

### Conclusion

Some fairly general procedures have been worked out for the preparation of several different types of complexes for a variety of phosphine ligands. Unfortunately, the differences in the electronic and steric properties of the various tertiary phosphines are so large as to preclude any completely general procedures. In spite of this, however, several series of complexes were prepared. There do not seem to be any really discernible trends within these groups with respect to stability, color, melting points, or carbonyl stretching frequencies.

Several interesting anomalies were noted. Whereas most of the rhodium(III) species appear to be six-coordinate as expected, the five-coordinate  $\text{RhHCl}_2(\text{P}(i\text{-Pr})_3)_2$  is the most stable complex of this ligand. It was

also of interest to note that this compound is capable of decarbonylating both alcohols and carboxylic acids to form  $\text{RhClCO}(\text{P}(i\text{-Pr})_3)_2$ .

The oxidative addition of  $\text{HCl}$  to  $\text{RhCl}(\text{PR}_3)_3$  to yield the hydride compound  $\text{RhHCl}_3(\text{PR}_3)_3$  was observed to proceed *via* a *cis* addition followed by a less rapid rearrangement to the product which would occur from *trans* addition.

Finally, evidence has been obtained for the structure of the dinuclear complexes. These are postulated as the dinuclear, chlorine-bridged isomer with all *trans* phosphines.

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## Spectroscopic Studies of Metal-Metal Bonding. III. Vibrational Spectra and Analyses of $\text{M}[\text{Co}(\text{CO})_4]_2$ ( $\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$ )

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The vibrational spectra of the recently studied  $\text{Zn}[\text{Co}(\text{CO})_4]_2$  and its congeners  $\text{Cd}[\text{Co}(\text{CO})_4]_2$  and  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  have been measured in the infrared (33–4500  $\text{cm}^{-1}$ ) and laser-Raman ( $\Delta\omega = 0\text{--}4000 \text{ cm}^{-1}$ ) regions. The infrared and Raman fundamentals are assigned on the basis of  $D_{3d}$  symmetry, under which no coincidences are allowed, but infrared-Raman band "pairs" are observed which are separated by interactions across the metal-metal system. The normal-coordinate analyses of these species also demonstrate significant coupling across the trinuclear  $\text{M-M}'\text{-M}$  bond and permit evaluation of vibrational coupling of coterminal metal-metal bonds as well as the strengths of the  $\text{M-Co}$  bonds. The metal-metal force constants are nearly identical, although they fall in the order  $k(\text{Zn-Co}) \geq k(\text{Cd-Co}) \geq k(\text{Hg-Co})$ . This result is discussed in terms of the reported trends in  $k(\text{M-Co})$  from very approximate treatments and reported mass spectral results.

### Introduction

The  $\text{Hg}$ ,  $\text{Cd}$ , and  $\text{Zn}$  derivatives of  $\text{Co}(\text{CO})_4^-$ ,  $\text{M}[\text{Co}(\text{CO})_4]_2$ , have occupied an interesting position in the study of metal-metal bonded compounds. Their relatively early known existence<sup>4,5</sup> has made them the subject of several vibrational spectroscopic investigations,<sup>6–12</sup> of which the earliest<sup>6–8</sup> were attempts to elucidate the structures of the compounds. Subsequent X-ray crystallographic determinations<sup>13,14</sup> confirmed the spectroscopic conclusions of a linear, un-

supported  $\text{Co-M-Co}$  bonding framework. The more recent interest in the nature of metal-metal bonding in such systems has prompted reports<sup>15–19</sup> of the low-frequency vibrational spectra of the  $\text{M}[\text{Co}(\text{CO})_4]_2$  compounds, with particular emphasis on those bands which primarily involve  $\text{M-Co}$  stretching vibrations. Using vibrational frequency data and localized mode calculations with varying approximations in the calculations, several authors<sup>7,15,16,20</sup> have reported for these compounds metal-metal "force constants" which range from a high<sup>7</sup> of 2.6 and 2.3  $\text{mdyn}/\text{\AA}$  for  $k(\text{Hg-Co})$  and  $k(\text{Cd-Co})$ , respectively, to a low<sup>20</sup> of 0.77  $\text{mdyn}/\text{\AA}$  for  $k(\text{Cd-Co})$ . The several approximate treatments give the order of force constants to be  $k(\text{Hg-Co}) > k(\text{Cd-Co})$  or  $k(\text{Zn-Co}) > k(\text{Hg-Co}) > k(\text{Cd-Co})$ .

Recently J. M. B.<sup>21,22</sup> reported studies of the ionic dissociation reactions and the mass spectra of the

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three  $M[\text{Co}(\text{CO})_4]_2$  compounds. Two results of these studies are relevant to the previous spectroscopic work. First, the compounds are dissociated, to varying extents, in polar solvents. Second, the mass spectra qualitatively indicate that the order of metal-metal bond strength is  $\text{Zn-Co} > \text{Cd-Co} > \text{Hg-Co}$ .

Since the reported vibrational analyses of the  $M[\text{Co}(\text{CO})_4]_2$  compounds were based on incomplete data and widely varying approximations, since the orders of metal-metal bond strengths from vibrational and mass spectral studies are inconsistent, and since the true order is of interest in light of the ionic dissociation and metal-exchange results, we have undertaken a study of the complete vibrational spectra. In this paper we report the infrared and laser-Raman spectra and vibrational analysis of the three compounds  $\text{Zn}[\text{Co}(\text{CO})_4]_2$ ,  $\text{Cd}[\text{Co}(\text{CO})_4]_2$ , and  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ .

