CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
BROWN UNIVERSITY, PROVIDENCE, RHODE ISLAND 02912

Spectroscopic Studies of Metal–Metal Bonding. I. Absorption and Laser Raman Spectra and Vibrational Analyses of Cl₃MCo(CO)₄ (M = Sn, Ge, Si)[1]

BY KENNETH L. WATTERS,[2a] JOHN N. BRITTAIN, AND WILLIAM M. RISEN, JR.[2b]

The complete absorption spectra (33–55,000 cm^{-1}) are reported for the three analogous metal–metal or metal–metalloid bound molecules Cl₃SnCo(CO)₄, Cl₃GeCo(CO)₄, and Cl₃SiCo(CO)₄, and the laser Raman spectra, including band polarization, have been measured for $\Delta\omega$ = 0–4000 cm^{-1}. The symmetry types of the vibrational bands are assigned for the 48 observed of the 60 allowed fundamentals, the overtone and combination bands observed are tentatively assigned, including the ν_{CO} type of overtones and combinations in the 4000–4250-cm^{-1} region, and the electronic ultraviolet transitions giving rise to the colors are reported. Vibrational normal-coordinate analyses for the molecules are reported which yield close agreement between calculated and validly assigned spectra and which are based on both reasonable spectroscopic assumptions and valence force field. The different k_{Co-M} values found (k_{Co-Sn} = 1.23 mdyn/Å, k_{Co-Ge} = 1.05 mdyn/Å, k_{Co-Si} = 1.32 mdyn/Å) do not appear to be significantly reflected in the 5-μ (ν_{CO}) spectra. The vibrational eigenvectors indicate that approximate methods of calculating k_{MM} from one assigned "ν_{MM}" are not reliable.

Introduction

The nature of metal–metal and metal–metalloid bonding is being studied by a number of techniques on a variety of systems which range from vapor-phase n-mers to metals and alloys. In the recent few years the syntheses of a number of relatively stable discrete metal–metal bonded molecules have led to the expenditure of considerable effort at the study of these bonds. To date, the studies have been primarily in survey form,[3] with the exception of structural studies and a few mass spectral studies. The potential of vibrational analysis leading to determination of the strengths of the bonds of interest is well recognized, but its fulfillment has been approached in only few cases.[4] The reasons for this are evident; the molecules and consequently the numbers of vibrations and sizes of force fields are large, and the larger they are the greater the disparity which must be overcome between the number of unknown force field elements and known experimental data.

Since finding a sufficiently complete valence force field which is both in complete agreement with the observed spectra and which can claim to be a substantially valid measure of bond strengths is a problem which normally demands somewhat more than spectral information for one molecule, we have selected a very favorable series of molecules, Cl₃MCo(CO)₄ (M = Sn, Ge, Si), to consider.

Its members can be prepared in high purity, structural information is available, spectra in important regions can be measured in the vapor as well as liquid phase, the spectral assignments of fundamentals are theoretically unambiguous because of the selection rules and polarization behavior of the Raman bands, and a relatively large fraction of the vibrational bands is allowed. There is strong spectral evidence that a large portion of the force field is constant through the series, there is a systematic change in the extent of mixing between the modes involving and not involving the constant portion as the series is descended, and the moieties of each molecule have very close parallels in other vibrationally analyzed molecules.[5,6]

We report the infrared and laser Raman spectra of the three molecules Cl₃MCo(CO)₄ (M = Sn, Ge, Si), their vibrational analyses, and the conclusions we have reached from these analyses concerning their bonding and the treatment of metal–metal bonded compounds.

Experimental Section

The compounds Cl₃SiCo(CO)₄,[7] Cl₃GeCo(CO)₄,[8] and Cl₃SnCo(CO)₄[9] were prepared by referenced reported routes from reagents carefully prepurified in all cases by repeated vacuum

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Table I
Observed Infrared and Raman Spectra

