Journal of Organometallic Chemistry, 142 (1977) C58—C60
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

THE STRUCTURES OF ORGANOTIN(IV) TRICHLORIDE ADDUCTS WITH *N,N'*-ETHYLENEBIS(SALICYLIDENEIMINATO)-NICKEL(II) AND -COPPER(II) BY MÖSSBAUER SPECTROSCOPY

D. CUNNINGHAM* and M. LITTLE
Department of Chemistry, University College, Galway (Ireland)

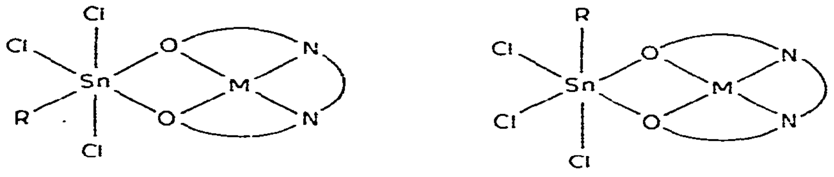
(Received October 19th, 1977)

Summary

Definite structural assignments may be made for adducts referred to in the title by Mössbauer spectroscopy.

The point charge model has been extensively used in the interpretation of Mössbauer quadrupole splitting data and has in many cases yielded valuable structural information, particularly in the case of organotin(IV) complexes [1]. Recently the applicability of the model to monoorganotin(IV) trihalide adducts has been examined [2] and it has been shown that while there generally was satisfactory agreement between calculated and experimental quadrupole splitting values the calculated data did not in any case allow an unambiguous distinction to be made between possible structural isomers. However, there also appeared to be situations where experimental and calculated data showed gross differences. Such was the position for adducts $RSnCl_3 \cdot Ni(salen)$ (R = Ph or Me; Ni(salen) = *N,N'*-ethylenebis(salicylideneiminato)nickel(II)). There is evidence to suggest that the most suitable choice of partial quadrupole splitting (p.q.s.) values had not been made in these instances [3]. Thus, in view of our general interest in the Mössbauer spectra of donor—acceptor complexes of tin(IV) in which the donor is a transition metal complex we have reexamined the quadrupole splitting data for the above nickel complexes and also for the n-butyl-tin and -copper analogs.

The two possible structures for the adducts are shown in Fig. 1 and quadrupole splittings calculated on the basis of both structures are given in Table 1. The difference between our calculated values and those previously reported stems entirely from the choice of p.q.s. values. The p.q.s. value for n-butyl used in the present calculation is an average estimate from quadrupole splitting data for the salts $(Et_4N)_2$-n-$BuSnCl_5$, (Δ 1.86 mm s^{-1}), $(Et_4N)_2$-n-$BuSnCl_3Br_2$, (Δ 1.85 mm s^{-1}) and $(Ph_4As)_2$-n-$BuSnCl_5$, (Δ 1.88 mm s^{-1}), and that for



(I)

(II)

R = alkyl or phenyl

M = nickel or copper

Fig. 1.

phenyl an average estimate from data for $(Et_4N)_2PhSnCl_5$, (Δ 1.65 mm s^{-1}), $(Ph_4As)_2PhSnCl_5$, (Δ 1.64 mm s^{-1}) and $(PyH)_2PhSnCl_5$, (Δ 1.72 mm s^{-1}).* It has been established [3] that these p.q.s. values are always more suitable for adducts $RSnCl_3 \cdot 2L$ and $(Et_4N)(RSnCl_4 \cdot L)$ (R = Ph or n-Bu; L = donor) than those previously employed (see Table 1). As quadrupole splitting data are not available for salts of $(MeSnCl_5)^{2-}$ the p.q.s. value for methyl used in the present calculation is an average estimate from quadrupole splitting data for $K_2(Me_2SnCl_4)$ [4,5], $Cs_2(Me_2SnCl_4)$ [4,5], $(PyH)_2(Me_2SnCl_4)$ [6] and $Cs_2(Me_2SnBr_4)$ [4]. The choice of a p.q.s. value for Ni(salen) gives rise to the greatest source of discrepancy between the two sets of calculated data in Table 1. The previous choice was made from quadrupole splitting data for the adducts $Me_2SnCl_2 \cdot$Ni(salen) and $Ph_2SnCl_2 \cdot$Ni(salen) whereas the present values for both Ni(salen) and Cu(salen) were estimated from data for stannic

