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^{119}Sn Mössbauer Quadrupole Splittings in Compounds with Sn-Mn Bonds

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Onaka, Sasaki, and Sano1) have recently reported ^{119}Sn Mössbauer data for the four series of compounds $(CO)_5MnSnR_{3-n}X_n$, where R=Me, Ph, and X=Cl, Br. The quadrupole splitting values (Δ) for $n=1$, 2 are always higher than those for $n=0$, 3, rather than showing a monotonic change as n increases, but no explanation was offered for this unexpected order. We have recently suggested2) that a similar trend in Δ for the compounds $(\pi\text{-}C_5H_5)Fe(CO)_2SnPh_{3-n}Cl_n$ is due to a change in sign of the quadrupole coupling constant, which can be explained on the basis of point-charge calculation. We wish to show that the results of Onaka, *et al.*1) are susceptible to a like explanation.

The point-charge model assumes that the electric field gradient (EFG) is an additive quantity,3) so that the quadrupole splitting can be evaluated from partial quadrupole splitting (PQS) values, [L], for the various ligands. Since the EFG at tin is largely due to an imbalance in the polarity of the tin-ligand σ-bonds, [L] values are related to this polarity and can be correlated with the Taft inductive constants for the ligands.4) The model has been discussed in detail by Parish and Platt,4) who also derived a number of PQS values from data for pentacoordinate tin compounds. It has been suggested that these PQS values should not be applied to compounds in which the tin atom has a different coordination number.5) For the

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1) S. Onaka, Y. Sasaki, and H. Sano, This Bulletin, **44**, 726 (1971).

2) B. V. Liengme, M. J. Newlands, and J. R. Sams, *Inorg. Nucl. Chem. Lett.*, **7**, 1223 (1971).

3) M. G. Clark, *Mol. Phys.*, **20**, 257 (1971).

4) R. V. Parish and R. H. Platt, *Inorg. Chim. Acta*, **4**, 65 (1970).

5) A. G. Maddock and R. H. Platt, *J. Chem. Soc.*, *A*, **1971**, 1191.

present tetracoordinate derivatives we have therefore derived a self-consistent set of PQS values. If we assume an arbitrary value for [Cl], then point-charge expressions for molecules of the types $SnAB_3$ and $SnA_2B_2$4) with experimental Δ values2) for $(CO)_5MnSnCl_3$, $(CO)_5MnSnMe_3$, and $[(CO)_5Mn]_2SnPh_2$ yields PQS values for $(CO)_5Mn$, Me, and Ph, respectively.2) A value for [Br] is obtained from the measured1) splitting in $(CO)_5MnSnBr_3$. These [L] values are given in footnote (a) to Table 1. It should be noted that our results are independent of the value chosen for [Cl].2) These PQS values are used to compute the EFG tensor elements, assuming tetrahedral bond angles.6) After diagonalising the tensor, the nonvanishing elements are ordered such that $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$, then the asymmetry parameter $\eta = (V_{yy} - V_{xx})/V_{zz}$ and

$$\Delta = \frac{1}{2}eQV_{zz}\left(1+\frac{\eta^2}{3}\right)^{1/2}$$

are calculated. The results for a number of compounds with Sn–Mn bonds are presented in Table 1, along with experimental Δ values.

TABLE 1. MEASURED AND PREDICTED QUADRUPOLE SPLITTINGS FOR SOME COMPOUNDS WITH Sn–Mn BONDSa)

Compound	Δ_{obs}b) (mm sec^{-1})	Δ_{pred} (mm sec^{-1})	η_{pred}
$(CO)_5MnSnCl_3$	1.57	+	0
$(CO)_5MnSnMeCl_2$	2.62	+2.37	0.85
$(CO)_5MnSnMe_2Cl$	2.66	−2.24	0.48
$(CO)_5MnSnMe_3$	0.61	−	0
$(CO)_5MnSnPhCl_2$	2.36	+2.13	0.93
$(CO)_5MnSnPh_2Cl$	2.49	−1.95	0.34
$(CO)_5MnSnPh_3$	0c)	−0.50	0
$(CO)_5MnSnBr_3$	1.41	+	0
$(CO)_5MnSnMeBr_2$	2.51	+2.22	0.83
$(CO)_5MnSnMe_2Br$	2.54	−2.11	0.51
$(CO)_5MnSnPhBr_2$	2.63	+1.97	0.92
$(CO)_5MnSnPh_2Br$	2.28	−1.82	0.36
$[(CO)_5Mn]_3SnCl$	1.55d)	−1.56	0
$(CO)_5MnSn(Cl)$ $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$	2.02e)	−1.73	0.18

a) PQS values used in the calculations are (in mm sec^{-1}): [Cl] = +0.63, [Br] = +0.56, [Me] = −0.56, [Ph] = −0.40, $[(CO)_5Mn]$ = −0.15.

b) Experimental values from Ref. 1) except as noted.

c) Splitting not resolved.

d) Reference 15.

e) Reference 16.

