geometry comes from the optical spectra. It shows one band centered at 19,275 cm^{-1} (ϵ 476). This is most likely due to the transition $(d_{x^2-y^2})^2 \rightarrow (d_{x^2-y^2})^1(d_{xy})^1$ in planar d^8 complexes.

The methinotetraphenyldithiodiphosphinate ligand shows a very close resemblance to the isoelectronic imidothiodiphosphinate particularly with respect to the similarity of the spectral and magnetic parameters of the iron(II) and cobalt(II) complexes. It gives the expected behavior of a sterically unencumbered bidentate ligand toward nickel(II), whereas the imidodiphosphinate gives the anomalous tetrahedral geometry. These results show conclusively that the factors which dictate the stereochemistry of coordination number 4 with bidentate ligands about nickel(II) are more complex than those previously anticipated.

Selenium Complexes.—The complex $[((C_6H_5)_2PSe)_2CH]_2Fe^{II}$ is obtained as small yellow crystals which decompose rapidly in air. It has been shown to be monomeric in toluene solutions which are extremely air sensitive. The magnetic moment and electronic spectrum indicate that it has a tetrahedral FeSe$_4$ unit. The spectral and magnetic data (Table I) for the green complex $[((C_6H_5)_2PSe)_2CH]_2Co^{II}$ show that it is also tetrahedral and like the iron complex is air sensitive in both solid and solution phases. These are the first examples of this geometry found for four-coordinate iron(II) and cobalt(II) complexes with selenium donor functions. The only other four-coordinate complexes of these metals are the 1,2-diselenolenes[10] $MSe_4C_4(CF_3)_4^-$ (M = Fe or Co) which are involved in monomer–dimer equilibria in solution and undoubtedly have planar monomeric units.

Considerable difficulty was experienced in preparing pure samples of the dark red complex $[((C_6H_5)_2PSe)_2CH]_2Ni^{II}$. Pure samples are diamagnetic; however it is frequently contaminated by a paramagnetic impurity. The optical spectrum and its diamagnetism indicate that like the sulfur analog it is planar.

Conclusions.—The two ligands, described in this work, give compounds of similar properties. The selenium ones are more soluble and more prone to decomposition in a number of solvents. The electronic spectra show slight shifts to lower energy of the d–d transitions of the CoSe$_4$ chromophore compared to the sulfur complex. The NiSe$_4$ complex, on the other hand, shows a slight shift to higher energy *vs.* the sulfur complex for the band usually assigned to the $(d_{x^2-y^2})^2 \rightarrow (d_{x^2-y^2})^1(d_{xy})^1$ transition. Previous spectral comparisons[21] of a variety of transition metal chromophores with selenium and sulfur donors usually show small shifts to longer wavelengths of both d–d and charge-transfer bands for the selenium derivatives. However, the separation of the mainly metal $d_{x^2-y^2}$ and d_{xy} orbitals for planar d^8 complexes is expected to be a sensitive function of both in-plane π and σ interactions. Thus, the slight blue shift found in this case is not unreasonable. Lastly, the "methinodiphosphinate" complexes are less stable than the related "imidodiphosphinate" ones with respect to decomposition of their solutions in air.

[21] C. K. Jørgensen, *Inorg. Chim. Acta*, **2**, 65 (1968).

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Spectroscopic Studies of Metal–Metal Bonding. II. The Variation of Metal–Metal Bond Strengths with Substituents from the Vibrational Analyses of $X_3MCo(CO)_4$ (M = Sn, Ge; X = I, Br, Cl)

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The complete absorption spectra (33–55,000 cm^{-1}) for the four metal–metal bonded molecules $Br_3SnCo(CO)_4$, $I_3SnCo(CO)_4$, $Br_3GeCo(CO)_4$, and $I_3GeCo(CO)_4$ and the results of laser Raman measurements, where obtainable, are reported. From 16 to 12 of the 20 predicted Raman- and infrared-active fundamentals for each molecule have been observed and the symmetry type of each vibration was assigned. Assignments of the ν(CO) overtone bands in the 4050–4250-cm^{-1} region are given. Vibrational normal-coordinate analyses for each of these molecules yield close agreement between the calculated and assigned spectra and are based upon a valence force field and reasonable spectroscopic assumptions including the transfer to this study of the portions of the force fields for the $Co(CO)_4$ moieties obtained in an earlier work. Series of solutions to the equations of motion have been obtained by continuously varying only four force field elements directly associated with the Co–M and M–X motions to give the correct calculated spectra while all other force field elements were left unchanged. Solutions obtained in this manner yield loci of the many acceptable values of k_{Co-M} and k_{M-X} for each molecule. The experimental evidence accumulated from other types of studies on these molecules is discussed along with the bonding implications of the values found for k_{Co-M}: $k_{Co-Ge}(X = Cl) = 1.10$, $k_{Co-Ge}(X = Br) = 0.96$, $k_{Co-Ge}(X = I) = 0.52$, $k_{Co-Sn}(X = Cl) = 1.23$, $k_{Co-Sn}(X = Br) = 1.05$, $k_{Co-Sn}(X = I) = 0.64$ mdyn/Å, each of which falls at the minimum of the accceptable range of values of k_{Co-M} as discussed in the text.

Introduction

The series of molecules $X_3MCo(CO)_4$ (X = I, Br, Cl; M = Sn, Ge, Si) is well suited for the investigation of metal–metal bond strengths and the dependence of these strengths upon the nature of the ligand X and of the metal M because the vibrational problem can be made tractable and also because both M and X can be

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systematically varied. We have reported the spectra and the values of the force field elements k_{M-Co} for the three trichloro derivatives $Cl_3MCo(CO)_4$ (M = Sn, Ge, Si)[3] and have reviewed the C–O stretching region spectra of $L_3MCo(CO)_4$ and related metal–metal bonded compounds.[4] We report here the spectra and vibrational analyses of the molecules $X_3MCo(CO)_4$ (X = I, Br; M = Sn, Ge) which, with the trichloro results, show the effect of changing X on k_{M-Co}.

Brown, *et al.*,[5,6] have reported that the ^{59}Co nqr spectra of most members of this series and the ^{35}Cl spectra of several members provide evidence that the degree of Co–Sn π bonding is nonzero and varies with X. However, the values of $eQq_{zz}(^{59}Co)$ for $Cl_3SnCo(CO)_4$ (163.4 MHz) and $Br_3SnCo(CO)_4$ (160.0 MHz) are essentially the same, differing by only 5% of the range of such values for $L_3SnCo(CO)_4$ compounds studied. Considering the differences in ligand electronegativity, the authors concluded "that chlorine is a relatively stronger π-bonded atom toward tin in these compounds than bromine, thus compensating for its somewhat greater σ-electron withdrawal."[6]

Of further interest are the linear correlations reported[7] between polarity constants σ^* of substituents and the carbonyl stretching frequencies for molecules of the type $L_3MCo(CO)_4$ (L = ethyl, phenyl, methoxy, Cl) and also the linear correlations reported between the sum of the L electronegativities and ν(CO).[8] Both π *and* σ characters of the Co–M bond have been discussed in terms of formal partitioning of the effects and in terms of specific experiments in an *ad hoc* manner and the nature of the Co–Si bonding in related $R_3SiCo(CO)_4$ compounds has recently been studied.[9] In light of these postulates, results, and discussions concerning the nature of the Co–M bond, the variation of k_{M-Co} with X is of special interest.

In order to employ a value of k_{M-Co} as a measure of the Co–M bond strength, it is particularly important to determine the ranges of k_{M-Co} values which lead to good calculated–observed spectral agreement and the way in which they depend upon other portions of the force field.

We report the vibrational spectra of $I_3SnCo(CO)_4$, $Br_3SnCo(CO)_4$, $I_3GeCo(CO)_4$, and $Br_3GeCo(CO)_4$, the assignments and vibrational analysis of these spectra, and their electronic spectra. We also report the way in which the force fields and k_{M-Co} values were obtained from the loci of a number of the theoretically permitted solutions to the vibrational equations for the molecules $X_3MCo(CO)_4$ (X = I, Br, Cl; M = Sn, Ge). The interpretation of the values of k_{M-Co} obtained is discussed.

