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THE PURE NUCLEAR QUADRUPOLE RESONANCE SPECTRUM  
OF COBALT-59 IN ADDUCTS OF COBALT TETRACARBONYL,  
 $MX_3Co(CO)_4$

Theodore L. Brown, P. A. Edwards, Charles B. Harris  
and Joseph L. Kirsch

October, 1968

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Contribution from the Inorganic Materials Research Division,  
Lawrence Radiation Laboratory and the Department of Chemistry,  
University of California, Berkeley and Materials Research Laboratory  
and Noyes Chemical Laboratory, University of Illinois, Urbana

The Pure Nuclear Quadrupole Resonance Spectrum of Cobalt-59

in Adducts of Cobalt Tetracarbonyl,  $\text{MX}_3\text{Co}(\text{CO})_4$ <sup>1</sup>

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and Joseph L. Kirsch<sup>2a</sup>

#### ABSTRACT

The <sup>59</sup>Co pure nuclear quadrupole resonance spectra of a series of trigonally coordinated cobalt complexes,  $\text{MX}_3\text{Co}(\text{CO})_4$ , where M = Si, Ge, Sn, Pd, and X = Cl, Br, I, and C<sub>6</sub>H<sub>5</sub>, are reported. The <sup>35,37</sup>Cl quadrupole resonance in  $\text{SiCl}_3\text{Co}(\text{CO})_4$  are also reported. The variation in field gradients obtained from the quadrupole coupling constants in these molecules can be interpreted in terms of  $\sigma$  and  $\pi$  bonding of  $\text{MX}_3$  to the cobalt. In certain cases explicit  $\sigma$  or  $\pi$  effects can be separated. Finally, strong evidence for the existence of Si-Cl  $d\pi-p\pi$  bonding is presented.

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- (1) Paper III in the series Transition Metal Nuclear Quadrupole Resonance by CBH and co-workers.
  - (2) a. Noyes Chemical Laboratory, University of Illinois, Urbana, 61801.  
b. Department of Chemistry, University of California, Berkeley.
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## INTRODUCTION

Recently a series of compounds,  $\text{MX}_3\text{Co}(\text{CO})_4$  (M = a group IV element and X = halide or organic group), have been synthesized. These organometallic complexes represent a general class of trigonally coordinated ( $\text{C}_{3v}$ ) cobalt<sup>4-6</sup> characterized by heteronuclear M-Co metal-metal bonds.

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- (4) W. T. Robinson and J. A. Ibers, Inorg. Chem., 6, 1208 (1967).  
(5) G. M. Shedrick and R. N. F. Simpson, J. Chem. Soc., 1005, 1968A.  
(6) B. T. Kilbourn, T. L. Blundell and H. M. Powell, Chem. Comm., 444, 1965.

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Unlike alkyl and hydride derivatives of cobalt tetracarbonyl, they exhibit high thermal stability. It has been suggested that this can be associated or correlated with strong M-Co  $\pi$  bonding since it is only when M is characterized as  $\pi$  acceptor that the compounds appear to be more stable. Infrared studies of the carbonyl modes and other physical data have been reported to provide evidence for the existence of extensive  $\pi$  bonding,<sup>7-10</sup>

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- (7) a. D. J. Patmore and W. A. G. Graham, Inorg. Chem., 6, 981 (1967).  
b. Ibid., 7, 771 (1968).  
(8) A. P. Hagen and A. G. McDairmid, Inorg. Chem., 6, 686 (1967).  
(9) L. Marko, G. Bor, G. Almasy and P. Szabo, Brennstoff. Chem., 44, 194 (1963).  
(10) O. Kahn and M. Bigorgne, J. Organometal. Chem., 10, 137 (1967).
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however, no conclusive results have heretofore been put forth to separate  $\pi$  from the  $\sigma$  effects.

Because nuclear quadrupole resonance provides a probe capable of elucidating small changes in the electron distribution in molecules, it can, along with other spectroscopic and structural information, provide new insights into the nature of the Co-M bond for a variety of  $\text{MX}_3$  species. Furthermore, when the quadrupole nucleus,  $^{59}\text{Co}$ , is at the origin of a molecular point group, as in the present case, it is possible in principle to separate changes in  $\sigma$  and  $\pi$  bonding in a series of isoelectronic and isostructural molecules.<sup>11</sup> We therefore report here the study of the pure

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(11) See C. B. Harris, Inorg. Chem., 7, 1517 (1968), and references therein.