The calculated Δ values are in only moderately good numerical agreement with the measured1) ones. The lack of better agreement between Δ_{pred} and Δ_{obs} may be due largely to distortions from tetrahedral symmetry. Although insufficient structural data are available to allow a quantitative estimate of such effects, X-ray data for related compounds7–11) suggest that the distortions are likely to be such as to increase the calculated $|V_{zz}|$ values.6,12) Another possible source of discrepancy is a variation in the σ-character of the tin-halogen bonds as the number of halogens bonded to tin changes. Such an effect has been suggested13) for the compounds $RSnCl_3$ and R_2SnCl_2 (R=*n*-Bu, Ph) on the basis of ^{35}Cl NQR data.

More important than the actual numerical agreement is the fact that in all four series $(CO)_5MnSnR_{3-n}X_n$ the magnitude of Δ is predicted to be greater for $n=1$ and 2 than for $n=0$ and 3, as observed experimentally. The sign of Δ_{pred} is the sign of the quadrupole coupling constant, eQV_{zz}. This sign has recently been shown to be positive for both $(CO)_5MnSnCl_3$ and $(CO)_5MnSnCl_2Me$,14) but the signs of eQV_{zz} for the remaining derivatives in Table 1 have not yet been reported. The positive eQV_{zz} for $(CO)_5MnSnCl_3$ shows that the charge distribution about tin is prolate, *i.e.*, there is greater electron density near the tin atom along the *z*-(Sn–Mn bond) direction than in the *xy*-plane, as expected from the greater electronegativity of Cl. The increase in Δ upon replacing one halogen by an organic group is due in part to the non-zero η, but the largest contribution comes from a reorientation of the *z*-axis of the EFG and a concomitant increase in $|V_{zz}|$. When there are two or three organic groups attached to tin, our calculations predict a negative eQV_{zz} (oblate charge distribution). We hope to verify these predictions in the near future. It is relevant to note that eQV_{zz} for tin is positive in $YSnCl_3$ and negative in $YSnBu_3$ ($Y = (\pi\text{-}C_5H_5)Fe(CO)_2$14)) as predicted by the point-charge model.2)

The small (or zero) observed splittings for $(CO)_5MnSnR_3$1) and $[(CO)_5Mn]_2SnPh_2$2) suggest that the σ-bonding characteistics of the $(CO)_5Mn$ group and Me or Ph are quite similar. This presumably accounts for the fact that the predicted value of η is less than ~0.5 for the cases $(CO)_5MnSnR_2X$, and greater than ~0.8 for $(CO)_5MnSnRX_2$. The former molecules approximate to the stoichiometry SnA_3B (for which $\eta = 0$), whilst the latter approximate to SnA_2B_2 (for which $\eta = 1$ if tetrahedral bond angles are assumed).

Finally, it should be noted that our calculations give an adequate estimate of $|\Delta|$ for $(CO)_5MnSn(Cl)[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, in which the tin atom is bonded to two different transition metals.

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6) G. N. Bancroft, K. D. Butler, and A. T. Rake, *J. Organometal. Chem.*, **34**, 137 (1972).

7) R. F. Bryan, *J. Chem. Soc., A*, **1967**, 172, 192.

8) J. E. O'Connor and E. R. Corey, *Inorg. Chem.*, **6**, 968 (1967).

9) P. T. Greene and R. F. Bryan, *J. Chem. Soc., A*, **1970**, 1696, 2261.

10) H. P. Weber and R. F. Bryan, *Acta Crystallogr.*, **22**, 822 (1967).

11) R. F. Bryan, *J. Chem. Soc., A*, **1968**, 696.

12) J. R. Sams and J. C. Scott, unpublished results.

13) E. D. Swiger and J. D. Graybeal, *J. Amer. Chem. Soc.*, **87**, 1464 (1965).

14) B. A. Goodman, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc., A*, **1971**, 1868.

15) A. N. Karasev, N. E. Kolobova, L. S. Polak, V. S. Shpinel, and K. A. Anisimov, *Teor. Eksp. Khim.*, **2**, 126 (1966).

16) V. I. Gol'danskii, B. V. Borshagovskii, E. F. Makarov, R. A. Stukan, K. A. Anisimov, N. E. Kolobova, and V. V. Skripkin, *Teor. Eksp. Khim.*, **3**, 478 (1967).