Ir	State	Intens	Raman	State	Intens	Pol	Symmetry	Assignment
				$Cl_3SiCo(CO)_4$				
4235	a	w	...		...	...	A_1	$2\nu_1$
4175	a	w	...		...	...	A_1	$\nu_1 + \nu_2$
4150	a	w	...		...	...	E	$\nu_{10} + \nu_1$
4120	a	w	...		...	...	A_1	$2\nu_2$
4105	a	w	...		...	...	E	$\nu_{10} + \nu_2$
4070	a	w	...		...	...	$A_1 + E$	$2\nu_{10}$
2663	a	vw	...				A_1	$\nu_1 + \nu_4$
2634	a	vw	...				E	$\nu_2 + \nu_{11}$
2610	a	vw	...				$A_1 + E$	$\nu_{10} + \nu_{11}$
2550	a	vw	...				E	$\nu_2 + \nu_{13}$ or $\nu_{10} + \nu_{12}$
2530	a	vw	...				A_1	$\nu_2 + \nu_5$
2498	a	vw	...				E	$\nu_{10} + \nu_5$
2472	a	vw	...				A_1	$\nu_2 + \nu_6$
2444	a	vw	...				E	$\nu_{10} + \nu_6$
2118	a	s	2121	a	w	P	A_1	ν_1
2066	a	s	2067	a	w	P	A_1	ν_2
2039	a	vs	2040	a	w	Dp	E	ν_{10}
1999	a	w	...				A' or A'' (C_s)	^{13}C isotope
641	a	vw	...				A_1	ν_3
612	a	vw	...				A_1	$2\nu_7$
571	a	s	573	a	w	Dp	E	ν_{11}
549	a	m	552	a	w	P	A_1	ν_4
506	a	m	...				E	ν_{12}
483	a	m	...				E	ν_{13}
471	a	m	469	b	w	P	A_1	ν_5
437	a	vw	438	b	vw		E	ν_{14}
411	a	w	412	a	m	P	A_1	ν_6
372	a	w	...				E	ν_{15}
309	c	m	309	b	s	P	A_1	ν_7
200	d	w	200	b	w	Dp	E	ν_1
179	d	m	180	b	s	P	A_1	ν_8
138	d	w	138	a	w	Dp	E	ν_{17}
100	d	w	100	a	s	P	A_1	ν_9
65	d	vw	...				E	ν_{20}
45	d	w	...					Libration
				$Cl_3GeCo(CO)_4$				
4239	a	w	...		...	...	A_1	$2\nu_1$
4177	a	w	...		...	...	A_1	$\nu_1 + \nu_2$
4163	a	w	...		...	...	E	$\nu_1 + \nu_{10}$
4125	a	w	...		...	...	A_1	$2\nu_2$
4115	a	w	...		...	...	E	$\nu_2 + \nu_{10}$
4048	a	w	...		...	...	$A_1 + E$	$2\nu_{10}$
2673	a	vw					E	$\nu_1 + \nu_{11}$
2617	a	vw					E	$\nu_2 + \nu_{11}$
2560	a	vw					E	$\nu_2 + \nu_{13}$
2540	a	vw					A_1	$\nu_2 + \nu_5$
2518	a	vw					A_1 or E	$\nu_1 + \nu_4$ or $\nu_{10} + \nu_5$
2460	a	vw					A_1 or E	$\nu_{10} + \nu_6$ or $\nu_2 + \nu_4$
2442	a	vw					E	$\nu_{10} + \nu_4$ or $\nu_2 + \nu_{15}$
2123	a	s	2123	b	w	P	A_1	ν_1
2070	a	s	2070	b	w	P	A_1	ν_2
2050	a	vs	2048	b	w	Dp	E	ν_{10}
2012	a	w					A' or A'' (C_s)	^{13}C isotope
548	a	s					E	ν_{11}
485	a	m					E	ν_{13}
465	a	m					A_1	ν_5
441	a	vw					E	ν_{14}
411	a	w	410	b	w	P	A_1	ν_6
391	a	m	390	b	m	P	A_1	ν_4
371	a	w					E	ν_{15}
240	a	m	240	b	s	P	A_1	ν_7

TABLE I (*Continued*)

Ir	State	Intens	Raman	State	Intens	Pol	Symmetry	Assignment
160	d	m–s	162	b	s	P	A_1	ν_8
129	d	m					E	ν_{17}
107	d	w	106	b	m	...	E	ν_{18}
89	d	w					A_1	ν_9
45	d	m					E	ν_{20} + lattice
				$Cl_3SnCo(CO)_4$				
4237	a	w	...	...	...	...	A_1	$2\nu_1$
4175	a	w	...	...	...	...	A_1	$\nu_1 + \nu_2$
4160	a	w	...	...	...	...	E	$\nu_1 + \nu_{10}$
4125	a	w	...	...	...	...	A_1	$2\nu_2$
4115	a	w	...	...	...	...	E	$\nu_2 + \nu_{10}$
4081	a	w	...	...	...	...	$A_1 + E$	$2\nu_{10}$
2665	a	vw	...	...	...	...	E	$\nu_1 + \nu_{11}$
2610	a	vw	...	...	...	...	E	$\nu_2 + \nu_{11}$ or $\nu_1 + \nu_{13}$
2440	a	vw	...	...	...	...	A_1	$\nu_2 + \nu_4$
2121	c	s					A_1	ν_1
2069	c	s					A_1	ν_2
2048	c	vs					E	ν_{10}
545	b	s					E	ν_{11}
490	b	m					E	ν_{13}
463	b	m					A_1	ν_5
405	b	w					A_1	ν_6
365	b	m	365	b	m	...	A_1	ν_4
360	b	w					E	ν_{15}
204	b	ms	204	b	m	P	A_1	ν_7
125	d	ms					A_1	ν_8
107	d	m					E	ν_{17}
69	d	m					E	ν_{19}
50	d	m					E	ν_{20}

^{a} CCl$_4$ solution. ^{b} C$_6$H$_6$ solution. ^{c} Cyclohexane solution. ^{d} Nujol mull.

sublimation, distillation, and fractionation, where applicable. The Co$_2$(CO)$_8$ used was freshly sublimed from material purchased from Strem Chemical Co.

Purity of samples was determined by elemental analysis and physical (melting points, color) and spectral (5-μ infrared) properties, which agreed well with the expected or published values.[7–9] Elemental analyses including metal analyses, conducted by Baron Consulting Co., agreed with calculated values to within 0.5% for C and Cl and 0.8% in M in each case.

Solutions for spectroscopic studies were prepared and handled in a dry nitrogen atmosphere or *in vacuo* using carefully dried and deaerated solvents and were placed in infrared or Raman cells which had been purged with nitrogen and were then sealed. Fused-silica Raman cells, KBr, CsI, high-density polyethylene, and crystal quartz infrared liquid cells and 10-cm vapor cells were used where appropriate.

Considerable decomposition of Cl$_3$SnCo(CO)$_4$ in solution was found to occur when samples were exposed to the intense He–Ne laser source during Raman spectral measurements. This occurs despite the observation that there is no absorption band in the region of the Raman excitation line. The use of neutral density filters (25, 50, and 75% T in the exciting beam) reduced the problem somewhat but did not eliminate it. Therefore, the only Raman data reported for this compound are those which have been carefully verified by duplication with several different samples on both laser Raman instruments.