Experimental Section

The compounds $Br_3SnCo(CO)_4$, $I_3SnCo(CO)_4$, $Br_3GeCo(CO)_4$, and $I_3GeCo(CO)_4$ were prepared by the methods of Patmore and Graham.[10] The reagents used were carefully prepurified by sublimation, distillation, and recrystallization, as appropriate, and reactions were carried out under dry Ar or N_2 atmosphere. While the reactions progressed as described, the products were sufficiently impure to require extensive purification. Pure $X_3MCo(CO)_4$ was separated from contaminants which appeared to be predominantly $X_2M[Co(CO)_4]_2$ in each case by extracting the product several times with cold *n*-pentane and recrystallizing it repeatedly from *n*-pentane at −23°. The identity and purity of each compound were established by elemental analysis (Co, M, X, C) and by physical (melting points, color) and spectral (5-μ infrared) properties. The analyses, performed by Baron Consulting Co. and Midwest Microlab, Inc., agreed with expected values to within 0.3% for Co, X, and C, 0.5% for Sn, and 1.0% for Ge in all cases. Physical and spectral properties agreed with reported work.[10] The experimental details of the study of $Cl_3MCo(CO)_4$ (M = Sn, Ge, Si) have been reported earlier.[3]

Solutions, powders, and mulls for spectroscopic studies were prepared and handled in a dry nitrogen atmosphere or *in vacuo* using carefully dried and deaerated solvents and were sealed in infrared or Raman cells which had been purged with nitrogen. Sealed capillary and fused-silica Raman cells or sealed KBr, CsI, and high-density polyethylene far-infrared liquid cells[11] were used where appropriate.

The infrared spectra were measured on Beckman IR-11 and IR-12 spectrophotometers with a resolution and accuracy of better than 1 cm^{-1} as determined by standard resolution tests and wave number calibration.[12] The Hg arc source was filtered with black polyethylene when used. The laser Raman spectra were measured on the Jarrell-Ash 25-300 Raman spectrometer with He–Ne 632.8-nm and Ar^+ 488.0-nm laser radiation and a constant spectral slit width of *ca.* 3 cm^{-1} and an accuracy of 1 cm^{-1}. Ultraviolet–visible and near-infrared spectra were measured using a Cary 14 spectrophotometer.

It was possible to obtain Raman spectra in the critical low-frequency region on powdered solid samples and solutions of $Br_3GeCo(CO)_4$ and on powdered solid samples of $Br_3SnCo(CO)_4$. However, photochemical degradation problems precluded measurement of complete solution spectra of the bromides and iodides or of complete solid spectra of the iodides. Due to the importance of the bands, we report several intense low-frequency bands which were repeatedly observed, which are always present in freshly prepared samples, which decrease in intensity relative to bands from decomposition products with increasing exposure to the laser radiation, and which correspond to infrared bands.

The observed infrared and Raman spectra are given in Table I, and the uv–visible band maxima are given in Table II. The carbonyl overtone and combination region for one of the molecules, $I_3GeCo(CO)_4$, is shown in Figure 1. The important 150–300-cm^{-1} regions, both in the infrared and in the Raman spectra, are shown in Figure 2 for $Br_3SnCo(CO)_4$.

Results

The molecular symmetries of the tribromo and triiodo compounds are assumed to be C_{3v} because of the close agreement of their vibrational spectra and physical and chemical properties with those of the previously reported $Cl_3GeCo(CO)_4$ and $Cl_3SnCo(CO)_4$[3] and of $Cl_3SiCo(CO)_4$ and $F_3SiCo(CO)_4$ which have been shown by X-ray structural studies to have C_{3v} molecular symmetry.[13,14]

The vibrational representation for these molecules in C_{3v} is Γ_{vib} = 9 A_1 (infrared active, Raman active, polarized) + 2 A_2 (inactive), + 11 E (infrared active, Raman active, depolarized). Between 12 and 16 of the 20 predicted infrared- and Raman-active fundamen-

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[3] K. L. Watters, J. N. Brittain, and W. M. Risen, Jr., *Inorg. Chem.*, **8**, 1347 (1969).

[4] K. L. Watters and W. M. Risen, Jr., *Inorg. Chim. Acta Rev.*, **3**, 129 (1969).

[5] T. L. Brown, P. A. Edwards, C. B. Harris, and J. L. Kirsch, *Inorg. Chem.*, **8**, 763 (1969).

[6] D. D. Spencer, J. L. Kirsch, and T. L. Brown, *ibid.*, **9**, 235 (1970).

[7] J. Dalton, I. Paul, J. G. Smith, and F. G. A. Stone, *J. Chem. Soc. A*, 1199 (1968).

[8] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **6**, 981 (1967).

[9] A. D. Berry, E. R. Corey, A. P. Hagen, A. G. MacDiarmid, F. E. Saalfeld, and B. B. Wayland, *J. Amer. Chem. Soc.*, **92**, 1940 (1970).

[10] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **7**, 771 (1968).

[11] A. T. Tsatsas and W. M. Risen, Jr., *Appl. Spectrosc.*, **24**, 383 (1970).

[12] For the region 4000–600 cm^{-1} see "Tables of Wavenumbers for the Calibration of Infrared Spectrometers," IUPAC Commission on Molecular Spectroscopy, Butterworths, London, 1961. Calibration in the region 600–33 cm^{-1} was performed with the results of L. R. Blaine, *J. Res. Nat. Bur. Stand., Sect. C*, **67**, 207 (1963), and L. R. Blaine, E. K. Plyler, and W. S. Benedict, *ibid., Sect. A*, **66**, 223 (1962).

[13] W. T. Robinson and J. A. Ibers, *Inorg. Chem.*, **6**, 1208 (1967).

[14] K. Emerson, P. R. Ireland, and W. T. Robinson, *ibid.*, **9**, 436 (1970).