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nuclear quadrupole resonance spectra of  $^{59}\text{Co}$  in the above compounds.

#### EXPERIMENTAL

Synthesis. Synthetic procedures for the substituted tetracarbonyl compounds were taken from the literature.<sup>7,10,12</sup> Reactions were carried out

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(12) A. J. Chalk and J. H. Harrod, J. Amer. Chem. Soc., 87, 1133 (1965).

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on a scale large enough to provide 3-5 grams of pure products. All samples were identified by carbon, hydrogen, and where appropriate, halogen analysis and their purity was further confirmed by infrared spectra usually taken after repeated sublimation to insure the absence of bands in the carbonyl

stretching region due to impurities in the form of other cobalt carbonyl compounds. All compounds were sealed under a nitrogen atmosphere to insure against decomposition.

Nuclear Quadrupole Resonance Spectra. The spectra obtained at the University of Illinois were obtained with a self-quenching zeeman modulated super-regenerative spectrometer. The oscillator is similar to that described by Graybeal and Croston,<sup>13</sup> but incorporates a number of minor changes.

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(13) J. D. Graybeal and R. P. Croston, Rev. Sci. Instr., 37, 376 (1966).

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A coherence control system, designed at the University of Illinois but patterned after that reported by Peterson and Bridenbough<sup>14</sup> was employed

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(14) a. G. E. Peterson and P. M. Bridenbough, Rev. Sci. Instr., 35, 698 (1964).

b. Ibid., 36, 702 (1965).

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to maintain the appropriate oscillator conditions for wide range scanning. A modulation frequency of 100 Hz was applied to a pair of Helmholtz coils which provided a magnetic field of approximately 50 gauss. Phase sensitive detection was accomplished through a Princeton Applied Research Laboratory Model JB5 lock-in-amplifier. Spectra were normally obtained using a sweep rate of about 1 MHz per hour, and an 8 second time constant.

Frequencies were measured in most instances to an accuracy of approximately 1 KHz, utilizing a Drake Model R-4A receiver fitted with a frequency converter which permitted continuous tuning of the receiver over

a wide range of frequencies by selection of a suitable crystal. The receiver was equipped with a 100 KHz calibrator and the dial is scribed units of KHz. Using this arrangement, it was possible to place calibrating markers on the recorder chart paper with an event marker at convenient intervals. Interpolation between such markers provides a measure of any desired frequency to an accuracy of 1 KHz. When problems of distinguishing the center frequency from the side band frequency arose, accuracy to about 0.05 MHz could be obtained by a Tektronix spectrum analyzer coupled to a convenient frequency reference.

The spectrometer employed at the University of California is a high power push-pull super-regenerative spectrometer.<sup>15</sup> In the case of

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(15) C. B. Harris, unpublished work; G. E. Peterson, private communication.

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$\text{SnBr}_3\text{Co}(\text{CO})_4$  the frequencies were detected and measured by a fast-sweep marginal oscillator.<sup>16</sup> Frequencies were measured by spectrum analyzing

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(16) M. D. Fayer and C. B. Harris, unpublished work.

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techniques.<sup>17</sup>

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(17) G. E. Peterson and P. M. Bridenbough, Rev. Sci. Instr., 37, 1081 (1966).

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Variable temperature measurements (University of Illinois) were carried out using the cold cell depicted in Figure 1. The cell consists of a pair of coaxial, rectangular pipes fabricated of Plexiglass, which

provide for the passage of nitrogen (obtained from boiling off liquid nitrogen) over the sample, through the surrounding cell compartments, and out. Temperatures to  $-170^{\circ}\text{C}$  were readily obtained by control of the nitrogen boil-off rate. Using a 20 liter dewar with a short run of insulated line to the cold chamber permitted the maintenance of a temperature of  $-130^{\circ}\text{C}$  for a period of 8 hours with no attendance.

