halogen compounds on going from Cl to Br to I (*e.g.*, CH_3X,[12] HX,[12] X_2[13]). Thus, our assignment of band IV as an ionization from the X level leads to a more acceptable X_π-X_σ separation with respect to the trend on variation of halogen.

We believe that our results and line of reasoning (applicable to both the Mn and Re complexes) clearly establish the ordering $X_\pi > b_2 > e > X_\sigma$ for the $M(CO)_5X$ molecules under discussion. The advantages of varying the metal as well as the ligand as an aid to interpreting photoelectron spectra of transition metal complexes have been clearly demonstrated.

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Registry No. $Re(CO)_5Cl$, 14099-01-5; $Re(CO)_5Br$, 14220-21-4; $Re(CO)_5I$, 13821-00-6.

(12) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, London, 1970, Chapter 8.

(13) D. C. Frost, C. A. McDowell, and D. A. Vroom, *J. Chem. Phys.*, 46, 4255 (1967).

Contribution from the Department of Chemistry,
Colorado Women's College, Denver, Colorado 80220
and New England Institute, Ridgefield, Connecticut 06877

Tin-119m Mossbauer Spectra of Para-Substituted Dichlorotetraphenylporphinatotin(IV) Complexes

Nordulf W. G. Debye* and Alan D. Adler

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In a previous report of the Mossbauer spectra of various tin complexes of phthalocyanine and tetraarylporphins,[1] Curran and O'Rourke indicated their inability to resolve a possible quadrupolar splitting in the spectra of four dichlorotetraarylporphinatotin(IV) compounds. We now wish to report the successful resolution of the quadrupolar splittings in seven such compounds including those studied by Curran and O'Rourke. The compounds are all derivatives of dichlorotetraphenylporphinatotin(IV), hereafter identified as Cl_2Sn-TPP, differing by various substitutions at the para positions of the four phenyl groups. The seven substituents studied were F, Cl, Br, CH_3, OCH_3, and i-C_3H_7, in addition to the H of the parent compound, and were prepared and characterized by previously reported methods.[2]

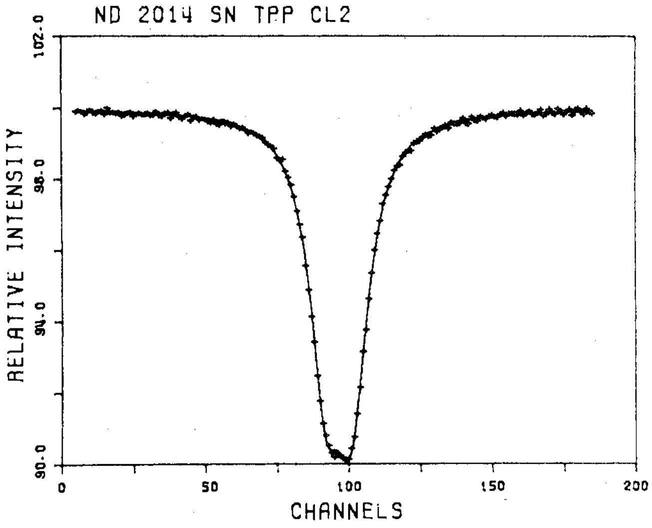

Figure 1. ^{119m}Sn Mossbauer spectrum of dichlorotetraphenylporphinatotin(IV), Cl_2SnTPP, at 80 K.

Table I. ^{119m}Sn Mossbauer Spectral Parameters of Para-Substituted Cl_2SnTPP

Compd	IS^{a-c}	QS^{a,b,d}	Area ratio^e
$Cl_2SnT(p\text{-}i\text{-}C_3H_7)PP$	0.160 (0.010)	0.512 (0.012)	0.65
$Cl_2SnT(p\text{-}CH_3)PP$	0.153 (0.008)	0.592 (0.010)	0.77
Cl_2SnTPP	0.146 (0.007)	0.588 (0.008)	0.73
$Cl_2SnT(p\text{-}OCH_3)PP$	0.147 (0.008)	0.555 (0.010)	0.75
$Cl_2SnT(p\text{-}Br)PP$	0.147 (0.005)	0.659 (0.007)	0.80
$Cl_2SnT(p\text{-}Cl)PP$	0.154 (0.006)	0.642 (0.007)	0.87
$Cl_2SnT(p\text{-}F)PP$	0.165 (0.013)	0.463 (0.018)	0.60

[a] Isomer shift (with respect to $BaSnO_3$) and quadrupole splitting in mm/sec, defining the room-temperature parameters of our $(CH_3)_2$-SnF_2 calibration sample to be IS = 1.2455 mm/sec and QS = 4.4945 mm/sec. All spectra were recorded at 80 K. [b] Numbers in parentheses represent the *ca.* 68% confidence level in the precision. [c] Correlation index for the two wing positions taken to be +1.0 during calculation of σ. [d] Correlation index for the two wing positions taken to be 0.0 during calculation of σ. [e] Area of high-energy wing divided by area of low-energy wing.