TABLE I

OBSERVED INFRARED AND RAMAN SPECTRA

Ir	State	Intens	Raman	State	Intens	Polarizn	Symmetry	Assignment
$Br_3GeCo(CO)_4$								
4235	a	w	...				A_1	$2\nu_1$
4175	a	w	...				A_1	$\nu_1 + \nu_2$
4162	a	w	...				E	$\nu_{10} + \nu_1$
4122	a	w	...				A_1	$2\nu_2$
4115	a	w	...				E	$\nu_2 + \nu_{10}$
4085	a	w	...				A_1 + E	$2\nu_{10}$
2118	c	s	...				A_1	ν_1
2066	c	s	...				A_1	ν_2
2048	c	vs	...				E	ν_{10}
548	c	s	...				E	ν_{11}
543	a	s	...				E	ν_{11}
498	c	w	...				E	ν_{12}
497	a	w	...				E	ν_{12}
483	c	m	...				E	ν_{13}
482	a	m	...				E	ν_{13}
461	c	s	...				A_1	ν_4
459	a	s	...				A_1	ν_4
404	c	w	407	e	m–w	...	A_1	ν_5
403	a	w	...				A_1	ν_5
369	c	vw	...				A_1	$(\nu_4 - \nu_9)^f$
368	a	vw	...				A_1	$(\nu_4 - \nu_9)^f$
303	c	s	294	e	m–w	...	A_1	ν_6
292	c	s	287	e	m–w	...	E	ν_{15}
...			200	b	vs	p	A_1	ν_7
...			200	c	s	p	A_1	ν_7
...			196		vs	...	A_1	ν_7
126	d	s	126		m	...	A_1	ν_8
...			108		m	...	E	ν_{17}
97	d	m	93		m	...	A_1	ν_9
67	d	m	74		s	...	E	ν_{18}
...			51		w	...	E	ν_{19}
...			44		s	...	...	Lattice
$I_3GeCo(CO)_4$								
4223	a	w	...				A_1	$2\nu_1$
4158	a	w	...				A_1	$\nu_1 + \nu_2$
4149	a	w	...				E	$\nu_1 + \nu_{10}$
4111	q	w	...				A_1	$2\nu_2$
4103	a	w	...				E	$\nu_2 + \nu_{10}$
4073	a	w	...				A_1 + E	$2\nu_{10}$
2113	c	s	...				A_1	ν_1
2062	c	s	...				A_1	ν_2
2042	c	vs	...				E	ν_{19}
610	a	vw	...				A_1	ν_3
544	a	s	...				E	ν_{11}
480	a	m	...				E	ν_{12}
459	a	s	...				A_1	ν_4
403	a	w	...				A_1	ν_5
368	a	vw	...				A_1	$(\nu_4 - \nu_9)^f$
266	c	w	...				A_1	ν_6
250	c	s	...				E	ν_{15}
161	c	w	165	e	vs		A_1	ν_7
117	d	m	...				E	ν_{17}
80	d	s	...				A_1	ν_8
$Br_3SnCo(CO)_4$								
4219	a	w	...				A_1	$2\nu_1$
4167	a	w	...				A_1	$\nu_1 + \nu_2$
4155	a	w	...				E	$\nu_1 + \nu_{10}$
4120	a	w	...				A_1	$2\nu_2$
4105	a	w	...				E	$\nu_2 + \nu_{10}$
4073	a	w	...				A_1 + E	$2\nu_{10}$
2116	c	s	...				A_1	ν_1
2063	c	s	...				A_1	ν_2
2043	c	vs	...				E	ν_{10}
547	c	s	540	e	w	...	E	ν_{11}
547	a	s	...				E	ν_{11}
488	a	m	...				E	ν_{13}
487	c	m	...				E	ν_{13}
462	c	s	453	e	w	...	A_1	ν_4
462	a	s	...				A_1	ν_4
407	c	w	408	e	s	...	A_1	ν_5
407	a	w	...				A_1	ν_5
368	c	vw	...				A_1	$(\nu_4 - \nu_9)^f$
368	a	vw	...				A_1	$(\nu_4 - \nu_9)^f$
261	c	m	257	e	m	...	A_1	ν_6
...			249	e	m	...	E	ν_{15}
247	c	s	246	e	m	...	E	ν_{15}
187	c	vw	182	e	vs	...	A_1	ν_7
116	d	s	117	e	m	...	E	ν_{17}
...			106	e	m	...	A_1	ν_8
83	d	s	77	e	s	...	A_1	ν_9
55	d	m	62	e	s	...	E	ν_{18}
$I_3SnCo(CO)_4$								
4214	a	w	...				A_1	$2\nu_1$
4154	a	w	...				A_1	$\nu_1 + \nu_2$
4139	a	w	...				E	$\nu_1 + \nu_{10}$
4105	a	w	...				A_1	$2\nu_2$
4092	a	w	...				E	$\nu_2 + \nu_{10}$
4061	a	w	...				A_1 + E	$2\nu_{10}$
2109	c	s	...				A_1	ν_1
2058	c	s	...				A_1	ν_2
2037	c	vs	...				E	ν_{10}
544	c	s	...				E	ν_{11}
543	a	s	...				E	ν_{11}
487	a	m	...				E	ν_{13}
486	c	m	...				E	ν_{13}
464	a	s	...				A_1	ν_4
462	c	s	...				A_1	ν_4
408	a	w	...				A_1	ν_5
406	c	w	...				A_1	ν_5
369	c	vw	...				A_1	$(\nu_4 - \nu_9)^f$
366	a	vw	...				A_1	$(\nu_4 - \nu_9)^f$
222	c	w	...				A_1	ν_6
208	c	s	...				E	ν_{15}
156	c	w	153	e	vs		A_1	ν_7
67	d	s	...				A_1	ν_8
60	d	m	...				E	ν_{17}

[a] CCl_4 solution. [b] Benzene solution. [c] Cyclohexane solution. [d] Nujol mull. [e] Solid powder. [f] Weakest observed bands in the middle-frequency spectrum are assigned here as difference bands.

TABLE II

ULTRAVIOLET–VISIBLE BAND MAXIMA OF $X_3MCo(CO)_4$ COMPOUNDS IN CYCLOHEXANE SOLUTION

Molecule	Obsd max, nm
$Cl_3SnCo(CO)_4$	270.0
$Cl_3GeCo(CO)_4$	261.0
$Cl_3SiCo(CO)_4$	235.0
$Br_3SnCo(CO)_4$	302.5 m, 251.2 m, 222.5 s
$Br_3GeCo(CO)_4$	295.0 m, 252.5 m, 212.5 s
$I_3SnCo(CO)_4$	385.0 m, 302.5 sh, 257.5 s, sh, 227.5 s
$I_3GeCo(CO)_4$	390.0 m, 312.5 m, 220.0 s

TABLE III

SYMMETRIES OF VIBRATIONAL MODES FOR $X_3MCo(CO)_4$ (C_{3v})

C–O str	2 A_1 + E	MX_3 def	A_1 + 2 E
Co–C str	2 A_1 + E	C–Co–C def	A_1 + 2 E
Co–C–O def	A_1 + A_2 + 3 E	M–Co–C_{ax} def	E
M–X str	A_1 + E	Torsion	A_2
Co–M str	A_1		

tals have been observed and assigned for each of the compounds discussed here. All observed vibrational frequencies and the conditions under which they were obtained are listed in Table I for $Br_3GeCo(CO)_4$, $Br_3SnCo(CO)_4$, $I_3GeCo(CO)_4$, and $I_3SnCo(CO)_4$.

Spectral Assignments.—For $X_3MCo(CO)_4$ molecules of the C_{3v} symmetry assumed[3,13,14] there are, as shown in Table III, eleven symmetry coordinates involving C–O stretching, Co–C stretching, and Co–C–O deformation motions for each of these molecules. The vibrational fundamentals involving these internal coordinates are expected, on the basis of many studies of metal carbonyl compounds, to have frequencies above 350 cm^{-1}. Table I shows that the vibrational spectra above 350 cm^{-1} are nearly identical for these four molecules. In addition, they are nearly identical with the bands reported earlier for $Cl_3SnCo(CO)_4$ and Cl_3-

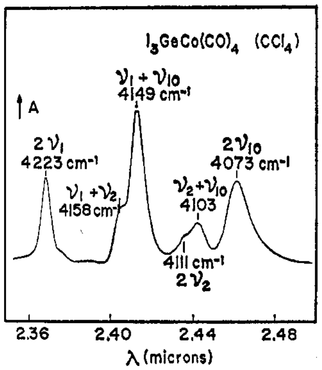

Figure 1.—The ν(CO) overtone and combination region spectrum of $I_3GeCo(CO)_4$.

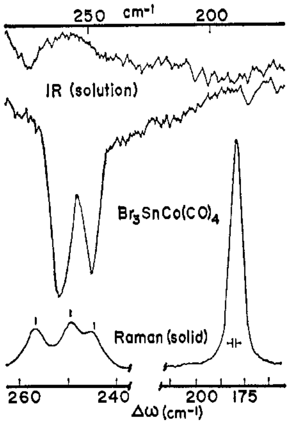

Figure 2.—Laser Raman and far-infrared spectra in the 150–300-cm^{-1} region of $Br_3SnCo(CO)_4$ in the solid state and in cyclohexane solution, respectively. The top spectrum is pure cyclohexane.

$GeCo(CO)_4$[3] above 400 cm^{-1}. All bands above 400 cm^{-1} in these molecules are thus considered to be due mainly to motions of the $Co(CO)_4$ moiety, and since these assignments are the same as those given previously for the trichloro derivatives,[3] they will not be discussed further here.

The spectral region 150–350 cm^{-1} is expected to contain three fundamentals which are largely M–X and Co–M stretching motions for these molecules, two of A_1 symmetry and one of E symmetry. The two predicted A_1 stretching modes in this region are expected to be, to some degree, a mixture of both the M–X and the Co–M stretches. Each of the tribromo and triiodo compounds displays a broad, intense infrared absorption with a maximum between 200 and 300 cm^{-1}. A second band usually occurring as a shoulder is found at 10–20 cm^{-1} higher frequency than this strong band. These are assigned as fundamentals of E and of A_1 symmetry, respectively. There is also a very weak infrared band between 150 and 200 cm^{-1} in the spectrum of $Br_3SnCo(CO)_4$, $I_3SnCo(CO)_4$, and $I_3GeCo(CO)_4$. The corresponding band was not observed in the infrared spectrum of $Br_3GeCo(CO)_4$.

The strongest band in the Raman spectrum of $Br_3SnCo(CO)_4$, shown in Figure 2, occurs at 182 cm^{-1}, approximately the same frequency as the very weak band in the infrared solution spectrum, while a very intense Raman band is found at about 200 cm^{-1} in the spectrum of $Br_3GeCo(CO)_4$ both as a solid powder and in solution. This solution band is polarized and this, as well as the intensity of the Raman band in this region for solid $Br_3SnCo(CO_4)$ and $Br_3GeCo(CO)_4$, leads to an A_1 assignment for the band in the 150–200-cm^{-1} region in each molecule. It is also seen in Figure 2 that the E mode of $Br_3SnCo(CO)_4$ is split in the solid state. These assignments in the 150–350-cm^{-1} region are consistent with those previously given for M–Cl and Co–M stretching modes of $Cl_3SnCo(CO)_4$ and $Cl_3GeCo(CO)_4$[3] when the effect of increased mass of the halogen is considered, as shown in Figure 3.

