Signs of Quadrupole Coupling Constants for the Tin(IV) Adducts with Acetonitrile, Triethylphosphine, and Triethylarsine

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The signs of the quadrupole coupling constants are positive for *cis*-$SnCl_4$,2MeCN, *trans*-$SnCl_4$,2PEt_3, and *trans*-$SnCl_4$,2$AsEt_3$ and this is consistent with the order of bond polarity Sn–N (*sp*-hybridized) > Sn–Cl > Sn–P or Sn–As.

WE have recently reported Mössbauer parameters for adducts of tin(IV) halides with amines, nitriles, phosphines, and arsines and found that among the nitrogen donor complexes only those with nitrile groups gave rise to resolved quadrupole splitting.[1] Triphenylphosphine and triphenylarsine adducts gave single-line spectra but quadrupole splitting was induced in the spectra by replacing phenyl by alkyl groups. We tentatively explained the results for these compounds in terms of σ-bonding effects by assuming that the order of bond polarities to tin is $Sn{-}PEt_3 \simeq Sn{-}AsEt_3 < Sn{-}PPh_3 < Sn{-}Cl < Sn{-}N$ (*sp*-hybridized). Without a knowledge of the signs of the quadrupole coupling constants it was not possible to confirm this order. We have now determined the sign of the quadrupole coupling constants (eQV_{zz}) for $SnCl_4$,2PEt_3, $SnCl_4$,2$AsEt_3$, and $SnCl_4$,2MeCN by recording the spectra of powdered samples in an applied magnetic field. The results are in the Table. These are the first reported signs of quadrupole coupling constants for complexes of this type.

Mössbauer data for the complexes

Compound	Δ/mm s^{-1} (observed at liquid-nitrogen temperature)	Δ/mm s^{-1} (computed at 4·2 K)	Sign of eQV_{zz}
$SnCl_4$,2MeCN	0·91	1·03	+
$SnCl_4$,2$AsEt_3$	0·90	0·93	+
$SnCl_4$,2PEt_3	1·15	1·11	+

The field gradient arises both from imbalance in the distribution of electrons in the valence shell of the metal (the valence contribution) and from effects of charges in the crystal lattice (the lattice contribution). Lattice contributions are very small[2] for organotin(IV) compounds, and the contribution of π-bonding to the valence term is small compared with that of σ-bonding.[2–7] For these compounds the sign of the principal component of the field gradient (V_{zz}) will therefore be determined largely by the distribution of electron density in the 5*p* orbitals.[7,8] An excess of negative charge in the p_z orbitals will make a negative contribution to V_{zz} whereas an excess of negative charge in p_x and p_y will give a positive contribution.

An *X*-ray single-crystal analysis[9] of $SnCl_4$,2MeCN has shown that the nitrogen atoms are in *cis*-positions. The octahedral environment of tin is considerably distorted but the *z*-axis is approximately perpendicular to the plane defined by the metal and nitrogen atoms and lies along the unique Cl–Sn–Cl direction. Thus the positive sign observed for the quadrupole coupling constant (which means V_{zz} is negative because *eQ* for ^{119}Sn is negative) can be visualized as arising from a concentration of *p*-electron density in this direction. This charge distribution can be accounted for if it is assumed that the Sn–N bond is more polar, *i.e.*, $Sn^{\delta+}{-}N^{\delta-}$, than the Sn–Cl bonds. There are no *X*-ray structural data available for $SnCl_4$,2PEt_3 or $SnCl_4$,2$AsEt_3$ but i.r. and Raman spectroscopic data strongly suggest that the bulky phosphine[1,10] and arsine[1] groups occupy *trans*-positions. The quadrupole coupling constants are also positive for both these complexes. This means that there is again a concentration of *p*-electron density along the direction of V_{zz}, but in these complexes V_{zz} is directed towards donor groups and not along a Cl–Sn–Cl direction. This is consistent with our previous suggestion that the Sn–Cl bonds are much more polar than the Sn–P or Sn–As bonds. Hence the signs of the quadrupole coupling constants are consistent with an overall order of bond polarity in the direction Sn–N (*sp*-hybridized) > Sn–Cl > Sn–As or Sn–P.

Asymmetry parameters (η) of the order of 0·5 were indicated for each of the three complexes which suggest a distorted octahedral environment for tin in all cases. For $SnCl_4$,2MeCN a value of 0·5—0·6 for η is obtained from a point-charge calculation based on the known structure.

EXPERIMENTAL

The preparation of the complexes has been reported.[1] The Mössbauer spectra were recorded at P.C.M.U., Harwell. Least-squares fits of the spectra were obtained by use of proven routines to simulate the spectra[11] and to minimize the sum of squares.[12]

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