by Cowley and collaborators.[5] We agree with those arguments. Model A, which is also a C_{3v} model, can be treated by our crude MO arguments because one of the ionization potentials can always be equated to P_0, while the others may be fit by only two parameters, e.g.

$$I_1 = N_0 - 2\beta^\sigma_{NN} \tag{12}$$

$$I_2 = P_0 \tag{13}$$

$$(I_3 + I_4)/2 = N_0 + \beta^\sigma_{NN} \tag{14}$$

The parameters obtained for all of the combinations of N_0 and P_0 using this model were inconsistent with the data. Furthermore, Cowley and co-workers have studied recently[5] the photoelectron spectrum of the caged compound $P[N(CH_3)-CH_2]_3CCH_3$ for which model A must apply. The spectrum obtained for this compound did not even remotely resemble those for I–III, and the Jahn–Teller splitting was too small to be resolved. Model C can be treated by our MO method; again all combinations of P_0 and N_0 produced results inconsistent with the data for I–III. Recent results in these laboratories on the photoelectron spectrum of the molecule
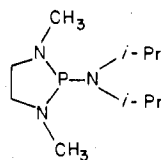
which has been demonstrated[9] by low-temperature ^{13}C NMR to have a structure consistent with model C, indicate that model C cannot be the correct one for I–III. It should be noted that attempts in these laboratories to freeze out II and III in the low-temperature ^{13}C NMR spectra in hopes of obtaining additional proof of their structures has not been successful to date, although considerable line broadening was observed near 130 K.

Conclusions

Our results indicate that the interpretation originally proposed by Cowley et al.[2] is basically correct. Namely,

tris(dialkylaminophosphines) have local C_s symmetry with only one nitrogen lone pair interacting with the phosphorus lone pair. However, we propose that bands I_2 and I_3 refer to the phosphorus–nitrogen lone pair interaction rather than bands I_2 and I_4 as concluded by Cowley et al. or bands I_1 and I_4 as concluded by Lappert et al.[4]

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Periodic Trends in Metal–Metal Bond Character Based on Cobalt-59 Nuclear Quadrupole Resonance Spectroscopy

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^{59}Co nuclear quadrupole resonance data in the $-Co(CO)_4$ group bound to the elements bismuth, silicon, germanium, tin, lead, gallium, indium, thallium, zinc, cadmium, mercury, gold, manganese, and cobalt are discussed. The metal–cobalt bound covalency is found to increase going vertically down the periodic chart in groups 2B, 3A, and 4A. The horizontal trend is to increase covalency from left to right; that is, M–Co covalency is group 1B < group 2B < group 3A < group 4A < group 5A. There is no strong evidence for metal–metal π bonding in the majority of the compounds. The σ-bond character overall is the dominating feature. However, an interaction of the π^* level of the equatorial CO groups in $-Co(CO)_4$ with the metal–cobalt bond or the heterometal itself appears to exist based on (1) the lack of correlation between the highest frequency symmetric CO stretching mode and the cobalt coupling constants and (2) the ^{115}In NQR data in $In[Co(CO)_4]_3$ compared to those in $In[Mn(CO)_5]_3$.

Introduction

The determination of differences in metal–metal bond characteristics for a wide range of metals requires a technique that is able to sample electron density information at the bond itself. In this paper, nuclear quadrupole resonance spectroscopy was used to examine the ^{59}Co electric field gradient

in a series of $M-Co(CO)_4$ compounds where M is varied through as wide a series of metals as possible. The electric field gradient detected in the NQR experiment is sensitive to changes in the orbital populations on the cobalt atom. Through electric field gradient changes it should be possible to qualitatively order metal–cobalt bond covalency both vertically and

Table I. ^{59}Co NQR Data in Metal–Cobalt Bonds at 298 K[a]

Compd	$\nu(^3/_2 \leftrightarrow ^1/_2)$	$\nu(^5/_2 \leftrightarrow ^3/_2)$	$\nu(^7/_2 \leftrightarrow ^5/_2)$	e^2Qq_{zz}/h, MHz	η	Ref
(CO)$_5$MnCo(CO)$_4$				128.44	0.094	4
				129.15	0.156	4
(C$_6$H$_5$)$_3$PAuCo(CO)$_4$		8.160 (2)	12.41 (2)	58.10	0.179	This work
Zn[Co(CO)$_4$]$_2$	6.120 (2)	11.95 (3)	17.96 (5)	83.85	0.067	This work
Cd[Co(CO)$_4$]$_2$		12.89 (4)	19.46 (4)	90.96	0.136	This work
		12.74 (4)	19.26 (4)	90.04	0.119	This work
Hg[Co(CO)$_4$]$_2$		15.99	24.00	112.0	0.05	3
		15.81	23.75	110.8	0.00	3
(C$_6$H$_5$)$_4$AsHg[Co(CO)$_4$]$_3$		11.50 (5)	17.56 (2)	82.30	0.21	This work
		11.06 (3)	17.16 (2)	80.90	0.32	This work
		10.94 (5)	16.92 (2)	79.64	0.30	This work
In[Co(CO)$_4$]$_3$[b]	9.082 (10)	14.52 (9)	22.35 (60)	105.0	0.26	This work
	8.313 (9)	14.57 (9)	22.21 (45)	104.0	0.19	This work
	11.40 (10)	13.50 (9)	21.32 (15)	101.8	0.47	This work
Tl[Co(CO)$_4$]$_3$	9.760 (6)	16.83 (250)	25.67 (35)	120.3	0.20	This work
	11.00 (6)	16.25 (200)	25.18 (40)	118.7	0.31	This work
	9.130 (6)	16.66 (250)	25.25 (40)	118.1	0.16	This work
Sn[Co(CO)$_4$]$_4$		18.47	27.69	129.2	0.00	3
Bi[Co(CO)$_4$]$_3$	9.657 (2)	18.90 (3)	28.42 (4)	132.7	0.074	This work
	9.408 (2)	18.72 (3)	28.09 (4)	131.1	0.035	This work
	10.24 (2)	18.26 (3)	27.75 (5)	129.9	0.175	This work

