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Registry No. $PW_{12}O_{40}^{4-}$, 12534-78-0; $SiW_{12}O_{40}^{5-}$, 12504-06-2; $GeW_{12}O_{40}^{5-}$, 59965-05-8; $BW_{12}O_{40}^{6-}$, 39326-57-3; $H_2W_{12}O_{40}^{7-}$, 12501-12-1; $P_2W_{18}O_{62}^{7-}$, 12504-08-4; $As_2W_{18}O_{62}^{7-}$, 59965-04-7; $PMo^{V}W_{11}O_{40}^{4-}$, 12776-99-7; $PMo^{V}Mo_{11}O_{40}^{4-}$, 53850-86-5; $P^{95}Mo^{V95}Mo_{11}O_{40}^{4-}$, 59965-02-5; $P^{95}Mo^{V}W_{11}O_{40}^{4-}$, 59965-03-6; $PW_{12}O_{40}^{3-}$, 12534-77-9; $SiW_{12}O_{40}^{4-}$, 12363-31-4; $GeW_{12}O_{40}^{4-}$, 37369-87-2; $BW_{12}O_{40}^{5-}$, 12513-03-0; $H_2W_{12}O_{40}^{6-}$, 12207-61-3; $P_2W_{18}O_{62}^{6-}$, 12269-70-4; $As_2W_{18}O_{62}^{6-}$, 12267-69-5.

References and Notes

(1) The words "isotropic", "axial", and "rhombic" are used in this paper to describe the *appearance* of an ESR spectrum and do not necessarily imply that the species responsible for the spectrum is respectively isotropic, axial, or rhombic. As will become apparent, all of the complexes under discussion have rhombic symmetries but give "axial" or "isotropic" spectra when exchange broadening increases the line widths beyond the separation of the rhombic components.

(2) M. T. Pope, *Inorg. Chem.*, **11**, 1973 (1972); the term "heteropoly blue" is generic rather than descriptive. The reduced anions are blue, purple, brown, green, etc. according to the energies of the intervalence charge-transfer transitions.

(3) D. P. Smith, H. So, J. Bender, and M. T. Pope, *Inorg. Chem.*, **12**, 685 (1973).

(4) H. So and M. T. Pope, *Inorg. Chem.*, **11**, 1441 (1972).

(5) J. J. Altenau, M. T. Pope, R. A. Prados, and H. So, *Inorg. Chem.*, **14**, 417 (1975).

(6) G. M. Varga, Jr., E. Papaconstantinou, and M. T. Pope, *Inorg. Chem.*, **9**, 662 (1970).

(7) P. Stonehart, J. G. Koren, and J. S. Brinen, *Anal. Chim. Acta*, **40**, 65 (1968).

(8) P. Rabette, C. Ropars, and J. -P. Grivet, *C. R. Hebd. Seances Acad. Sci, Ser. C*, **265**, 153 (1967).

(9) R. A. Prados, P. T. Meiklejohn, and M. T. Pope, *J. Am. Chem. Soc.*, **96**, 1261 (1974).

(10) M. T. Pope and G. M. Varga, Jr., *Inorg. Chem.*, **5**, 1249 (1966).

(11) M. T. Pope and E. Papaconstantinou, *Inorg. Chem.*, **6**, 1147 (1967).

(12) P. Souchay, *Ann. Chim. (Paris)*, **20**, 96 (1945).

(13) R. K. Motorkina, *Zh. Neorg. Khim.*, **2**, 92 (1957).

(14) P. T. Meiklejohn, M. T. Pope, and R. A. Prados, *J. Am. Chem. Soc.*, **96**, 6779 (1974).

(15) D. P. Smith and M. T. Pope, *Inorg. Chem.*, **12**, 331 (1973).

(16) J. H. Kennedy, *J. Am. Chem. Soc.*, **82**, 2701 (1960).

(17) P. Souchay and G. Hervé, *C. R. Hebd. Seances Acad. Sci.*, **261**, 2486 (1965).

(18) Rabette et al.[8] reported a similar spectrum for the one-electron blue of $SiMo_{12}O_{40}^{4-}$ at 77 K.

(19) For example the envelope of 61 Gaussian lines with component widths as large as 80 G is still only ca. 100 G peak to peak.

(20) M. T. Pope, *Inorg. Chem.*, **15**, 2008 (1976), and references cited therein.

(21) E. Papaconstantinou and M. T. Pope, *Inorg. Chem.*, **9**, 667 (1970).

(22) H. Wu, *J. Biol. Chem.*, **43**, 189 (1920).

(23) P. Souchay, R. Contant, and J. M. Fruchart, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **264**, 976 (1967).

(24) R. Strandberg, *Acta Chem. Scand., Ser. A*, **29**, 350 (1975).

(25) Note that in the recent structure determination of Wu's A-$P_2W_{18}O_{62}^{6-}$, the anion is labeled as the α isomer: K. Y. Matsumoto and Y. Sasaki, *J. Chem. Soc., Chem. Commun.*, 691 (1975).

(26) H. Kon and N. G. Sharpless, *J. Phys. Chem.*, **70**, 105 (1966).

(27) R. S. Abdrakhmanov, N. S. Garif'yanov, and E. I. Semenova, *Zh. Strukt. Khim.*, **9**, 530 (1968).

(28) N. S. Garif'yanov, B. M. Kozyrev, and V. N. Fedotov, *Dokl. Akad. Nauk SSSR*, **156**, 641 (1964).

(29) P. M. Smith, Ph.D. Thesis, Georgetown University, 1972; *Diss. Abstr. B*, **32**, 5136 (1972).

(30) R. Strandberg, *Acta Chem. Scand., Ser. A*, **29**, 359 (1975).

(31) H. T. Evans, Jr., *Perspect., Struct. Chem.*, **4**, 1 (1971).

(32) B. Dawson, *Acta Crystallogr.*, **6**, 113 (1953).

(33) Very recent structure determinations of $Na_4H_2[P_2Mo_{18}O_{62}]\cdot 20H_2O$ and α-$(NH_4)_6[P_2W_{18}O_{62}]\cdot 9H_2O$ confirm earlier results for the molybdate but show that the corresponding distortions in the tungstate are much less pronounced. The symmetry of the latter ion more nearly approaches D_{3h}: H. D'Amour, *Acta Crystallogr., Sect. B*, **32**, 729 (1976).

(34) N. S. Hush, *Prog. Inorg. Chem.* **8**, 391 (1967).

