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VIBRATIONAL ASSIGNMENT OF SOME $X_3MCo(CO)_4$ MOLECULES ($M = Si$, Ge, Sn AND $X = Cl$, Br, I)

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SUMMARY

The infrared and Raman vibrational spectra of $X_3MCo(CO)_4$ compounds ($M = Si$, Ge, Sn and $X = Cl$, Br, I) including depolarization measurements are presented. These spectra result in complete vibrational assignments which are different from those reported previously.

INTRODUCTION

In the last few years several papers have been published dealing with the subject of metal–metal bonding in tetracarbonylcobalt derivatives[1–16], but the discussions therein do not provide a definite solution to the problem of vibrational assignments. Earlier investigations dealt with the possible relationship between frequency shifts in the carbonyl stretching region and the bond character of the metal–metal bond. With one exception force-field calculations have been limited to the carbonyl stretching frequencies[1–4], and valence force-field calculations on the series $X_3MCo(CO)_4$ ($M = Si$, Ge, Sn and $X = Cl$, Br, I) have been performed by Watters *et al.*[12,13]. The purpose of the work described here was to obtain more information about the bond character for this series of complexes. A new vibrational assignment in terms of internal valence symmetry coordinates, which is in particular based upon extended Raman data, is proposed. The interpretation of the vibrational spectra has been assisted by calculations based upon the units X_3M– and $-Co(CO)_4$ and other related molecules[17–21]. The explanation of all observed bands in the solid will be the subject of a further single crystal study including site-symmetry and factor-group splitting. However, the knowledge of the complete structure in the solids is an absolute necessity for this study. Valence force-field calculations based upon the new assignment will also be presented in a forthcoming paper, together with an interpretation of the bond parameters.

EXPERIMENTAL

The complexes were prepared by published procedures[14–16]. All compounds were handled in a nitrogen atmosphere and purified by vacuum sublimation or by recrystallization from pentane. Infrared spectra were recorded on Beckman IR-11 and IR-12 spectrophotometers at room and liquid nitrogen temperatures using several techniques. In the region 2200–200 cm^{-1} CsI-windows were used, while in the frequency region below 250 cm^{-1} powdered polyethylene pressed disks and highly concentrated cyclohexane solutions between polyethylene windows gave the best results. Both spectrometers were calibrated using the IUPAC wave-number tables[22]. Raman spectra were recorded on a Coderg PH1 spectrometer with a CRL 53 mixed gas (Ar/Kr) laser, using 6471 Å as the exciting line. The solids were studied at room and liquid nitrogen temperatures. From solution spectra depolarization values were obtained. The reproducibility of the peak positions was ± 1 cm^{-1} in the Raman spectra.

RESULTS AND DISCUSSION

The Raman spectra of the solids Cl_3Si–, Cl_3Ge–, Cl_3Sn–, I_3Ge– and I_3Sn–$Co(CO)_4$, not reported previously in the literature, proved to be of excellent quality, although complicated by site-symmetry and factor-group splitting (especially in the CO-stretching region) and by lattice vibrations in the low frequency region.

The Raman spectra of the solids at liquid nitrogen temperature are reproduced in Fig. 1–7 from 0–650 cm^{-1} for all compounds. No decomposition could be detected when the samples were exposed to the intense laser source (up to 1000 mW) during the measurements in the solid state, even at room temperature.

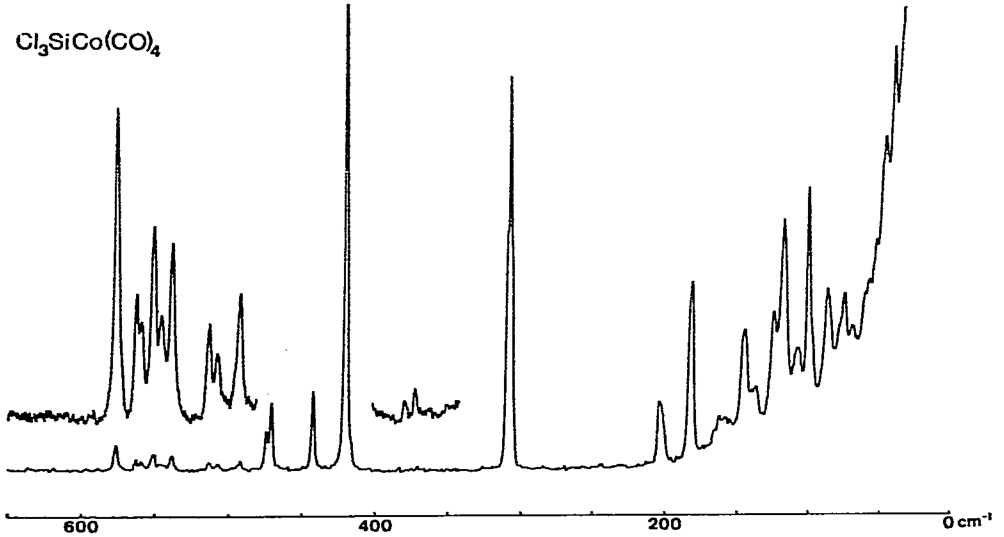

Fig. 1. Raman spectrum at $-160°$ of $Cl_3SiCo(CO)_4$.

The infrared and Raman data are given in Tables 1–7, together with the assignment of the vibrational modes.

The frequency shifts of almost all bands for the various spectra of each molecule proved to be proportionally small.