### RESULTS AND DISCUSSION

In nuclear quadrupole resonance, one measures the interaction of a nuclear quadrupole moment,  $Q$ , with a field gradient,  $q$ , around a given nucleus. A requirement for a nucleus having a quadrupole moment is that its nuclear spin be greater than  $1/2$ ; for  $^{59}\text{Co}$ ,  $I = 7/2$  and the requirement for an finite field gradient is that the total electronic potential surrounding the given nucleus be neither spherical nor cubic in symmetry; in the case of the  $\text{MX}_3\text{Co}(\text{CO})_4$  compounds, the symmetry is  $\text{C}_{3v}$ . One expects, therefore, to measure a field gradient which can be related via a valence bond or molecular orbital interpretation to the electron distribution indicative of the bonding in these compounds. Because the cobalt is located on the principal axis of the  $\text{C}_{3v}$  point group, the populations of various valence orbitals can be related in a simple way to the angular momentum functions of the electrons which diagonalize the field gradient tensor. In this way, one can, in principle, distinguish electron populations representative of  $\pi$  and  $\sigma$  bonding. Three radio frequency transitions are expected for a nucleus with a spin of  $7/2$ . When the cobalt nucleus experiences an axially symmetric field gradient tensor due to the three-fold axis, relative transition frequencies of 3:2:1 are expected for the nuclear transitions from

Table I. Pure Quadrupole Resonance Data for  $^{59}\text{Co}$ ,  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  in Tetracarbonyl  
Cobalt Compounds,  $\text{Co}(\text{CO})_4\text{MX}_3$

Ligand, L	Temperature °C.	$^{59}\text{Co}$ Resonance <sup>a</sup> (MHz)			$\eta$	$eQq_{zz}$ <sup>b</sup> (MHz)	$^{35}\text{Cl}$	$^{37}\text{Cl}$
		$\nu_3$	$\nu_2$	$\nu_1$				
$\text{SiCl}_3^-$	25	27.957 (100)	18.500 (50)	9.825(3)	0.13	130.67	19.225(25)	15.137(5)
							*19.060(25)	15.000(5)
							18.975(25)	14.950(5)
							*19.175(25)	
	-88		18.675 (50)				*19.175(25)	
	-124		18.750 (12)				*19.275(5)	
	-150		18.800 (5)				*19.307(5)	
$\text{GeCl}_3^-$	25	34.620 (5)	23.090 (10)		0	161.56		
		34.150 (5)	22.770 (10)			159.37		
$\text{GeBr}_3^-$	25	34.573 (10)	22.918 (5)		0.12	161.34		
$\text{GeI}_3$	25	34.078 (10)	22.694 (5)		0.04	159.08		
$\text{SnCl}_3^-$	25	35.025 (10)	23.375 (20)	11.675(5)	0	163.45	19.880(3)	
			23.687 (15)					
			23.785 (7)					
			23.835 (7)					
	-90							
	-133							
	-154							
$\text{SnBr}_3^-$	25	34.2692(100)	22.7900(100)	11.650(4)	0.06	159.91		
$\text{SnI}_3^-$	25	32.786 (100)	21.815 (100)	11.052(4)	0.06	153.04		
$(\text{C}_6\text{H}_5)_3\text{Si}-$	25	21.662 (14)	14.434 (9)		0	101.09		
$(\text{C}_6\text{H}_5)_3\text{Sn}-$	25	22.304 (7)	14.852 (10)		0.05	104.11		
$(\text{C}_6\text{H}_5)_3\text{Pb}-$	25	23.741 (11)	15.806 (9)		0.05	110.82		

<sup>a</sup>Figures in parenthesis are signal to noise ratios.

<sup>b</sup> $eQq_{zz}$  is calculated from the observed values for  $\nu_2$  and  $\nu_3$  using the Dehmelt and Kruger expressions.<sup>18</sup>

\*The temperature dependence of the central  $^{35}\text{Cl}$  resonance was observed.

$\pm 5/2 \rightarrow \pm 7/2$ ,  $\pm 3/2 \rightarrow \pm 5/2$ , and  $\pm 1/2 \rightarrow \pm 3/2$ , respectively.<sup>18,19</sup> In all

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(18) H. Demelt and H. Kruger, Z. Physik., 130, 385 (1951).

(19) M. H. Cohen, Phys. Rev., 96, 1278 (1954).

---

cases, the deviations from axial symmetry as measured by the asymmetry parameter,  $\eta$ , are small, and can be attributed to the packing of the molecules in the solid state. Chlorine resonances (both  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ ) were detected in a number of compounds. For these nuclei ( $I = 3/2$ ) only one transition, the  $\pm 1/2 \rightarrow 3/2$ , is observed. The ratio of the  $^{35}\text{Cl}$  to  $^{37}\text{Cl}$  resonant frequencies is 1.269 for nuclei in equivalent lattice sites. The quadrupole resonance data obtained are listed in Table I. The lowest  $^{59}\text{Co}$  resonance is always of low intensity and could not be located in some cases.