The infrared spectra were measured on Beckman IR-11, IR-12, and Perkin-Elmer 621 spectrophotometers with a resolution and accuracy of better than 0.5 cm^{-1} as determined by resolution standard tests and wave number calibration.[10] The laser Raman spectra were measured on both the Jarrell–Ash and the Spex Ramalog laser Raman systems with an accuracy of *ca.* 1 cm^{-1} and resolution of *ca.* 3 cm^{-1}. Visible–uv spectra were recorded using a Cary 14 spectrophotometer.

Results

The molecular symmetry of Cl$_3$SiCo(CO)$_4$ has been determined by X-ray structural studies to be C$_{3v}$.[11] The molecular symmetry of the other two molecules in the study is also assigned as C$_{3v}$ by direct analogy, by close agreement of their vibrational spectra, and by the similarity of synthetic and physical properties. M–Cl bond lengths used in the calculation for Cl$_3$SnCo(CO)$_4$ and Cl$_3$GeCo(CO)$_4$ were based upon values reported for the M–Cl bond lengths in the corresponding Sn and Ge tetrachlorides.[12] It is felt that this assumption is accurate, since the Si–Cl bond distance reported for Cl$_3$SiCo(CO)$_4$ is very nearly equal to that for SiCl$_4$.[13] All angles for Cl$_3$GeCo(CO)$_4$ and Cl$_3$SnCo(CO)$_4$ were the same as those for Cl$_3$SiCo(CO)$_4$. The values used for r_{Co-Sn} and r_{Co-Ge} were 2.50 and 2.40 Å, respectively, as estimated by considering the values for r_{Mn-Ge},[14] r_{Mn-Sn},[15] and r_{Fe-Sn}[16] in similar molecules.

For these molecules in C$_{3v}$ symmetry the vibrational representation is

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

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$\Gamma_{\text{vib}} = 9\,A_1\,(\text{ir, R, pol}) + 2\,A_2\,(\text{ia}) + 11\,E\,(\text{ir, R, depol})$

(ir, infrared active; R, Raman active; pol, polarized; depol, depolarized; ia, inactive). Thus the 33 normal modes occur as 22 vibrational fundamentals of which 20 are both infrared and Raman active. Raman polarization studies provide theoretically definitive, unique symmetry assignments of the fundamentals by differentiating between A_1 and E modes. Of the 20 predicted active fundamentals, 18 have been observed and assigned for $Cl_3SiCo(CO)_4$, 16 for $Cl_3GeCo(CO)_4$, and 14 for $Cl_3SnCo(CO)_4$. The entire observed vibrational spectra for the three molecules are given in Table I with qualitative indications of intensity and Raman polarization. All three molecules have sufficient vapor pressures at room temperature to yield vapor-phase infrared spectra in the 5-μ region, but many weaker vibrational bands in the middle- and low-frequency regions (700–$33\ cm^{-1}$) could be observed only in solution or as mull samples and thus all reported frequencies and assignments are based upon spectra observed under conditions noted in Table I.

The six overtones and combinations of the 5-μ region bands are observed, as expected from C_{3v} symmetry. These results, in the region 4050–$4250\ cm^{-1}$, are included in Table I.

Spectral Assignments.—Symmetry coordinates, formulated in the usual manner using the molecular geometry shown in Figure 1, are useful as a starting
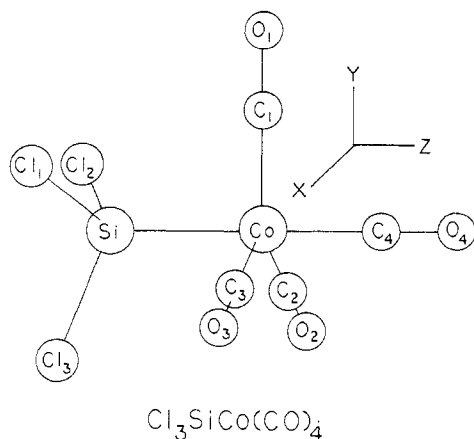

Figure 1.—Molecular geometry of $Cl_3SiCo(CO)_4$ as found by Ibers and Robinson.[11] Atomic labels are those used for all three homologous molecules. Atomic cartesian coordinates are parallel to the molecular coordinate system in this figure.

point in a spectral assignment. As shown in Table II, we expect three fundamental frequencies in the 2000-cm^{-1} region: two A_1 modes due to axial and equatorial C–O stretches and an E mode involving a stretch of the equatorial C–O's. Nine fundamentals, four A_1 and five E modes, are expected in the 300–700-cm^{-1} region. The A_1 modes are based upon axial Co–C, equatorial Co–C and M–Cl stretching motions, and Co–C–O bending out of the plane of the equatorial carbonyls. The five E modes in this region include equatorial Co–C and M–Cl stretching motions and three Co–C–O bending motions. At the low end of the middle-

TABLE II

SYMMETRIES OF VIBRATIONAL MODES
FOR $Cl_3MCo(CO)_4$ (C_{3v})

C–O str	$2\,A + E$	MCl_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–Cl str	$A_1 + E$	Torsion	A_2
Co–M str	A_1		

frequency region or in the upper part of the low-frequency (33–300-cm^{-1}) region an A_1 mode which is predominantly Co–M stretching is expected to occur. The low-frequency region should also contain three modes which are deformations of the MCl_3 group and four skeletal C–Co–C or M–Co–C bending motions.