In order to elucidate the site-symmetry and factor-group splitting, crystallographic determination of the structures is in progress.

TABLE 1

VIBRATIONAL FREQUENCIES (CM^{-1}) AND ASSIGNMENTS FOR $Cl_3SiCo(CO)_4$

Infrared		*Raman*		*Assignment*
Solution[a]	*Solid* (−160°)	*Solution*[b]	*Solid* (−160°)	
2117 s	2120 s	2122 m, p	2127 m	A_1 ν(CO)
			2081 s	
2063 s	2064 s	2067 m, p	2072 m	A_1 ν(CO)
2040 vs	2039 vs	2039 m, dp	2039 m	E ν(CO)
			2030 m	
			2023 m	
2000 vw	2002 w		2008 vw	$\nu(^{13}CO)$
612 w				Impurity
569 vs	575 vs	575 w, dp	577 mw	E ν(SiCl)
			563 w	
			560 w	E $\delta(CoCO)_{out}$
550 s	551 s	551 w, p	552 w	A_1 $\delta(CoCO)_{out}$
			547 w	
			540 w	
			513 w	
506 s	506 s	506 w, p	507 w	A_1 ν(SiCl)
483 vw	483 vw		492 w	E $\delta(CoCO)_{ax}+\nu(CoC)_{eq}$
			473 m	
471 vw	473 w	474 m, dp	470 m	E $\nu(CoC)_{eq}+\delta(CoCO)_{ax}$
441 vw	441 vw	438 m, p	442 m	A_1 $\nu(CoC)_{ax}$
	414 w	413 s, p	420 vs	A_1 $\nu(CoC)_{eq}$
			379 vw	
372 w	376 vw		372 vw	E $\delta(CoCO)_{in}$
307 w	308 w	307 s, p	308 s	A_1 ν(SiCo)
202 w	202 w	202 w, dp	203 w	E $\delta(SiCl_3)$
182 m	180 s	181 m, p	182 m	A_1 $\delta(SiCl_3)$
			159 w	Impurity
			144 w	
138 m	137 w	139 w, dp	137 vw	E δ(ClSiCo)
			124 m	
			117 m	E δ(CCoC)
112 w			108 w	E δ(CCoC)
100 w		103 m	100 m	
			86 m	A_1 δ(CCoC)
			74 w	
			69 w	
			59 w	E δ(SiCoC)
			46 vw	
			40 vw	

[a] Infrared solutions in cyclohexane or benzene. [b] Raman solutions in CCl_4 or benzene, p=polarized dp=depolarized.

Vibrational assignment

The molecules $Cl_3SiCo(CO)_4$, $F_3SiCo(CO)_4$ and $H_3SiCo(CO)_4$ possess C_{3v} symmetry as shown by X-ray and electron diffraction studies[23–25]. Since the vibrational spectra of all molecules of our series are in close agreement with those of the former three, a C_{3v} trigonal bipyramidal configuration is assumed for the tetracarbonyl

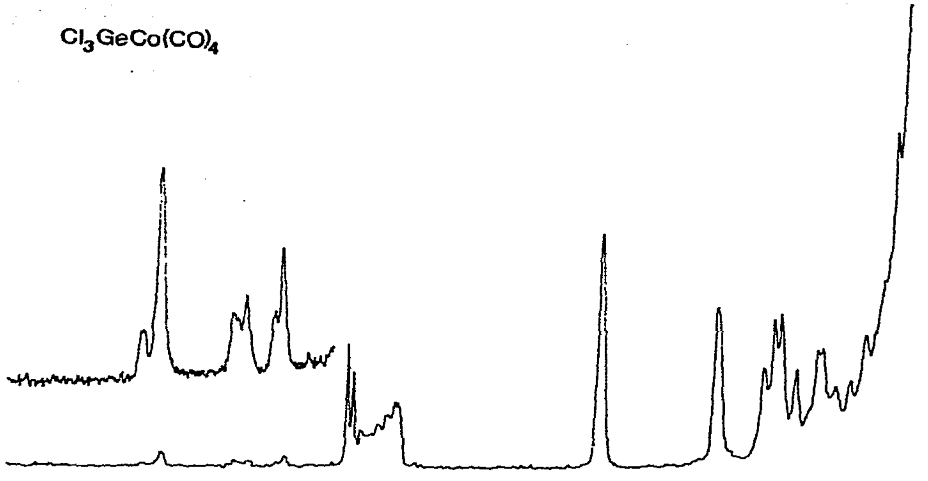

Fig. 2. Raman spectrum at −160° of $Cl_3GeCo(CO)_4$.