[a] Parenthetical numbers are signal-to-noise ratios. [b] A forbidden transition, $\nu(^1/_2 \leftrightarrow ^5/_2)$, was observed at 24.91 (5) MHz.

horizontally in the periodic chart. The details of metal–metal bond trends can be made most specific when a series of closely related compounds is available where only the ligands are varied, and both metals can be studied by NQR spectroscopy.[1] The supply of these idealized systems is limited by both synthetic constraints and by the number of NQR-active elements. Nevertheless, a reasonably broad range of comparisons can be made when the data from this work are combined with the results already known for M–Co(CO)$_4$ systems.[1–3] In most cases M is a metal whose bonding role is controlled mostly by the valence s- and p-electron density. The following periodic block of metals bound to the –Co(CO)$_4$ group have now been studied and can be compared.

1B	2B	3A	4A	5A
			Si	P
	Zn	Ga	Ge	
	Cd	In	Sn	
Au	Hg	Tl	Pb	Bi

The formalism of "B" group elements refers here to transition metals while "A" group elements are from the main group. In addition to these elements, –Mn(CO)$_5$ bound to –Co(CO)$_4$[4] and Co–Co bonds in [R$_3$PCo(CO)$_3$]$_2$ complexes[5] can be included in the comparisons. ^{115}In NQR spectra for In[Co(CO)$_4$]$_3$ and In[Mn(CO)$_5$]$_3$ were observed and are compared with previous data for triorganoindium compounds.[6,7]

The results lead to a qualitatively useful picture of the variation in the metal–metal bond covalency when viewed in the context of general trending. However, more specific details of metal–metal bond characteristics can be extracted when limited sets of compounds are scrutinized. For example, spectroscopic evidence of the interaction between the π^* orbitals of equatorial CO groups and the metal–metal bond[8] or the π^* orbitals and the metal to which cobalt is bound[9] has been obtained. It is hoped that these results will clearly point to the utility of NQR spectroscopy as a tool for experimentally examining the periodic differences in selected systems containing metal–metal bonds.

Experimental Section

All manipulations involving compounds in this work were carried out under an atmosphere of nitrogen using standard Schlenk-line techniques or in a Vacuum Atmospheres drybox. Solvents were dried and degassed prior to use and either stored in the drybox or distilled directly into the reaction vessel.

The compounds of interest in this work have been reported previously. In[Co(CO)$_4$]$_3$,[10] Cd[Co(CO)$_4$]$_2$,[11] and Zn[Co(CO)$_4$]$_2$[11] were prepared by transmetalation with Hg[Co(CO)$_4$]$_2$ and the appropriate metal. Hg[Co(CO)$_4$]$_2$ was prepared by the method of Hieber et al.,[12] as described by King.[13] (C$_6$H$_5$)$_3$PAuCo(CO)$_4$[14] and In[Mn(CO)$_5$]$_3$[15] were prepared by metathesis of (C$_6$H$_5$)$_3$PAuCl and InCl$_3$, respectively, with the appropriate metal carbonyl–sodium salt. Tl[Co(CO)$_4$]$_3$ was prepared by insertion of Tl[Co(CO)$_4$] into Co$_2$(CO)$_8$.[16] (C$_6$H$_5$)$_4$-AsHg[Co(CO)$_4$]$_3$ was prepared by the method of Conder and Robinson.[17] Bi[Co(CO)$_4$]$_3$ has been mentioned previously[18] and was prepared by combining BiI$_3$ (1.77 g, 3 mmol) in 20 mL of THF with NaCo(CO)$_4$ (9 mmol). The resulting red-brown solution was evaporated to dryness under vacuum, and the residue extracted with CH$_2$Cl$_2$/hexane. After filtration and cooling of the mixture slowly to -80 °C, 1.0 g (46%) of black crystals of Bi[Co(CO)$_4$]$_3$ was isolated (mp 88–90 °C). IR: 2071 (s), 2016 (m), 2004 (m), 199 (w, sh) cm^{-1}. Anal. Calcd for C$_{12}$O$_{12}$BiCo$_3$: C, 19.97; H, 0.0; Bi, 28.95. Found: C, 20.17; H, 0.33; Bi, 28.49.

All compounds except Bi[Co(CO)$_4$]$_3$ were identified by the correspondence of their IR spectra, melting points, and properties with the reports published previously. Infrared spectra were recorded on a Perkin-Elmer 180 grating spectrophotometer using sealed 0.15-mm KBr cells. Frequency measurements were accurate to within ± 1 cm^{-1}. Melting point values were obtained in sealed nitrogen-filled capillary tubes.

The nuclear quadrupole resonance spectra were recorded on 1–2 g of polycrystalline material sealed under nitrogen in glass vials. The spectral data were taken at room temperature (296–298 K) using a spectrometer system described before.[19] The spectrum analyzer frequency measurements are accurate to ± 0.005 MHz, but the uncertainty identifying the center line of the resonance multiplet causes us to report the resonance frequency data to four significant figures.