All assigned fundamentals, their symmetry, and partial descriptions of the motions involved are given in Table III for $Cl_3SnCo(CO)_4$, $Cl_3GeCo(CO)_4$, and $Cl_3SiCo(CO)_4$. Our assignments of the three $\nu(CO)$ fundamentals in the 5-μ region agree with previous assignments which have been made in this region for all three molecules[8,9,17] but which did not have the experimental verification of Raman polarization studies.

All fundamentals predicted to occur in the middle-frequency region for $Cl_3SiCo(CO)_4$ are observed in the infrared spectrum. The very weak band observed at $641\ cm^{-1}$ is assigned as the A_1 Co–C–O bending motion.[18] The bands at 549, 471, and $411\ cm^{-1}$ in $Cl_3SiCo(CO)_4$ are polarized (A_1) and are assigned as Si–Cl, axial Co–C, and equatorial Co–C stretching motions, respectively, while the polarized band at $309\ cm^{-1}$ is assigned mainly to Co–Si stretching motion. This leaves the other five bands in the middle-frequency region as the five predicted depolarized E modes.

In the low-frequency region for $Cl_3SiCo(CO)_4$, bands at 200, 179, and $138\ cm^{-1}$ are assigned mainly to $SiCl_3$ deformation, in agreement with recent studies of Si_2Cl_6.[19] The bands observed at 100 and $65\ cm^{-1}$ are assigned as C–Co–C or Si–Co–C skeletal bending. The two predicted fundamentals not observed for $Cl_3SiCo(CO)_4$ are believed to be C–Co–C bending motions of E symmetry which should occur at approximately $100\ cm^{-1}$.

The spectral assignments for $Cl_3GeCo(CO)_4$ and $Cl_3SnCo(CO)_4$ are in agreement with those for $Cl_3SiCo(CO)_4$ taking into account frequency shifts in the region 120–$600\ cm^{-1}$ which are the result of changes in the mass of M, the force field associated with the MCl_3 group, and the mixing between modes of the same symmetry. The greatest frequency shifts of assigned fundamentals occur for bands assigned as M–Cl and Co–M stretches; thus, the bands at 549 and $309\ cm^{-1}$ in the spectrum of $Cl_3SiCo(CO)_4$ are shifted to 391 and $240\ cm^{-1}$ for $Cl_3GeCo(CO)_4$ and to 365 and $204\ cm^{-1}$ for $Cl_3SnCo(CO)_4$. The assignments of the M–Cl stretching fundamentals for each molecule are quite consistent with reported, valid assignments for MCl_4,

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TABLE III
OBSERVED AND CALCULATED FUNDAMENTALS

Obsd (ir)	Calcd	Symmetry	Description
		$Cl_3SiCo(CO)_4$	
2118	2121	A_1	$\nu_{C-O(ax)} + \nu_{C-O(eq)}$
2066	2069	A_1	$\nu_{C-O(eq)} + \nu_{C-O(ax)}$
2039	2044	E	$\nu_{C-O(eq)}$
641	634	A_1	δ_{Co-C-O}
571	568	E	$\delta_{Co-C-O(ax)}$
549	546	A_1	$\nu_{Si-Cl} + \nu_{Co-Si}$
506	503	E	$\nu_{Co-C} + \nu_{Si-Cl} + \delta_{Co-C-O}$
483	483	E	δ_{Co-C-O}
471	469	A_1	$\nu_{Co-C(ax)}$
437	438	E	δ_{Co-C-O}
411	410	A_1	$\nu_{Co-C(eq)}$
372	373	E	$\nu_{Si-Cl} + \nu_{Co-C}$
309	310	A_1	$\nu_{Co-Si} + \nu_{Si-Cl} + \delta_{SiCl_3}$
200	199	E	δ_{SiCl_3}
179	177	A_1	$\delta_{SiCl_3} + \nu_{Co-Si}$
138	139	E	$\delta_{SiCl_3} + \delta_{Co-Co-CO}$
. . .	118	E	$\delta_{CO-Co-CO} + \delta_{SiCl_3}$
100	99	A_1	$\delta_{CO-Co-CO} + \delta_{SiCl_3}$
. . .	80	E	$\delta_{CO-Co-CO}$
65	61	E	$\delta_{Si-Co-CO(ax)} + \delta_{Co-Si-Cl}$
		$Cl_3GeCo(CO)_4$	
2123	2121	A_1	$\nu_{C-O(ax)} + \nu_{C-O(eq)}$
2070	2069	A_1	$\nu_{C-O(eq)} + \nu_{C-O(ax)}$
2050	2044	E	$\nu_{C-O(eq)}$
. . .	637	A_1	δ_{Co-C-O}
548	555	E	$\delta_{Co-C-O(ax)}$
485	488	E	$\nu_{Co-C} + \delta_{Co-C-O}$
. . .	484	E	$\nu_{Co-C} + \delta_{Co-C-O}$
465	467	A_1	$\nu_{Co-C(ax)}$
441	443	E	δ_{Co-C-O}
411	408	A_1	$\nu_{Co-C(eq)}$
391	393	A_1	ν_{Ge-Cl}
371	365	E	ν_{Ge-Cl}
240	240	A_1	$\nu_{Co-Ge} + \nu_{Ge-Cl} + \delta_{GeCl_3}$
. . .	182	E	δ_{GeCl_3}
160	162	A_1	$\delta_{GeCl_3} + \nu_{Co-Ge}$
129	130	E	$\delta_{GeCl_3} + \delta_{Co-Co-CO}$
107	113	E	$\delta_{CO-Co-CO} + \delta_{GeCl_3}$
89	94	A_1	$\delta_{CO-Co-CO}$
. . .	87	E	$\delta_{CO-Co-CO}$
45	51	E	$\delta_{Ge-Co-CO(ax)} + \delta_{Co-Ge-Cl}$
		$Cl_3SnCo(CO)_4$	
2121	2121	A_1	$\nu_{C-O(ax)} + \nu_{C-O(eq)}$
2069	2069	A_1	$\nu_{C-O(eq)} + \nu_{C-O(ax)}$
2048	2044	E	$\nu_{C-O(eq)}$
. . .	639	A_1	δ_{Co-C-O}
545	542	E	$\delta_{Co-C-O(ax)}$
490	489	E	$\nu_{Co-C} + \delta_{Co-C-O}$
. . .	484	E	$\nu_{Co-C} + \delta_{Co-C-O}$
463	468	A_1	$\nu_{Co-C(ax)}$
. . .	449	E	δ_{Co-C-O}
405	406	A_1	$\nu_{Co-C(eq)}$
365	364	A_1	ν_{Sn-Cl}
360	357	E	ν_{Sn-Cl}
204	205	A_1	ν_{Co-Sn}
. . .	129	E	δ_{SnCl_3}
125	128	A_1	$\delta_{SnCl_3} + \delta_{Co-Co-CO}$
107	114	E	$\delta_{SnCl_3} + \delta_{Co-Co-CO}$
. . .	92	E	$\delta_{CO-Co-CO}$
. . .	89	A_1	$\delta_{CO-Co-CO}$
69	80	E	$\delta_{CO-Co-CO}$
50	. . .	. . .	**Libration**
. . .	29	E	$\delta_{Sn-Co-C(ax)} + \delta_{Co-Sn-Cl}$