TABLE 1

EXPERIMENTAL AND CALCULATED MÖSSBAUER QUADRUPOLE SPLITTING DATA

	Δ_{exp} (mm s^{-1})^a	Δ_{calc} (mm s^{-1})^d	
		Structure I	Structure II
$MeSnCl_3 \cdot$Ni(salen)^c	1.63^b	1.89	2.72
		(2.08)	(2.01)
n-$BuSnCl_3 \cdot$Ni(salen)	1.53	1.61	2.47
$PhSnCl_3 \cdot$Ni(salen)	1.38	1.42	2.27
		(1.92)	(1.85)
n-$BuSnCl_3 \cdot$Cu(salen)	1.67	1.68	2.36
$PhSnCl_3 \cdot$Cu(salen)	1.45	1.49	2.16

^{a}±0.03 mm s^{-1}. ^{b}Data from ref. 8. ^{c}Nomenclature as in text. ^{d}For present calculations partial quadrupole splitting values (mm s^{-1}) were: methyl −1.06; n-butyl −0.935; phenyl−0.835; Ni(salen)/2 +0.30; Cu(salen)/2 +0.245. Previous calculated data (shown in brackets) were obtained using the partial quadrupole splitting values (mm s^{-1}): alkyl −1.03; phenyl −0.95; Ni(salen)/2 −0.05.

---

*Quadrupole splitting data for the organopentachlorostannate(IV) species are new except those for $(Et_4N)_2$-n-$BuSnCl_5$ and $(Et_4N)_2$-n-$BuSnCl_3Br_2$ [9]. A quadrupole splitting of 1.92 mm s^{-1} has previously been reported for $(PyH)_2PhSnCl_5$ [6].

halide adducts $SnX_4 \cdot M(salen)$ (X = Cl, Br and I; M = Ni and Cu) [7]. The latter choice is based on the experience [3] that p.q.s. parameters for donor groups obtained from quadrupole splitting data for stannic halide adducts are always suitable for adducts $RSnCl_3 \cdot 2L$ and $(Et_4N)(RSnCl_4 \cdot L)$ and this seems to be further substantiated by the data in Table 1.

It is seen (see Table 1) that the calculated quadrupole splitting values based on structures I and II are always significantly different, differences being in the range 0.67—0.86 mm s^{-1}. Furthermore, the values based on structure I are always in remarkably good agreement with experimental data (a more suitable choice of p.q.s. value for the methyl group based on quadrupole splitting data for salts of $(MeSnCl_5)^{2-}$ might have resulted in better agreement in the case of $MeSnCl_3 \cdot Ni(salen)$). Thus, in view of the large differences in the values predicted for both structures and the good agreement in all cases between values calculated on the basis of structure I and experimental data (which rules out any fortuitous agreement that might have resulted from one calculation) it can be confidently assumed that all adducts have structure I.

The structural assignments for the above adducts from Mössbauer quadrupole splitting data are particularly valuable since these could not be readily made on the basis of infrared data [8].

Acknowledgement

The authors are indebted to Dr. M.J. Conneely, Department of Mathematical Physics, University College, Galway for valuable assistance with the computer analysis of the Mössbauer spectra.

References

1 See for example N.N. Greenwood and T.C. Gibb, Mössbauer Spectroscopy, Chapman and Hall, London, 1971 or R.V. Parish, Progr. Inorg. Chem., 15 (1972) 101.
2 R. Barbieri, L. Pellerito, N. Bertazzi and G.C. Stocco, Inorg. Chim. Acta, 11 (1974) 173.
3 K. McLaughlin, M.Sc. Thesis, National University of Ireland, 1977.
4 R.V. Parish and R.H. Platt, Inorg. Chim. Acta, 4 (1970) 65.
5 R.V. Parish and C.E. Johnson, J. Chem. Soc. A, (1971) 1906.
6 B.W. Fitzsimmons, N.J. Seeley and A.W. Smith, J. Chem. Soc. A, (1969) 143.
7 D. Cunningham and M. Little, unpublished work.
8 L. Pellerito, R. Cefalù, A. Gianguzza and R. Barbieri, J. Organometal. Chem., 70 (1974) 303.
9 A.G. Davies, L. Smith and P.J. Smith, J. Organometal. Chem., 23 (1970) 135; N.W.G. Debye, E. Rosenberg and J.J. Zuckerman, J. Amer. Chem. Soc., 90 (1968) 3234.