(35) Direct determination of such activation energies may be possible using individual stereoisomers of substituted anions such as $PMo^{V}Mo^{VI}W_{10}O_{40}^{4-}$: M. T. Pope, S. E. O'Donnell, and R. A. Prados, *J. Chem. Soc., Chem. Comm.*, 22 (1975).

(36) R. Massart and G. Hervé, *Rev. Chim. Miner.*, **5**, 501 (1968).

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A Cobalt-59, Indium-115, Gallium-69, Gallium-71, Bromine-79, Bromine-81, and Chlorine-35 Nuclear Quadrupole Resonance Study of Structure and Bonding in Four-Coordinate Gallium and Indium Compounds Containing Metal–Metal Bonds

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Pure nuclear quadrupole resonance spectra are reported for a series of four-coordinate gallium and indium compounds having as ligands $Co(CO)_4$, Br, Cl, THF, acac, and $(C_6H_5)_3PO$. The ^{59}Co, ^{115}In, ^{69}Ga, ^{71}Ga, ^{79}Br, ^{81}Br, and ^{35}Cl NQR parameters when taken together and separately lead to qualitative structural inferences and a coherent picture of the ground-state electron distribution in these molecules. The ^{59}Co and ^{115}In coupling constants and the ^{115}In asymmetry parameters suggest that ligand angle changes in the In(III) coordination sphere account for some of the trends. ^{59}Co asymmetry parameters suggest cobalt–indium (gallium) π bonding is not a major factor in these compounds. The presence of bridging and terminal halogens can be determined using ^{79}Br, ^{81}Br, and ^{35}Cl NQR frequencies. The halogen frequency shifts are consistent with orbital population changes on indium as evidenced by the ^{115}In coupling constants. The number of examples is limited but partial quadrupole splitting values for ligands derived from Sn(IV) Mössbauer spectra appear to predict the trends in In(III) coupling constants. The EFG trends and carbonyl ir frequency shifts in $Co(CO)_4$–In(Ga) bonds compared to $(CO)_4Co$–Sn(Ge) bonds are entirely consistent but show ν_{CO} to be much less sensitive than the electric field gradient to substitutions.

Introduction

Cobalt-59 nuclear quadrupole resonance spectra for a large number of M–$Co(CO)_4$ molecules have been obtained and analyzed on the basis of the effect of M on the cobalt electric field gradient (EFG).[1-10] In most cases M has been a group 4A or group 5A atom based moiety with Si, Ge, Sn, Pb, and P at the bonding site. Although many interesting inferences about σ- and π-bonding character have been extracted from these data, none of these group 4A and 5A elements bound to $Co(CO)_4$ possesses quadrupolar nuclei in the ground state. Hence it has not been possible to probe both ends of the metal–metal bond by NQR spectroscopy. In providing an

Table I. ^{115}In, ^{69}Ga, and ^{71}Ga NQR Data[a]

Compd[b]	Cryptic notation	$\nu(^{115}\text{In})$, MHz				e^2Qq_{zz}/h, MHz	η	$\nu(^{69}\text{Ga})$, MHz	$\nu(^{71}\text{Ga})$, MHz
		$^9/_2 \leftrightarrow {}^7/_2$	$^7/_2 \leftrightarrow {}^5/_2$	$^5/_2 \leftrightarrow {}^3/_2$	$^3/_2 \leftrightarrow {}^1/_2$				
$\{\text{ClIn}[\text{Co(CO)}_4]_2\}_x$	Co_2InCl_2	72.99 (2)	52.07 (2)	36.82 (10)	48.33 (2)	450.6	0.61		
$\{\text{BrIn}[\text{Co(CO)}_4]_2\}_x$	Co_2InBr_2	68.83 (4)	48.97 (7)	35.07 (12)	47.80 (6)	427.7	0.65		
$\text{ClIn}[\text{Co(CO)}_4]_2\cdot\text{THF}$	Co_2InOCl	61.28 (4)	44.02 (7)	30.11 (12)	39.01 (4)	378.2	0.58		
$\text{BrIn}[\text{Co(CO)}_4]_2\cdot\text{THF}$	Co_2InOBr	59.24 (2)	41.99 (4)	30.70 (3)	42.55 (2)	369.2	0.67		
$\text{acacIn}[\text{Co(CO)}_4]_2$	Co_2InO_2	57.19 (4)	42.12 (8)	26.79 (12)	27.14 (7)	347.0	0.39		
$\text{In}_3\text{Br}_3\text{Co}_4\text{(CO)}_{15}$	Co_2InBr_2		63.55 (7)	40.44 (8)	32.78 (10)	516.0	0.27		
			59.85 (7)	38.00 (10)	33.48 (5)	487.9	0.31		
			58.08 (7)	36.85 (12)	37.01 (12)	478.4	0.38		
$\text{Br}_2\text{GaCo(CO)}_4\cdot\text{THF}$	CoGaOBr_2							51.65 (3)	81.90 (2)

[a] Parenthetical numbers are signal-to-noise ratios. [b] The compound $(\text{C}_6\text{H}_5)_3\text{POIn}[\text{Co(CO)}_4]_3$ gives a resonance at 24.52 MHz which may be an ^{115}In resonance.

internally coherent picture of electron density flow and geometry changes it would be valuable to situate probes at as many sites in molecules as is possible.

In the present paper we discuss the results of an NQR study of M–Co(CO)_4 type systems where M is one of the group 3A elements, gallium or indium. The motivation for this study comes along two fronts. First, ^{115}In, ^{69}Ga, and ^{71}Ga are quadrupolar nuclei that can be investigated along with ^{59}Co in order to probe both ends of the metal–metal bond. Second, ^{119}Sn Mössbauer results on tetrahedrally coordinated Sn(IV) compounds are available[11] and allow comparisons to be made to these structurally and electronically similar four-coordinate In(III) compounds.

Perhaps the most unfortunate feature of the group 3A–Co(CO)_4 compounds is that the results cannot be made more quantitative in part for lack of x-ray crystal structure determinations. Nevertheless, with these compounds it has been possible to make an internally consistent account of structures and electron density flow by using ^{59}Co, ^{115}In, ^{69}Ga, ^{71}Ga, ^{79}Br, ^{81}Br, and ^{35}Cl NQR parameters.