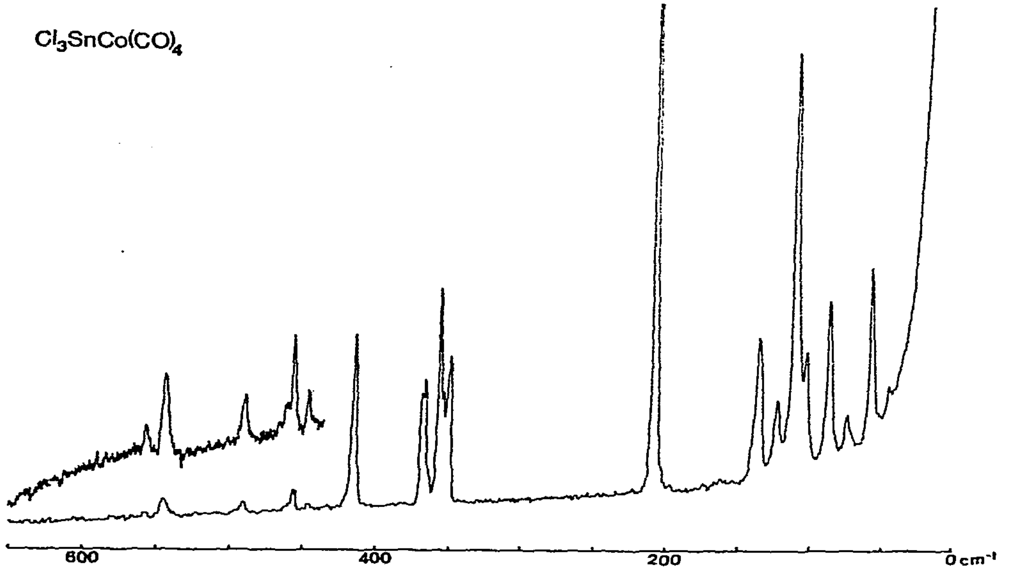

Fig. 3. Raman spectrum at −160° of $Cl_3SnCo(CO)_4$.

cobalt complexes herein.

In this case the vibrational representation is:

$$\Gamma_{vib} = 9\,A_1 + 2\,A_2 + 11\,E$$

A_1 = infrared active, Raman allowed, polarized
A_2 = inactive
E = infrared active, Raman allowed, depolarized

Table 8 enumerates the irreducible representations of each vibrational mode in terms

TABLE 2

VIBRATIONAL FREQUENCIES (CM^{-1}) AND ASSIGNMENTS FOR $Cl_3GeCo(CO)_4$

Infrared		*Raman*		*Assignment*
Solution	*Solid* (−160°)	*Solution*	*Solid* (−160°)	
	2142 w		2141 m	
	2136 w		2135 s	
2123 s	2124 m	2126 m, p	2122 vw	A_1 ν(CO)
			2091 m	
	2088 vw		2088 s	
	2083 vw		2082 s	
2070 s	2072 m	2072 m, p	2068 w	A_1 ν(CO)
			2063 m	
2052 vs	2050 s	2053 m, dp	2056 m	E ν(CO)
			2052 m	
	2038 w		2038 s	
2034 (sh)			2035 m	
2013 w	2011 w		2008 w	$\nu(^{13}CO)$
	554 vs		560 w	E $\delta(CoCO)_{out}$
549 vs	547 vs	547 w, p	548 m	A_1 $\delta(CoCO)_{out}$
	496 m		497 w	
487 m	487 m		490 w	E $\delta(CoCO)_{ax}+\nu(CoC)_{eq}$
463 s	464 s		467 w	E $\nu(CoC)_{eq}+\delta(CoCO)_{ax}$
			461 w	
	442 (sh)		444 vw	A_1 $\nu(CoC)_{ax}$
			418 s	
			415 s	A_1 $\nu(CoC)_{eq}$
405 s	409 m	410 m, p	409 m	E ν(GeCl)
			404 m	
	399 s		398 m	
390 s	392 s	390 s, p	392 m	A_1 ν(GeCl)
	385 (sh)		387 m	
370 vw	372 m		373 vw	E $\delta(CoCO)_{in}$
	368 m			
243 m	242 m	241 vs, p	244 vs	A_1 ν(GeCo)
162 m	163 m	161 s, p	163 s	A_1+E $\delta(GeCl_3)$
	131 w		131 m	
124 m		123 w	123 m	E δ(CCoC)
			119 m	
112 m	109 w	104 m	109 m	E δ(CCoC)
89 w	91 (sh)		91 m	E δ(ClGeCo)
	81 w		80 w	A_1 δ(CCoC)
			70 w	
	58 vw		59 w	E δ(GeCoC)
			46 vw	
			39 vw	

of internal coordinates. The vibrational assignment will be discussed for several specific regions.

CO stretching region

The 2200–1900 cm^{-1} region for this type of molecule has been the subject of

TABLE 3

VIBRATIONAL FREQUENCIES (CM^{-1}) AND ASSIGNMENTS FOR $Cl_3SnCo(CO)_4$

Infrared		*Raman*		*Assignment*
Solution	*Solid* (−160°)	*Solution*	*Solid* (−160°)	
			2146 w	
	2132 m		2133 w	
2122 s	2123 w		2127 m	A_1 ν(CO)
2069 s	2075 m		2078 s	A_1 ν(CO)
			2062 w	
	2052 s			
2049 vs	2041 s		2033 s	E ν(CO)
2010 w			2005 vw	$\nu(^{13}CO)$
			558 vw	E $\delta(CoCO)_{out}$
549 vs	549 vs		545 w	A_1 $\delta(CoCO)_{out}$
487 m	489 m		491 w	E $\delta(CoCO)_{ax}+\nu(CoC)_{eq}$
			462 (sh)	
458 s	459 s		458 w	E $\nu(CoC)_{eq}+\delta(CoCO)_{ax}$
			447 vw	A_1 $\nu(CoC)_{ax}$
	416 w		416 s	A_1 $\nu(CoC)_{eq}$
			370 m	E $\delta(CoCO)_{in}$
363 s	360 s	362 s	368 m	E ν(SnCl)
			358 s	
			356 w	
	352 s		352 m	A_1 ν(SnCl)
204 m	206 m	206 s, p	210 vs	A_1 ν(SnCo)
135 m	134 s		138 m	E $\delta(SnCl_3)$
126 (sh)	122 w		125 m	E δ(CCoC)
			112 s	A_1 $\delta(SnCl_3)$
108 m	105 w		105 m	E δ(CCoC)
			88 m	E δ(ClSnCo)
			75 w	A_1 δ(CCoC)
			59 m	E δ(SnCoC)
			42 w	

