a value extrapolated over a very large distance. The choice of aromatic hydrocarbons as standards was suggested by the consideration that Franck–Condon factors in aromatic hydrocarbons would approximate those in the metal acetylacetonates better than those in smaller molecules would, and of course those in noble gases! These points may account for the discrepancy between our values and the values reported earlier[3b] for compounds **1** and **4**.[18–21]

Data were obtained on a modified Hitachi RMU-6E mass spectrometer in at least sextuplicate on at least two different days for each of the sets of experimental data summarized in Figure 1. The sets of data were repeated with different ion sources. They were recorded at the same accelerating voltage; the closest standard, anthracene, has mol wt 178, and therefore mass discrimination effects should be less than in other studies. Internal correlations for this set and others[5,19] suggest that the data within themselves are good to about ±0.03 eV, as measured by the closeness of fit of data points to correlation lines. While our precision is ±0.02 eV in general, and our internal accuracy for the set 0.03 eV, we of course do not claim absolute accuracy greater than what is generally found for electron-impact methods, ±(0.1–0.2) eV.

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[18] The energy compensation technique gave a high value for the IP of benzene in the original investigation on a time-of-flight instrument.[14] On the other hand, our single-point results were reproduced in another study[19] to within ±0.05 eV on the average by a semilogarithmic-plot[20] method on an MS902 mass spectrometer in which different standards were used.[21]

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Nuclear Quadrupole Coupling in Bis(tetracarbonylcobalt)tin Compounds

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Prior studies of a series of compounds formed by insertion of a metal-containing group into a $Co_2(CO)_8$ molecule have revealed several features regarding the stretching frequencies and the intensities of the infrared spectra of these compounds.[3] These features include (1) the observation that there is appreciable coupling between the $Co(CO)_4$ groups, (2) a shift to higher frequencies of the CO stretching frequencies with increasing halogen substitution on the metal atom, and (3) an increase in the Co–M–Co bond angle as determined by relative intensity measurements of the infrared bands. The ^{59}Co and ^{35}Cl pure quadrupole resonances have been observed and measured in dichlorobis(tetracarbonylcobalt)tin(IV), $Cl_2Sn[Co(CO)_4]_2$, chlorophenylbis(tetracarbonylcobalt)tin(IV), $Cl(C_6H_5)Sn[Co(CO)_4]_2$, and diphenylbis(tetracarbonylcobalt)tin(IV), $(C_6H_5)_2Sn[Co(CO)_4]_2$. This study of these compounds was made in order to correlate the ir and nqr data and to provide a basis for the establishment of a model of the bonding in the system.

Experimental Section

The compounds studied were prepared by the procedure of Patmore and Graham.[3] Their identity was ascertained by colors, melting points, and infrared spectra. Observations and measurements of the frequencies of the resonances were made using a noise-controlled superregenerative spectrometer.[4] Three-gram samples were used. All measurements were made at 25°. Frequency measurements were made by switching the oscillator to continuous wave operation *via* application of a high voltage to the control grid and measurement of the oscillator frequency with a Hewlett Packard 5245L frequency counter. For known resonances this method gives agreement to ±0.002 MHz.

Results and Discussion

The observed resonances are given in Table I. Also given are the nuclear quadrupole coupling constants, e^2Qq_{zz}, and the asymmetry parameters. For ^{59}Co, which has a nuclear spin $I = {}^7/_2$, both e^2Qq_{zz} and η were obtained from the experimental frequencies by use of series approximations for the transition frequencies.[5] The values were further confirmed by use of a frequency ratio plot.[6]

The occurrence of two resonances for each compound indicates two inequivalent crystallographic sites for the Co atoms in each. If the Co atom is in a trigonal-bipyramidal configuration, then the threefold axis dictates that $\eta = 0$. The values of η observed experimentally are small and are undoubtedly due to intermolecular forces in the crystal and/or nonsymmetrical sites due to crystal packing eliminating the strict C_{3v} site symmetry. This view is substantiated by the fact that there are differences in η for the two crystalline sites in these compounds and that these differences are of the same order of magnitude as the values of η. Were the magnitudes of the η's dependent primarily on the intramolecular bonding, then η should be nearly the same for all sites with the differences being due to intermolecular effects.

To discuss the bonding in this compound one can proceed *via* two paths: (1) comparison of the experimental parameters with those of similar compounds; (2) comparison of experimental coupling constants with calculated coupling constants, based on some molecular model.

The e^2Qq_{zz}'s and η's for the compounds studied along with those of several related compounds are given in Table II. A comparison of the data given in this table leads to several observations. (1) The inductive effect of a Cl atom bonded to a Sn atom will increase the electron affinity of the empty 4d orbitals of the Sn

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TABLE I

NQR PARAMETERS FOR BIS(TETRACARBONYLCOBALT)TIN(IV) COMPOUNDS

Compound	^{59}Co resonance freq,[a] MHz $\nu_1(S/N)$	$\nu_2(S/N)$	$\nu_3(S/N)$	e^2Qq_{zz}, MHz	η	^{35}Cl resonance freq, MHz $\nu(S/N)$
$Cl_2Sn[Co(CO)_4]_2$	10.853 (5)	21.243 (8)	31.926 (8)	149.1 ± 0.2	0.065	17.676 (3)
	10.516 (5)	20.607 (8)	30.988 (8)	144.8 ± 0.2	0.074	17.150 (3)
$ClC_6H_5Sn[Co(CO)_4]_2$	*b*	18.356 (2)	27.500 (2)	128.4 ± 0.2	0.051	*b*
	b	18.100 (2)	27.250 (2)	126.9 ± 0.2	0.089	
$(C_6H_5)_2Sn[Co(CO)_4]_2$	*b*	16.075 (2)	24.219 (2)	113.1 ± 0.2	0.094	
	b	16.030 (2)	24.089 (2)	112.7 ± 0.2	0.063	

[a] Experimental error for all frequencies is ±0.004 MHz. [b] Not observed.