Experimental Section

Synthetic procedures for the In(III) and Ga(III) compounds were taken from the literature.[12] Identification of the compounds was made by the correspondence of the melting points and infrared spectra between this work and previously reported values.[12] It was necessary to purify all solvents prior to use and perform synthetic manipulations in Schlenk tubes and a drybox containing an N_2 atmosphere. $(\text{C}_6\text{H}_5)_3\text{POIn}[\text{Co(CO)}_4]_3$ has been mentioned[13] and was prepared by stirring a THF solution of $\text{In}[\text{Co(CO)}_4]_3$ (1.3 g, 2.04 mmol) and $(\text{C}_6\text{H}_5)_3\text{PO}$ (0.65 g, 2.33 mmol) for 0.5 h under N_2 and at room temperature. The THF was removed under vacuum and the resulting residue extracted with petroleum ether (bp 30–60 °C) and filtered. Evaporation of the petroleum ether under vacuum gave 1.25 g (65% yield) of bright orange crystals of $(\text{C}_6\text{H}_5)_3\text{POIn}[\text{Co(CO)}_4]_3$.

The nuclear quadrupole resonance spectra were recorded on 0.5–2 g of polycrystalline material in tightly sealed vials. All samples were held under an N_2 atmosphere to ensure against decomposition. The NQR data were taken at room temperature (296–298 K) using a spectrometer facility which has been described before.[14] The frequency measurements are believed to be accurate to 0.003 MHz but the occasional uncertainty in selecting the center line of the resonance multiplet leads us to report the frequency to four significant figures below 100 MHz and to five significant figures above 100 MHz. No NQR frequencies were observed for $(\text{C}_6\text{H}_5)_4\text{AsIn}[\text{Co(CO)}_4]_4$,[12] $(\text{C}_6\text{H}_5)_4\text{AsTl}[\text{Co(CO)}_4]_4$,[12] $(\text{C}_2\text{H}_5)_4\text{NBr}_2\text{In}[\text{Co(CO)}_4]_2$,[15] and $(\text{C}_6\text{H}_5)_4\text{AsBr}_3\text{InCo(CO)}_4$.[16] All of these compounds are salts as opposed to the neutral complexes where NQR signals were detected.

Infrared spectra were taken on a Perkin-Elmer 180 grating spectrometer. The solvent used was cyclohexane so that the frequencies could be compared to those reported earlier.[12] The cells used were sealed KBr cells with 0.15-mm path length. Frequency measurements were accurate to within ±1 cm^{-1}.

NQR Spectra and Structural Information

In terms of their stoichiometry the compounds studied here appear rather formidable. However, the basic structural units are believed to be based on four-coordinate In(III) and Ga(III), with either bridging or terminal halogen atoms and terminal Co(CO)_4 groups.[12] The one exception is $\text{In}_3\text{Br}_3\text{Co}_4\text{(CO)}_{15}$ whose crystal structure[17] shows that one of the cobalt atoms occurs as a Co(CO)_3 group bound to three indium atoms. The various structural possibilities are illustrated in Figure 1.

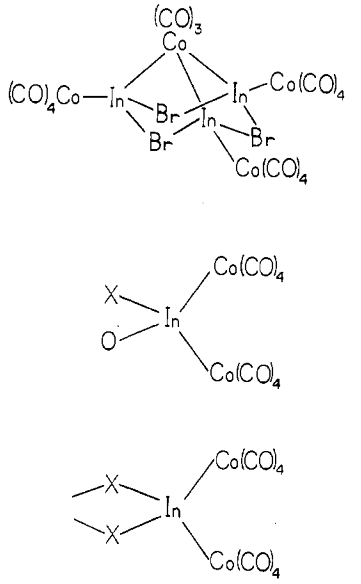

Figure 1. Known and proposed structural arrangements for compounds in Tables I–III.

Indium-115 with a nuclear spin of $^9/_2$ yields four resonances per chemically and crystallographically different nucleus. The nuclear quadrupole coupling constant, e^2Qq_{zz}/h, in MHz, and the electric field gradient asymmetry parameter, $\eta = (q_{xx} - q_{yy})/q_{zz}$, can be redundantly computed by fitting the frequencies to the secular equations for $I = {}^9/_2$.[18] Q is the nuclear quadrupole moment and q_{zz} is the largest component of the EFG tensor. Table I summarizes the ^{115}In NQR data extracted from these compounds. Cobalt-59 is an $I = {}^7/_2$ nucleus giving three NQR frequencies per inequivalent nucleus. e^2Qq_{zz}/h and η can again be readily computed[18] and the data appear in Table II. Gallium-69, gallium-71, bromine-79, bromine-81, and chlorine-35 are all $I = {}^3/_2$ nuclei which can give only one NQR absorption per inequivalent nucleus. It is not possible to compute the two unknowns, e^2Qq_{zz}/h and η, from these polycrystalline spectra. Nevertheless, from a comparative point of view some $I = {}^3/_2$ spectra are of value in these systems. For example, in the case of terminal halogen atoms, the NQR frequency roughly parallels the electron density change on the halogen. Also the frequency for an $I = {}^3/_2$ nucleus is not very sensitive to changes in η. An η variation of 0 → 1 causes only about a 15% increase in the

Table II. ^{59}Co NQR Data[a]