numerous papers[1-5,14,15]. In agreement with the assignment of Bor[4], for $H_3CCo(CO)_4$, the A_1 stretching mode for CO with the highest frequency is believed to be the in-phase combination of the equatorial and axial CO bonds for the whole series, whilst the next highest is the out-of-phase combination. This is the only possible combination of the two symmetry coordinates which will account for the observed unexpected high intensity of the former CO stretching mode in all the infrared spectra and, additionally, for the abnormal depolarization ratio found in the Raman spectra of solutions of Cl_3Si–, Cl_3Ge– and Br_3Ge–$Co(CO)_4$. Notably, the observed depolarization ratio for ν_1 and ν_2 is ρ 0 and ρ 0.65 respectively.

The ratio of participation of both symmetry coordinates in these vibrations will be the subject of a normal coordinate analysis (in progress). The third strong band in this region is the degenerate equatorial CO stretching mode which has a high infrared intensity and is depolarized in the Raman spectrum. A very weak band at ca. 2005 cm^{-1} is found in all the infrared spectra. This band can be assigned to an equatorial ^{13}CO stretching mode. The frequency shift of ca. 40 cm^{-1} is consistent with

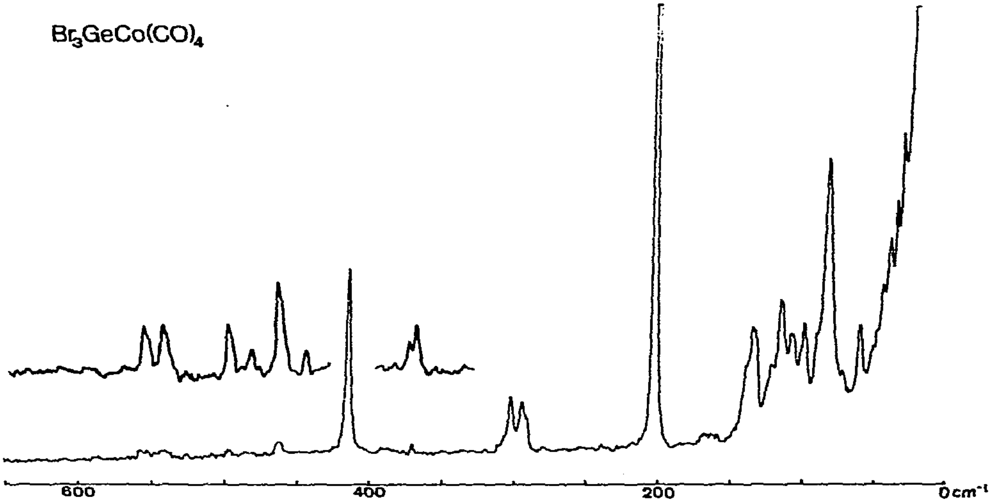

Fig. 4. Raman spectrum at −160° of $Br_3GeCo(CO)_4$.

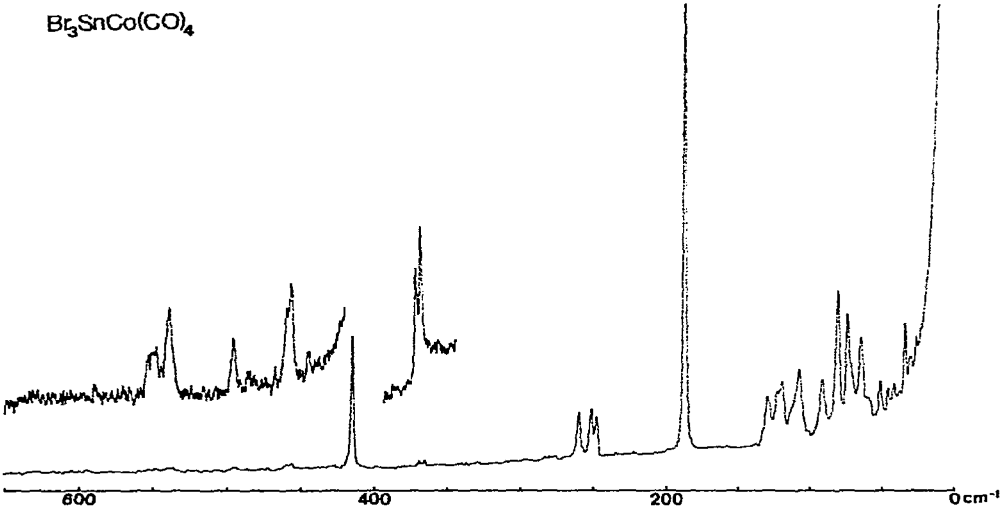

Fig. 5. Raman spectrum at −160° of $Br_3SnCo(CO)_4$.

frequency calculations from the mass ratio and with the shifts found for the metal carbonyls which never exceed 45 cm^{-1} [26,27].