It is evident from the data that the asymmetry parameter for cobalt in all compounds studied is zero or nearly so. This result is in keeping with the trigonal symmetry expected for the molecular species. Deviations from trigonal symmetry as in  $\text{SiCl}_3\text{Co}(\text{CO})_4$  for which crystal structure information is available,<sup>4</sup> results from crystal packing, i.e., the molecule occupies a lattice site of lower than trigonal symmetry and is slightly distorted. This distortion, which results in a small non-zero value for the asymmetry parameter leads to a multiplicity of closely spaced chlorine resonances.

It is apparent from the data that the  $^{59}\text{Co}$  resonances are strongly dependent upon the nature of the ligand bonded on the three-fold axis. In order to simplify the interpretation of the changes in the quadrupole

coupling constant with variation of the ligand, it is useful to assume that the geometry of the molecules is constant. Variables in the geometry which might be important are the angle made between the equatorial CO and radial CO, and the departure from three-fold symmetry of the equatorial carbonyls (cf., Fig. 2). If these angles were to vary considerably from one substituent to the next, the interpretation of the field gradient would be complicated considerably. It does not appear, however, that these angles are subject to a great deal of change. In  $\text{SiCl}_3\text{Co}(\text{CO})_4$ ,<sup>4</sup>  $(\text{C}_6\text{H}_5)_3\text{PAuCo}(\text{CO})_4$ ,<sup>6</sup> and  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ ,<sup>5</sup> the equatorial CO-M-radial CO angle is  $89^\circ$ , somewhat greater than  $90^\circ$ , and  $98^\circ$ , respectively. Although the mercury case is somewhat extreme, the available data as well as the data for analogous manganese compounds,  $\text{LMn}(\text{CO})_5$ , suggest that the angle is about  $90^\circ$  to  $95^\circ$  for the ligands studied there. This range is sufficiently small so that changes in the orbital population resulting from angle variations should be small. The departure from three-fold symmetry of the equatorial carbonyls is likewise small.

It is convenient to consider the quadrupole coupling constants in terms of the occupancy of valence atomic orbitals since it is the electron density in these orbitals which determines field gradient in molecular solids. On the basis of arguments presented elsewhere<sup>11</sup> applicable to the present series of compounds it is possible to proceed by accounting for the variations in the field gradient in terms of changes in the populations of only the 3d orbitals of cobalt. It can be shown from various arguments, that the field gradient due to an electron in the 4p orbitals is at least a factor of 4 or 5 lower than for an electron in the 3d orbital. In addition, the 4p orbitals would be expected to have a low population of electrons

relative to the population of the 3d orbitals in these trigonal structures. Because of the spherical symmetry of the 4s orbital, its electron populations does not contribute to the field gradient.

The molecular field gradient,  $q_{zz}$ , can be expressed in terms of the various types of 3d electrons using the relationship of the field gradient to angular momentum, i.e.

$$q_{nlm} = q_{nlo} (1 - 3m^2/l(l+1)) \quad (1)$$

In a valence bond<sup>20</sup> or molecular orbital theory,<sup>21</sup>  $q_{zz}$  arising from the 3d

(20) C. H. Townes and B. P. Dailey, J. Chem. Phys., 17, 782 (1949).

(21) F. A. Cotton and C. B. Harris, Proc. Natl. Acad. Sci. U.S., 56, 12 (1966).

electrons, can be expressed in terms of atomic orbital populations,<sup>22</sup>

(22) R. S. Mulliken, J. Chem. Phys., 23, 1841 (1955);

$$N_j = \sum_k^{\text{occ}} N_k C_{jk}^2 + \sum_k^{\text{occ}} \sum_l N_k C_{ik} C_{jk} S_{ij}$$

$N_i$  i.e.

$$q_{zz} = q_{320} [N_{d_{z^2}} + 1/2 (N_{dxz} + N_{dyz}) - (N_{dxy} + N_{dx^2-y^2})] \quad (2)$$