A representative spectrum clearly showing such a resolved splitting is shown in Figure 1 and a summary of all the ^{119m}Sn Mossbauer spectral parameters obtained at 80 K is given in Table I. All spectra were obtained with a $Ba^{119m}SnO_3$ source held at room temperature and the isomer shift (IS) values are reported with respect to a $BaSnO_3$ absorber at room temperature. The uncertainties indicated in parentheses for both the IS and the quadrupole splitting (QS) represent the 1σ confidence range for the precision of the evaluated parameters; we estimate the overall 1σ confidence level, including both uncertainties in the precision and the accuracy, to require the addition of 0.01 mm/sec to the stated numbers. The total count accumulation per data point for these spectra range from one to ten million and all compounds demonstrated a large resonance effect. Spectrometer calibration spectra were "time-sandwiched" about each sample spectrum and the expressed uncertainties are the pooled uncertainties of each sample spectrum and two calibration spectra. The spectral parameters were obtained with the aid of the PARLOR computer program[3] which assumes that the spectra represent independent lorentzian absorption curves on a parabolic base line.

The seven compounds clearly exhibit variations in the quadrupole splitting outside of the stated uncertainties in addition to more poorly defined variations in their isomer shifts. The presence of these resolvable splittings is somewhat surprising as the tin atom is bonded only to other atoms which all possess lone-pair electrons, a bonding situation which usually results in a singlet spectrum. Correlations of both spectral parameters (IS, QS) with the following empirical

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* To whom correspondence should be addressed at Colorado Women's College.

(1) M. O'Rourke and C. Curran, *J. Amer. Chem. Soc.*, 92, 1501 (1970).

(2) A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Org. Chem.*, 32, 476 (1967); A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, 32, 2443 (1970); A. D. Adler and J. L. Harris, *Anal. Biochem.*, 14, 472 (1966).

(3) E. Rhodes, W. O'Neal, and J. J. Spijkerman, *Nat. Bur. Stand. (U. S.), Tech. Note*, No. 104, 108 (1966); further information concerning this program may be obtained from Dr. John C. Travis, National Bureau of Standards, Washington, D. C. 20234.

characteristics of the substituents have been attempted: Hammett σ_P constants,[4] substituent electronegativities from ν_{PO} bond vibrations,[5] empirically derived mutually consistent group electronegativities using various data,[5] Hammett σ_I constants,[6] and substituent steric requirements. The advantages and disadvantages of these materials in looking for such correlation phenomena have been recently considered in some detail.[7,8]

We find only a weak positive correlation of the IS with the substituent electronegativities indicating a slightly increasing total s-electron density at the tin nucleus with increasing electron-withdrawing capacity of the para substituent. In addition, we find some correlation of the IS with the QS as the magnitude of the observed splitting generally decreases with increasing shift values.[7] Such behavior is consistent with slightly decreasing coordination abilities of the nitrogen atoms toward the central tin atom.[9] Both of the above correlations would be consistent with the conclusion that the degree of coordination between the tin and the nitrogens in these compounds varies due to the inductive transmittal of electronic effects from the phenyl para positions. One might thus expect to find a slightly larger central hole in the F-substituted compound than in the parent Cl_2SnTPP. Unfortunately, only the structure of the latter has been reported.[10]

All seven compounds studied here exhibit distinct asymmetries in their doublet Mossbauer spectra. The ratio of the high-energy wing area to the low-energy wing is indicated for each sample spectrum in Table I. It is quite apparent that increased area asymmetries are accompanied by decreased splittings. Such asymmetry variations (if indeed due to variations in the bonding environment of the tin) should represent variations in the spatial anisotropy of the recoil-free fraction of the tin atoms.[11] One might expect the tin to be more tightly bound in the "plane" roughly defined by the nitrogen atoms rather than along the Cl–Sn–Cl axis. All of the Mossbauer measurements were obtained with finely powdered samples but, because nonrandom orientations of the microcrystals could also lead to spectral asymmetries, several of the compounds were repeatedly reground and reexamined. No significant changes in the doublet asymmetries were observed, thus indicating a random orientation of the polycrystalline absorbers.