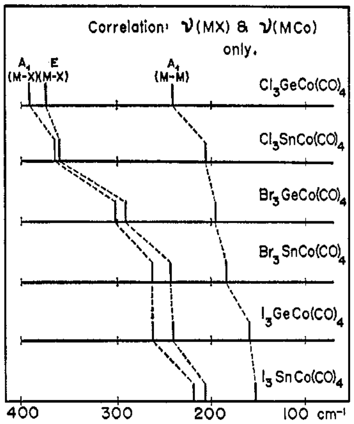

Figure 3.—Correlation diagram of observed ν(M–X) and ν(M–Co) modes with their assigned symmetries for all members of the series $X_3MCo(CO)_4$ (M = Sn, Ge).

The vibrational modes which are primarily deformations of the MX_3 group and the skeletal C–Co–C and M–Co–C deformations are expected to occur below 150 cm^{-1} for these molecules. Several bands are observed and assigned in this region for each compound. The strongest infrared band in the very low-frequency region varies in frequency from 126 cm^{-1} in $Br_3GeCo(CO)_4$ to 67 cm^{-1} for $I_3SnCo(CO)_4$. This is just the manner in which the MX_3 deformation frequencies are expected to vary for this series of molecules and is consistent with assignments for the infrared spectra of corresponding MX_4 species.[15] Other members of the series contain one or more bands in this region of the vibrational spectrum which vary in frequency in this same way and which have been assigned as primarily MX_3 deformation modes. One or more bands located in the 80–120-cm^{-1} region for each compound are assigned to C–Co–C skeletal deformations consistent with the results of related studies.[3,16]

The assigned fundamentals, their symmetries, and partial descriptions of the motions involved are given in Table IV for $Br_3GeCo(CO)_4$, $Br_3SnCo(CO)_4$, $I_3GeCo(CO)_4$, and $I_3SnCo(CO)_4$.

Molecular Valence Force Fields.—As is illustrated in Table I the spectra of these molecules are nearly identical above 400 cm^{-1}. In addition, the spectra in this region are in close agreement with those of $Cl_3SnCo(CO)_4$ and $Cl_3GeCo(CO)_4$. This agreement for vibrational modes primarily associated with the motions

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[15] (a) Landolt–Börnstein, "Physikalische-chemische Tabellen," Vol. I. Part 2, Springer-Verlag, 1951; (b) H. Stammreich, Y. Tavares, and D. Bassi, *Spectrochim. Acta*, **17**, 661 (1961); (c) X. Gerbaux and A. Hadni, *J. Phys. Radium*, **23**, 877 (1962); (d) D. M. Adams, "Metal-Ligand and Related Vibrations," St. Martin's Press, New York, N. Y., 1968.

[16] (a) C. O. Quicksall and T. G. Spiro, *Inorg. Chem.*, **7**, 2365 (1968); (b) H. Stammreich, K. Kawai, and Y. Tavares, *J. Chem. Phys.*, **32**, 1482 (1960); (c) R. J. H. Clark and B. C. Crosse, *J. Chem. Soc. A*, 224 (1969); (d) L. H. Jones, R. S. McDowell, and M. Goldblatt, *Inorg. Chem.*, **8**, 2349 (1969).

TABLE IV

OBSERVED AND CALCULATED FUNDAMENTALS

Ir, cm^{-1}				Ir, cm^{-1}			
Obsd	Calcd	Symmetry	Description	Obsd	Calcd	Symmetry	Description
		$Br_3GeCo(CO)_4$				$Br_3SnCo(CO)_4$	
2118	2121	A_1	$\nu_{\mathrm{C-O(ax)}} + \nu_{\mathrm{C-O(eq)}}$	2116	2121	A_1	$\nu_{\mathrm{C-O(ax)}} + \nu_{\mathrm{C-O(eq)}}$
2066	2070	A_1	$\nu_{\mathrm{C-O(eq)}} + \nu_{\mathrm{C-O(ax)}}$	2063	2070	A_1	$\nu_{\mathrm{C-O(eq)}} + \nu_{\mathrm{C-O(ax)}}$
2048	2034	E	$\nu_{\mathrm{C-O(eq)}}$	2043	2044	E	$\nu_{\mathrm{C-O(eq)}}$
. . .	623	A_1	$\delta_{\mathrm{Co-C-O}}$	. . .	623	A_1	$\delta_{\mathrm{Co-C-O}}$
543	546	E	$\delta_{\mathrm{Co-C-O}}$	547	537	E	$\delta_{\mathrm{Co-C-O}}$
497	496	E	$\delta_{\mathrm{Co-C-O}} + \nu_{\mathrm{Co-C(eq)}}$	488	493	E	$\delta_{\mathrm{Co-C-O}} + \nu_{\mathrm{Co-C(eq)}}$
482	476	E	$\nu_{\mathrm{Co-C-O}} + \delta_{\mathrm{Co-C(eq)}}$	462	459	A_1	$\nu_{\mathrm{Co-C(ax)}}$
459	459	A_1	$\nu_{\mathrm{Co-C(ax)}}$	. . .	461	E	$\nu_{\mathrm{Co-C(eq)}} + \delta_{\mathrm{Co-C-O}}$
. . .	444	E	$\nu_{\mathrm{Co-C(eq)}}$	. . .	444	E	$\nu_{\mathrm{Co-C(eq)}} + \delta_{\mathrm{Co-C-O}}$
403	410	A_1	$\nu_{\mathrm{Co-C(eq)}}$	407	409	A_1	$\nu_{\mathrm{Co-C(eq)}}$
303	303	A_1	$\nu_{\mathrm{Ge-Br}} + \nu_{\mathrm{Ge-Co}}$	261	261	A_1	$\nu_{\mathrm{Sn-Br}} + \nu_{\mathrm{Sn-Co}}$
292	292	E	$\nu_{\mathrm{Ge-Br}}$	247	247	E	$\nu_{\mathrm{Sn-Br}}$
200	200	A_1	$\nu_{\mathrm{Ge-Co}} + \nu_{\mathrm{Ge-Br}}$	182	182	A_1	$\nu_{\mathrm{Sn-Co}} + \nu_{\mathrm{Sn-Br}}$
. . .	134	E	$\delta_{\mathrm{C-Co-C}} + \delta_{\mathrm{GeBr_3}}$	. . .	120	E	$\delta_{\mathrm{C-Co-C}}$
126	127	A_1	$\delta_{\mathrm{GeBr_3}}$	116	113	E	$\delta_{\mathrm{C-Co-C}}$
108	108	E	$\delta_{\mathrm{C-Co-C}}$	106	106	A_1	$\delta_{\mathrm{SnBr_3}} + \delta_{\mathrm{C-Co-C}}$
97	78	A_1	$\delta_{\mathrm{C-Co-C}} + \nu_{\mathrm{Ge-Co}}$	. . .	78	E	$\delta_{\mathrm{Sn-Co-C}} + \delta_{\mathrm{SnBr_3}}$
67	78	E	$\delta_{\mathrm{Ge-Co-C}} + \mathrm{GeBr_3}$	83	77	A_1	$\delta_{\mathrm{SnBr_3}}$
51	67	E	$\delta_{\mathrm{Br-Ge-Br}}$	55	55	E	$\delta_{\mathrm{Br-Sn-Br}}$
. . .	22	E	$\delta_{\mathrm{Co-Ge-Br}}$	. . .	25	E	$\delta_{\mathrm{Co-Sn-Br}}$
		$\lvert\nu_{\mathrm{obsd}} - \nu_{\mathrm{calcd}}\rvert_{\mathrm{av}} = 5.3$ cm^{-1}				$\nu_{\mathrm{obsd}} = \nu_{\mathrm{calcd}}\rvert_{\mathrm{av}} = 3.1$ cm^{-1}	
		$I_3GeCo(CO)_4$				$I_3SnCo(CO)_4$	
2113	2121	A_1	$\nu_{\mathrm{C-O(ax)}} + \nu_{\mathrm{C-O(eq)}}$	2109	2121	A_1	$\nu_{\mathrm{C-O(ax)}} + \nu_{\mathrm{C-O(eq)}}$
2062	2064	A_1	$\nu_{\mathrm{C-O(eq)}} + \nu_{\mathrm{C-O(ax)}}$	2058	2070	A_1	$\nu_{\mathrm{C-O(eq)}} + \nu_{\mathrm{C-O(ax)}}$
2042	2044	E	$\nu_{\mathrm{C-O(eq)}}$	2037	2044	E	$\nu_{\mathrm{C-O(eq)}}$
610	616	A_1	$\delta_{\mathrm{Co-C-O}}$	. . .	621	A_1	$\delta_{\mathrm{Co-C-O}}$
544	545	E	$\delta_{\mathrm{Co-C-O}}$	543	541	E	$\delta_{\mathrm{Co-C-O}}$
. . .	496	E	$\delta_{\mathrm{Co-C-O}} + \nu_{\mathrm{Co-C(eq)}}$	487	495	E	$\delta_{\mathrm{Co-C-O}} + \nu_{\mathrm{Co-C(eq)}}$
480	476	E	$\nu_{\mathrm{Co-C(eq)}} + \delta_{\mathrm{Co-C-O}}$	. . .	474	E	$\nu_{\mathrm{Co-C(eq)}} + \delta_{\mathrm{Co-C-O}}$
459	456	A_1	$\nu_{\mathrm{Co-C(ax)}}$	464	457	A_1	$\nu_{\mathrm{Co-C(ax)}}$
. . .	446	E	$\nu_{\mathrm{Co-C(eq)}} + \delta_{\mathrm{Co-C-O}}$	. . .	444	E	$\nu_{\mathrm{Co-C(eq)}} + \delta_{\mathrm{Co-C-O}}$
403	409	A_1	$\nu_{\mathrm{Co-C(eq)}}$	408	409	A_1	$\nu_{\mathrm{Co-C(eq)}}$
266	266	A_1	$\nu_{\mathrm{Ge-I}} + \nu_{\mathrm{Ge-Co}}$	222	222	A_1	$\nu_{\mathrm{Sn-I}} + \delta_{\mathrm{Sn-Co}}$
249	249	E	$\nu_{\mathrm{Ge-I}}$	208	208	E	$\nu_{\mathrm{Sn-I}}$
161	161	A_1	$\nu_{\mathrm{Ge-Co}} + \nu_{\mathrm{Ge-I}}$	156	156	A_1	$\nu_{\mathrm{Sn-Co}} + \nu_{\mathrm{Sn-I}}$
. . .	134	E	$\delta_{\mathrm{C-Co-C}}$	. . .	120	E	$\delta_{\mathrm{C-Co-C}}$
. . .	129	A_1	$\delta_{\mathrm{C-Co-C}} + \delta_{\mathrm{GeI_3}}$	. . .	111	E	$\delta_{\mathrm{C-Co-C}}$
117	103	E	$\delta_{\mathrm{C-Co-C}}$	. . .	90	A_1	$\delta_{\mathrm{SnI_3}}$
. . .	77	E	$\delta_{\mathrm{Ge-Co-C}} + \delta_{\mathrm{GeI_3}}$	. . .	77	E	$\delta_{\mathrm{Sn-Co-C}} + \delta_{\mathrm{SnI_3}}$
80	67	A_1	$\nu_{\mathrm{Ge-Co}} + \delta_{\mathrm{C-Co-C}}$	67	68	A_1	$\delta_{\mathrm{SnI_3}}$
. . .	70	E	$\delta_{\mathrm{GeI_3}}$	60	49	E	$\delta_{\mathrm{I-Sn-I}}$
. . .	18	E	$\delta_{\mathrm{Co-Ge-I}}$	. . .	19	E	$\delta_{\mathrm{Co-Sn-I}}$
		$\lvert\nu_{\mathrm{obsd}} - \nu_{\mathrm{calcd}}\rvert_{\mathrm{av}} = 4.5$ cm^{-1}				$\lvert\nu_{\mathrm{obsd}} - \nu_{\mathrm{calcd}}\rvert_{\mathrm{av}} = 5.1$ cm^{-1}	