TABLE II

NQR DATA FOR TIN COMPOUNDS

Compound	$e^2Qq_{zz}(^{59}Co)$,[a] MHz	$e^2Qq_{zz}(^{35}Cl)$,[a] MHz	(Co)	(Cl)	Ref
$Cl_2Sn[Co(CO)_4]_2$	146.9	30.0[f]	0.070		
$ClC_6H_5Sn[Co(CO)_4]_2$	127.7	. . .	0.070		
$(C_6H_5)_2Sn[Co(CO)_4]_2$	112.9		0.078		
$Cl_3SnCo(CO)_4$	163.45	39.76[f]	0.0		*b*
$(C_6H_5)_3SnCo(CO)_4$	104.11		0.05		*b*
$SnCl_4$		47.7		0.25	*c*
$Cl_2Sn(CH_3)_2$		30.8		0.34	*d*
$Cl_2Sn(C_6H_5)_2$		35.7[f]		. . .	*e*

[a] Average for multiple resonances. [b] T. L. Brown, P. A. Edwards, C. B. Harris, and J. L. Kirsch, *Inorg. Chem.*, **8,** 763 (1969). [c] J. D. Graybeal and P. J. Green, *J. Phys. Chem.*, **73,** 2948 (1969). [d] J. D. Graybeal and B. A. Berta, Proceedings of the 2nd Materials Research Symposium, National Bureau of Standards, U. S. Government Printing Office, Washington, D. C., 1967, p 393. [e] P. J. Green and J. D. Graybeal, *J. Amer. Chem. Soc.*, **89,** 4305 (1967). [f] Assumed $\eta = 0$.

atom. This will tend to drain electron density from the filled Co 3d orbitals and in turn will remove electron density from the CO π^* orbital. The net effect will be to (a) free some of the s character of the tin atoms from the Sn–Cl bond and make it more available in the Sn–Co bond, (b) decrease the net electron population of the Co atom, and (c) strengthen the C≡O bond. These effects will result in (a) an increase of the Co–Sn–Co bond angle, (b) an increase in e^2Qq_{zz}(Co), and (c) an increase in the C–O stretching frequency with increased Cl substitution. The first and third points have been substantiated by Patmore and Graham[3] while this work confirms the second. (2) The replacement of a $Co(CO)_4$ group by a Cl atom shows a substantial increase in e^2Qq_{zz}(Co) further confirming the concept of reduced electron density on the Co atoms due to halogen inductive effect. (3) The value of e^2Qq_{zz}(Cl) increases going from $Cl_2Sn[Co(CO)_4]_2$ to $SnCl_4$ rather than decreases as one might expect if the Cl atom gained electron density. This observed change indicates that the net electron density change on the Sn atoms is relatively small and is insufficient to provide any net increase of electron density on the Cl atoms in view of the increased competition of the large number of Cl atoms.

The magnitude of the observed coupling constants can be rationalized on the basis of a simplified calculation of the electric field gradient (EFG) tensor components and the use of an electronically analogous system to estimate orbital populations. By using a hydrogen-like wave function for a $3d_{z^2}$ orbital and the effective atomic number of Co given by Korol'kov and Makhanek,[7] the EFG tensor component, expressed as a coupling constant component, e^2Qq_{320}, is estimated to be 615 MHz. The total coupling constant is found by summing the contributions of all electrons present

$$e^2Qq_{zz} = e^2Qq_{320}\left[N_{d_{z^2}} + \frac{N_{d_{xz}} + N_{d_{yz}}}{2} - N_{d_{xy}} - N_{d_{x^2-y^2}}\right] + e^2Qq_{410}\left[N_{p_z} - \frac{N_{p_x} + N_{p_y}}{2}\right]$$

The magnitude of q_{410} is less than one-fifth that of q_{320}.[7] Using the electron densities calculated by Schreiner and Brown[8] for $Fe(CO)_5$ and $q_{410} = 0.2q_{320}$, the estimated value of e^2Qq_{zz} is 204 MHz.

This calculated value is related to the observed value by

$$(e^2Qq_{zz})_{\text{obsd}} = (e^2Qq_{zz})_{\text{calcd}}(1 - R)$$

where R is the Steinheimer shielding factor for an open-shell system. Calculations to date show $-0.3 < R < 0.2$.[9] When one considers that the lower electronegativity of tin as compared to carbon would probably result in $N_{d_{z^2}}$ being larger in these compounds as compared to the completely symmetric type, this estimate of e^2Qq_{zz} is reasonable.

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