The 650–350 *cm*$^{-1}$ *region*

In this region mainly a fixed pattern of bands throughout the whole series is expected due to the $-Co(CO)_4$ moiety of the molecule. The three Co–C stretching and four Co–C–O deformation modes (the only vibrations usually found in this region) must be assigned to 3 A_1 and 4 E symmetry species. For the chloro derivatives one more A_1 and E vibration due to the M–Cl stretching mode has been observed. There

TABLE 4

VIBRATIONAL FREQUENCIES (CM^{-1}) AND ASSIGNMENTS FOR $Br_3GeCo(CO)_4$

Infrared		*Raman*		*Assignment*
Solution	*Solid* (−160°)	*Solution*	*Solid* (−160°)	
			2127 m	
2119 s	2122 s	2123 m, p	2122 vw	A_1 $\nu(\mathrm{CO})$
	2083 w		2083 s	
	2077 w	2075 m, p	2076 m	
2067 s	2068 m		2065 vw	A_1 $\nu(\mathrm{CO})$
2050 vs	2047 vs	2049 m, dp	2052 s	E $\nu(\mathrm{CO})$
			2045 vw	
			2039 m	
	2030 w		2030 s	
2011 w				$\nu(^{13}\mathrm{CO})$
547 s	549 vs		554 w	E $\delta(\mathrm{CoCO})_{\mathrm{ont}}$
	539 (sh)	543 w, p	540 w	A_1 $\delta(\mathrm{CoCO})_{\mathrm{out}}$
	495 w		495 w	
484 w	481 w		481 vw	E $\delta(\mathrm{CoCO})_{\mathrm{ax}}+\nu(\mathrm{CoC})_{\mathrm{eq}}$
460 m	459 s		460 w	E $\nu(\mathrm{CoC})_{\mathrm{eq}}+\delta(\mathrm{CoCO})_{\mathrm{ax}}$
	440 (sh)		443 w	A_1 $\nu(\mathrm{CoC})_{\mathrm{ax}}$
	410 w	407 s, p	412 s	A_1 $\nu(\mathrm{CoC})_{\mathrm{eq}}$
	372 w		371 w	
	366 w		367 w	E $\delta(\mathrm{CoCO})_{\mathrm{in}}$
302 m	304 m		300 m	E $\nu(\mathrm{GeBr})$
293 s	292 s	294 w	291 m	A_1 $\nu(\mathrm{GeBr})$
		199 s, p	200 vs	A_1 $\nu(\mathrm{GeCo})$
			164 w	Impurity
130 m	128 w		131 m	E $\delta(\mathrm{CCoC})$
			119 w	
			111 m	E $\delta(\mathrm{CCoC})$
			104 w	
97 m	98 m		96 w	E $\delta(\mathrm{GeBr_3})$
	83 w		80 s	A_1 $\delta(\mathrm{GeBr_3})$
	65 w		69 w	A_1 $\delta(\mathrm{CCoC})$
			57 w	E $\delta(\mathrm{GeCoC})$
	47 w		41 w	E $\delta(\mathrm{BrGeCo})$
			36 w	
			32 w	
			28 w	

has been much discussion in several articles dealing with the middle frequency region for these or for related molecules concerning a definite vibrational assignment[5-13].

A positive contribution to this discussion can now be made, since our Raman spectra yield much more information. Raman depolarization measurements result in the following statements:

(*i*). For $Cl_3SiCo(CO)_4$ the bands at 551, 506, 438 and 413 cm^{-1} are polarized (A_1 species), the other bands in this region are of E symmetry under which the 474 cm^{-1} band is undoubtedly depolarized (in contrast to Watters[12,13] assignment).

(*ii*). The spectra of the $Cl_3GeCo(CO)_4$ show 3 of the 4 A_1 bands in this region at 547, 410 and 390 cm^{-1}.

TABLE 5

VIBRATIONAL FREQUENCIES (CM^{-1}) AND ASSIGNMENTS FOR $Br_3SnCo(CO)_4$

Infrared		*Raman*		*Assignment*
Solution	*Solid* (−160°)	*Solution*	*Solid* (−160°)	
2117 s	2118 s		2123 m	A_1 ν(CO)
	2081 m		2078 s	
	2074 m		2073 m	
2065 s	2067 m			A_1 ν(CO)
	2059 w		2059 w	
2045 vs	2043 s		2048 s	E ν(CO)
			2036 m	
	2025 w		2029 s	
2006 w				ν(^{13}CO)
			552 w	E δ(CoCO)$_{out}$
546 s	545 s		542 w	A_1 δ(CoCO)$_{out}$
	496 w		496 w	
487 w	486 w			E δ(CoCO)$_{ax}$ + ν(CoC)$_{eq}$
460 m	459 m		461 w	E ν(CoC)$_{eq}$ + δ(CoCO)$_{ax}$
			459 w	
	443 (sh)		445 vw	A_1 ν(CoC)$_{ax}$
407 vw	413 w		413 m	A_1 ν(CoC)$_{eq}$
			370 w	
362 w	366 w		367 w	E δ(CoCO)$_{in}$
256 m	262 m		259 m	E ν(SnBr)
249 m	252 s	252 w	252 m	A_1 ν(SnBr)
			249 m	
		185 s, p	187 s	A_1 ν(SnCo)
130 m			128 m	E δ(CCoC)
			120 m	
114 w	117 w		107 m	E δ(CCoC)
86 s	88 s		91 m	E δ($SnBr_3$)
			80 m	A_1 δ($SnBr_3$)
	73 vw		74 m	A_1 δ(CCoC)
	62 vw		65 m	
			52 w	E δ(SnCoC)
			47 w	E δ(BrSnCo)
			43 w	
			36 m	
			32 w	
			29 w	

(*iii*). $Br_3GeCo(CO)_4$ shows only two polarized bands at 543 and 407 cm^{-1}.