of the $Co(CO)_4$ group suggests that the molecular force fields for that moiety may initially be assumed identical in all six molecules. Thus the $Co(CO)_4$ moiety force field elements used in the normal-coordinate calculations are those which were obtained in calculations previously reported for $Cl_3SnCo(CO)_4$, $Cl_3GeCo(CO)_4$, and $Cl_3SiCo(CO)_4$.[3] It was found that calculated spectra above 400 cm^{-1} remained in excellent agreement with the observed spectra throughout the $X_3MCo(CO)_4$ series without making any alterations in that portion of the force field which determines the vibrational modes of the $Co(CO)_4$ moiety. This constant portion of the field is given in Table V, which includes necessary and more detailed information than our earlier report.

The interatomic distances used for the $Co(CO)_4$ moiety in the calculations were those found in the X-ray structural analysis of $Cl_3SiCo(CO)_4$.[13] The M-X distances used were those from X-ray studies of the corresponding MX_4 species[17] while the Co-M distances were estimated from the literature values of

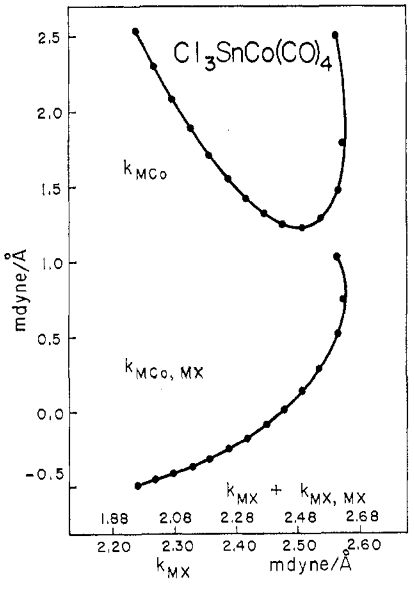

Figure 4.—The variation of $k_{\mathrm{M-Co}}$ and $k_{\mathrm{M-Co,M-X}}$ with $k_{\mathrm{M-X}}$ or $k_{\mathrm{M-X}} + k_{\mathrm{M-X,M-X}}$ for the molecule $Cl_3SnCo(CO)_4$.

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(17) (a) B. T. Kilbourn and H. M. Powell, *Chem. Ind.* (*London*), 1578 (1964); (b) J. D. Cotton, *Chem. Commun.*, 253 (1966).

TABLE V

NONZERO FORCE FIELD ELEMENTS[a] FOR THE SERIES $X_3MCo(CO)_4$

Elements Held Constant for the Series

$k_{C-O(ax)}$	17.98[b]	$k_{Co-C-O(ax)}$	0.293[b]
$k_{C-O(eq)}$	17.05[b]	$k_{Co-C-O(ip)}$	0.32[b]
$k_{C-O,C-O}$	0.17	$k_{Co-C-O(op)}$	0.28[b]
$k_{Co-C(eq)}$	2.62[b]	$k_{Co-C-O(op),Co-C-O(op)}$	0.05
$k_{Co-C(ax)}$	2.51[b]	$k_{Co-C-O,Co-C-O}$	0.025[d]
$k_{Co-C,Co-C}$	0.105	$k_{M-Co-C(eq)}$	0.13[b]
$k_{Co-C,C-O}$	0.735	$k_{M-Co-C(ax)}$	0.02[b]
$k_{C-Co-C(ax)}$	0.195[b]	$k_{M-Co,Co-C}$	0.10
$k_{C-Co-C(eq)}$	0.09	$k_{M-X,X-M-X}$	0.001
$k_{C-Co-C,C-Co-C}$	−0.008[c]	$k_{X-M-X,X-M-X}$, $k_{Co-M-X,Co-M-X}$	0.017
$k_{torsion}$	0.002		

