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VIBRATIONAL ASSIGNMENTS FOR SOME $X_3MCo(CO)_4$ MOLECULES

II*. M = C, Ge, AND X = H, D, F

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Summary

The infrared and Raman vibrational spectra of $X_3MCo(CO)_4$ compounds (M = C, Ge and X = H, D, F), including depolarization measurements, are presented, and complete vibrational assignments are made.

Introduction

In an earlier paper [1] complete vibrational assignments for some $X_3MCo(CO)_4$ molecules were described, and herein we report preparations and vibrational spectra of some other members of this series, viz. $H_3GeCo(CO)_4$, $D_3GeCo(CO)_4$, $F_3CCo(CO)_4$ and $F_3GeCo(CO)_4$. These were studied for the following reasons. Firstly, to obtain useful information on the character of the Group IV element —cobalt bond, by means of force-field calculations; this was the main purpose of our investigations, and can be achieved by a study of the complete series of $X_3MCo(CO)_4$ complexes. Secondly, the only published complete vibrational spectra or vibrational assignments were those for $H_3GeCo(CO)_4$ and $D_3GeCo(CO)_4$ [2]. Thirdly, in the frequency region below 150 cm^{-1} for the complexes studied previously [1], only a tentative assignment could be given, because strong mixing occurred between the MX_3 deformation and the C—Co—C deformation modes. In the case of our new complexes, the C—Co—C deformation modes are the only modes in the low frequency region, and thus it was expected that a definitive assignment could be made for the vibrations concerned.

Experimental

Synthesis

Starting materials were either commercially available or prepared by standard

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[*] For part I see ref. 1.

methods. All compounds were handled under argon. The salt $NaCo(CO)_4$ was prepared by the method of Edgell and Lyford [3].

The germylcobalt tetracarbonyl was obtained through reaction of germyl bromide with $NaCo(CO)_4$ in dimethyl ether [2]. Final distillations from a bath at 0° to a trap of —45° gave the pure colourless product. The instability of the complex towards light forced us to carry out all distillations in complete darkness. $D_3GeCo(CO)_4$ was prepared similarly.

Trifluoromethylcobalt tetracarbonyl was prepared by a method similar to that used for the methyl compound [4]. From trifluoroacetic anhydride and $NaCo(CO)_4$ the trifluoroacetyl complex is formed. At 60° this complex loses CO on pumping, to give the trifluoromethyl compound, m.p. $\approx$ 10°. It proved to be much more stable (even at room temperature in a powerful laser beam) than was expected.

According to Baay and MacDiarmid [5], trifluorogermylcobalt tetracarbonyl can be prepared by treating $(CH_3)_3SiCo(CO)_4$ with GeF_4, but no experimental details were given. In a heavy-walled glass tube (2.4 cm o.d. × 30 cm with a wall thickness of 2.5 mm and capacity of about 100 ml) 6.5 g freshly sublimed $(CH_3)_3SiCo(CO)_4$ was dissolved in 15 ml pentane. The tube was attached to a vacuum line, cooled to —120°, and evacuated. Into this tube was then condensed 12 ml GeF_4. The tube was sealed and, with explosion-proof protective shielding, permitted to warm slowly during 1-2 hours to room temperature. It was kept at room temperature for 24 hours, and then cooled to —70°, opened under argon, and attached to a vacuum line. Volatile compounds were pumped off at —50°, and the impure trifluorogermylcobalt tetracarbonyl was purified by several vacuum sublimations at room temperature. Sublimation of the compound resulted in little decomposition, and the final product was obtained as pale yellow crystals (3.5 g). The complex was kept at room temperature under argon with no apparent decomposition during 24 hours.

Spectra

Infrared spectra were recorded on Beckman I.R. 11 and I.R. 12 spectrophotometers. The instruments were calibrated with standard gases [6]. Gas phase infrared spectra were obtained, where possible, using cells with a path length of 30 cm. CsI windows were employed from 2200—200 cm^{-1} and polyethylene windows from 300—40 cm^{-1}.

