyl-1-amino-1,3-butadienes

Preliminary Communication

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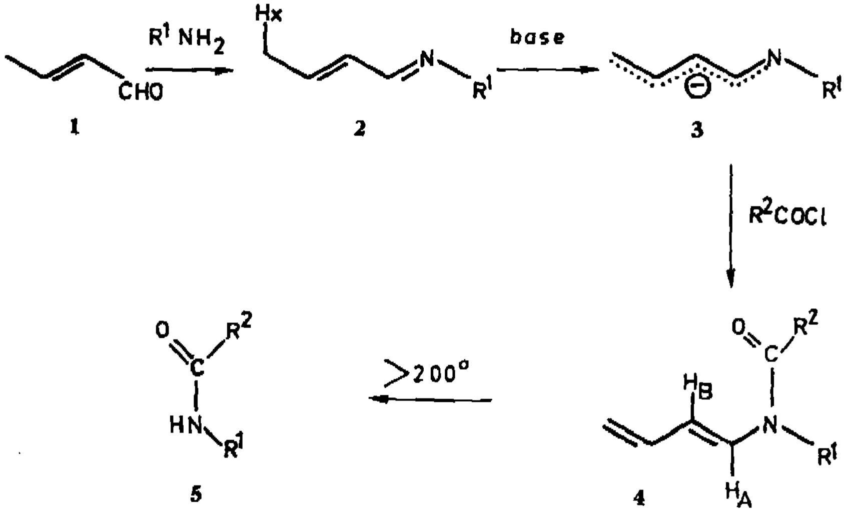
(24. I. 75)

Zusammenfassung. In der vorliegenden Mitteilung wird erstmals ein Zugang zu *trans*-N-Acyl, N-alkyl-1-amino-1,3-butadienen **4**, sowie zu *trans*-N-Acyl, N-aryl-1-amino-1,3-butadienen **4** beschrieben. Deprotonierung von N-substituierten 1-Imino-2-butenen **2** führt vermutlich zu den nicht isolierten delokalisierten Anionen **3**, die anschliessend regioselektiv am Stickstoffatom acyliert werden.

In order to achieve the stereocontrolled synthesis of substituted decahydro quinolines [1] a general approach to *trans*-N-acyl, N-alkyl-1-amino-1,3-butadienes[1])

Scheme



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[1]) A multi step preparation of an endocyclic N-acyl-1-amino-4-cyano-1,3-butadiene has been described in connection with the synthesis of anthramycin [2].