Elements Which Vary through the Series

	$Cl_3GeCo(CO)_4$	$Br_3GeCo(CO)_4$	$I_3GeCo(CO)_4$	$Cl_3SnCo(CO)_4$	$Br_3SnCo(CO)_4$	$I_3SnCo(CO)_4$
k_{M-Co}[b,e]	1.10 (1.18 ± 0.08)	0.96 (1.02 ± 0.06)	0.52 (0.57 ± 0.05)	1.23 (1.29 ± 0.06)	1.05 (1.11 ± 0.06)	0.64 (0.68 ± 0.04)
k_{M-X}[b,e]	2.82 (2.81 ± 0.10)	2.23 (2.21 ± 0.15)	2.15 (2.10 ± 0.20)	2.51 (2.50 ± 0.06)	2.01 (1.98 ± 0.09)	1.99 (1.96 ± 0.10)
$k_{M-X,M-X}$[e]	−0.04 (−0.05 ± 0.10)	0.51 (0.49 ± 0.15)	0.61 (0.56 ± 0.20)	−0.01 (−0.02 ± 0.06)	0.26 (0.23 ± 0.09)	0.28 (0.25 ± 0.10)
$k_{M-Co,M-X}$[e]	0.33 (0.36 ± 0.29)	0.34 (0.39 ± 0.27)	0.32 (0.31 ± 0.24)	0.16 (0.15 ± 0.25)	0.19 (0.21 ± 0.22)	0.15 (0.15 ± 0.17)
k_{X-M-X}[b]	0.225	0.120	0.108	0.074	0.070	0.076
k_{Co-M-X}[b]	0.045	0.045	0.042	0.020	0.040	0.040
$k_{M-X,Co-M-X}$	0.022	0.022	0.022	0.012	0.012	0.012
$k_{M-Co,Co-M-X}$	0.022	0.022	0.007	0.030	0.080	0.080

[a] All force constants are in mdynes per ångström. All internal valence coordinates are defined as positive for bond stretching and for angle opening; thus all elements have unique sign. [b] Diagonal element; corresponds to k_{ii} for internal valence coordinate r_i. [c] Includes M–Co–C(eq) bend–bend interaction. [d] Defined as β,β interaction. Includes β(ip), β(ip); β(ax), β(ax); β(ax), β(ip); β(ax), β(op); and β(op), β(ip), same CO. Abbreviations: ip, in plane; op, out of plane; ax, axial; eq, equatorial. [e] Elements corresponding to k_{M-Co} at the minimum of the k_{M-Co} *vs.* k_{M-X} curves. Numbers in parentheses define the optimum range of values.

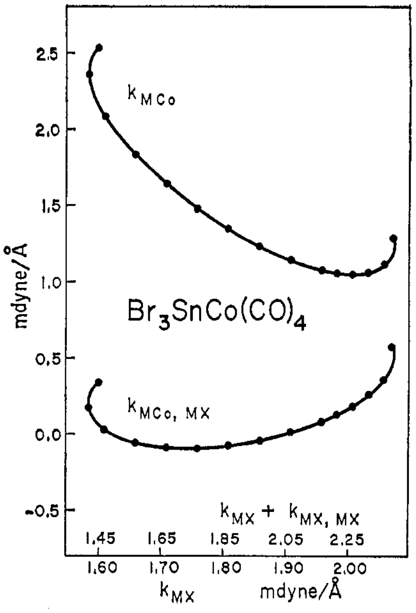

Figure 5.—The variation of k_{M-Co} and $k_{M-Co,M-X}$ with k_{M-X} or $k_{M-X} + k_{M-X,M-X}$ for the molecule $Br_3SnCo(CO)_4$.

r_{Mn-Sn}, r_{Fe-Sn}, and r_{Mn-Ge}[18] as 2.40 Å for r_{Co-Ge} and 2.50 Å for r_{Co-Sn}. Stalick and Ibers[19] have found r_{Co-Ge} to be 2.34 ± 0.02 Å in the related compound $Co[Ge(C_6H_5)_3](CO)_3[P(C_6H_5)_3]$. Although it is difficult to know whether this provides a better basis for estimation, an error of *ca.* 0.05 Å in estimating this distance would have only a negligible effect on the vibrational analysis.

In the vibrational calculations only the force field elements for Co–M stretching, M–X stretching, MX_3 deformation, and associated interaction constants were varied to obtain agreement between the calculated and observed spectra. These calculations show that M–X stretching and M–Co stretching motions together provide most of the potential energy in the three vibrational fundamentals in the spectral region 150–350 cm^{-1}. The frequencies calculated[20] for these three modes are thus largely determined by the four force constants k_{M-Co}, k_{M-X}, $k_{M-Co,M-X}$, and $k_{M-X,M-X}$.

The force field elements for MX_3 deformation were first adjusted to obtain substantial agreement between the calculated and observed spectra in the very low-frequency (<150 cm^{-1}) region. The values of the four force field elements listed above could then be continuously varied to obtain an infinity of force fields yielding calculated spectra that agree closely with the observed in both the 150–350-cm^{-1} region and the middle- and low-frequency regions where the calculated frequencies are primarily determined by other force field elements. A total of more than 150 force fields has been obtained, collectively, for $Br_3GeCo(CO)_4$, $Br_3SnCo(CO)_4$, $I_3GeCo(CO)_4$, and $I_3SnCo(CO)_4$ and for $Cl_3GeCo(CO)_4$ and $Cl_3SnCo(CO)_4$. Figures 4–9 show the loci of values of k_{M-Co} and $k_{M-Co,M-X}$ as functions of k_{M-X} and $k_{M-X} + k_{M-X,M-X}$ for each of these six molecules. Each set of values in these loci yields calculated frequencies in the 150–400-cm^{-1} spectral region which are within 1 cm^{-1} of the observed values and are a part of molecular force fields which give $|\nu_{calcd} - \nu_{obsd}|_{av} \simeq 5$ cm^{-1} in all cases.

The linear relationship between k_{M-X} and $k_{M-X,M-X}$ evident in Figures 4–9 results from the symmetry-required exclusion of M–Co stretching motion from modes of E symmetry. Thus, the contribution from k_{M-Co} and $k_{M-Co,M-X}$ to the E mode frequencies is identically zero, so that the frequency of the E mode in the 200–400-cm^{-1} region is primarily (*ca.* 95%) determined by k_{M-X} and $k_{M-X,M-X}$. The *C*-matrix elements[20] for this E mode which are obtained from the solutions to the equations of motion led to the relationship $\lambda^{E}_{15} = C_{15},\ k_{MX}(k_{MX} - k_{MX,MX})$.

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(18) (a) R. F. Bryan, *J. Chem. Soc. A*, 172 (1967); (b) R. F. Bryan, *ibid.*, *A*, 192 (1967).

(19) J. K. Stalick and J. A. Ibers, *J. Organometal. Chem.*, **22**, 213 (1970).

(20) The vibrational analysis program of W. F. Edgell and coworkers has been employed in these calculations: see R. L. Yantis, M.S. Thesis, Purdue University, 1964; see also ref 3 of this paper.

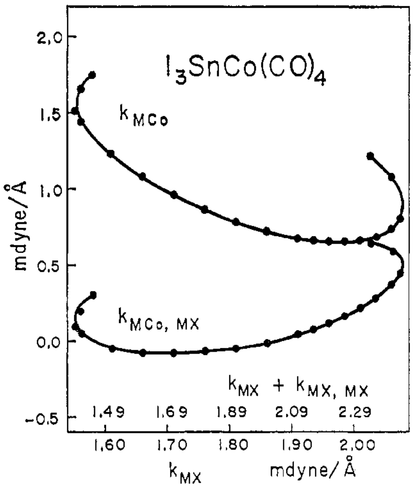

Figure 6.—The variation of $k_{\mathrm{M-Co}}$ and $k_{\mathrm{M-Co,M-X}}$ with $k_{\mathrm{M-X}}$ or $k_{\mathrm{M-X}} + k_{\mathrm{M-X,M-X}}$ for the molecule $I_3SnCo(CO)_4$.

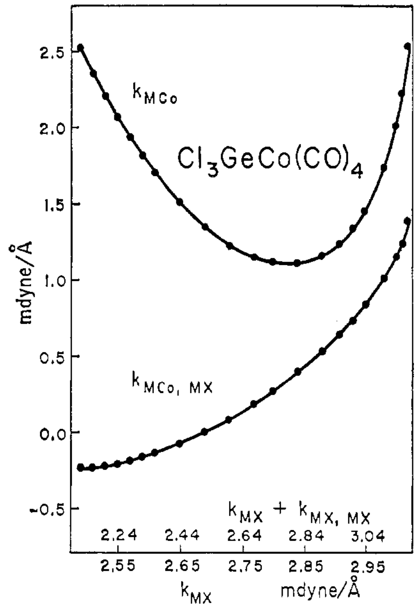

Figure 7.—The variation of $k_{\mathrm{M-Co}}$ and $k_{\mathrm{M-Co,M-X}}$ with $k_{\mathrm{M-X}}$ or $k_{\mathrm{M-X}} + k_{\mathrm{M-X,M-X}}$ for the molecule $Cl_3GeCo(CO)_4$.