Solutions for spectroscopic studies were prepared and handled under dry argon, and carefully dried and deoxygenated solvents were used. Raman spectra were recorded on a Coderg Ph 1 spectrometer with a C.R.L. 53 mixed gas (Ar/Kr) laser, using 6471 Å as the exciting line. The solids were studied at liquid nitrogen temperature, and from the liquid phase spectra depolarization values were obtained.

Vibrational assignments

Since the vibrational spectra of the molecules closely resemble those of our first series [1], a C_{3v} trigonal bipyramidal configuration is assumed for the tetracarbonylcobalt complexes herein. In this case the vibrational representation is

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

TABLE 1

SYMMETRY OF THE VIBRATIONAL MODES

$\nu(\mathrm{CO})$	$2A_1 + E$	$\nu(\mathrm{MX})$	$A_1 + E$
$\nu(\mathrm{CoC})$	$2A_1 + E$	$\nu(\mathrm{MM})$	A_1
$\delta(\mathrm{CoCO})$	$A_1 + A_2 + 3E$	$\delta(\mathrm{MX_3})$	$A_1 + E$
$\delta(\mathrm{CCoC})$	$A_1 + 2E$	$\delta(\mathrm{XMCo})$	E
Torsion	A_2	$\delta(\mathrm{MCoC})$	E

TABLE 2

VIBRATIONAL FREQUENCIES ($\mathrm{cm^{-1}}$) AND ASSIGNMENTS FOR $H_3GeCo(CO)_4$

Infrared			Raman		Assignment
Vapor	Liquid	Solid—100°	Liquid	Solid —160°	
2110s	2108m	2105m	2102m (P)	2102s	$A_1\,\nu(\mathrm{CO})$
		2086m		2086m	
					$E\,\nu(\mathrm{GeH})$
2074m	2072m				
2066m		2068m		2063m	$A_1\,\nu(\mathrm{GeH})$
2061m					
2057m	2055m		2052m (P)	2054w	$A_1\,\nu(\mathrm{CO})$
2045m	2041m	2038m	2040m (DP)	2045s	
					$E\,\nu(\mathrm{CO})$
2024s				2032s	
				2018w	
	2004s	2004s	2000w (DP)	1999m	
				1990w	
876w	873m	873m	874m	874w	
					$E\,\delta(\mathrm{GeH_3})$
				870m	
812m				816m	
808m		809s	808w		$A_1\,\delta(\mathrm{GeH_3})$
804m	805m			799w	
				570vw	$E\,\delta(\mathrm{CoCO})_{out}$
562vs	554vs	557s	555w(P)	552vw	$A_1\,\delta(\mathrm{CoCO})_{out}$
530m	530(sh)	535w	532w(P)	535w	$E\,\delta(\mathrm{HGeCo})$
				505w	
					$E\,\delta(\mathrm{CoCO})_{ax} + \nu(\mathrm{CoC})_{eq}$
	499w	498w		499w	
481s	476s	478s	480w(DP)	481w	$E\,\nu(\mathrm{CoC})_{eq} + \delta(\mathrm{CoCO})_{ax}$
460(sh)		464(sh)		467vw	$A_1\,\nu(\mathrm{CoC})_{ax}$
416w	420m	421m	420vs(P)	423vs	$A_1\,\nu(\mathrm{CoC})_{eq}$
				382vw	
377m	374m	376m		378vw	
					$E\delta(\mathrm{CoCO})_{in}$
363w	361w	363w		365vw	
				227s	$A_1\,\nu(\mathrm{GeCo})$
223m			222vs(P)	223vs	
				128s	$E\delta(\mathrm{CCoC})$
			102s(DP)	107s	$E\delta(\mathrm{CCoC})$
				84s	$A_1\,\delta(\mathrm{CCoC})$
				70m	
					$E\delta(\mathrm{GeCoC})$
			60m(DP)	63w	
				56m	
				50w	
				37s	
				28m	