Since the field gradient arising from a  $3d_{z^2}$  electron or  $q_{320}$  is itself a negative quantity, it is instructive to consider the sign of the molecular field gradient,  $q_{zz}$ . Assuming no covalency, one would predict a positive

molecular field gradient insofar as the orbital populations, [N], would be  $3d_{z^2}$ , [0],  $3d_{xy}$ ,  $3d_{x^2-y^2}$ , [4], and  $3d_{xz}$ ,  $3d_{yz}$ , [4]. This value, however, is far too great to account for the observed field gradients in these trigonal complexes. The relative populations of the 3d orbitals in  $\text{MX}_3\text{Co}(\text{CO})_4$  compounds should be similar to those in the isoelectronic and

Table II. Orbital Populations in  $\text{Fe}(\text{CO})_5$

Orbital	Population
$3d_{z^2}$	1.23
$3d_{xz}$ , $3d_{yz}$	1.32
$3d_{xy}$ , $3d_{x^2-y^2}$	1.43
$4p_z$	0.07
$4p_x$ , $4p_y$	0.17
$4s$	0.27

isostructural  $\text{Fe}(\text{CO})_5$ . Table II lists the orbital populations<sup>23</sup> calculated

(23) A. F. Schreiner, Ph.D. thesis, University of Illinois, 1967.

See A. F. Schreiner and T. L. Brown, J. Amer. Chem. Soc., 90, 3366 (1968) for details of the MO model.

for  $\text{Fe}(\text{CO})_5$  and illustrates that indeed, the calculated field gradient still remains positive. We may therefore expect that the molecular field gradient in the cobalt complexes is also positive.

Utilizing Eq. 2, it can be seen that the change in the magnitude of  $q_{zz}$ , can be related to the bonding interactions of the cobalt with the  $\text{MX}_3$  group in three ways. First, there can be a change in the population of the  $3d_{z^2}$  orbital as a result of variable  $\sigma$  donating properties of  $\text{MX}_3$ . In general,  $q_{zz}$  increases with a decreased  $\sigma$  donation to Co from  $\text{MX}_3$ . Secondly, there may be a decrease in the population of the  $3d_{xz}$ ,  $3d_{yz}$  orbitals because of increased  $\pi$  bonding to the  $\text{MX}_3$  group. This would also result in an increased molecular field gradient,  $q_{zz}$ . Thirdly, it is, of course, well recognized that there is a complimentary character in the relative  $\sigma$  donor- $\pi$  acceptor characteristics of a given ligand system; therefore, inductive release on the part of  $\text{MX}_3$  through the  $\sigma$  M-Co bond, resulting in a decreased  $q_{zz}$ , should occur with increased M-X  $\pi$  bonding. This is consistent with the general notion that  $\pi$  acceptor characteristics of M places charge in the ligand from either X or Co, which in turn induces greater  $\sigma$  donor strength to the Co. Since the  $\pi$  and  $\sigma$  forms of bonding have opposite effects on  $q_{zz}$ , it is not clear, a priori, that there will be evidence of  $\pi$  bonding from the values obtained from the  $^{59}\text{Co}$  nuclear quadrupole resonance. At any rate we cannot quantitatively separate the two effects. However, from the general trends seen for the  $^{59}\text{Co}$  nuclear quadrupole resonances as tabulated in Table I, one can in a qualitative fashion, assign the effects based predominantly on a  $\sigma$ ,  $\pi$ , or  $\pi$  induced  $\sigma$  interaction.

From the analysis of the data in Table I it is possible to make some unambiguous generalizations concerning the bonding of the  $MX_3$  group to the cobalt.

It can be seen that the more electron releasing triphenyl substituents lead to much lower frequencies indicative of the increased  $\sigma$  bond order between cobalt and M. The small differences that exist between the silicon, tin, and lead triphenyl substituted compounds cannot at this point be interpreted as being due to differences in the  $\sigma$  or  $\pi$  framework of the Co-M bond.

In the halo-substituted tin complexes, changes in the field gradient in the series  $SnCl_3$ ,  $SnBr_3$ , and  $SnI_3$ , represents an increase in the relative electron-releasing ability of the ligand as the halogen varies.