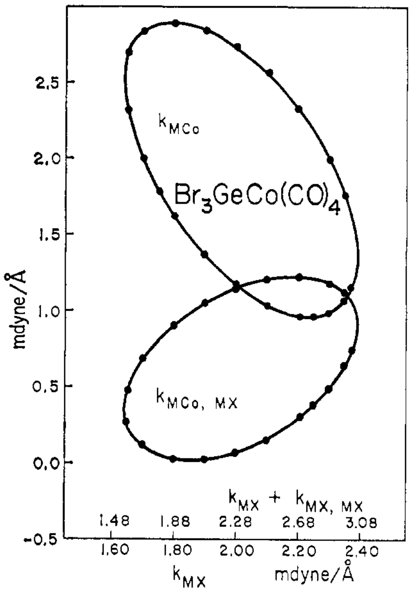

Figure 8.—The variation of $k_{\mathrm{M-Co}}$ and $k_{\mathrm{M-Co,M-X}}$ with $k_{\mathrm{M-X}}$ or $k_{\mathrm{M-X}} + k_{\mathrm{M-X,M-X}}$ for the molecule $Br_3GeCo(CO)_4$.

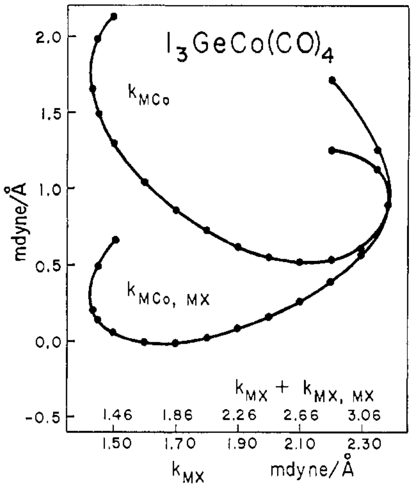

Figure 9.—The variation of $k_{\mathrm{M-Co}}$ and $k_{\mathrm{M-Co,M-X}}$ with $k_{\mathrm{M-X}}$ or $k_{\mathrm{M-X}} + k_{\mathrm{M-X,M-X}}$ for the molecule $I_3GeCo(CO)_4$.

The loci in Figures 4–9 of stretching force field elements pertaining to the $CoMX_3$ moiety describe ellipses or segments of ellipses. These curves are analogous to the force constant relationships found for pairs of modes of the same vibrational symmetry type in triatomic,[21] tetrahedral,[22] and other small molecules. The $k_{\mathrm{M-X}}$ extrema on a complete ellipse correspond to force fields whose eigenvectors show total separation of the M–Co stretching motion from the M–X stretching motion in one of the two A_1 bands in the 150–400-cm^{-1} region. At the $k_{\mathrm{M-X}}$ maximum, the higher of the two A_1 modes is predominantly ν(M–X) with no ν(M–Co) contribution and the lower A_1 is predominantly ν(M–Co), while at the $k_{\mathrm{M-X}}$ minimum the lower A_1 is predominantly ν(M–X) with no ν(M–Co) contribution. The force fields of interest, based on this information and the spectral interpretation of the lower frequency A_1 mode as predominantly ν(M–Co), lie in the lower right-hand portion of the ellipse, which is that segment we have found for all the molecules.

At the extremal values of $k_{\mathrm{M-Co}}$ found for the complete ellipses, the vibrational eigenvectors show complete separation of the M–X from the M–Co stretching motions on one of the relevant A_1 modes. In the segment of interest, where $k_{\mathrm{M-Co}}$ is at a minimum, the lower frequency A_1 is predominantly ν(M–Co) with no ν(M–X) contribution, and the higher frequency A_1 is predominantly ν(M–X). For the $Cl_3MCo(CO)_4$ derivatives the energy separation of these modes involving the $Co(CO)_4$ moiety from the M–Co and M–X dependent modes in the 150–400-cm^{-1} region is not sufficient to permit obtaining the complete ellipses, although it is in the tribromo and triiodo derivatives where the M–Co and M–X modes all lie below 305 cm^{-1}. All of the points describing the loci in Figures 4–9 correspond to fields resulting in $|\nu_{\mathrm{calcd}} - \nu_{\mathrm{obsd}}|_{\mathrm{av}} \simeq 5$ cm^{-1} for the entire molecule.

The high intensity and Raman polarization of the lower frequency A_1 band in the 150–250-cm^{-1} region

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[21] P. Torkington, *J. Chem. Phys.*, **17**, 357 (1949).

[22] S. J. Cyvin, "Molecular Vibrations and Mean Square Amplitudes," Elsevier, Amsterdam, 1968, p 176.

for each compound and the similarity of the higher frequency A_1 band in the 150–350-cm^{-1} region to the MX_4 spectra have led us to assign the lower energy A_1 band to the predominantly M–Co stretching motion.

The optimum range of k_{M-Co} values may accordingly be found to be those for which the ν(M–Co) contribution to the potential energy of the lower frequency A_1 mode in the 150–400-cm^{-1} region is much greater than the ν(M–X) contribution. In these ranges we find that the important interaction constants ($k_{MX,MX}$ and $k_{MCo,MX}$) are much smaller than the associated diagonal constants. This is consistent with studies of MX_2, MX_3^-, and MX_4 analogs of the MX_3 moieties of the compounds studied here and the fact that the magnitude of bond stretching force constants is generally severalfold greater than the absolute magnitude of the associated stretch–stretch interaction constants.

The solid line connecting the filled symbols in Figures 4–9 corresponds to the optimum range of force constant values as listed in Table V. For all calculated solutions in this range, none of the frequency deviations caused by mixing above 400 cm^{-1} and below 150 cm^{-1} are more than 5 cm^{-1} from the frequency calculated at k_{M-Co} (min). Also listed in Table V are the values obtained for force field elements associated with deformation of the MX_3 group.[23]

The specified ranges for k_{M-Co} are $k_{Ge-Co}(X = Cl) = 1.18 \pm 0.08$, $k_{Ge-Co}(X = Br) = 1.02 \pm 0.06$, $k_{Ge-Co}(X = I) = 0.57 \pm 0.05$, $k_{Sn-Co}(X = Cl) = 1.29 \pm 0.06$, $k_{Sn-Co}(X = Br) = 1.11 \pm 0.06$, and $k_{Sn-Co}(X = I) = 0.68 \pm 0.04$.

Discussion

The principal feature of the results of the vibrational analyses of these compounds is the variation of k(M–Co) as the metal M and the halide X are varied. The values of k(M–Co) are higher for the Sn derivatives than for the corresponding Ge derivatives, and for both the $X_3SnCo(CO)_4$ and the $X_3GeCo(CO)_4$ compounds the k(M–Co) values fall in the order chloride > bromide > iodide. Another feature is the roughly twofold difference between the largest and smallest values of k(M–Co), an occurrence only indirectly reflected by the small variations in the 5-μ (ν(CO)) spectra of these compounds.

It is of interest to investigate the bonding implications of these results and the previously reported experimental work. It is clear that the minimum metal–metal bonding requirement for these molecules is the presence of a filled molecular σ-type orbital of A_1 symmetry in which the principal overlap is between orbitals of the two metals and that there will be 4 A_1 and 2 E filled bonding σ molecular orbitals (excluding the C–O σ from these considerations). Since all of the A_1 orbitals must, in general, involve both X and M orbitals to a nonzero extent, the nature of both X and M will affect the character of the M–Co bond. In particular, as the energies of the X-orbital set are lowered, the energies of all of the A_1 σ-bonding orbitals are lowered. Thus, we would expect that if σ bonding were the primary determinant, it would be found that k(M–Co) would increase linearly with the electronegativity of X (or equivalently the sum of the X electronegativities). In fact, a plot of k(M–Co) *vs.* the electronegativity of X is nearly linear, giving essentially parallel lines for the Sn and Ge derivatives. We take this to mean that the M–Co bond strength and its variation with X appear to contain an important contribution from the molecular σ-bonding system. However, since the Co–Sn strengths are higher than the Co–Ge strengths, while the electronegativities of Sn and Ge are quite similar, other factors must be considered.