TABLE 3

VIBRATIONAL FREQUENCIES (cm^{-1}) AND ASSIGNMENTS FOR $D_3GeCo(CO)_4$

Infrared	Raman		Assignment
Vapor	Liquid	Solid −160°	
2107s	2100m(P)	2099m	$A_1\,\nu(CO)$
2070w			
2047s			$A_1\,\nu(CO)$
	2034m	2035s	
			$E\ \nu(CO)$
		2031m	
2026vs		2020	
	2000m	1998s	
1988w		1992s	
1522vw			
1495m	1492m(DP)	1502s	$E\ \nu(GeD)$
		1489w	
		1486m	
		1483w	
1478m	1472m(P)	1470vs	$A_1\,\nu(GeD)$
		777vw	
		732vw	
		724vvw	
623m	626w(DP)	624m	$E\,\delta(GeD_3)$
		612w	
590s	584w(P)	588m	$A_1\delta(GeD_3)$
		583vw	
560vs		568vvw	$E\ \delta(CoCO)_{out}$
	550vw(DP)?	551vw	$A_1\delta(CoCO)_{out}$
		545vw	
		516w	
510s	505vw (DP)	506vw	$E\ \delta(CoCO)_{ax} + \nu(CoC)_{eq}$
492m		492w	
	487vw(DP)	490w	$E\ \nu(CoC)_{eq} + \delta(CoCO)_{ax}$
468w		466vw	$A_1\,\nu(CoC)_{ax}$
415w	419vs(P)	422vs	$A_1\,\nu(CoC)_{eq}$
		387vw	
385w		383vw	$E\ \delta(DGeCo)$
		372vw	
365w		364vvw	$E\ \delta(CoCO)_{in}$
		227s	
	221vs(P)	223vs	$A_1\,\nu(GeCo)$
		128s	$E\ \delta(CCoC)$
		118m	
	102s(DP)	105s	$E\ \delta(CCoC)$
		84s	$A_1\delta(CCoC)$
		70m	
		62w	
	58m(DP)	57m	$E\ \delta(GeCoC)$
		50m	
		37s	
		28m	

(A_1 = infrared active, Raman allowed, polarized; A_2 = inactive; E = infrared active, Raman allowed, depolarized).

Table 1 lists the irreducible representations of each vibrational mode in terms of internal coordinates. The vibrational assignments will be discussed for each molecule.

$H_3GeCo(CO)_4$ *and* $D_3GeCo(CO)_4$

Our infrared and Raman data are summarized in Tables 2 and 3. The Raman spectra of the solid $H_3GeCo(CO)_4$ at −160° and its deuterated analog are shown in Fig. 1.

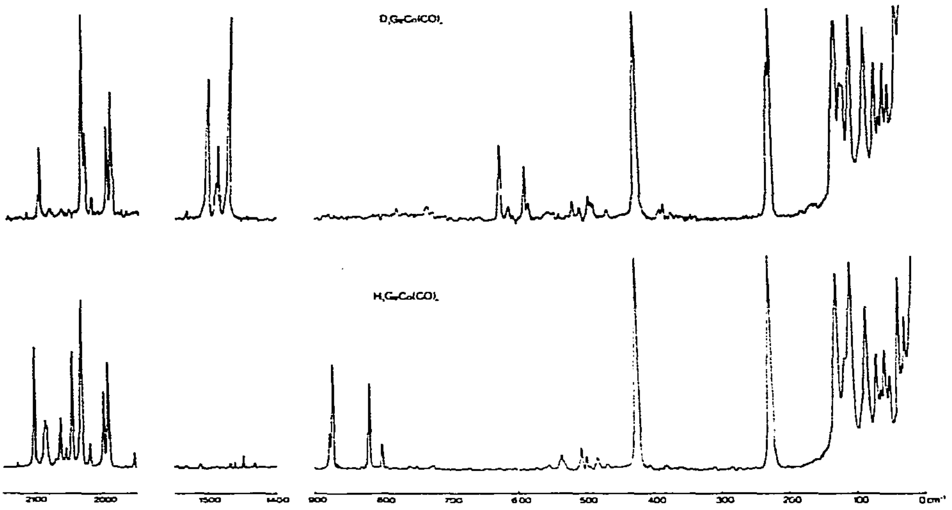

Fig. 1. Raman spectra of solid $H_3GeCo(CO)_4$ and $D_3GeCo(CO)_4$ at −160°.