The trihalo substituents are all grouped closely together, with the exception of the low frequency for  $SiCl_3Co(CO)_4$ . The low frequency must arise from an enhanced  $\sigma$  donor character for the  $SiCl_3$  group. This enhanced  $\sigma$  donor character might, however, be a property of the  $SiCl_3$  moiety itself, or might arise as a result of  $d\pi-d\pi$  interaction between Co and Si. It is unlikely that the latter mechanism is operative, since there is no evidence for it in the triphenyl series. The more plausible explanation, therefore, is that the increased  $\sigma$  donation of the  $SiCl_3$  group to cobalt arises from bonding effects within the  $SiCl_3$  group. If extensive Si-Cl  $d\pi-p\pi$  bonding occurs in chlorosilane compounds, negative charge is transferred from chlorine to silicon. This electron density on the silicon inductively increases the  $\sigma$  donor character of the  $SiCl_3$  moiety. It is interesting to note that the variation in the molecular field gradient in the series  $SnCl_3$ ,  $GeCl_3$  and  $SiCl_3$  parallels the variations

Table III. Comparative  $^{35}\text{Cl}$  nqr Frequencies for  
Chloro Derivatives

Compound	$^{35}\text{Cl}$ (MHz)	$\Delta$ (MHz)	Ref.
$\text{SiCl}_4$	20.41		27, 28
$\text{Co}(\text{CO})_4\text{SiCl}_3$	19.08	1.33	---
$\text{C}_2\text{H}_5\text{SiCl}_3$	19.11	1.30	27
$\text{GeCl}_4$	25.66		28
$\text{Co}(\text{CO})_4\text{GeCl}_3$	--- <sup>a</sup>	---	---
$\text{C}_2\text{H}_5\text{GeCl}_3$	22.42	3.24	28
$\text{SnCl}_4$	24.14		---
$\text{Co}(\text{CO})_4\text{SnCl}_3$	19.88	4.26	29
$n\text{-C}_4\text{H}_7\text{SnCl}_3$	21.56	2.58	30

<sup>a</sup> Not observed.

(27) I. P. Biryukov, M. G. Voronkov and I. A. Safin, Dokl. Akad. Natur. SSSR, 165, 857 (1965).

(28) M. G. Voronkov and I. P. Biryukov, Teor. Eksp. Khim, 1, 124 (1965).

(29) H. O. Hooper and P. J. Bray, J. Chem. Phys., 33, 335 (1960).

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

in the  $^{13}\text{C}$ -H coupling constants in the series  $\text{CH}_3\text{SnCl}_3$ <sup>24</sup> (143 Hz),

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(24) K. Stark and T. L. Brown, J. Phys. Chem., 69, 2679 (1965).

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$\text{CH}_3\text{GeCl}_3$ <sup>25</sup> (138 Hz), and  $\text{CH}_3\text{SiCl}_3$ <sup>24</sup> (126 Hz). The  $^{13}\text{C}$ -proton coupling

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(25) D. F. Van de Vondel, J. Organometal. Chem., 3, 400 (1965).

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constants reflect the effective  $\sigma$  donating ability of the group bonded to the  $\text{CH}_3$ <sup>26</sup> and thus, are a measure of the  $\sigma$  (as opposed to  $\pi$ ) bonding

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(26) T. L. Brown and J. C. Puchett, J. Chem. Phys., 44, 2238 (1966).

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properties. Secondary support for this contention can be obtained from the  $^{35}\text{Cl}$  nuclear quadrupole frequencies for these compounds (Table III). It is to be noted that the  $^{35}\text{Cl}$  frequency is essentially unchanged upon replacement of a chlorine in going from  $\text{SiCl}_4$  to  $\text{SiCl}_3\text{Co}(\text{CO})_4$  or  $\text{C}_2\text{H}_5\text{SiCl}_3$ . This suggests that the Si-Cl  $d\pi$ - $p\pi$  bonding effectively blocks field gradient changes with group substitution. In the corresponding series with  $\text{SnCl}_4$ ,  $\text{SnCl}_3\text{Co}(\text{CO})_4$  and  $n\text{-C}_4\text{H}_7\text{SnCl}_3$  by contrast, it is observed that there is a substantial change in the  $^{35}\text{Cl}$  quadrupole resonance. This is indicative that the Sn-Cl bond does not determine the interactions via  $\pi$  bonding nearly as extensively as in the analogous silicon compounds.