Possible line shape model errors in the spectrum-fitting routine have been considered and we are quite confident that they are negligible in the determination of the IS and QS from these well-fitted spectra. The distribution of the calculated residuals is uniform across the absorption peak of each spectrum. The supposed quadrupolar-split spectra may, however, actually be the result of two very closely spaced singlets originating from two crystal forms of each compound; the two forms differ, perhaps, by the orientations of the phenyl groups. We have no evidence to support such a supposition and these data indicate that both crystal forms would be equally prevalent, which on stereochemical considerations of the possible structures would be unlikely. Careful analyses of these spectra in a strong external magnetic field would, however, differentiate between a genuine doublet and two closely spaced singlets. Chemical impurities at a 50% level are known not to be significant in these chromatographically purified and analytically characterized compounds.[2]

We conclude, therefore, that though all of these complexes exhibit discernible doublet ^{119m}Sn Mossbauer spectra with various magnitudes of the splitting, the causes are not completely clear. The doublets might be two singlets, closely spaced and representing two structural forms of the complexes, although we consider this unlikely. Differences in the crystal packing arrangements of these solid-state complexes might also yield variations in the electric field gradient (EFG) at the tin nuclear site, but such sensitivity of the EFG to long-range interactions would be highly unusual for such molecular solids. As a further consideration, we have estimated the effect of slight movements of the tin atom along the Cl–Sn–Cl axis on the basis of the point-charge model[12] and found that if the atom were to pop out of the central hole by up to 0.2 Å, then the QS might be expected to vary by about 10–15%, as observed. The effect of such a distortion upon the IS would probably be very small as the accompanying rehybridization of the tin bonding orbitals would not substantially affect the total s-electron density at the tin nucleus. However, an independent test (and confirmation) of this explanation of the data requires further X-ray structural analyses of some of the substituted complexes.

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Registry No. $Cl_2SnT(p\text{-}i\text{-}C_3H_7)PP$, 52628-87-2; $Cl_2SnT(p\text{-}CH_3)PP$, 26334-83-8; Cl_2SnTPP, 26334-85-0; $Cl_2SnT(p\text{-}OCH_3)PP$, 26334-82-7; $Cl_2SnT(p\text{-}Br)PP$, 52628-86-1; $Cl_2SnT(p\text{-}Cl)PP$, 26334-84-9; $Cl_2SnT(p\text{-}F)PP$, 52628-88-3.

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(4) H. H. Jaffe, *Chem. Rev.*, 53, 191 (1953).

(5) P. R. Wells, *Progr. Phys. Org. Chem.*, 6, 111 (1968).

(6) R. W. Taft, *J. Chem. Phys.*, 64, 1805 (1960); P. R. Wells, *Chem. Rev.*, 63, 171 (1963).

(7) A. D. Adler, *Ann. N. Y. Acad. Sci.*, 206, 7 (1973).

(8) M. Meot-Ner and A. D. Adler, *J. Amer. Chem. Soc.*, 94, 4763 (1972).

(9) R. L. Collins and J. C. Travis, *Mossbauer Eff. Methodol.*, 3, 123 (1967).

(10) J. L. Hoard, *Science*, 174, 1295 (1971); D. M. Collins, W. R. Scheidt, and J. L. Hoard, *J. Amer. Chem. Soc.*, 94, 6689 (1972).

(11) S. V. Karyagin, *Dokl. Akad. Nauk SSSR*, 148, 110 (1963).

(12) B. W. Fitzsimmons, N. J. Seeley, and A. W. Smith, *Chem. Commun.*, 390 (1968); R. V. Parish and R. H. Platt, *Inorg. Chim. Acta*, 4, 65 (1970); N. W. G. Debye and J. J. Zuckerman in "Determination of Organic Structures by Physical Methods," Vol. 5, F. C. Nachod and J. J. Zuckerman, Ed., Academic Press, New York and London, 1973, p 235.

Contribution from the Department of Chemistry,
University of Georgia, Athens, Georgia 30602

Some Studies on Tungsten Carbonyl Nitrosyl Derivatives

R. B. King,* M. S. Saran,[1] and S. P. Anand[2]

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Cleavage of the metal–metal bond in bimetallic metal carbonyl derivatives such as $[C_5H_5M(CO)_3]_2$ (M = Mo, W), $M_2(CO)_{10}$ (M = Mn, Re), and $[C_5H_5M(CO)_2]_2$ (M = Fe, Ru) by reagents such as halogens and alkali metals provides useful routes to interesting monometallic transition metal derivatives.[3] In this connection, the recently reported[4] unsymmetrical bimetallic tungsten carbonyl nitrosyl hydride

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(1) Postdoctoral research associate, 1969–1974.

(2) Postdoctoral research associate, 1973–1974.

(3) R. B. King, "Transition Metal Organometallic Chemistry: An Introduction," Academic Press, New York, N. Y., 1969.

(4) M. Andrews, D. L. Tipton, S. W. Kirtley, and R. Bau, *J. Chem. Soc., Chem. Commun.*, 181 (1973).