Results and Discussion

In not all cases is it possible to prepare compounds where the coordination sphere of the central element is saturated with –Co(CO)$_4$ groups. The central elements in the compounds Zn[Co(CO)$_4$]$_2$, Cd[Co(CO)$_4$]$_2$, Hg[Co(CO)$_4$]$_2$, In[Co(CO)$_4$]$_3$, Tl[Co(CO)$_4$]$_3$, Sn[Co(CO)$_4$]$_4$, and Bi[Co(CO)$_4$]$_3$ have their primary bonding affinity saturated by –Co(CO)$_4$ ligands. However, when the central element is Au^{I}, Ga^{III}, Si^{IV}, Ge^{IV}, or Pb^{IV}, this type of complex is not yet known. As a result, for these elements it is necessary to make comparisons using compounds having other ligands in the central metal coordination sphere. The ^{59}Co NQR data in Table I, in most cases, are for compounds where the central M is saturated with –Co(CO)$_4$ groups. The data in Table II allow comparisons to be made among group 3A and 4A elements in compounds having the same stoichiometry.

Table II. Comparison of NQR Data in Stoichiometrically Similar Ga and In Compounds and Si, Ge, Sn, and Pb Compounds[a]

Compd	e^2Qq_{zz}/h, MHz	η	Ref
acacGa[Co(CO)$_4$]$_2$	96.40[b]	0.055	1
acacIn[Co(CO)$_4$]$_2$	101.5[b]	0.09	1
BrGa[Co(CO)$_4$]$_2$·THF	103.3	0.16	1
BrIn[Co(CO)$_4$]$_2$·THF	105.9[b]	0.11	1
ClGa[Co(CO)$_4$]$_2$·THF	102.2	0.15	1
ClIn[Co(CO)$_4$]$_2$·THF	105.5[b]	0.10	1
Cl$_3$SiCo(CO)$_4$	130.67	0.13	2
Cl$_3$GeCo(CO)$_4$	160.47[b]	0.0	2
Cl$_3$SnCo(CO)$_4$	163.45	0.0	2
(C$_6$H$_5$)$_3$SiCo(CO)$_4$	101.09	0.0	2
(C$_6$H$_5$)$_3$SnCo(CO)$_4$	104.11	0.05	2
(C$_6$H$_5$)$_3$PbCo(CO)$_4$	110.82	0.05	2

[a] Data at room temperature. [b] Average of 2 resonances.

For rationalizing the changes in ^{59}Co coupling constants, e^2Qq_{zz}/h, in terms of electron density changes, the electric field gradient at the metal nucleus in the –Co(CO)$_4$ fragment can be expressed to a good approximation in terms of the populations of the d orbitals on cobalt, N_{d_i}

$$e^2Qq_{zz}/h = (e^2Qq_{320}/h)\{N_{d_{z^2}} + [(N_{d_{xz}} + N_{d_{yz}})/2] - N_{d_{xy}} - N_{d_{x^2-y^2}}\} \qquad (1)$$

q_{320} is the electric field gradient produced by a single d electron, and q_{zz} is the maximum-value component of the electric field gradient tensor for the –Co(CO)$_4$ group. It is not necessary to know the exact value of e^2Qq_{320}/h when making trending comparisons because the term is constant. The d$_{z^2}$ orbital is assumed to be coincident with the metal–cobalt bond axis (a C_3 axis in the –Co(CO)$_4$ unit). Evidence from other studies is very strong that the sign of the bracketed quantity in eq 1 is negative for –Co(CO)$_4$.[1-3] Hence a decrease in the population of orbitals carrying a positive sign will increase the coupling constant. This would correspond to migration of σ- and π-electron density from cobalt atom to the heterometal, M. The metal–metal bond would become more covalent in this case. It should be mentioned that p-orbital contributions to bonding may be significant in the absolute magnitude of the electric field gradient. MO calculations on Fe(CO)$_5$ show that 10–20% of the total electric field gradient may come from p-orbital effects.[20] This contribution is not of very great concern to the arguments made here because the effects of p$_z$ orbital population changes will parallel those of d$_{z^2}$, and p$_x$ and p$_y$ will parallel d$_{xy}$ and d$_{x^2-y^2}$.[20] The data will be discussed in terms of the trends rather than absolute magnitudes.

Should the M–Co(CO)$_4$ bond axis be nonaxially symmetric because of the ligands bound to M, the population of the d$_{xz}$ and d$_{yz}$ orbitals on the cobalt atom may become inequivalent. In this case, a nonzero value of the electric field gradient asymmetry parameter, η, occurs. Equation 2 expresses η in

$$\eta = \frac{^3/_2\left[N_{d_{xy}} - N_{d_{yz}}\right]}{e^2Qq_{zz}/h} \qquad (2)$$

terms of the orbital populations but requires caution in its use because the orientation of q_{zz} may no longer coincide with the metal–metal bond axis for nonzero η values. The symmetry of the compounds in Tables I and II leads us to strongly suspect that q_{zz} and the metal–metal bond are still reasonably well aligned, however.