Compd	Cryptic notation	$\nu(^{59}\text{Co})$, MHz			e^2Qq/h, MHz	η
		$^7/_2 \leftrightarrow {}^5/_2$	$^5/_2 \leftrightarrow {}^3/_2$	$^3/_2 \leftrightarrow {}^1/_2$		
$\{\text{BrIn[Co(CO)}_4]_2\}_x$	Co_2InBr_2	24.85 (12)	16.42 (10)	8.920 (2)	116.2	0.15
$\{\text{ClIn[Co(CO)}_4]_2\}_x$	Co_2InCl_2	24.70 (6)	16.32 (4)	8.860 (2)	115.5	0.15
$In_3Br_3Co_4(CO)_{15}$	Co_2InBr_2	24.87 (4)	16.56 (5)	8.377 (2)	116.1	0.05
		24.67 (4)	16.32 (5)	8.740 (2)	115.3	0.13
		50.89 (3)				
$\text{BrIn[Co(CO)}_4]_2\cdot\text{THF}$	Co_2InOBr	23.39 (5)	15.58 (4)	7.943 (2)	109.2	0.07
		21.93 (3)	14.49 (4)	7.894 (2)	102.6	0.15
$\text{ClIn[Co(CO)}_4]_2\cdot\text{THF}$	Co_2InOCl	23.25 (14)	15.48 (12)	7.842 (5)	108.5	0.06
		21.78 (12)	14.40 (10)	7.685 (5)	101.8	0.14
$\text{acacIn[Co(CO)}_4]_2$	Co_2InO_2	22.06 (9)	14.60 (7)		104.3	0.08
		21.12 (7)	13.98 (6)		98.70	0.12
$\text{(C}_6\text{H}_5)_3\text{POIn[Co(CO)}_4]_3$	Co_3InO	21.60 (4)	14.30 (3)		101.0	0.12
		20.69 (6)	13.74 (6)		96.60	0.09
		19.93 (3)	13.00 (3)		93.50	0.24
$\text{BrGa[Co(CO)}_4]_2\cdot\text{THF}$	Co_2GaOBr	22.09 (8)	14.53 (5)	7.934 (2)	103.3	0.16
		22.27 (6)				
$\text{ClGa[Co(CO)}_4]_2\cdot\text{THF}$	Co_2GaOCl	21.85 (7)	14.42 (3)		102.2	0.15
			14.28 (5)			
$\text{acacGa[Co(CO)}_4]_2$	Co_2GaO_2	20.85 (7)	13.86 (8)		97.34	0.07
		20.44 (6)	13.56 (6)		95.46	0.10
$\text{Br}_2\text{GaCo(CO)}_4\cdot\text{THF}$	$CoGaOBr_2$	23.50 (12)	15.64 (20)	7.938 (3)	109.7	0.06
$\text{Cl}_2\text{GaCo(CO)}_4\cdot\text{THF}$	$CoGaOCl_2$	22.94 (6)	15.23 (10)	7.925 (3)	107.2	0.10
acacGaBrCo(CO)_4	$CoGaO_2Br$	21.78 (6)	14.46 (6)		101.7	0.10

[a] Parenthetical numbers are signal-to-noise ratios.

Table III. Halogen NQR Data (MHz)[a]

Compd	$\nu(^{79}\text{Br})$	$\nu(^{81}\text{Br})$	$\nu(^{35}\text{Cl})$
$\text{BrIn[Co(CO)}_4]_2\cdot\text{THF}$	109.54 (2)	91.54 (2)	
$In_3Br_3Co_4(CO)_{15}$	85.50 (4)	71.45 (2)	
	78.78 (8)	65.80 (5)	
	73.25 (4)	61.20 (4)	
CH_3InBr_2[b]	101.59		
	102.92		
$InBr_3$[c]	103–104		
	123–127		
$\text{Br}_2\text{Ga[Co(CO)}_4]\cdot\text{THF}$	124.10 (10)	103.62 (20)	
	134.53 (5)	112.18 (3)	
$\text{BrGa[Co(CO)}_4]_2\cdot\text{THF}$	119.45 (4)	99.83 (9)	
$\text{BrGa[Co(CO)}_4]\cdot\text{acac}$	125.37 (2)	104.94 (3)	
$GaBr_3$[d]	168.5		
	120.6		
$\text{Cl}_2\text{GaCo(CO)}_4\cdot\text{THF}$			15.15 (15)
			15.20 (5)
$GaCl_3$[e]			19.01–20.23
			14.67

[a] Parenthetical numbers are signal-to-noise ratios. [b] Reference 23. [c] References 27, 28. [d] Reference 26. [e] Reference 36.

frequency.[18] Assignment of gallium and bromine resonance frequencies can be made on the basis of nuclear quadrupole moment ratios of the isotopes. For gallium $Q_{71}/Q_{69} = 1.587$, and for bromine $Q_{79}/Q_{81} = 1.197$. Table I contains the gallium data, and Table III, the halogen results.

In most of the compounds where two or more $Co(CO)_4$ groups are present in the formula unit, the NQR spectra show inequivalence of the cobalt atoms in the crystal lattice. The cobalt atoms seem to lie in an approximately regular trigonal-bipyramidal field and thus connect at an axial position on cobalt to the group 3A atom. This inference is based on the relatively small η values (0.05–0.24) for ^{59}Co. These η values are in line with those seen in other M–$Co(CO)_4$ compounds.[1-10] However, in terms of the additional groups bound to the group 3A elements gallium and indium, the Co–M bond is not axially symmetric in any of these compounds. Yet $\eta(^{59}\text{Co})$ is only slightly greater than values in R_3M–$Co(CO)_4$ compounds and within the range of their values on average (0.0–0.285).[19] It appears that significant electron population asymmetry in the cobalt orbitals lying off the Co–M bond axis (M = Ga, In) is not produced by groups more than one bond away from the cobalt atom when M is four-coordinate.

$In_3Br_3Co_4(CO)_{15}$ gives ^{59}Co resonances for only two of the three $Co(CO)_4$ groups even though spectra for all of the In(III) atoms were observed. The crystal structure of the compound[17] indicates that all of the cobalt atoms are inequivalent but that one $Co(CO)_4$ group is twisted roughly 20° about the Co–In axis compared to the other two. While we cannot be certain, it may be that this $Co(CO)_4$ group is the one for which we see no ^{59}Co frequencies. The reason for this is not at all clear, however. One additional distinct but weak resonance was seen at 50.98 MHz in this compound and is not assignable to ^{115}In, ^{79}Br, ^{81}Br, or the $Co(CO)_4$ groups. It has the wrong frequency to be a forbidden transition of In(III). We believe that this frequency might be the $^7/_2 \leftrightarrow {}^5/_2$ transition of the approximately axial $\equiv Co(CO)_3$ group. The lower frequency resonances for this ^{59}Co nucleus could easily be overlapping the ^{115}In resonances which blanket the 32–33-MHz range in the case of $^5/_2 \leftrightarrow {}^3/_2$ and could be too weak to observe in the case of $^3/_2 \leftrightarrow {}^1/_2$. In several other instances the $^3/_2 \leftrightarrow {}^1/_2$ transition of ^{59}Co could not be seen because it often tends to be of lower intensity than the others. If this assignment is correct, the resonance would be the highest yet reported for ^{59}Co.

A complete set of ^{115}In resonances were observed in most compounds and these are reported in Table I. In $In_3Br_3Co_4(CO)_{15}$ no $^9/_2 \leftrightarrow {}^7/_2$ transitions appear. Gallium signals could be found in only one compound. The value of having gallium NQR data is small because by comparison to the analogous indium compounds the EFG asymmetry parameter may be large and variable. The gallium frequencies are indeterminably susceptible to changes in q_{zz} and η. The single set of indium and gallium resonances in most cases indicates that only one type of group 3A element is present in the unit cell. However, the sizable asymmetry parameters for ^{115}In imply severe distortion of the tetrahedral environment. The crystal structures of $In_3Br_3Co_4(CO)_{15}$[17] and $(C_2H_5)_4NBr_2$-$\text{In[Co(CO)}_4]_2$,[15] the latter for which no NQR spectrum was seen, bear out this fact.