There is evidence of Co-Ge and Co-Sn  $\pi$  bonding from the analysis of the data presented in Table III. The substitution for a Cl by  $\text{Co}(\text{CO})_4$  compared to an  $n\text{-C}_4\text{H}_7$  moiety in  $\text{SnCl}_4$  results in a substantially smaller

field gradient at chlorine. If the  $\text{SnCl}_3$  group acts as a  $\pi$  acceptor towards Co, one would expect this form of charge transfer to the tin to result in an additional polarization of the Sn-Cl bond; thus, a lower  $^{35}\text{Cl}$  nuclear quadrupole frequency, as observed. This result is also consistent with the trend of  $^{59}\text{Co}$  frequencies in  $\text{SiCl}_3$ ,  $\text{SnCl}_3$  and  $\text{GeCl}_3$  derivatives.  $\pi$  bonding between cobalt and tin or germanium should result in an increased  $q_{zz}$  at the cobalt. Such is observed; however, it is difficult to place quantitative estimates on the importance of  $\pi$  bonding between the cobalt and tin, since other variable factors, in particular the  $\sigma$  bonding, contributes to the field gradient at the cobalt. It is interesting that the Co frequencies are essentially invariant in the series  $\text{GeCl}_3$ ,  $\text{GeBr}_3$ ,  $\text{GeI}_3$ . In terms of a simple halogen  $\sigma$  effect as observed in the tin series, one would expect  $q_{zz}$  at cobalt to decrease in the order listed. The fact that this does not occur cannot, however, be accounted for in terms of  $d\pi$ - $d\pi$  bonding from cobalt to germanium. In the absence of chlorine-germanium  $\pi$  bonding one would expect such an interaction to be greatest for  $\text{GeCl}_3$ . But a cobalt-germanium  $\pi$  interaction would lead to a higher  $q_{zz}$ , through depopulation of  $d_{xz}$  and  $d_{yz}$  on cobalt, contrary to the observed results. It must be concluded, therefore, that the essential constancy of  $q_{zz}$  in the halogermanium series is due to a variation in the germanium-halogen  $\pi$  bonding, in the order  $\text{Cl} > \text{Br} > \text{I}$ .

In principle, it should be possible to obtain a reflection of the difference in the degree of Co-Sn versus Co-Si  $\pi$  bonding from the temperature dependence of the  $^{59}\text{Co}$  quadrupole frequency. The observed temperature dependence of the cobalt in  $\text{SnCl}_3\text{Co}(\text{CO})_4$  is greater than that for  $\text{SiCl}_3\text{Co}(\text{CO})_4$ . Whether this results from the presence of lower frequency vibrational modes in the tin compound, or is a reflection of more extensive  $\pi$  bonding,

is not possible to say at this juncture. It would be expected, however, that intermolecular motions should have a particularly small effect on the field gradient in the cobalt since it is the central atom of the molecules.

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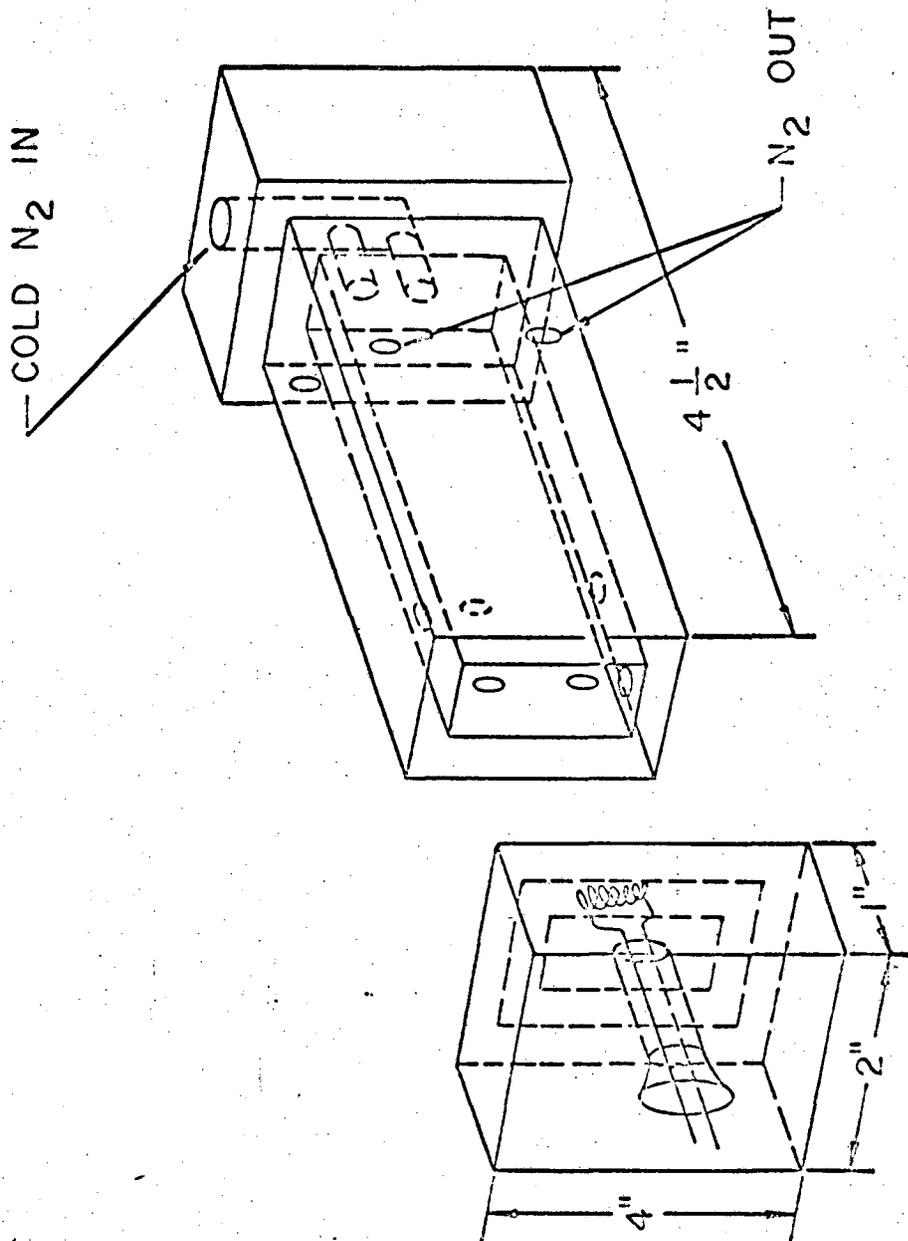


