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Geometrical Isomerism in a Monoorganotin(IV) Complex

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While it is now clear that many tin complexes can exist as equilibrium isomeric mixtures in solution it is surprising that there are so few examples of separate isomeric forms of a tin complex which can be isolated in the solid state. To our knowledge strong evidence for the isolation of both *cis* and *trans* isomers (about tin) has been presented for only two complexes, these being $SnCl_4 \cdot 2THT$ [1] (THT = tetrahydrothiophene) and $Me_2Sn(salen)$ [2] (salen = N,N′-ethylenebis(salicylideneiminato)) and there are no examples of separate geometrical isomers of a monoorganotin(IV) complex existing in the solid state. In the course of our studies of adducts of tin(IV) Lewis acids with transition metal complexes as bases we have isolated what we believe to be isomeric forms of an adduct of $BuSnCl_3$.

We recently reported that adducts $RSnCl_3 \cdot M(salen)$ (R = butyl or phenyl; M(salen) (see Fig. 1a) = N,N′-ethylenebis(salicylideneiminato)nickel(II) and -copper (II)) have the *mer* structure of Fig. 2a [3]. As an extension of this work adducts were prepared with N,N′-*o*-phenylenebis(salicylideneiminato)nickel(II) and -copper(II) (see Fig. 1b) as bases [4]. Not surprisingly these latter ligands gave 1:1 adducts with tin(IV) halides which exhibited Mössbauer quadrupole splittings of the same order of magnitude as those for analogous adducts containing M(salen) ligands. However, adducts $RSnCl_3 \cdot M(salphen)$ (R = Bu or Ph) had substantially greater quadrupole splittings than analogous adducts $RSnCl_3 \cdot M(salen)$ and in fact the quadrupole splittings of the former adducts were, in all cases, in good agreement with those calculated for the *fac* structure of Fig. 2b. The changeover from *mer* to *fac* structure is difficult to rationalize since M(salen) and M(salphen) presumably exert essentially the same steric influence in the immediate tin environment and the Mössbauer data for the tin(IV) halide adducts do not point to any large difference in Lewis basicity between both types of base. It may be that the energy difference between both isomeric forms is quite small in these instances; bearing this possibility in mind we attempted to isolate both *mer* and *fac* isomers for all of the adducts of this study. This appears to be possible for the adduct $BuSnCl_3 \cdot$ Ni(salphen).

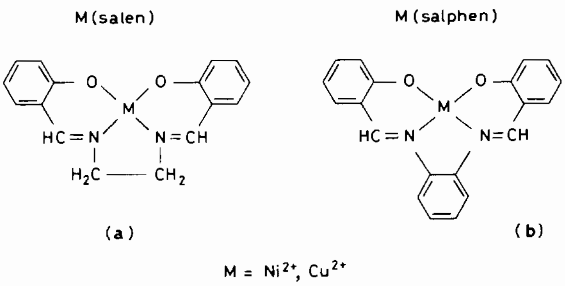

Fig. 1. Structures of M(salen) and M(salphen).

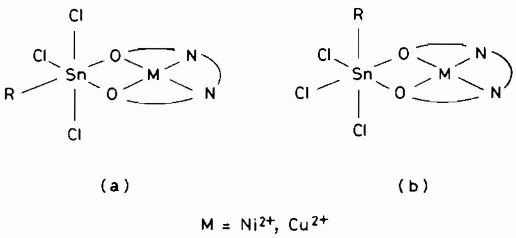

Fig. 2. Structure of organotin adducts.

TABLE I. Mössbauer Data for $BuSnCl_3 \cdot Ni(salphen)$.

	δ/ mm s^{-1} [a] (±0.03)	Δ_{obs}/ mm s^{-1} (±0.03)	Δ_{calc}/ mm s^{-1} [b]
$BuSnCl_3 \cdot Ni(salphen)$ (A)	1.21	2.13	2.32[c]
$BuSnCl_3 \cdot Ni(salphen)$ (B)	1.05	1.48	1.69[d]

[a] Relative to $BaSnO_3$. [b] The following partial quadrupole splitting values were employed: Chloride 0.0; Butyl –0.93 (see ref. 3); Ni(salphen)/2 + 0.225 (value from quadrupole splitting data for $SnCl_4 \cdot Ni(salphen)$). [c] Calculated for the *fac* structure. [d] Calculated for the *mer* structure. (A) and (B) refer to preparations in dichloromethane and acetonitrile respectively.