Samples of H_3 GeCo(CO)$_4$ and D_3 GeCo(CO)$_4$ showed some decomposition in the liquid phase at 0° in the laser beam, while decomposition did not occur in the fluorine complexes.

The vibrational assignment given by George et al. [2] was based upon infrared spectra in the gas phase and the solid state, and Raman frequencies of the liquid. Our Raman data of the liquid phase and solid state at −160° are much more complete, especially in the low frequency region. The vibrational assignments made by George are undoubtedly correct as far as the C—O stretching modes, Ge—H and Ge—D stretching modes, and GeH_3 and GeD_3 bending and rocking modes are concerned. The three expected C—O stretching modes occur at about 2105 cm^{-1} (A_1), 2045 cm^{-1} (A_1) and 2030 cm^{-1} (E). The GeH_3 and GeD_3 vibrations are in the usual regions, with the Ge—H stretching modes obscuring the C—O stretching region. As usual, the lower of the two vibrational bands belongs to the A_1 species: ν(Ge—H) 2080 cm^{-1} (E) and 2060 cm^{-1} (A_1); ν(Ge—D) 1490 cm^{-1} (E) and 1475 cm^{-1} (A_1). For the bending modes the following frequencies are found: GeH_3 872 cm^{-1} (E), 808 cm^{-1} (A_1) and 532 cm^{-1} (E, rock); GeD_3 622 cm^{-1} (E), 588 cm^{-1} (A_1) and 383 cm^{-1} (E, rock). For the vibrational modes which have their frequencies in the 560—350 cm^{-1} region, the same pattern is expected as for the first series of molecules, although in this case some mixing may occur between modes of the Co(CO)$_4$ moiety and the rocking modes. This mixing can be different for the hydride and deuteride. Furthermore, it seems quite reasonable that the Co—C stretching modes are somewhat higher in frequency than in the first series, because the C—O stretching frequencies are lowered. This can be explained by postulating that there is more Co—CO π-backbonding, this seems always to be the case when hydrides are compared with the analogous halogen molecules. The Co—CO bending modes will not be much affected by these changes in bonding. So the following assignment can be made for both molecules:

≈ 560 cm^{-1}	$\delta(CoCO)_{out}$	A_1 and E
505 cm^{-1}	$\delta(CoCO)_{ax} + \nu(CoC)_{eq}$	E
480 cm^{-1}	$\nu(CoC)_{eq} + \delta(CoCO)_{ax}$	E
460 cm^{-1}	$\nu(CoC)_{ax}$	A_1
420 cm^{-1}	$\nu(CoC)_{eq}$	A_1
365 cm^{-1}	$\delta(CoCO)_{in}$	E

The strong polarized Raman band at 220 cm^{-1} is assigned as the Ge—Co stretching mode.

The frequency region below 150 cm^{-1} gives more certainty about the correctness of the assignment made for our first series of compounds. The C—Co—C deformation modes are assigned at:

~125 cm^{-1} $\delta(C{-}Co{-}C)$ E
105 cm^{-1} $\delta(C{-}Co{-}C)$ E
84 cm^{-1} $\delta(C{-}Co{-}C)$ A_1

This leaves the band at ~ 70 cm^{-1} as the Ge—Co—C deformation mode.

$F_3CCo(CO)_4$

The trifluoromethylcobalt tetracarbonyl was prepared for the first time. by Hieber et al. [4]; the only infrared spectrum given referred to a solution in cyclohexane and the range 2200—1000 cm^{-1}. We have recorded infrared and Raman spectra over the whole range in various aggregation states. These spectra enable us to make a complete and unequivocal assignment of the vibrational modes.