(*iv*). Solutions of the other molecules of the series proved to be too unstable in the laser beam to permit reliable depolarization measurements.

At this stage it is relatively easy to solve the assignment problem *viz.* 3 A_1 and 4 E bands, for the $Co(CO)_4$ moiety fixed throughout the series of molecules and 1 A_1 and 1 E band for the M–Cl stretching modes, as summarized in Table 9.

For the chlorosilyl derivative, the 506 cm^{-1} band has a strong infrared counterpart not observed in any of the other molecules. Therefore, this band must be assigned to the Si–Cl stretching vibration although the Raman intensity is remarkably low.

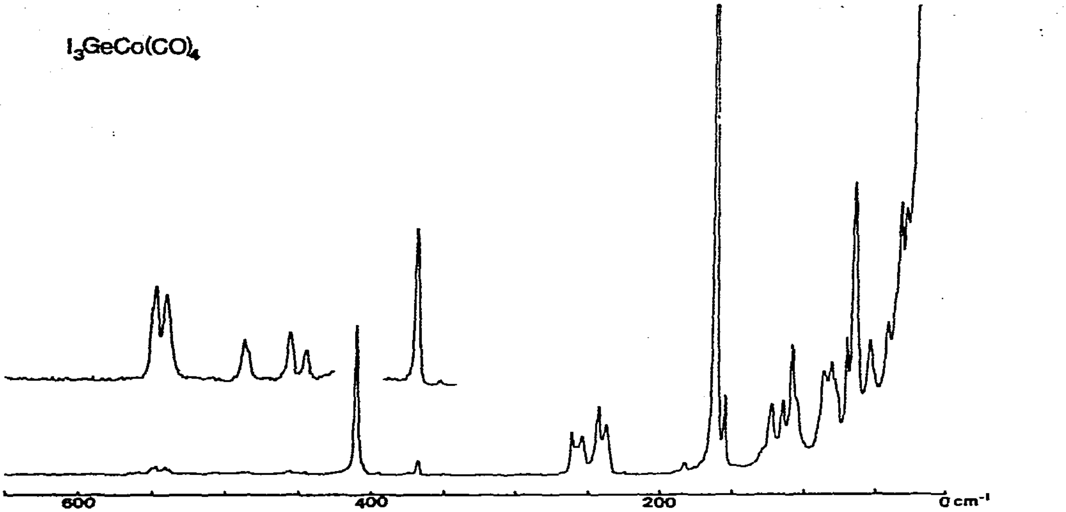

Fig. 6. Raman spectrum at −160° of $I_3GeCo(CO)_4$.

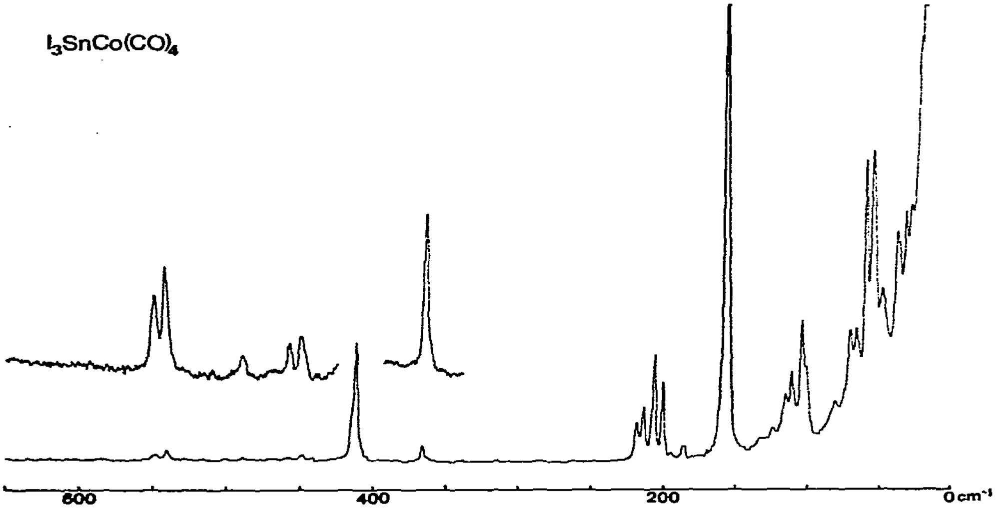

Fig. 7. Raman spectrum at −160° of $I_3SnCo(CO)_4$.

For the Cl_3Ge analogue the assignment of the 390 cm^{-1} band to the Ge–Cl stretching mode seems reliable and is in close agreement with values for other $GeCl_3X$ molecules[17–19].

From the remaining bands in this region, having *E* symmetry, four possess a fixed frequency in each molecule whereas for the chloro-compounds, one band varies.

One of the four fixed bands (at 370 cm^{-1}), previously assigned to a difference band[13], proved to be one of the fundamentals since the intensity did not decrease on lowering the temperature. The mutual assignment in the A_1 and *E* block is presented on the basis of the following arguments.