NQR Data and Crystal Structure Relationships. It is informative to know how the NQR data in this work compare with the known crystal structures in several of the compounds. The structure of (C$_6$H$_6$)$_3$PAuCo(CO)$_4$ reveals a linear P–Au–Co linkage[21] yet the ^{59}Co asymmetry parameter is 0.179. This rather large value probably results from lat-

Table III. Highest Frequency Totally Symmetric Carbonyl Stretching Mode in a Series of M–Co(CO)$_4$ Systems

Compd	ν(CO), cm^{-1}	Ref
(C$_6$H$_5$)$_3$PAuCo(CO)$_4$	2055[a]	d
(C$_6$H$_5$)$_4$AsHg[Co(CO)$_4$]$_3$	2063[b]	17
Tl[Co(CO)$_4$]$_3$	2068[a]	16
In[Co(CO)$_4$]$_3$	2070[c]	e
Cd[Co(CO)$_4$]$_2$	2071[a]	11
Bi[Co(CO)$_4$]$_3$	2071[a]	This work
Hg[Co(CO)$_4$]$_2$	2072[a]	11
Zn[Co(CO)$_4$]$_2$	2077[a]	11
Sn[Co(CO)$_4$]$_4$	2104[a,f]	3

[a] Hexane. [b] Tetrahydrofuran. [c] Cyclohexane. [d] L. M. Bower and M. H. B. Stoddard, *J. Chem. Soc. A*, 706 (1968). [e] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 5, 1587 (1966). [f] Two other papers [D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 7, 773 (1968); M. Bigorgne and A. Quintin, *C. R. Hebd. Seances Acad. Sci.*, 264, 2055 (1967)] list 2079 cm^{-1} as the highest frequency mode in cyclohexane. The mode at 2104 cm^{-1} is reported to be very weak and possibly could have been overlooked in these two studies

tice-induced distortions in the –Co(CO)$_4$ unit, but the structure was not refined to the level required to identify them. Inasmuch as reasonably large asymmetry parameters in other seemingly axially symmetric M–Co(CO)$_4$ systems, such as Cd[Co(CO)$_4$]$_2$ and Cl$_3$SiC$_0$(CO)$_4$, are also found, little intramolecular bonding significance can be attached to η values in the range of 0.2 or less in these cobalt carbonyls. The structures of Zn[Co(CO)$_4$]$_2$[22] and Hg[Co(CO)$_4$]$_2$[23] show linear Co–M–Co linkages within 1 or 2°. In accordance with this, small η values are observed. The two ^{59}Co coupling constants found in Hg[Co(CO)$_4$]$_2$ agree with the fact that the cobalt atoms are crystallographically inequivalent in the crystal lattice.

In[Co(CO)$_4$]$_3$ contains discrete tricoordinate indium atoms.[10] The cobalt atoms are crystallographically inequivalent and no longer possess an axially symmetric electric field gradient tensor because of the planarity of the InCo$_3$ framework. It is consistent then that η values of 0.19–0.47 are observed for the cobalt atoms and three different coupling constants are observed. The resonances were sufficiently strong that a forbidden $m_I^2 = \,^1/_2 \leftrightarrow \,^5/_2$ transition was detected for the cobalt atom having the largest asymmetry parameter. The probability of these forbidden transitions becomes greater as η increases.[24] The crystal structures of Tl[Co(CO)$_4$]$_3$ and Hg[Co(CO)$_4$]$_3^-$ salts have not yet appeared. The η values in these two systems are significant but are somewhat less than those in In[Co(CO)$_4$]$_3$. Since the cobalt coupling constants for the Hg^{II} and Tl^{III} compounds straddle those in the In^{III} compound, it would seem that the η values arise more from differences in the space available to the –Co(CO)$_4$ group as controlled by the size of the central metal element than from differences in the nature of the metal–metal bonds.

NQR Data and CO Infrared Stretching Frequencies. Carbonyl infrared stretching frequencies might be used to learn about the metal–metal bond character in these compounds. Metal NQR coupling constants have been noted to correlate with the highest energy A mode of ν_{CO} for compounds of the type X$_n$Sn[Co(CO)$_4$]$_{4-n}$ and R$_n$Sn[Co(CO)$_4$]$_{4-n}$ containing Sn–Co bonds[3] and for (CH$_3$)$_n$C$_6$H$_{6-n}$Mn(CO)$_3^+$ compounds,[25] where no metal–metal bond is present. On the other hand, X–Mn(CO)$_5$ compounds are found not to yield a correlation between ν_{CO} and the ^{55}Mn coupling constants.[26,27]

From the CO stretching frequencies in Table III we find that the highest frequency A mode is not very sensitive to the heterometal, M, yet $e^2Qq_{zz}/h(^{59}$Co) is very sensitive to M. Moreover, in the crystal structures discussed above,[10,21-23] the CO groups in the equatorial plane of the –Co(CO)$_4$ group "umbrella" toward the central metal such that the M–Co–CO

(equatorial) angle is 80–85°. Two reasons for these facts may be (1) a secondary interaction between the equatorial carbonyl π^* orbitals and the metal–metal σ bond or (2) interactions between the π^*(CO) level with the heterometal, M. The first type of interaction has been discussed in $Mn(CO)_5X$ compounds, X = Cl, Br, I,[8] while the second has been proposed in the silicon–metal bond.[9] Migration of the density to the π^* levels of the CO group directly from the metal–metal bond or from the π^* level into an empty orbital on the central atom (in each case bypassing the cobalt atom) would cause ν_{CO} and $e^2Qq_{zz}/h(^{59}Co)$ to follow different courses. For example, $e^2Qq_{zz}/h(^{59}Co)$ is greater in $Tl[Co(CO)_4]_3$ than in $In[Co(CO)_4]_3$ which suggests that less electron density resides on a cobalt atom involved in the Tl–Co bond than in the In–Co bond. However, following the idea then that the π^* orbitals of the CO groups should be less populated in $Tl[Co(CO)_4]_3$ we find, in contradiction, that ν_{CO} is about the same in $Tl[Co(CO)_4]_3$ and $In[Co(CO)_4]_3$. The same behavior is observed in $M[Co(CO)_4]_2$, M = Zn, Cd, Hg.