A reasonable assumption is that the other compounds in this work contain four-coordinate group 3A atoms in light of their stoichiometry and the bulky nature of the $Co(CO)_4$ group. Making this assumption allows an EFG analysis to be made

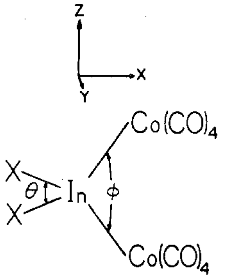

Figure 2. Structural relationships used in eq 1 and 2.

using a model derived[20,21a] and used[22,23] with some success previously. The angles of ϕ and θ are defined as Co–M–Co and X(O)–M–(O)X, respectively in Figure 2. The electron population of M orbitals used in Co–M bonds (=a) and Co–X(O) bonds (=b) are related to q_{zz} at M according to eq 1. The EFG asymmetry parameter at M is defined in eq 2.

$$q_{zz} = (q_{zz})_{\text{atomic}}(a - b)(1 + \eta/3)^{-1} \qquad (1)$$

$$\eta = -3 \cos \theta \qquad (2)$$

Equation 2 completely defines η because $\cot^2 (\theta/2) + \cot^2 (\phi/2) = 1$. These equations cannot be thought of as quantitative because they involve the usual assumptions necessary to interpret EFG parameters in large molecules.[21] To test their applicability the NQR data for $In_3Br_3Co_4(CO)_{15}$ can be put to the test of the known structure of the complex.[17] The Br–In–Br angles lie in the range of 92.6–98.3° which gives an η value range according to eq 2 of 0.14–0.43. Table I shows the experimental values to be 0.27–0.38 in $In_3Br_3Co_4(CO)_{15}$ and thus to be in quite satisfactory agreement. The entire range of ^{115}In asymmetry parameters is 0.27–0.67 in Table I which would indicate Br–In–Br angles in the 92–105° range. The two relevant crystal structures[15,17] show angles spanning this range. η is obviously very sensitive to small changes in geometry as has been noted before.[24,25] It is quite encouraging, however, that reasonable agreement can be obtained between model and experiment. It will be noted shortly that the model also allows interpretation of electronic changes.

Bromine resonances were observed much more often than chlorine resonances but they could not be detected in all compounds. Halogen resonances have been used with considerable success in the past to distinguish bridging and terminal halogen atoms.[26–32] For main-group elements, the bridging halogen atoms give resonances lying markedly lower in frequency than terminal halogen resonances.[26–30,32] The gallium compounds are better to use as bench marks than the indium compounds because more halogen NQR signals were seen in them. $GaBr_3$ gives a widely separated set of ^{79}Br resonances at 168.5 and 120.6 MHz[26] corresponding respectively to terminal and bridging halogen atoms of the Ga_2Br_6 unit. In the metal–metal bonded systems in Table III, the stoichiometries are very suggestive of the presence of terminal halogen atoms, and, further, Ga(III) rarely has higher than four-coordinate geometry with any ligands,[33] much less the bulky $Co(CO)_4$ group. A substantial decrease (10–30%) in $\nu(^{79}Br)$ occurs when $Co(CO)_4$ groups replace halogens in the coordination sphere of Ga(III). This decrease should be characteristic of both bridging and terminal halogens. Turning to indium, two distinct classes of ^{79}Br resonances have been reported in In_2Br_6 at 123–127 and 103–104 MHz on two separate occasions.[27,28] A third study[34] found only the ^{79}Br resonances in the 103-MHz range. The first two reports indicate that bridging and terminal halogen atoms are present while the third suggests that all of the bromine atoms in the crystal lattice of $InBr_3$ are bridging. A sizable decrease in $\nu(^{79}Br)$ is again seen when $Co(CO)_4$ replaces a halogen in the In(III) coordination sphere but now two classes of resonances emerge in those in the 73–85 MHz range which we know are due to bridging bromine atoms on the basis of the crystal structure data[17] and the resonance at 109.5 MHz in $BrIn[Co(CO)_4]_2 \cdot THF$ which is suggestive of a terminal halogen resonance on the basis of the stoichiometry. Again the pattern seems to emerge that a 10–30% decrease in $\nu(Br)$ accompanies the presence of $Co(CO)_4$ in the coordination sphere. An additional compound for reference is CH_3InBr_2. This compound is believed to be dimeric with terminal CH_3 groups,[3] although it is by no means proven to be so because CH_3InCl_2 contains five-coordinate indium.[35] Bromine-79 resonances have been observed in the 100–103-MHz region[23] and hence appear to be in the range of bridging halogen atoms compared to those of In_2Br_6 but in range of terminal halogen atoms considering the nucleophilic CH_3^- group present in the coordination sphere. In the present work, except for $In_3Br_3Co_4(CO)_{15}$, all of the compounds for which halogen NQR frequencies could be found appear to contain terminal halogen atoms. Regrettably no halogen signals for the $\{InX[Co(CO)_4]_2\}_x$ systems appeared.

These comments seem extendable to ^{35}Cl where a 20% decrease in frequency is found in $Cl_2Ga[Co(CO)_4]_2 \cdot THF$ compared to the frequencies of the terminal halogen atoms[36] in dimeric $GaCl_3$.

Electronic Effects

In addition to structural indications the NQR data of all atoms taken together yield an internally consistent view of electronic changes in these compounds as the coordination sphere is varied. Because of the distracting complexity of the stoichiometries, the cryptic notation in Tables I and II will be invoked to indicate only the atoms present in the group 3A element coordination sphere. The consistency in the general trend indicates the qualitative validity of this approach. Naturally some details which would appear if a more extensive set of compounds were available are lost.

The periodic trends found in comparing four-coordinate Sn(IV) to four-coordinate In(III) compounds are useful to note. We were unable to obtain spectra on any In(III) systems that are entirely isoelectronic with those of Sn(IV). The present compounds are neutral as are the Sn(IV) compounds. In a way, however, this is an advantage because it eliminates the possibility of potentially important ionic crystal lattice contributions to the electric field gradient.