MCl_3^-, and M_2Cl_6 species.[19,20] The expected frequency shifts also occur for the bands between 100 and 200 cm^{-1} which are assigned as MCl_3 deformation fundamentals. Figure 2 contains a correlation diagram of
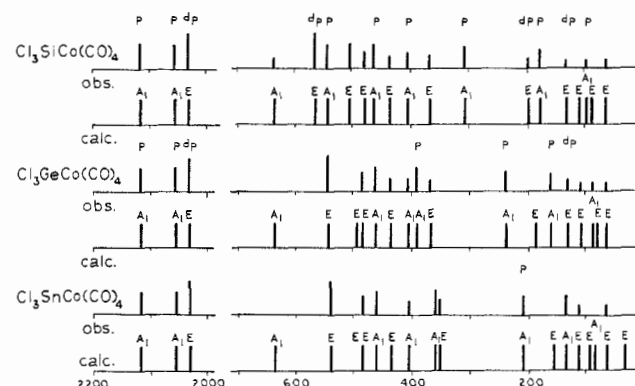
Figure 2.—Correlation diagram of observed and calculated spectra for the three molecules. Results of Raman polarization measurements are shown above the corresponding observed bands. Symmetries of calculated frequencies are as given.

the observed and calculated fundamentals for each of the molecules.

A recent discussion of a portion of the middle-frequency spectrum of $Cl_3SiCo(CO)_4$ and of Cl_3GeCo-$(CO)_4$[21] is somewhat different from that given in this work, but that discussion was not supported by Raman polarization data and did not extend to force field work.

Molecular Valence Force Fields.—The vibrational spectra of all three molecules are nearly identical in both the 2000-cm^{-1} C–O stretching region and the low-frequency (<120 cm^{-1}) far-infrared region involving mainly C–Co–C bending motion. This is a strong indication that the molecular force fields for the $Co(CO)_4$ moiety are nearly identical for all three molecules. Notable differences in the vibrational spectra of the three molecules were observed only in the region 120–600 cm^{-1}. These differences are, of course, attributable to the changes in the reduced mass and in that portion of the force field which accompanies the introduction of a different MCl_3 group and to consequent differences in the mixing of the M–Cl and Co–M stretching motions with middle-frequency vibrations of the $Co(CO)_4$ group. It is, in fact, observed that the vibrational spectra of $Cl_3SnCo(CO)_4$ and $Cl_3GeCo(CO)_4$ agree to within 5 cm^{-1} throughout the 400–600-cm^{-1} region which contains only $Co(CO)_4$ group vibrations; however, they are quite different from the $Cl_3SiCo(CO)_4$ spectrum in this region since the $Co(CO)_4$ vibrations for this molecule are extensively mixed with the Si–Cl and Co–Si stretching motions. Thus, a test of the assumed identity of the $Co(CO)_4$ group force field for the three molecules is to observe whether the middle-

(20) (a) "Landolt-Bornstein Physikalische-Chemische Tabellen," Vol. I, Part 2, Springer-Verlag, Berlin, 1951; (b) L. P. Lindeman and M. K. Wilson, *Spectrochim. Acta*, **9**, 47 (1957); (c) H. Kriegsman and S. Pauley, *Z. Anorg. Allgem. Chem.*, **330**, 275 (1964); (d) F. K. Butcher, *et al.*, *J. Organometal. Chem.* (Amsterdam), **1**, 431 (1964); (e) P. Taimsalu and J. L. Wood, *Spectrochim. Acta*, **20**, 1043 (1964); (f) A. L. Smith, *J. Chem. Phys.*, **21**, 1997 (1953).

(21) O. Kahn and M. Bigorgne, *Compt. Rend.*, **C266**, 792 (1968).