Table 4 contains the infrared and Raman frequencies together with the vibrational assignment for $F_3CCo(CO)_4$. Again in the C—O stretching region, three strong bands are found in the infrared and Raman: 2135 cm^{-1} $\nu(CO)$ A_1, 2075 cm^{-1} $\nu(CO)$ A_1 and 2050 cm^{-1} $\nu(CO)$ E. A weaker band at 2013 cm^{-1} may be assigned as a ^{13}C counterpart of the $\nu(CO)$ E. The assignment of the modes belonging to the CF_3 moiety is relatively simple, by comparison with other CF_3X compounds [9, 10, 11] and by means of depolarization measurements: 1080 cm^{-1} $\nu(CF)$ E, 1040 cm^{-1} $\nu(CF)$ A_1, 710 cm^{-1} $\delta(CF_3)$ A_1, 532 cm^{-1} $\delta(CF_3)$ E and 258 cm^{-1} $\rho(CF_3)$ E. For the trifluoro compound, the Co—C stretching modes would be expected to be somewhat lower in frequency than for the germylcobalt tetracarbonyl, as the C—O stretching modes are shifted about 30 cm^{-1} to higher frequency. This is probably because the strong electron withdrawing capacity of the CF_3 group results in less electrons available for metal—CO π-backbonding. The following assignment can therefore be made in the 600—350 cm^{-1} region:

563 cm^{-1}	$\delta(CoCO)_{out}$	E
555 cm^{-1}	$\delta(CoCO)_{out}$	A_1
475 cm^{-1}	$\delta(CoCO)_{ax} + \nu(CoC)_{eq}$	E
458 cm^{-1}	$\nu(CoC)_{eq} + \delta(CoCO)_{ax}$	E

TABLE 4

VIBRATIONAL FREQUENCIES (cm^{-1}) AND ASSIGNMENTS FOR $F_3CCo(CO)_4$

Infrared			Raman		Assignment
Vapor	Liquid	Solid −160°	Liquid	Solid −115°	
2137 s	2130 s	2141 s	2134 s(P)	2141 s	$A_1\nu(CO)$
2106 vw					
		2085 s			
			2078 s		
2065 vs	2068 s		2070(sh)		$A_1\nu(CO)$
2030 m	2055 vs	2046 w	2053 (br)	2049 vs	$E\nu(CO)$
2012 w	2015 w	2015 w		2013 w	$\nu(^{13}CO)$
1096 vs	1080 s	1063 (sh)		1071 w	$E\,\nu(CF)$
1057 vs	1047 s	1045 s	1038 m(P)	1041 m	$A_1\nu(CF)$
717 m	712 m	710 m	711 m(P)	710 m	$A_1\delta(CF_3)$
565 vs	561 vs	563(sh)		564 vw	$E\delta(CoCO)_{out}$
		557 vs			
			554 w	555 w	$A_1\delta(CoCO)_{out}$
		541 w			
	533 m	531 w	531 w(DP)	532 w	$E\,\delta(CF_3)$
513 w		517 vw		516 vw	
480 (sh)				483 vw	$E\delta(CoCO)_{ax}+\nu(CoC)_{eq}$
	470 sh	469 m	474 vw(DP)	473 vw	
		463 m		462 w	$E\,\nu(CoC)_{eq}+\delta(CoCO)_{ax}$
459 s	457 s	458 m	456 w(DP)	457 w	
		438 w	435 w(P)	440 w	$A_1\nu(CoC)_{ax}$
		405 vw	393 vs(P)	404 vs	$A_1\nu(CoC)_{eq}$
	381 m			382 vw	$E\,\delta(CoCO)_{in}$
375 m		375 m		376 vw	
280 vw	282 w	282 w	279 vs(P)	282 s	$A_1\,\nu(CoC)$
256 w	258 w	259 w	258 m(DP)	259 m	$E\,\delta(FCCo)$
			157 w(P)	160 m	Impurity
				126 vs	$E\,\delta(CCoC)$
	112 s			113 s	$E\,\delta(CCoC)$
			103 s(DP)		
				78 s	$A_1\,\delta(CCoC)$
			65 s(DP)		
				52 m	