^{59}Co NQR data are popularly treated by eq 3 which relates

$$e^2Qq_{zz}/h = (e^2Qq_{zz}/h)_{\text{at}}\left[N_{d_{z^2}} + \frac{N_{d_{xz}} + N_{d_{yz}}}{2} - N_{d_{x^2-y^2}} - N_{d_{xy}}\right] \qquad (3)$$

the coupling constant of the molecule, e^2Qq_{zz}/h, to the atomic coupling constant, $(e^2Qq_{zz}/h)_{\text{at}}$, by the populations of the d orbitals on cobalt, N_{d_i}. The bracketed term of eq 3 is known to have a negative sign for the $Co(CO)_4$ group[1] if d_{z^2} is taken to be coincident with the Co–M axis. An increase in Co→M σ bonding and/or an increase in Co→M π bonding will cause an increase in the ^{59}Co coupling constant. e^2Qq_{zz}/h values for ^{59}Co in Co_2SnX_2 compounds, X = halogens, fall in the range of 138–149 MHz.[1] For Co_2InX_2 compounds the range is 115–116 MHz. Hence the In–Co bond is substantially more ionic than the Sn–Co bond. As a general rule it appears that the group 3A element–cobalt bonds are all more ionic than the group 4A–cobalt bonds. The vertical trend in Co–M bonds, M = Ge, Sn and M = Ga, In, produces very little difference in the ^{59}Co orbital population distribution. The ^{59}Co asymmetry parameter measures the difference in the population of the d_{xz} and d_{yz} orbitals. The fact that $\eta(^{59}Co)$ does

Table IV. Comparison of In(III) and Sn(IV) Coupling Constants (MHz)

Stoichiometry	$\lvert e^2Qq\rvert_{\text{exptl}}$ for In(III)	$\lvert e^2Qq\rvert_{\text{calcd}}$ for Sn(IV)
Co_2MX_2	427–516	31.4
Co_2MOX	369–378	27.5
Co_2MO_2	347	26.9

not vary greatly upon changing the groups bound to gallium and indium through $Co(CO)_4$, Cl, Br, and oxygen donors, suggests that π bonding in the In–Co bond and Ga–Co bond is not an important factor in these four-coordinate complexes.

The trend in e^2Qq/h of ^{59}Co of $Co_2MX_2 > Co_2MOX > Co_2MO_2$ (M = Ga, In; X = Cl, Br) is readily apparent from the data in Table II. The differences are about 15% of the overall effect and it is unlikely that such a regular trend would be of random origin. The orbitals on M used in bonding to cobalt seem to become less electronegative as the number of oxygen atoms in the coordination sphere increases. A consistent interpretation of this change follows from the regular geometry change that should occur about the group 3A atom. Acetylacetonate complexes of d^{10} metals show O–M–O angles in the 90° range (cf. $Al(acac)_3$ at 91.8 °C).[37] In contrast the Br–In–Br angles in the complexes appear to be larger (vide supra) and are in the 93–105° range. Thus replacement of halogen by oxygen seems to result in a decrease in θ in eq 2. A change in the X(O)–In–(O)X angle in the order $Co_2InX_2 > Co_2InOX > Co_2InO_2$ should cause a change in the Co–In–Co angle in the same order. With the closing of the Co–In–Co angle, the In(III) (or Ga(III)) orbitals have less s character and become less electronegative.[38] Hence the ^{59}Co coupling constant decreases in this order. According to eq 2 the asymmetry parameter of In(III) will decrease as θ decreases toward 90°. This trend is borne out by the data in Table I, where $\eta(Co_2InX_2) \approx \eta(Co_2InOX) > \eta(Co_2InO_2)$. Further, the ^{115}In EFG is likely to increase according to eq 1 because as the X(O)–In–(O)X angle decreases, the Co–In bond orbitals become more populated as judged by the ^{59}Co coupling constants. This would correspond to an increase in the term "a". Since it is quite reasonable to expect that $a > b$ in these compounds, e^2Qq/h for ^{115}In is expected to increase. The order of e^2Qq/h for ^{115}In in Table I is indeed $Co_2InX_2 > Co_2InOX > Co_2InO_2$. Certainly this latter trend has also to do with the different partial field gradient contributions of X and O as well as angle changes. An evaluation of these partial field gradient trends follows.

The partial quadrupole splitting (PQS) model has been extensively used in Sn(IV) Mössbauer spectroscopy.[39] While it is possible to generate a similar model for In(III),[40] we have chosen here instead to use the PQS values for four-coordinate Sn(IV) compounds to see if they can reproduce the *trends* we observe in the coupling constants of four-coordinate In(III). PQS values for $Co(CO)_4$ of −0.71 mm/s and for Cl and Br of 0.00 have been worked out.[11] A problem arises with the oxygen donors. In octahedral Sn(IV) compounds PQS values for oxygen donors are in the +0.16 to −0.03 mm/s range with weaker donors having the more positive values.[41] The PQS values in T_d complexes should be somewhat lower.[39] A donor such as CH_3COO^- is believed to have a value of −0.15 mm/s in four-coordinate Sn(IV) complexes.[39,42] It would seem reasonable then that acac be assigned a value of about −0.10 mm/s and the weaker donor THF a value of 0.00. Without apologies, this treatment must be considered as quite approximate. Table IV contains the ^{115}In coupling constants for three compounds along with the PQS values calculated from Sn(IV) after converting them to MHz (for ^{119}Sn, 1 mm/s = 19.26 MHz). Naturally the magnitudes of the indium and tin values are very different because Q_{Sn}, Q_{In}, $q_{\text{at}}(\text{In})$, and $q_{\text{at}}(\text{Sn})$ have not been introduced. The ratio of the PQS values to e^2Qq_{zz}/h for ^{115}In is found to be less than but in the range of $Q_{\text{Sn}}q_{\text{at}}(\text{Sn})/Q_{\text{In}}q_{\text{at}}(\text{In})$ using literature values.[43] While the range of field gradients is small, the PQS values do reproduce the trend in ^{115}In coupling constants using reasonable assumptions. The correlation may be fortuitous but does seem to exist to the extent of demonstrating that electronic effects are important in producing the large change in ^{115}In coupling constants.