Unfortunately, either of the secondary interactions of the CO group mentioned above could be used to rationalize these experimental observations because both ν_{CO} and e^2Qq_{zz}/h are affected by competitive σ and π bonding. More evidence for secondary carbonyl bonding will be presented shortly on the basis of indium electric field gradients. It is not surprising that no simple experimental correlation exists between ν_{CO} and e^2Qq_{zz}/h over a wide range of compounds.

Vertical Trends in Groups 2B, 3A, and 4A. The trends in NQR data among the group 4A elements Si, Ge, Sn, and Pb have been considered elsewhere.[2,28] The $(C_6H_5)_3M-$ ligand produces small differences in e^2Qq_{zz}/h of cobalt when M = Si, Sn, and Pb, but the Cl_3M- ligand leads to a very large increase upon going from M = Si to M = Ge. The lower ^{59}Co EFG produced by the Cl_3Si- group is compatible with considerably greater ionicity in the Co–Si bond compared to Co–Ge. Co–Sn and Co–Ge bonds may have some π character in the trichloro derivatives.[2,28] On the whole, though, e^2Qq_{zz}/h for cobalt generally increases upon descending the periodic table in group 4A.

The group 3A elements Ga and In can be compared in several stoichiometrically similar compounds[1] given in Table II. The differences are again small but the regularity would suggest that there is a real nonaccidental source to the fact that in each instance the ^{59}Co electric field gradient is lower in the Co–Ga bond than in the Co–In bond. The effect of indium and thallium on the $-Co(CO)_4$ group can be directly compared with data for $In[Co(CO)_4]_3$ and $Tl[Co(CO)_4]_3$ given in Table I. The lower frequency in the former compound indicates that in the In–Co bond is the more ionic of the two. Hence, the covalency of the metal–cobalt bond in the heavier group 3A elements increases upon descending the periodic table. Metal–metal π bonding in $In[Co(CO)_4]_3$ and $Tl[Co(CO)_4]_3$ could exist in principle by involving the empty valence shell p_z orbital on indium or thallium with the populated d_{xz} or d_{yz} orbital on cobalt. Such an interaction would have the effect of increasing the ^{59}Co electric field gradient by decreasing $N_{d_{xz}}$ or $N_{d_{yz}}$ in eq 1. According to eq 2, η would increase because only one of these two cobalt d orbitals has the correct symmetry for metal–metal π interaction. The fact that the η values are lower in $Tl[Co(CO)_4]_3$ than in $In[Co(CO)_4]_3$, whereas the reverse is true of e^2Qq_{zz}/h, is good evidence that direct dp_π overlap is not an important factor in the ground-state electronic description of those molecules.

In group 2B, the results for $M[Co(CO)_4]_2$ compounds, M = Zn, Cd and Hg, are directly comparable. As in groups 4A and 3A, the data in Table I are consistent with an increase in the metal–metal bond covalency going down the group from zinc to mercury. This result can be compared to a detailed

force constant analysis of the same compounds[29] which shows that the metal–metal stretching force constants are nearly identical but fall in the order $k(Zn-Co) \geq k(Cd-Co) \geq k(Hg-Co)$. The mass spectra of these compounds qualitatively indicate that the order of metal–metal bond strength is Zn–Co > Cd–Co > Hg–Co.[11] Hence all of these techniques give a consistent trend but they are not quantitatively correlatable. No doubt the lack of quantification is at least partly due to the fact that the observables should not necessarily be related in the first place. The force constant of a bond and the strength of a bond are not fundamentally related to one another, and the NQR data here are being discussed in terms of covalency rather than strength of the bond. It is interesting, if not fortuitous, that the trends in these three bond parameters—covalency, strength, and stretching force constant—which are often considered to be related, vary in the same direction for this limited series of metal–metal bonds. In this series as before the EFG data indicate that the σ bond vastly dominates any π bonding in the ground-state description. Co–M π charge migration would drain electron density from the d_{xz} or d_{yz} orbitals on the cobalt atom which would lead to an increase in e^2Qq_{zz}/h. Experimentally, the cobalt coupling constant is lowest in the Zn–Co bond and increases steadily to the Hg–Co bond. This provides no evidence for π bonding.

Returning to periodic electric field gradient differences, e^2Qq_{zz}/h for cobalt shows a slightly greater difference between Zn–Co and Cd–Co bonds than what is found when cobalt is bonded to Ga and In or Ge and Sn. The difference between the effect of Cd and Hg on the $-Co(CO)_4$ group is not significantly different from the effect of In and Tl. However, the 15–20-MHz difference in e^2Qq_{zz}/h between the period 5 and period 6 elements in this part of the table is no doubt a result of the lanthanide contraction, which makes Z_{eff} of row 6 elements abnormally great and the metal–metal bond more covalent than would otherwise be the case. Taking all of these ideas together, *the vertical trend in the metal–cobalt bond character is to increase the covalency upon descendng the periodic table in groups 2B, 3A, and 4A.* The σ-bonding interaction dominates the metal–metal bond in these systems, although some π character may exist when the central element has a high formal charge and is also bound to relatively electronegative elements, as in $Cl_3MCo(CO)_4$.