TABLE IV

NONZERO FORCE FIELD ELEMENTS FOR $Cl_3SnCo(CO)_4$, $Cl_3GeCo(CO)_4$, $Cl_3SiCo(CO)_4$

Force Field Elements[a,b] Constant for the Series

k_{C-O}^{ax}	17.98[c]	k_{Co-C-O}^{op}	0.27[c]	$k_{M-Co,M-Cl}$	0.19
$k_{Co-C,C-O}$	0.735	$k_{Co-C-O,Co-C-O}$	0.02	$k_{C-Co-C,C-Co-C}$	-0.008
k_{Co-C}^{eq}	2.62[c]	k_{C-Co-C}^{ip}	0.09[c]	$k_{Cl-M-Cl,Cl-M-Cl}$	0.02
k_{Co-C}^{ax}	2.51[c]	k_{Co-C-O}^{op}	0.19[c]	$k_{M-Cl,Cl-M-Cl}$	0.02
$k_{Co-C,Co-C}$	0.1	$k_{M-Co-C(eq)}$	0.13[c]	$k_{M-Co,Co-M-Cl}$	0.02
k_{Co-C-O}^{ax}	0.30[c]	$k_{M-Co-C(ax)}$	0.02[c]	$k_{M-Cl,Co-M-Cl}$	0.01
k_{Co-C-O}^{ip}	0.32[c]	$k_{M-Co,Co-C}$	0.1	k_{C-O}^{eq}[c]	17.05
				$k_{C-O,C-O}$	0.170

Force Field Elements[a,b] Which Vary for the Series

k^a	$Cl_3SnCo(CO)_4$	$Cl_3GeCo(CO)_4$	$Cl_3SiCo(CO)_4$
k_{M-Co}^c	1.23	1.05	1.32
k_{M-Cl}^c	2.46	2.48	2.82
$k_{Cl-M-Cl}^c$	0.080	0.27	0.35
$k_{Co-M-Cl}^c$	0.028	0.060	0.096
$k_{M-Cl,M-Cl}$	0.001	0.002	0.04

[a] All force field elements are in millidynes per ångström. [b] All internal valence coordinates are defined as positive for bond stretching or angle opening; thus all force field elements have unique signs. [c] Diagonal element, corresponds to k_{ii} for internal valence coordinate r_i.

frequency spectra of all three molecules can be reproduced from calculations based upon molecular force fields containing identical force field elements for the $Co(CO)_4$ group. This test requires that the $Co(CO)_4$ portion of the force field be valid in both the extensively mixed and reasonably separated cases.

Molecular force fields individually containing 27 unique force field elements were used for each of the three molecules (see Table IV). For these molecules, in C_{3v} symmetry, six unique valence force field elements for bond stretching and nine elements for angle bending are required for the diagonal, k_{ii}, elements with twelve nonzero interaction constants, k_{ij}, used in each force field.

The initial force field for the $Co(CO)_4$ group and most of the interaction constants, unchanged through the series, were obtained by transfer from force fields which were found consistent with validly assigned spectra of metal carbonyls.[5,22] Starting diagonal elements for the MCl_3 groups were also obtained in this manner[6] while reasonable starting values were assumed for k_{Co-M} and the interaction constants between Co-M stretching and other motions. For the first molecule, the transferred diagonal elements were varied slightly to obtain a solution while the interaction constants were, in general, not varied.

After obtaining a solution for one molecule, only five elements were varied to obtain solutions for the other two molecules. The force fields for the three molecules were allowed to differ only for the three diagonal elements associated with the MCl_3 group, for k_{Co-M}, and for the M-Cl,M-Cl stretching interaction constant. It was found that, by varying only these force field elements, calculated spectra were obtained which not only matched both the highest and the lowest frequency regions of the vibrational spectrum but also reproduced the observed differences between the middle-frequency spectrum of $Cl_3SiCo(CO)_4$ and those of $Cl_3GeCo(CO)_4$ and $Cl_3SnCo(CO)_4$. In addition, the changes required

in the three diagonal force field elements associated with the MCl_3 group to yield calculated spectra in agreement with our assigned observed spectra are, in each case, in the direction and of the magnitude expected from previously published force constants for the simple group IVa tetrahalides.[6] The interaction constant $k_{M-Co,M-Cl} = 0.19$ has been kept constant for the three molecules, in keeping with the above description, after having been determined for the Si analog. The extent of mixing of these types of motion is not strongly dependent upon the precise magnitude of this constant, as we have shown by its systematic variation. Those modes whose λ values do change somewhat upon such variation of this k_{ij} can most readily be brought to the assigned λ value by small changes in k_{M-Cl} rather than $k_{M-Co,M-Cl}$. Variation of this k_{ij} by $\pm 50\%$ simply changes, slightly, the already adjustable k_{M-Cl} and has insignificantly small effect on the magnitudes and no effect on the order of the k_{M-Co} values. The entire molecular valence force fields are given in Table IV. The values of k_{Co-M} which are part of these molecular force fields which give the calculated spectra listed in Table III are: $k_{Co-Sn} = 1.23$ mdyn/Å, $k_{Co-Ge} = 1.05$ mdyn/Å, $k_{Co-Si} = 1.32$ mdyn/Å. The average value of $|\nu_{calcd} - \nu_{obsd}|$ is 2.7 cm^{-1}. While we can show that very minor changes in other, nonvaried force field elements will give essentially exact numerical agreement between calculated and observed spectra, this would be meaningless since the numbers already agree to better than the harmonic oscillator approximation throughout the entire spectrum. In the 2000-cm^{-1} region in particular, though variation of the force field elements associated with the C-O stretching motion by no more than ± 0.05 mdyn/Å will obtain an exact fit of calculated to observed frequencies, not only are the vibrations more anharmonic[23] than the 10 cm^{-1} within which corresponding bands for each of the three molecules appear, but the differences observed are no greater than the shifts observed in this

(22) W. M. Risen, Jr., Ph.D. Thesis, Purdue University, 1967.