TABLE 6

VIBRATIONAL FREQUENCIES (CM^{-1}) AND ASSIGNMENTS FOR $I_3GeCo(CO)_4$

Infrared		*Raman*		*Assignment*
Solution	*Solid* (−160°)	*Solution*	*Solid* (−160°)	
2113 s	2117 s		2117 m	$A_1\ \nu(\mathrm{CO})$
	2072 w		2067 m	
2062 m	2063 m			$A_1\ \nu(\mathrm{CO})$
2043 s	2043 s		2040 m	$E\ \nu(\mathrm{CO})$
			2035 m	
2005 w				$\nu(^{13}\mathrm{CO})$
	549 s		550 w	$E\ \delta(\mathrm{CoCO})_{\mathrm{out}}$
543 s	543 s		543 w	$A_1\ \delta(\mathrm{CoCO})_{\mathrm{out}}$
486 w	488 w		487 vw	$E\ \delta(\mathrm{CoCO})_{\mathrm{ax}}+\nu(\mathrm{CoC})_{\mathrm{eq}}$
458 m	458 s		456 vw	$E\ \nu(\mathrm{CoC})_{\mathrm{eq}}+\delta(\mathrm{CoCO})_{\mathrm{ax}}$
	447 (sh)		444 vw	$A_1\ \nu(\mathrm{CoC})_{\mathrm{ax}}$
	411 w		411 s	$A_1\ \nu(\mathrm{CoC})_{\mathrm{eq}}$
	407 w			
	368 w		368 w	$E\ \delta(\mathrm{CoCO})_{\mathrm{in}}$
	257 s		262 m	
250 s	248 s		256 m	$E\ \nu(\mathrm{GeI})$
	241 s		244 m	$A_1\ \nu(\mathrm{GeI})$
			239 m	
			183 w	Impurity
	160 vw		162 vs	$A_1\ \nu(\mathrm{GeCo})$
			155 m	
130 w	130 w		122 m	$E\ \delta(\mathrm{CCoC})$
112 w	115 w		114 m	$E\ \delta(\mathrm{CCoC})$
			108 s	
82 m	82 m		85 m	$E\ \delta(\mathrm{GeI_3})$
			80 m	
			70 m	$A_1\ \delta(\mathrm{CCoC})$
63 vw	63 w		65 s	$A_1\ \delta(\mathrm{GeI_3})$
			55 m	$E\ \delta(\mathrm{GeCoC})$
			43 m	$E\ \delta(\mathrm{IGeCo})$
			35 m	
			31 w	

A_1 block. On the basis of theoretical arguments one expects that the equatorial Co–C stretching mode will be strong in the Raman and of almost zero intensity in the infrared spectrum. The band at ±410 cm^{-1} fulfils these requirements. In this case the band at ±440 cm^{-1} with nearly the same frequency should be assigned to the axial Co–C stretching mode. The spectra do not allow for an interpretation in terms of mixing in-phase and out-of-phase modes as for the CO-stretching region. This will be confirmed by force-field calculations. In that case the 550 cm^{-1} band remains for the symmetric Co–C–O eq deformation in agreement with assignment in related molecules[7,28].

E block. Noteworthy in the Raman spectra of the solids is a band-system which appears at ca. 550 cm^{-1} consisting of two components of which the weaker is located at higher frequency. Since the lower component is assigned to the A_1 bending mode,

TABLE 7

VIBRATIONAL FREQUENCIES (CM^{-1}) AND ASSIGNMENTS FOR $I_3SnCO(CO)_4$

Infrared		*Raman*		*Assignment*
Solution	*Solid* (−160°)	*Solution*	*Solid* (−160°)	
2111 s	2111 s		2114 m	A_1 ν(CO)
2059 m	1060 m		2061 s	A_1 ν(CO)
2037 s	2037 s		2032 m	E ν(CO)
	2033 s		2029 m	
	548 s		549 w	E $\delta(CoCO)_{out}$
543 s	542 s		541 w	A_1 $\delta(CoCO)_{out}$
	537 (sh)			
487 w	489 m		489 vw	E $\delta(CoCO)_{ax}+\nu(CoC)_{eq}$
460 m	458 m		458 vw	E $\nu(CoC)_{eq}+\delta(CoCO)_{ax}$
	450 (sh)		449 vw	A_1 $\nu(CoC)_{ax}$
407 w	410 w		414 s	A_1 $\nu(CoC)_{eq}$
363 w	366 w		367 w	E $\delta(CoCO)_{in}$
220 (sh)			219 m	E ν(SnI)
	212 m		214 m	
207 m	207 m		207 m	A_1 ν(SnI)
	201 m		201 m	
			183 w	Impurity
158 vw	157 w		158 vs	A_1 ν(SnCo)
130 w			125 w	E δ(CCoC)
114 vw			116 m	
			111 m	
105 vw			105 s	E δ(CCoC)
	100 w		101 m	
			82 w	A_1 δ(CCoC)
			71 m	
63 m	63 m		67 m	E $\delta(SnI_3)$
			60 s	
58 w			56 s	A_1 $\delta(SnI_3)$
			50 m	E δ(SnCoC)
			39 m	E δ(ISnCo)
			34 w	
			30 w	

a plausible explanation would be that the higher component, with lower Raman intensity, is assigned to the same internal coordinate with E type symmetry. An observation which supports this explanation is the very strong intensity in the infrared spectrum. Moreover, as substitution of the axial CO group by $P(Et)_3$ leaves this mode unchanged in related compounds[7], it must be an equatorial one. This argument is strengthened by results of force-field calculations for $Fe(CO)_5$[26] and our own calculations.