Now it is clear that there are symmetry-proper combinations of the (formally filled) primarily Co d orbitals which can form molecular π-type orbitals involving the CO and MX_3 group orbitals. It is well known that the C–O stretching frequencies are sensitive to the contributions to such orbitals from CO(π^*) orbitals and that a decrease in the π^*(CO) contribution to these molecular orbitals increases the values of ν(CO), as observed. Now, since the MX_3 orbitals, primarily symmetry-proper combinations of X p and M d orbitals, take part in this molecular π bonding, a nonzero $X_3M-Co(CO)_4$ π character is expected. In fact, it has been suggested that the existence of $Cl_3SnCo(CO)_4$ coupled with the nonexistence of $ClCo(CO)_4$ indicates the significance of the π-acceptor nature of Cl_3Sn.[24]

It is very difficult to estimate *a priori* the extent to which the changes in the ν(CO) spectrum reflect the importance of Co–MX_3 "π bonding" and the extent to which they simply reflect the overall lowering of the energies of the bonding orbitals, due to the lowering of the MX_3 levels through a series, with consequent decreasing π^*(CO) character in the π molecular orbitals. However, Graham[25] has devised a scale to indicate the importance of the σ and π bonding to MX_3 which is based on approximate vibrational analysis of the ν(CO) spectra. In the $LMn(CO)_5$ compounds considered, the π parameter is found to be higher for Cl_3Sn than for Cl_3Ge, while those for Cl_3Sn and Br_3Sn are about the same.

It is interesting to note in this regard that the ^{59}Co nqr data of Brown and coworkers[6] have been interpreted to require some π-type bonding between the X_3Sn and $Co(CO)_4$ groups in $X_3SnCo(CO)_4$ compounds. In a recent extended-Hückel limited-basis-set molecular orbital calculation on the analogous $Cl_3SiCo(CO)_4$ and $F_3SiCo(CO)_4$ compounds, MacDiarmid and coworkers[9] found that the σ bonding accounts for approximately 97 and 84%, respectively, of the Si–Co bonding. It is reasonable to expect that $X_3M-Co(CO)_4$ π bonding would be calculated on this basis to be as important in the cases of the Sn and Ge derivatives as in the Si compounds.

On the basis of these results for k(M–Co) and the discussion above, we conclude that the metal–metal bond is indeed predominantly σ in character, that although the π character of the M–M bond is relatively small, the Co–Sn bond has more π character

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[23] We are grateful to Professor W. A. G. Graham and Dr. R. Gay of the University of Alberta for suggesting that the more detailed form of specification of the force field of Table V, compared with that of ref 3, is useful to workers repeating these calculations. Note that in Table IV of ref 3, the value for k(M–Cl, Co–M–Cl) should read 0.1 rather than 0.01.

[24] R. Kummer and W. A. G. Graham, *Inorg. Chem.*, **7**, 310 (1968); see footnote 15 of this reference.

[25] W. A. G. Graham, *ibid.*, **7**, 315 (1968).

than the Co–Ge bond,[26] and that the Co–M bond strengths vary significantly (twofold or more) with changes in electronegativity of other atoms (X) to which the metals are bound. The latter conclusion will be of particular interest in extending this model work on discrete metal–metal bonded molecules to the study of intermetallic forces in dilute alloys.

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[26] It has been suggested by a reviewer that, in addition to the data and correlations concerning Co–Sn and Co–Ge π bonding, the greater Co–Sn π bonding can be rationalized in terms of greater X–M π bonding in the case of Ge as opposed to Sn, which could reduce the amount of effective Co–Ge π bonding with respect to Co–Sn π bonding.

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Electron Spin Resonance Studies of Low-Spin Cobalt(II) Complexes. Base Adducts of Cobalt Phthalocyanine

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The effects of the extraplanar ligands DMSO, pyridine, imidazole, and cyanide on the esr spectra of cobalt complexes of tetrasulfonated phthalocyanine have been studied. With the first three ligands, a marked change in the esr spin-Hamiltonian parameters was observed with increasing basicity. In the case of cyanide, the Co(II) species was found to be no longer stable. Evidence is presented for an "intramolecular" oxidation–reduction reaction to a Co(III) complex of the phthalocyanine anion. Efforts to prepare simple 1:1 oxygen adducts of these complexes were unsuccessful.

Introduction

Considerable recent work has been devoted to the reactions of a group of low-spin cobalt(II) complexes, many of which form cobalt hydrides, organocobalt complexes, oxygen adducts, and peroxo-bridged dimers under suitable conditions. Included in this group are vitamin B_{12r}, bis(dimethylglyoximato)cobalt, cobalt porphyrins, and cobalt phthalocyanines (CoPc). The reactions of all of these complexes are strongly influenced by extraplanar ligands, as has been shown in a comparison of B_{12r} and cobaloxime chemistry.[3]

Since the unpaired electron in these complexes is in a d_{z^2} orbital, the orbital directly involved in the coordination of extraplanar ligands, electron spin resonance (esr) provides a particularly sensitive tool for the study of these species. Thus, esr spectra provided strong evidence for the coordination of the 5,6-dimethylbenzimidazole "fifth ligand" to the central cobalt in vitamin B_{12r}.[4–6] Addition of either pyridine or imidazole had no effect on the spectra, indicating the absence of further sixth-position coordination by the free base. This behavior is in contrast to that of cobaloximes, of cobalt phthalocyanines,[7] and of derivatives of cobalt tetraphenylporphine (CoTPP),[8] which readily form six-coordinate bis-pyridine complexes. With imidazoles, however, only the monoadducts (of the cobaloximes and porphines) are formed. Esr studies of the coordination of imidazoles with CoPc have not been reported.

In the presence of air, many of these complexes reversibly form 1:1 adducts with molecular oxygen, and pronounced changes in the esr spectra are observed.[8–12] The equilibrium constants and reversibility of this adduct formation and the tendency toward further reaction to the peroxo-bridged dimers are functions both of the extraplanar ligand and of the specific cobalt complex. Increasingly basic ligands, for example, favor formation of the oxygen adduct.[8]

In an effort to elucidate the effect of axial ligands on the electronic structure of these B_{12} models and, hopefully, their oxygen adducts, we have undertaken an esr study of the base adducts of tetrasulfonated cobalt(II) phthalocyanine, Na_4CoPTS. In view of the earlier work cited above, the ligands pyridine, imidazole, and cyanide were chosen. Studies of sulfonated phthalocyanines in aqueous solution can be complicated by molecular association.[13] For this reason, dimethyl sulfoxide (DMSO) was used; in this solvent, association has been shown to be absent.[14]

The unambiguous interpretation of paramagnetic resonance spectra of polycrystalline or frozen-glass samples at a single frequency can be difficult or im-

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[3] G. N. Schrauzer and R. J. Windgassen, *Chem. Ber.*, **99**, 602 (1966).

[4] G. N. Schrauzer and L. P. Lee, *J. Amer. Chem. Soc.*, **90**, 6541 (1968).

[5] S. A. Cockle, H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, *Biochim. Biophys. Acta*, **177**, 686 (1969).

[6] J. H. Bayston, F. D. Looney, J. R. Pilbrow, and M. E. Winfield, *Biochemistry*, **9**, 2164 (1970).

[7] J. M. Assour, *J. Amer. Chem. Soc.*, **87**, 4701 (1965).

[8] F. A. Walker, *ibid.*, **92**, 4235 (1970).

[9] Y. Ogata, K. Marumo, and T. Kwan, *Chem. Pharm. Bull.*, **17**, 1194 (1969).

[10] J. H. Bayston, N. K. King, F. D. Looney, and M. E. Winfield, *J. Amer. Chem. Soc.*, **91**, 2775 (1969).

[11] G. N. Schrauzer and L. P. Lee, *ibid.*, **92**, 1551 (1970).

[12] K. Yamamoto and T. Kwan, *J. Catal.*, **18**, 354 (1970).

[13] K. Bernhauer and S. Fallab, *Helv. Chim. Acta*, **44**, 1287 (1961).

[14] L. D. Rollmann and R. T. Iwamoto, *J. Amer. Chem. Soc.*, **90**, 1455 (1968).