(23) J. M. Smith and L. H. Jones, *J. Mol. Spectry.*, **20**, 248 (1966).

TABLE V

Molecule	ν(calcd)	λ(calcd)	$C_{8n}k_{Co-M}$	$C_{9n}k_{M-Cl}$	$C_{4n}k_{Co-C}^{ax}$	$C_{3n}k_{Co-C}^{eq}$	$C_{6n}k_{\delta(Cl-M-Cl)}$	$C_{7n}k_{\delta(Co-M-Cl)}$
Cl₃SiCo(CO)₄	468.3	0.1292	0.0020	0.0053	0.0907	0.0041	0.0005	...
Cl₃SiCo(CO)₄	543.2	0.1738	0.0360	0.1001	0.0010	...	0.0334	0.0081
Cl₃SiCo(CO)₄	311.8	0.05725	0.01185	0.02020	0.00373	0.00006	0.01301	0.00317
Cl₃SiCo(CO)₄	177.3	0.01852	0.00702	0.00038	0.00088	...	0.00424	0.00102
Cl₃GeCo(CO)₄	467.0	0.1284	0.0046	...	0.0952	0.0043	...	...
Cl₃GeCo(CO)₄	392.9	0.09090	0.0044	0.0819	...	...	0.0055	0.0011
Cl₃GeCo(CO)₄	239.9	0.03388	0.01266	0.00280	0.0012	...	0.01183	0.002738
Cl₃GeCo(CO)₄	162.5	0.01554	0.00436	0.00079	0.00056	...	0.00377	0.00076
Cl₃SnCo(CO)₄	468.0	0.1290	0.0051	...	0.0950	0.0040	...	...
Cl₃SnCo(CO)₄	364.1	0.07809	0.0012	0.07921	...	...	0.00032	0.00009
Cl₃SnCo(CO)₄	204.7	0.02468	0.01839	0.00004	0.0018	...	0.0010	0.00031
Cl₃SnCo(CO)₄	127.6	0.00959	0.00004	0.00009	...	...	0.00302	0.00090

region on going from vapor to condensed phase. Of course, use of our 5-μ vapor-phase data would partially solve the problem, but we have vapor data only in this region and they are, in any event, not harmonic frequencies. It should be pointed out that force constants for C–O stretches in these molecules can be obtained from $^{12}C^{16}O$ data only by making at least two assumptions regarding the force field. First, a relationship between the force field elements $k_{C-O,C-O}^{eq,eq}$ and $k_{C-O,C-O}^{eq,ax}$ must be assumed (in these studies the two were assumed to be equal while in another study[17] $k_{C-O,C-O}^{eq,ax}$ was assumed to be zero), and, second, the value of the interaction constant, $k_{Co-C,C-O}$, must be set (this value is often set equal to zero). While k_{C-O} cannot be omitted from the molecular force field when considering the middle- and low-frequency bands without affecting the values obtained for k_{Co-C}, as shown by the contribution of C–O stretching motion to the eigenvalues for modes mainly involving Co–C stretch, the small differences in the values obtained for k_{C-O} resulting from different assumptions which are made regarding the $k_{C-O,C-O}$ interaction constants do not have a significant effect upon any of the calculated frequencies in the middle-frequency region. The one band we observed for the ^{13}CO monosubstituted species is an A′ or A″ mode of the molecule in the new point group C$_s$ since the substitution is most likely to occur among the equatorial CO's. This frequency now depends primarily upon the k_{C-O}^{eq} and $k_{C-O,C-O}^{eq,eq}$ and is calculated with our force constants.

An interesting feature of the Raman spectra in the 2000-cm^{-1} region should be mentioned. Although approximate bond dipole considerations predict that one of the infrared A₁ bands in this region, namely, that one associated with equatorial C–O stretch, should have very low intensity, both A₁ infrared bands are strong and of nearly equal intensity, and therefore the equatorial and axial C–O stretching motions are mixed. Our calculations show that the required mixing of these A₁ modes is obtained if a nonzero interaction constant between axial and equatorial stretch is included in the force field. The Raman spectra, however, show strikingly different polarizations for the two bands of A₁ symmetry with the band at 2065 cm^{-1} having ρ $\simeq$ 0.6 while the band at 2120 cm^{-1} has $\rho \simeq 0$. Similar results have been observed in Raman studies by Edgell, et al.,[24] and a theory has been derived by Edgell[19] which

promises to make calculation of the amount of axial and equatorial mixing possible from the observed Raman polarization ratios.

Vibrational Eigenvectors.—An important objective of this study has been to obtain the vibrational eigenvectors for the modes which involve Co–M stretching motion. The eigenvectors, a direct result of the vibrational analysis, clearly show that those modes involving Co–M stretch also extensively involve other motions, of particular importance the axial Co–C and the M–Cl distentions.

Contributions of the various internal coordinates with associated force constant k_i to the calculated normal coordinates can be assessed by obtaining the energy contribution from the motion along an internal coordinate to a given eigenvalue. These are given in Table V for the four modes which involve Co–M stretching, where $C_{ij}k_i$ is the contribution from k_i to the eigenvalue, λ_j for the jth normal mode. This convenient formulation is a consequence of using the vibrational analysis equations of Edgell[25] and the program of Yantis.[25] In that formalism $\Lambda = \mathbf{Ck}$, where Λ is a column array of eigenvalues, $\mathbf{k}$ is a column matrix of force constants, and $\mathbf{C}$ is related to the similarity and coordinate transformation matrices. This is similar in content to the Wilson, et al.,[26] equations.