When Ni(salphen) and $BuSnCl_3$ were stirred together in equimolar quantities in dichloromethane an insoluble product, A, with elemental analysis consistent with its formulation as $BuSnCl_3 \cdot$Ni(salphen) was obtained. An insoluble product, B, from a similar type reaction carried out in acetonitrile gave similar analyses and its infrared spectrum excluded the possibility of coordinated nitrile. Products A and B differed in their X-ray powder diffraction patterns, infrared and Mössbauer spectra (Mössbauer parameters are in Table I). There is no reason to doubt the adduct formulation of A since all other adducts of this study and of previous studies [3–6], including $Me_2SnCl_2 \cdot$ Ni(salen) for which X-ray data have confirmed the adduct structure [6], were prepared in dichlorome-

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thane. That the adduct formulation is also correct for B seems certain for the following reasons:

1. Other adducts of this study could be prepared in acetonitrile (giving identical products to those obtained from dichloromethane).

2. When B was added to methanol it yielded $BuSnCl_3$ (solvated) and free Ni(salphen). Product A and other adducts of this study behaved likewise.

3. Both A and B are similar in colour and contain diamagnetic nickel(II).

4. When A was stored for approximately six months in a sealed container it was found to have partially converted to B and there was no evidence for the formation of any other species in this transformation. Furthermore, A was totally converted to B when stirred in acetonitrile at room temperature for approximately twelve hours.

Thus, A and B are either two crystal modifications or isomeric forms of the same complex. The possibility that they are two crystal modifications is remote since their Mössbauer parameters differ so substantially. In Table I the quadrupole splittings of A and B are compared with values calculated (using the point charge model approach) for *mer* and *fac* isomers of $BuSnCl_3$-Ni(salphen). Bearing in mind the overall accuracy of the point charge model [7] the experimental values for A and B are in quite good agreement with the values estimated for the *fac* and *mer* structures respectively. The Mössbauer chemical shift of A is 0.16 mm s^{-1} greater than that of B and this is consistent with the fact that adducts $RSnCl_3 \cdot M$(salphen) (*fac* structure) consistently exhibited greater chemical shifts than analogous adducts $RSnCl_3 \cdot M$(salen) (*mer* structure). This order of chemical shifts is intuitively what would be expected since in the case of the *mer* structure an oxygen is *trans* to the Sn–C bond containing the greatest *s*-character and is hence likely to withdraw more *s*-electron density from tin than it would in a position *cis* to carbon [8].

Finally, it is noteworthy that in the case of $BuSnCl_3Cu$(salphen) it was only possible to obtain the *fac* isomer. Since Cu(salphen) and Ni(salphen) are sterically identical it is clear that the failure to isolate the *mer* isomer cannot in this case be attributed to steric factors.

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References

1 S. J. Ruzicka and A. E. Merbach, *Inorg. Chim. Acta, 20,* 221 (1976).
2 K. Kawakami, M. Miya-Uchi and T. Tanaka, *J. Organometal. Chem., 70,* 67 (1974).
3 D. Cunningham and M. Little, *J. Organometal. Chem., 142,* C58 (1977).
4 D. Cunningham and M. Little, unpublished work.
5 L. Pellerito, R. Cefatu, A. Gianguzza and R. Barbieri, *J. Organometal. Chem., 70,* 303 (1974).
6 M. Calligaris, L. Randaccio, R. Barbieri and L. Pellerito, *J. Organometal. Chem., 76,* C56 (1974).
7 M. G. Clark, A. G. Maddock and R. H. Platt, *J. Chem. Soc. Dalton,* 281 (1972).
8 L. A. Aslanov, V. M. Ionov, W. M. Attia, A. B. Permin and V. S. Petrosyan, *J. Organometal. Chem., 144,* 39 (1978).