Horizontal Trends in Metal–Cobalt Bond Character. The importance of the oxidation state, n, of the central metal in determining the cobalt electric field gradient can be extracted by comparing the $M^n[Co(CO)_4]_n$ compounds in Table I. For period 5 $Cd[Co(CO)_4]_2$, $In[Co(CO)_4]_3$, and $Sn[Co(CO)_4]_4$ represent two-, three-, and four-coordinate systems where the oxidation state of the central element increases from II to IV. The coupling constant for ^{59}Co increases by 13 MHz from Cd^{II} to In^{III} and 16 MHz from In^{III} to Sn^{IV}. The change is mostly a result of the increasing σ-bond electron density migration from the d_{z^2} orbital of cobalt to the central metal element, M, as the oxidation state of M increases.

An even broader horizontal comparison from gold to bismuth can be made in period 6 if a few corollary arguments are interjected. The ^{59}Co coupling constant for $(C_6H_5)_3P-AuCo(CO)_4$ is to our knowledge the lowest yet observed for the $-Co(CO)_4$ group. The presence of triphenylphosphine in the gold coordination sphere is no doubt a factor in making the Au^I-Co bond the least covalent of all the metal–metal bonds discussed here. However, the fact that e^2Qq_{zz}/h for cobalt is only slightly more than half that produced when cobalt is bonded to the neighboring element, mercury, in $Hg[Co(CO)_4]_2$ makes it highly probable that the Au^I-Co bond is inherently less covalent than the $Hg^{II}-Co$ bond anyway. The more directly comparable $Hg^{II}-Co$ and $Tl^{III}-Co$ bonds in $Hg[Co(CO)_4]_2$ and $Tl[Co(CO)_4]_3$ clearly show the $Tl^{III}-Co$

Table IV. ^{115}In NQR Data in Tricoordinate In(III) Compounds[a]

Compd	$\nu(^3/_2 \leftrightarrow {}^1/_2)$	$\nu(^5/_2 \leftrightarrow {}^3/_2)$	$\nu(^7/_2 \leftrightarrow {}^5/_2)$	$\nu(^9/_2 \leftrightarrow {}^7/_2)$	e^2Qq_{zz}/h	η
In[Co(CO)$_4$]$_3$	27.70 (40)	55.22 (30)	82.88 (55)	110.51 (45)	662.94	0.019
In[Mn(CO)$_5$]$_3$	25.83 (5)	51.62 (7)	77.43 (4)		619.5	0.009
In(CH$_3$)$_3$[b]	53.9	90.90	138.91		1115.1	0.14
In(C$_2$H$_5$)$_3$[b]	51.44	93.06	141.40	188.50	1135.2	0.107
	52.12	95.53	143.16	193.16	1159.6	0.096
In(C$_6$H$_5$)$_3$[c]	49.95 (10)	85.17 (5)	129.97 (10)	173.63 (4)	1043.5	0.133

[a] Parenthetical numbers are signal-to-noise ratios. [b] Reference 6 at 77 K. [c] Reference 7 at 298 K.

bond to be the more covalent one. In group 4A no directly comparable Pb^{IV}–Co bond exists, but an extrapolation can be made from Sn[Co(CO)$_4$]$_4$ where $e^2Qq_{zz}/h(^{59}$Co) is greater than that in Tl[Co(CO)$_4$]$_3$. It would follow from the vertical trends in group 4A discussed above that the M–Co bond covalency for M = Pb will be greater than when M = Sn. Hence it seems very safe to say that the Pb^{IV}–Co bond is more covalent than the Tl^{III}–Co bond. Finally, the Bi^{III}–Co bond in Bi[Co(CO)$_4$]$_3$ produces the largest cobalt coupling constant of all those in Table I. This strongly reinforces the expectation that Bi^{V}–Co bonds would be still more covalent than Pb^{IV}–Co bonds. In sum the trend in metal–cobalt bond covalency in period 6 increases in the series metal = group 1B < group 2B < group 3A < group 4A < group 5A. The same general trend over a narrower but more directly comparable set of compounds was noted above for period 5 elements bonded to the –Co(CO)$_4$ group. *The metal–cobalt bond covalency increases from left to right across the periodic chart for the heavier main-group elements.*

It is noteworthy that the phosphorus–cobalt bond in [R$_3$PCo(CO)$_3$]$_2$ and in [(C$_6$H$_5$)$_3$P]$_2$Co(CO)$_3^+$ salts produces cobalt coupling constants in the 140–160-MHz region.[5] These rather large values are compatible with the trends note above that group 5A elements form highly covalent bonds to the cobalt carbonyl group. The cobalt–cobalt bond in the [R$_3$PCo(CO)$_3$]$_2$ compounds leads to an electric field gradient almost as large as that produced by the group 5A–cobalt bond. The manganese–cobalt bond in (CO)$_5$MnCo(CO)$_4$ also fits this pattern because $e^2Qq_{zz}/h(^{59}$Co) in this compound is 128.5–129 MHz.[4] These Co–Co and Mn–Co bonds involve an interaction where the nucleophilic character of –Mn(CO)$_5$ and –Co(CO)$_3$PR$_3$ is known to be comparable to or greater than that of the cobalt carbonyl itself.[30] In general, many of the main-group metals and also those of groups 1B and 2B produce lower cobalt coupling constants than the Mn–Co and Co–Co bonds. It can be inferred, therefore, that they form less covalent metal–metal bonds than are found in Co–Co and Mn–Co. An assumption made here is that a large redistribution in the orbital population on cobalt in the –Co(CO)$_4$ group does not occur as the metal-containing ligand is varied. In the absence of significant metal–cobalt π bonding, for which in most cases there is little clear evidence, this assumption should be qualitatively valid.