It can be seen from Table V that only for Cl₃SnCo-(CO)₄ is the Co–M stretching motion localized, to any significant extent, in one normal mode. For Cl₃SiCo-(CO)₄ the Co–Si stretching motion is mixed with Si–Cl stretching and SiCl₃ deformation motions in the three A₁ vibrational modes at 549, 309, and 179 cm^{-1}, while for Cl₃GeCo(CO)₄ the Co–Ge stretching motion only mixes significantly with the GeCl₃ deformation to contribute to vibrational modes at 240 and 160 cm^{-1}. In general, each row in Table V would have an entry for each force field element; however, only important contributions to λ have been included. Thus, the discrepancy between λ and the series of the entries in the appropriate row of Table V is due primarily to interaction constant contributions. The observed decrease in the mixing of Co–M stretching with M–Cl

(24) W. F. Edgell and coworkers, Purdue University, private communication.

(25) W. F. Edgell and R. L. Yantis, to be submitted for publication; see also R. L. Yantis, M.S. Thesis, Purdue University, 1964.

(26) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, eq 5, Appendix VIII.

stretching on going from M = Si to M = Sn is, of course, consistent with increasing difference in the reduced masses of the Co–M and M–Cl pairs of atoms.

Table VI lists the values of k_{Co-M} obtained in this study and those obtained using the two approximate models most commonly employed in the literature[27,28] to determine metal–metal stretching force constants. Both of the models employ simple pseudodiatomic approximations. The first uses only the masses of the metal atoms as the pseudodiatoms[27] while the second model assumes that the entire masses of the halves of the molecule form the diatomic unit.[28] The vibrational eigenvectors obtained in this study indicate that these approximate model calculations, based upon the assignment of one observed vibrational band as *the* metal–metal stretching vibration, cannot possibly be accurate for either $Cl_3SiCo(CO)_4$ or $Cl_3GeCo(CO)_4$. The fact that Co–Sn stretching motion makes a large contribution to only one vibrational mode would predict that calculations which use approximate models might provide more reliable values for k_{Co-Sn} than for either k_{Co-Ge} or k_{Co-Si}; however, the values listed in Table V indicate that, although the normal-mode eigenvectors obtained as solutions to normal-coordinate analyses for the three molecules do show the expected increase in the separation of Co–M stretching motion from other motions as the mass of M increases, the amount of mixing, even when M is the relatively heavy tin atom, makes these approximate methods unreliable for metal–metal bonded molecules with ligands as heavy as chlorine. Of the two models used in Table VI, that one which uses only the masses of the metal atoms results in estimates of k_{Co-M} which are approximately the correct magnitude though the ordering of the magnitudes of the k_{Co-M} values in the three molecules is incorrect, while the model which assumes the "ν_{Co-M}" to arise from the halves of the molecule vibrating as a psuedodiatom predicts neither the ordering of k_{Co-M} values nor their approximate

(27) (a) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 1328 (1965); (b) C. O. Quicksall and T. G. Spiro, *Chem. Commun.*, 839 (1967).
(28) (a) D. Hartley, P. A. Kilty, and M. J. Ware, *ibid.*, 493 (1968); (b) H. M. Gager, J. Lewis, and M. J. Ware, *ibid.*, 616 (1966).

TABLE VI

APPROXIMATE "k_{Co-M}" VALUES FROM SEVERAL MODELS AND COMPARISON WITH "k_{Co-M}" FROM THIS WORK[a]

Compound	Band used, cm^{-1}	Model I (pseudo-diatomic) [M]–[Co]	Model II (pseudodiatomic) [L$_3$M]–[Co(CO)$_4$] Normal-ized to k_{Co-Sn} = 1.23	This work (whole molecule)
$Cl_3SiCo(CO)_4$	309	1.07	4.21	2.18	1.3$_2$
$Cl_3GeCo(CO)_4$	240	1.11	2.96	1.53	1.0$_5$
$Cl_3SnCo(CO)_4$	204	0.97	2.38	(1.23)	1.2$_3$

[a] k is expressed in millidynes per ångström.

magnitudes. Though neither approximate model is very reliable for molecules of this type, the first is at least able to predict the approximate magnitudes of k_{Co-M}. These results are supported by other very recent studies.[4,29]

One objective of complete vibrational analyses of metal–metal bonded carbonyls is to test assumptions concerning the value of the 5-μ spectra as a probe of metal–metal bond strengths in a closely related series of molecules. Clearly the nearly identical 5-μ spectra of these three molecules are not diagnostic of changes in Co–M bond strengths of the magnitude observed in this study. Studies are under way in this laboratory to determine what values of k_{Co-M} may result from replacing the chlorine atoms with other ligands.

The visible and ultraviolet spectra of each of the three molecules have been recorded in cyclohexane solution. In each there is a strong band in the near-ultraviolet region, with λ_{max} 2700, 2610, and 2350 Å for $Cl_3SnCo(CO)_4$, $Cl_3GeCo(CO)_4$, and $Cl_3SiCo(CO)_4$, respectively. These bands have high extinction coefficients and have significant absorption in the violet end of the visible region at even moderate concentrations.

(29) D. Hartley and M. J. Ware, *Chem. Commun.*, 912 (1967).