437 cm^{-1} $\nu(CoC)_{ax}$ A_1

400 cm^{-1} $\nu(CoC)_{eq}$ A_1

375 cm^{-1} $\delta(CoCO)_{in}$ E

The very strong Raman band at 280 cm^{-1}, with depolarization ratio 0.1, is without doubt the "metal"—metal stretching mode. In the low frequency region four C—Co—C bending modes are expected this time. Three of them occur at the expected frequencies, viz.:

126 cm^{-1} δ(C—Co—C) E

110 cm^{-1} δ(C—Co—C) E

78 cm^{-1} δ(C—Co—C) A_1

The "metal"—Co—C bending mode is not found.

$F_3GeCo(CO)_4$

The existence of the trifluorogermylcobalt tetracarbonyl was first reported by Baay and MacDiarmid [5] but no vibrational spectra have previously been

TABLE 5

VIBRATIONAL FREQUENCIES (cm^{-1}) AND ASSIGNMENTS FOR $F_3GeCo(CO)_4$

Infrared		Raman	Assignment	
Solution	Solid —160°	Solid —160°		
2128 s	2143 m	2149 m	A_1	$\nu(CO)$
	2103 w	2098 m	A_1	$\nu(CO)$
2077 m	2070 vw			
2059 vs		2064 m	E	$\nu(CO)$
2053	2050 m	2056 m		
	2030 m			
706 m				
695 m	687 (sh)	688 w	E	$\nu(GeF)$
678 m	673 s	673 w	A_1	$\nu(GeF)$
553 s	552 s	553 w	$E+A_1$	$\delta(CoCO)_{out}$
488 w	481 w	484 (sh)	E	$\delta(CoCO)_{ax}+\nu(CoC)_{eq}$
468 m	465 m	470 w	E	$\nu(CoC)_{eq}+\delta(CoCO)_{ax}$
	442 (sh)	440 (sh)	A_1	$\nu(CoC)_{ax}$
409 w	413 w	416 vs	A_1	$\nu(CoC)_{eq}$
370 w	372 w	368 vw	E	$\delta(CoCO)_{in}$
	365 w			
312 m	315 s	312 s	$E+A_1$	$\delta(GeF_3)$
	248 m			
	222 s	222 vs	A_1	$\nu(GeCo)$
	160 m	164 m	E	$\delta(FGeCo)$
	132 w	134 s		
	122 m	122 m	E	$\delta(CCoC)$
	117 w			
	105 w	104 m	E	$\delta(CCoC)$
	94 m	88 m	A_1	$\delta(CCoC)$
		63 m	E	$\delta(GeCoC)$
		48 m		
		36 w		

described. The infrared and Raman spectra have been recorded for different phases, and a complete vibrational assignment is possible. The data are shown in Table 5. The spectra are very much the same as those of $F_3CCo(CO)_4$, the same shift in the CO stretching region occur, whereas the shifts in the CoC stretching region are less obvious. The Ge—F stretching frequencies are somewhat lower than for GeF_4, and are assigned as 688 cm^{-1} ν(GeF) E, and 673 cm^{-1} ν(GeF)A_1. The GeF_3 deformation modes must have the same frequency, as only one band is observed at 312 cm^{-1}. For the GeF_3 rocking mode two possibilities are available, namely 164 cm^{-1} and 134 cm^{-1}. Forcefield calculations [12] show that a frequency of 164 cm^{-1} for this rocking mode is more likely.

For the remaining assignments, which are consistent with those for the other $X_3MCo(CO)_4$ molecules, see Table 5.

Conclusion

From the complete Raman and infrared spectra under various conditions, together with the observed depolarization values, it is possible to make reliable vibrational assignments for the $X_3MCo(CO)_4$ molecules. These assignments are consistent with and support those of the series of complexes we studied previously [1]. The CO stretching frequencies and, rather less obviously, the CoC stretching frequencies, reflect the electron withdrawing capacity of the MX_3 group.

With the aid of the assignment of the molecules studied so far, it seems easy to predict the spectra of any other member of the $X_3MCo(CO)_4$ series.

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