A consistency in the halogen NQR data with those of In(III) and Co(−I) should also exist. The EFG in terminal halogen atoms can be interpreted using the relative population difference of the p orbitals, N_{p_i}; i.e.

$$(e^2Qq_{zz}/h)_{\text{mol}} = (e^2Qq_{zz}/h)_{\text{at}}\left[N_{\text{p}_z} - \frac{N_{\text{p}_x} + N_{\text{p}_y}}{2}\right] \qquad (4)$$

The bracketed term is negative for a singly bonded halogen atom using its p_z orbital in the bond. The halogen frequencies in Table III undergo a 10–30% decrease when $Co(CO)_4$ replaces a halogen in the coordination sphere of MX_3 compounds. This corresponds to an increase in the ionicity of the metal–halogen bond because N_{p_z} has increased. The electron density change should show up on indium through an increased "a" term and decreased "b" term in eq 1. That is, e^2Qq_{zz}/h of ^{115}In should increase upon replacement of Br by $Co(CO)_4$. Table I shows that e^2Qq_{zz}/h for ^{115}In is in fact about 25% greater in Co_2InBr_2 than in $InBr_3$. Additionally, the In–Br bonds should be longer. The crystal structures of $In_3Br_3Co_4(CO)_{15}$[17] and $Br_2In[Co(CO)_4]_2^-$ [15] indeed contain dramatically increased In–Br bond lengths compared to In_2Br_6.[44] If the compound CH_3InBr_2 is included and assumed to involve a similar indium atom coordination sphere geometry, we expect the trend in ν(^{79}Br terminal) with substitution in the In(III) coordination sphere to be $CH_3 < Co(CO)_4 < Br$. The experimental data in Table III verify this expectation.

It is worthwhile to note that these observations carry over to the halogen resonances in group 4A based compounds. $Co(CO)_4$–SnX_3 and $Co(CO)_4$–GeX_3 give halogen resonances that are substantially lower than those in SnX_4 and GeX_4.[1]

Finally, the correlation between e^2Qq_{zz}/h and the carbonyl infrared stretching frequencies in cobalt[3] and manganese[45] carbonyls has been noted. We expect to find a similar relationship in these compounds. Previous correlations of $\nu_{\text{CO}}(A_1)$ with e^2Qq_{zz}/h for ^{59}Co involved 50% changes in the coupling constant which show 40-cm^{-1} shifts in ν_{CO}.[3] In accordance with this the small range of e^2Qq_{zz}/h for ^{59}Co here goes along with a very small range of ν_{CO} values. In fact the A_1 modes lie in the 2085–2095-cm^{-1} range with most lying in the 2092–2095-cm^{-1} region. The insensitivity of carbonyl stretching frequencies to electronic and geometry changes in these compounds makes a correlation impossible. Co–Sn and Co–Ge bonds do produce higher $\nu_{\text{CO}}(A_1)$ values in the $Co(CO)_4$ group than do Co–In and Co–Ga bonds. $\nu_{\text{CO}}(A_1)$ in Co_2SnX_2 compounds is at 2115 cm^{-1} [3] while in Co_2InX_2 compounds it appears at 2094 cm^{-1}. The increased electron density on cobalt in the Co–In bond compared to that in Co–Sn produces a lower coupling constant according to eq 3 and a greater σ^* and π^* orbital population on CO. The magnitude of this carbonyl frequency shift with the metal atom electric field gradient change is in line with that found for other cobalt carbonyls[3] and for manganese carbonyls.[45]

Registry No. $\{BrIn[Co(CO)_4]_2\}_x$, 59922-77-9; $\{ClIn[Co(CO)_4]_2\}_x$, 59922-78-0; $In_3Br_3Co_4(CO)_{15}$, 21107-15-3; $BrIn[Co(CO)_4]_2 \cdot THF$, 59922-92-8; $ClIn[Co(CO)_4]_2 \cdot THF$, 59922-86-0; $acacIn[Co(CO)_4]_2$, 59922-87-1; $(C_6H_5)_3POIn[Co(CO)_4]_3$, 59922-88-2; $BrGa[Co(CO)_4]_2 \cdot THF$, 59922-89-3; $ClGa[Co(CO)_4]_2 \cdot THF$, 59922-90-6; $acacGa[Co(CO)_4]_2$, 59922-91-7; $Br_2GaCo(CO)_4 \cdot THF$, 59922-93-9; $Cl_2GaCo(CO)_4 \cdot THF$, 59922-94-0; $acacGaBrCo(CO)_4$, 59922-95-1;

$In[Co(CO)_4]_3$, 15820-67-4; ^{71}Ga, 14391-03-8; ^{115}In, 14191-71-0; ^{69}Ga, 14391-02-7; ^{59}Co, 7440-48-4; ^{79}Br, 14336-94-8; ^{81}Br, 14380-59-7; ^{35}Cl, 13981-72-1.