An isoelectronic relationship exists between Hg[Co(CO)$_4$]$_3^-$ and Tl[Co(CO)$_4$]$_3$. Of most interest is the fact that an indication of the effect of a change in the formal oxidation state of the central element can be established in a structurally similar moiety. The cobalt coupling constant decreases from 118–120 MHz for Tl^{III} to 80–82 MHz for Hg^{II}. The source of this change is mostly an increase in $N_{d_z^2}$ on cobalt through an increase in ionicity and bond length of the Hg–Co bonds.

Indium Electric Field Gradient Measurements. NQR data for ^{115}In in two tricoordinate metal–metal bonded compounds were obtained and are reported in Table IV along with several organoindium compounds for comparison. No ^{55}Mn resonances were observed in In[Mn(CO)$_5$]$_3$. The relationship between indium metal p-orbital populations and the ^{115}In coupling constant can be understood in terms of eq 3. The

$$e^2Qq_{zz}/h = (e^2Qq_{510}/h)\{N_{p_z} - [(N_{p_x} + N_{p_y})/2]\} \qquad (3)$$

p$_z$ orbital is coincident with the C_3 axis in these compounds, and the p$_x$ and p$_y$ orbitals are used in hybridization to form the indium–metal σ bonds. Since N_{p_z} is close to zero, the sign of the bracketed quantity is negative for In^{III} in molecules of this symmetry. An increase in the σ-donor character of the ligands will increase e^2Qq_{zz}/h by increasing N_{p_x} and N_{p_y}.

The η values in the metal–metal bonded compounds are all very small in accordance with the presence of a C_3 axis at the indium atom. In (CH$_3$)$_3$In and (C$_6$H$_5$)$_3$In secondary coordination involving the axial position of the metal and organo groups in neighboring molecules causes the indium atom to be pseudo-five-coordinate with three short and two long indium–carbon bonds.[31,32]

The trend in the electric field gradient at indium produced by the ligands is –CH$_3$ > –C$_6$H$_5$ > –Co(CO)$_4$ > –Mn(CO)$_5$. This trend follows the order of nucleophilicity of the groups except in the case of –Mn(CO)$_5$ and –Co(CO)$_4$ where it is established property that –Mn(CO)$_5$ is better nucleophile than –Co(CO)$_4$.[30] For example, the partial quadrupole coupling constants for –CH$_3$, –C$_6$H$_5$, –Mn(CO)$_5$, and –Co(CO)$_4$ bound to Sn^{IV} in four-coordinate complexes are respectively –1.37, –1.26, –0.97, and –0.71 mm/s.[33] Chemical reactivity patterns also clearly indicate that –Mn(CO)$_5$ is a better nucleophile than –Co(CO)$_4$.[30] The ^{115}In NQR data seem at odds with this ordering if only the σ bond is considered to be important. However, the crystal structure of In[Co(CO)$_4$]$_3$ shows the In–Co bond length to be less than the sum of the covalent radii for indium and cobalt.[10] It might be tempting to ascribe this bond distance shortening to d$_{xy}$, d$_{yz}$(Co) → p$_z$(In) π bonding. But already we have discounted the η values of cobalt, which would be generated by dp$_\pi$ bonding, as arising from the In–Co bond characteristics. Instead, it has been proposed[10] that indium–carbon interactions between the π^*(CO) orbitals and the p$_z$ orbital of indium occur. An alternate explanation is that the In–Co bond donates electron density directly to the π^*(CO) level. Any increase in N_{p_z} will have the effect of lowering the indium coupling constant, as will a decrease in N_{p_x}, N_{p_y}. Further, either of these secondary interactions would cause the equatorial carbonyl groups to relocate closer to the indium atom and make the In–Co–CO (equatorial) angle less than 90°, as is observed.[10] Only six of the nine equatorial carbonyl groups (those above and below the InCo$_3$ plane) can engage in π^*(CO) → p$_z$(In) interactions in In[Co(CO)$_4$]$_3$. Although the crystal structure of In[Mn(CO)$_5$]$_3$ has not appeared, it is not difficult to see that more than six equatorial CO groups can have the right symmetry to interact with the p$_z$ orbital of indium. If only six interact, which is sterically unlikely because the remaining equatorial CO groups would have to point directly toward one another, maximal overlap between the π^*(CO)–p$_z$(In) system is achieved. More likely, rotation of one or more of the –Mn(CO)$_5$ groups occurs, which reduces the overlap but increases the number of CO groups available for the interaction. The importance of this secondary interaction would have to be sufficiently great to override the greater σ-donor power of –Mn(CO)$_5$ compared to –Co(CO)$_4$. The interaction of π^*(CO) with the metal–indium σ bond

could be greater in In–Mn than In–Co because of the greater nucleophilicity of $-Mn(CO)_5$ compared to $-Co(CO)_4$. The trend in N_{p_x}, N_{p_y} and thus $e^2Qq_{zz}/h(^{115}In)$ would be Co > Mn.