Figure 1. Schematic illustration of cold cell.

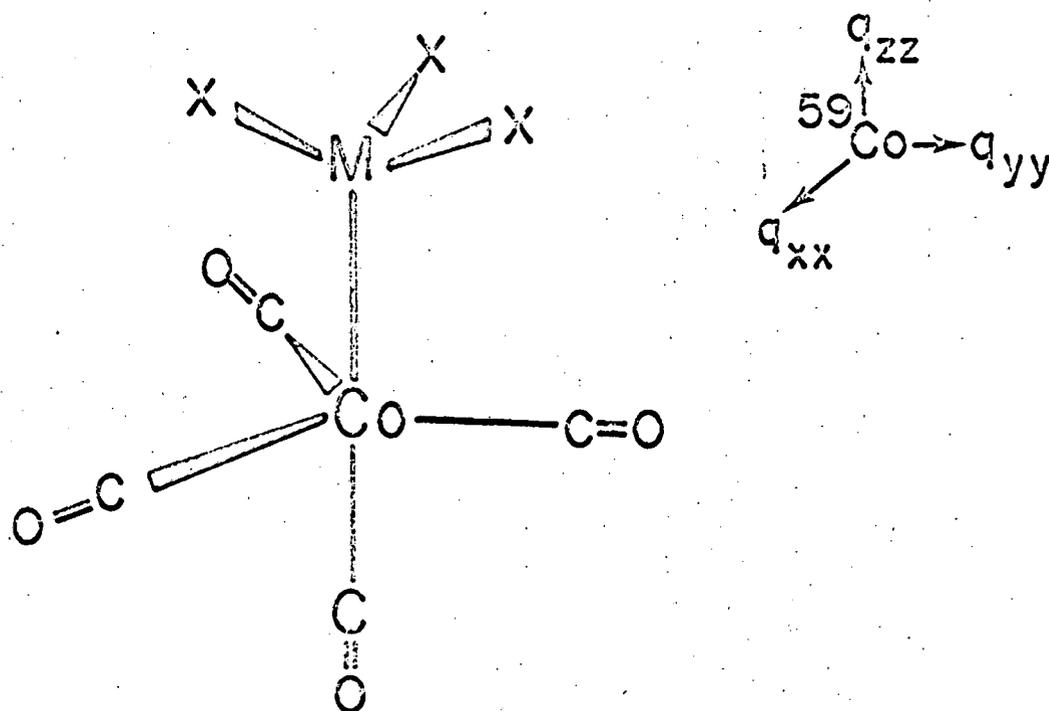


Figure 2. Field gradient coordinate system and geometry in  $\text{Co}(\text{CO})_4\text{MX}_3$  compounds.