The next two bands at ±490 and ±460 cm^{-1} exhibit considerable mixing in the two internal symmetry coordinates, *viz.* the axial Co–C–O deformation and the equatorial Co–C stretch as is indicated in Table 9. Therefore a mutual assignment in terms of internal symmetry coordinates is doubtful. This leaves the remaining band at ±370 cm^{-1} as the equatorial in-plane Co–C–O deformation mode.

TABLE 8

SYMMETRY OF THE VIBRATIONAL MODES

ν(CO)	$2A_1+E$	ν(MX)	A_1+E
ν(CoC)	$2A_1+E$	ν(MM)	A_1
δ(CoCO)	A_1+A_2+3E	$\delta(MX_3)$	A_1+E
δ(CCoC)	A_1+2E	δ(XMCo)	E
Torsion	A_2	δ(MCoC)	E

TABLE 9

VIBRATIONAL ASSIGNMENT IN THE 600–350 CM^{-1} REGION

		Cl_3Si–	Cl_3Ge–	Cl_3Sn–	Br_3Ge–	Br_3Sn–	I_3Ge–	I_3Sn–
$\delta(CoCO)_{out}$	A_1	551 p	547 p	545	543 p	542	543	540
$\nu(CoC)_{ax}$	A_1	438 p	440	447	440	444	444	450
$\nu(CoC)_{eq}$	A_1	413 p	410 p	415	407 p	412	410	412
$\delta(CoCO)_{out}$	E	560	558	558	549	545	550	548
$\delta(CoCO)_{ax}+\nu(CoC)_{eq}$	E	490	490	490	490	491	488	490
$\nu(CoC)_{eq}+\delta(CoCO)_{ax}$	E	474 dp	465	458	458	460	458	458
$\delta(CoCO)_{in}$	E	375	373	368	370	368	368	367
ν(MCl)	A_1	506 p	390 p	353				
ν(MCl)	E	575 dp	405	365				

TABLE 10

ASSIGNMENT OF MX, MCo AND MX_3 VIBRATIONS

		Cl_3Si–	Cl_3Ge–	Cl_3Sn–	Br_3Ge–	Br_3Sn–	I_3Ge–	I_3Sn–
ν(MX)	A_1	506	390	353	293	249	242	204
ν(MX)	E	575	405	365	302	256	248	213
ν(MCo)	A_1	307	242	205	199	185	161	157
$\delta(MX_3)$	A_1	181	162	112	80	76	65	58
$\delta(MX_3)$	E	203	162	138	96	91	82	69

The MX, MCo and MX_3-vibrations

The assignment of the M–X stretching modes is straightforward. All the values given in Table 10 are in good agreement with those observed for related MX_3Z molecules[17,19]. The degenerate stretching vibration is always higher in frequency than the symmetric one for such molecules.

The M–Co stretching modes have a very high intensity in the Raman spectrum, giving no problems of assignment. Even in this case, the assignment of internal symmetry coordinates is rather arbitrary since a considerable amount of mixing occurs, for the chloro-derivatives with the symmetric MX_3 deformations and for the bromides and iodides with the symmetric M–X stretching mode. Except for $Cl_3SiCo(CO)_4$ and $Cl_3GeCo(CO)_4$ the two MX_3 deformations belong to the frequency region below 150 cm^{-1}. Depolarization measurements for $Cl_3SiCo(CO)_4$ lead to the conclusion that 181 cm^{-1} is the A_1 and 203 cm^{-1} is the E-vibration. However, following the same scheme for $Cl_3GeCo(CO)_4$, the Raman spectrum shows only one band with ρ 0.3. This observation necessitates both A_1 and E modes having the same frequency.

From a comparison of the frequencies in the Raman spectra of the solids and on the basis of Raman intensity arguments (see Fig. 1–7) (*i.e.* A bands have greater intensity than E bands) the assignment of the bands in the spectra of the heavier molecules became possible, as is shown in Table 10.

The low frequency region

The remaining unassigned fundamentals are δ(C–Co–C) ($2A_1+E$), δ(M–Co–C) (E) and δ(X–M–Co) (E). All these vibrations occur between 0 and 150 cm^{-1}. This region is complicated by lattice vibrations. Examination of the observed values reveals only two frequencies in all molecules. Their mean values are ± 126 cm^{-1} and ± 111 cm^{-1}. These bands do show site-symmetry splitting. Force-field calculations make it clear that the degenerate C–Co–C deformations have no influence of the MX_3 part of the molecule. This fact and the observed site-symmetry splitting are good reasons for assigning the 126 and 111 cm^{-1} bands to the E fundamentals of this coordinate.

The symmetric δ(C–Co–C) couples with the A_1 $\delta(MX_3)$ when X=Br or I. The δ(X–M–Co) and δ(M–Co–C) will vary with M and X. Therefore, only a tentative assignment can be made for the last three vibrations, assisted by our frequency calculations.

CONCLUSION

On the basis of our Raman and infrared spectra under various conditions, together with the observed depolarization values, we are able to make a new vibrational assignment for the molecules of the series $X_3MCo(CO)_4$.

The corresponding results for X_3MZ and $YCo(CO)_4$, which give more detailed information, proved to be very useful for the interpretation of the spectra and for the first approximate calculation of force-field calculations (in progress).

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