References and Notes

(1) T. L. Brown, P. A. Edwards, C. B. Harris, and J. L. Kirsch, *Inorg. Chem.*, **8**, 763 (1969).
(2) A. N. Nesmeyanov, G. K. Semin, E. V. Bryukhova, K. N. Anisimov, N. E. Kilobova, and V. N. Khandozhko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1936 (1969).
(3) D. D. Spencer, J. L. Kirsch, and T. L. Brown, *Inorg. Chem.*, **9**, 235 (1970).
(4) J. D. Graybeal, S. K. Ing, and M. S. Hsu, *Inorg. Chem.*, **9**, 678 (1970).
(5) H. W. Spiess and R. K. Sheline, *J. Chem. Phys.*, **53**, 3036 (1970).
(6) K. Ogino and T. L. Brown, *Inorg. Chem.*, **10**, 517 (1971).
(7) T. E. Boyd and T. L. Brown, *Inorg. Chem.*, **13**, 422 (1974).
(8) L. S. Chia, W. R. Cullen, and M. C. L. Gerry, *Can. J. Chem.*, **52**, 3095 (1974).
(9) C. D. Pribula, T. L. Brown, and E. Münck, *J. Am. Chem. Soc.*, **96**, 4149 (1974).
(10) D. L. Lichtenberger, D. R. Kidd, P. A. Loeffler, and T. L. Brown, *J. Am. Chem. Soc.*, **98**, 629 (1976).
(11) G. M. Bancroft and K. D. Butler, *J. Chem. Soc., Dalton Trans.*, 1694 (1973).
(12) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 1586 (1966).
(13) W. R. Robinson and D. P. Schussler, *J. Organomet. Chem.*, **30**, C5 (1971).
(14) T. B. Brill and G. G. Long, *J. Phys. Chem.*, **75**, 1989 (1971).
(15) P. D. Cradwick, *J. Organomet. Chem.*, **27**, 251 (1971).
(16) J. K. Ruff, *Inorg. Chem.*, **7**, 1499 (1968).
(17) P. D. Cradwick and D. Hall, *J. Organomet. Chem.*, **22**, 203 (1970).
(18) T. P. Das and E. L. Hahn, *Solid State Phys., Suppl.*, **1**, Chapter 1 (1956). A computer program written by L. F. Hamilton and T. B. Brill was used to compute the eigenvalues for $I = {}^5/_2$, ${}^7/_2$, and ${}^9/_2$ nuclei in increments of $\eta = 0.001$.
(19) T. L. Brown, *Acc. Chem. Res.*, **7**, 408 (1974).
(20) P. A. Casabella, P. J. Bray, and R. G. Barnes, *J. Chem. Phys.*, **30**, 1393 (1959).
(21) (a) E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants", Academic Press, New York, N.Y., 1969, Chapter 12; (b) *ibid.*, Chapter 7.
(22) M. J. S. Dewar, D. B. Patterson, and W. I. Simpson, *J. Chem. Soc., Dalton Trans.*, 2381 (1973).
(23) D. B. Patterson and A. Carnevale, *Inorg. Chem.*, **13**, 1479 (1974).
(24) M. G. Clark, *Chem. Phys. Lett.*, **13**, 316 (1972).
(25) T. B. Brill, *J. Mag. Reson.*, **15**, 395 (1974).
(26) R. G. Barnes and S. L. Segal, *J. Chem. Phys.*, **25**, 180 (1956).
(27) G. W. Ludwig, *J. Chem. Phys.*, **25**, 159 (1956).
(28) R. G. Barnes, S. L. Segal, P. J. Bray, and P. A. Casabella, *J. Chem. Phys.*, **26**, 1345 (1957).
(29) J. C. Evans and G. Y.-S. Lo, *Inorg. Chem.*, **6**, 836 (1967).
(30) T. B. Brill, P. E. Garrou, and G. G. Long, *J. Inorg. Nucl. Chem.*, **33**, 3285 (1971).
(31) P. A. Edwards and R. E. McCarley, *Inorg. Chem.*, **12**, 900 (1973).
(32) D. J. Merryman, P. A. Edwards, J. D. Corbett, and R. E. McCarley, *Inorg. Chem.*, **13**, 1471 (1974).
(33) A. J. Carty, *Coord. Chem. Rev.*, **4**, 29 (1969).
(34) T. Okuda, Y. Furukawa, H. Shigemoto, and H. Negita, *Bull. Chem. Soc. Jpn.*, **46**, 741 (1973).
(35) K. Mertz, W. Schwartz, F. Zetler, and H. D. Hausen, *Z. Naturforsch., B*, **30**, 159 (1975).
(36) G. E. Peterson and P. M. Bridenbaugh, *J. Chem. Phys.*, **51**, 238 (1969).
(37) D. K. Hon and C. E. Pfluger, *J. Coord. Chem.*, **3**, 67 (1973).
(38) H. A. Bent, *J. Chem. Educ.*, **37**, 616 (1960).
(39) G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, **15**, 59 (1972), and references therein.
(40) T. B. Brill, *Inorg. Chem.*, **15**, 2558 (1976).
(41) G. M. Bancroft, V. G. Kumar Das, and K. D. Butler, *J. Chem. Soc., Dalton Trans.*, 2355 (1974).
(42) R. H. Herber, A. A. Stöckler, and W. T. Reichle, *J. Chem. Phys.*, **42**, 2447 (1965).
(43) R. G. Barnes and W. V. Smith, *Phys. Rev.*, **93**, 95 (1954).
(44) A. F. Wells, "Structural Inorganic Chemistry", Oxford University Press, London, 1962, p. 357.
(45) T. B. Brill and A. J. Kotlar, *Inorg. Chem.*, **13**, 470 (1974).

Notes

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Application of the Additive Electric Field Gradient Model to Nuclear Quadrupole Resonance Data in Indium(III) Compounds and the Relation to Tin(IV) Parameters

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Additive electric field gradient models have been the focus of recent attention in the effort to formalize and predict trends in Mössbauer quadrupole splittings[1,2] and nuclear quadrupole resonance data.[3,4] It has been possible to define individual ligand electric field gradient (EFG) contributions which, when combined appropriately, will approximate the EFG at a central atom. Sn(IV),[5] Sb(III),[6] Sb(V),[7] Ir(III),[8] and low-spin Fe(II)[9] complexes have been analyzed in this way using Mössbauer spectra. Nuclear quadrupole resonance data in five-[3,10] and six-coordinate[4] cobalt compounds have also been discussed in connection with partial ligand field gradients (PFG). There exist many specific exceptions to the PFG model because π bonding,[3,11] the assumption of constant PFG values for individual ligands,[12] secondary associations,[1,2] and geometry changes[1,2] all contribute significantly to the EFG. Moreover, Sternheimer factors (valence and core electron polarizations) are usually assumed to be, but may not be, constant for a particular geometry.[13] Exceptions not withstanding, the frequent success of the PFG model at least in rationalizing qualitative trends in the electric field gradient makes it of general value and utility.

The bonding in Sn(IV) and Sb(V) compounds seems to be dominated by σ-bonding terms, and they often have good agreement between calculated and observed electric field gradients. Similarly it should be possible to subject the In(III) atom to an additive ligand electric field gradient treatment. Only quite recently have enough ^{115}In nuclear quadrupole resonance data become available to permit a preliminary PFG analysis, and by no means is the present note meant to be a final description. It is unlikely, however, that modeling as extensive as has been possible for Sn(IV) will ever come about because the number of suitable In(III) compounds and their tractability seems more restricted. Also the sign of the ^{115}In nuclear quadrupole coupling constant cannot be obtained experimentally from NQR spectroscopy. Even under the best of circumstances important assumptions are always made in applying the PFG model. All of these considerations make the model for In(III) a necessarily crude one. Nevertheless, by making qualitative comparisons to Sn(IV) parameters as a guide, the EFG trends in In(III) complexes do seem understandable as arising mainly from ligand PFG contributions and coordination sphere geometry changes.

Discussion

Table I contains a number of inorganic and organometallic compounds for which nuclear quadrupole coupling constants, e^2Qq/h, and EFG asymmetry parameters, η, have been reported. In particular, these are compounds having roughly similar counterparts in Sn(IV) chemistry. The sample temperature differences do not cause shifts in the coupling constants that are large enough to warrant concern here.

The compounds referred to as "six-coordinate" are not in all cases proven to be so on the basis of crystal structure determinations. $(CH_3)_2InCl$,[14] $(CH_3)_2InBr$,[15] and $(CH_3)_2InOAc$[16] are known to contain six-coordinate In(III) atoms with approximately trans CH_3 groups and multiply associated anions. Other R_2InX compounds ($R = CH_3$, C_6H_5; X = F,