Registry No. $(C_6H_5)_3PAuCo(CO)_4$, 15154-50-4; $Zn[Co(CO)_4]_2$, 16985-99-2; $Cd[Co(CO)_4]_2$, 16986-00-8; $(C_6H_5)_4AsHg[Co(CO)_4]_3$, 37336-87-1; $In[Co(CO)_4]_3$, 38188-07-7; $Tl[Co(CO)_4]_3$, 41161-30-2; $Bi[Co(CO)_4]_3$, 62571-22-6; $acacGa[Co(CO)_4]_2$, 14242-69-4; acac-$In[Co(CO)_4]_2$, 14242-71-8; $BrGa[Co(CO)_4]_2$, 62571-21-5; Br-$In[Co(CO)_4]_2$, 59922-76-8; $ClGa[Co(CO)_4]_2$, 62601-29-0; Cl-$In[Co(CO)_4]_2$, 37707-06-5; $Cl_3SiCo(CO)_4$, 15693-80-8; Cl_3Ge-$Co(CO)_4$, 16560-96-6; $Cl_3SnCo(CO)_4$, 17523-00-1; $(C_6H_5)_3Si$-$Co(CO)_4$, 14095-19-3; $(C_6H_5)_3SnCo(CO)_4$, 13964-91-5; $(C_6H_5)_3$-$PbCo(CO)_4$, 16561-04-9; $In[Mn(CO)_5]_3$, 36539-52-3; ^{59}Co, 7440-48-4; ^{115}In, 14191-71-0.

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Electronic Structure of the Octahedral Hexachloroytterbate Ion

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The absorption spectrum of the $^2F_{7/2}(E_u') \rightarrow {}^2F_{5/2}(U_u' + E_u'')$ transitions in single crystals of $Cs_2NaYbCl_6$ has been measured at room temperature and 77 K. Extensive vibronic structure was resolved and assigned for both transitions. The intensity of the magnetic dipole induced no-phonon transition to the U_u' term was found to be $\sim 0.25 \ \mu_B^2$. The fourth-order crystal field parameter, b_4, was found to be $-21.1 \pm 2.3 \ cm^{-1}$ and the spin-orbit coupling parameter, ζ, to equal $2850 \pm 25 \ cm^{-1}$. The low value of ζ can be explained by assuming an increased interaction with the metal 5p orbitals in the six-coordinate species. Two ligand-to-metal charge-transfer transitions were measured in a single crystal of $Yb^{3+}:Cs_2NaYCl_6$ at ~ 10 K using absorption and MCD. The MCD results allow the first, at 38 315 cm^{-1}, to be assigned as the $E_u' \rightarrow {}^2T_{1g}(\pi)$ transition arising from the $t_{1g}(\pi) \rightarrow 4f(t_{1u})$ electron transfer. The second transition is tentatively assigned, based on intensity arguments, as the $E_u' \rightarrow {}^2T_{2g}(\pi)$ transition arising from the $t_{2g}(\pi) \rightarrow 4f(t_{1u})$ electron transfer.

Introduction

Compounds of the type $Cs_2NaLnCl_6$ (Ln = trivalent metal ion) have recently been the object of much study. These compounds have the cubic elposolite structure, space group $Fm3m$, with the Ln ion at a site of six-coordinate O_h symmetry.[1] As a consequence of this many interesting effects are observed.

Thus far the f–f transitions and vibronic structure have been studied using absorption and magnetic circular dichroism (MCD) spectroscopy for $Cs_2NaEuCl_6$,[2] $Cs_2NaPrCl_6$,[3] $Cs_2NaTbCl_6$,[4] and $Cs_2NaTmCl_6$.[5] The vibrational structure is similar in all cases studied so far and seems to be due to an interaction of the electrons with a density of vibrational states over the entire Brillouin zone. This contrasts with the results for $Cr^{3+}:Cs_2NaYCl_6$ where the vibrational structure was interpreted assuming interactions only within the $CrCl_6^{3-}$ moiety.[6] In that case progressions involving both the a_{1g} and, Jahn–Teller active, e_g modes were observed. No progression of any type has been seen in the f–f spectra of the lanthanides.

The luminescence of $Cs_2NaNdCl_6$ and $Nd^{3+}:Cs_2NaYCl_6$ have been studied and show the longest lifetimes yet reported for Nd^{3+}.[7] The luminescence of $Cs_2NaTbCl_6$ originating on the $^5D_4$ term showed vibrational structure on ΔJ even transitions and only magnetic dipole origins for the ΔJ odd transitions.[4] Long-range energy transfer from Tb^{3+} to Eu^{3+} has also been observed in this crystal system.[8]

The low-temperature EPR spectra of a number of ions doped into Cs_2NaYCl_6 have been reported. Ce^{3+}, Dy^{3+}, and Yb^{3+} show isotropic g values[9] but orientation-dependent line widths.[10] The orientation dependence of the Γ_8(quartet) ground term of Er^{3+} has been studied and the $\pm^1/_2 \rightarrow \pm^3/_2$ transition observed in addition to the usually studied $-^1/_2 \rightarrow +^1/_2$ transition.[11] The resonance of Gd^{3+} has been recorded as a function of host lattice (Ln = La, Pr, Tb, Yb, Y) and temperature.[11] A crystalline phase transition has been found to occur between room temperature and 77 K in those compounds with Ln = La–Eu and found not to occur down to 4.2 K for Ln = Tb–Yb and Y.[12] Finally no indications of