### Experimental Section

The compounds  $M[\text{Co}(\text{CO})_4]_2$  where  $M = \text{Hg}, \text{Cd},$  and  $\text{Zn}$  were prepared as previously described.<sup>22,23</sup> Samples employed in the spectroscopic studies were handled *in vacuo* or under a dry nitrogen or argon atmosphere and, when possible, in the absence of light. Solvents were carefully dried, as appropriate, vacuum deaerated, and vacuum distilled. Solid samples used for laser-Raman measurements were sealed in glass capillaries under high vacuum.

Laser-Raman spectra were measured using a Jarrell-Ash 25-300 spectrometer, with a calibrated accuracy of *ca.*  $1 \text{ cm}^{-1}$  and resolution of at least  $5 \text{ cm}^{-1}$ . The infrared spectra were measured on a Beckman IR-11-12 spectrophotometer, with resolution and accuracy of *ca.*  $1 \text{ cm}^{-1}$ . Calibration of infrared spectra was performed using standard vapor-phase spectra.<sup>24</sup>

Solutions and milled samples (Nujol or polyethylene matrix) of these compounds decompose when exposed to unfiltered radiation from the mercury-arc far-infrared source. This problem was eliminated by placing a carbon-black-filled polyethylene film between the source and sample when using this source in the  $33\text{--}400\text{-cm}^{-1}$  region and by employing a Nernst glower source in the  $300\text{--}800\text{-cm}^{-1}$  region.

Decomposition was also found to occur when the samples were exposed to the full power of our laser sources ( $\text{He-Ne}$ ,  $632.8 \text{ nm}$ ;  $\text{Ar}^+$ ,  $514.5 \text{ nm}$ ) during preliminary Raman spectral measurements. The use of neutral-density source filters to reduce the power at the sample eliminated the problem completely, and all Raman results reported here were made on samples which showed no evidence of decomposition.

### Spectral Results

The structures of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ <sup>14</sup> and  $\text{Zn}[\text{Co}(\text{CO})_4]_2$ <sup>13</sup> have been reported. In each case the molecule is found to have approximately  $D_{3d}$  molecular symmetry with a linear and symmetrical  $\text{MCo}_2$  unit. Because of the similarity of its properties and vibrational spectrum to those of the  $\text{Hg}$  and  $\text{Zn}$  compounds,  $\text{Cd}[\text{Co}(\text{CO})_4]_2$  is also taken to belong to the point group  $D_{3d}$ .

The vibrational representation of these molecules in  $D_{3d}$  symmetry is  $\Gamma_{\text{vib}} = 7 A_{1g}(\text{R}, \text{pol}) + 2 A_{1u}(\text{ia}) + 1 A_{2g}(\text{ia}) + 7 A_{2u}(\text{ir}) + 8 E_g(\text{R}, \text{depol}) + 9 E_u(\text{ir})$ , where the symbol meanings are as follows: ir, infrared active; R, Raman active; pol, polarized in the Raman; depol, depolarized in the Raman; ia, inactive in the infrared and Raman spectra. The 51 normal modes thus occur at 34 fundamental frequencies, of which 15 are Raman active and 16 are infrared active.

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Because the molecules possess a center of symmetry, none of the fundamentals is predicted to be both infrared and Raman active.

The infrared and laser Raman spectra of all three compounds are reported in Table I. Since the previously referenced<sup>6-12,15-19</sup> reports of spectral work give various incomplete portions of the spectra, we have not given specific reference to each frequency in Table I that has been reported earlier. Our infrared data are in good agreement with those frequencies that have been reported, but several reported Raman bands are erroneous, as discussed below.

As detailed in Table II, on the basis of symmetry coordinates and previous work on metal carbonyls, we expect six fundamental vibrations in the  $2000\text{-cm}^{-1}$  region due primarily to C-O stretching vibrations:  $2 A_{1g} + 2 A_{2u} + 1 E_g + 1 E_u$ . Of these, three are expected in the infrared and three in the Raman spectrum. Vibrations which are largely  $\nu(\text{M-C})$  and  $\delta(\text{M-C-O})$  are generally found in the middle-frequency region ( $350\text{--}700 \text{ cm}^{-1}$ ). Thus, seven infrared- and seven Raman-active vibrations should be observable in this region. Below  $350 \text{ cm}^{-1}$  the modes due primarily to metal-metal stretching vibrations [ $\nu_{\text{sym}}(\text{Co-M-Co})$ ,  $A_{1g}$ ;  $\nu_{\text{asym}}(\text{Co-M-Co})$ ,  $A_{2u}$ ] and nine skeletal distortion vibrations are expected to be active.

The observed bands assigned to fundamental vibrations are designated in Table I. The six  $\nu(\text{C-O})$  fundamentals, the fourteen<sup>25</sup> middle-frequency modes, the two predominantly metal-metal stretching modes, and several of the very low frequency skeletal modes are observed and assigned. The bases for the specific assignments can be discussed most readily by considering the three spectral regions separately. However, there is a general characteristic of the spectrum which clarifies the interpretation.

If the  $\text{Co}(\text{CO})_4$  moieties were vibrationally uncoupled, there would be many accidentally degenerate pairs of vibrations, of which one would be Raman active and one infrared active due to their phase relationship. Since the removal of such degeneracies results from interactions across the  $\text{Co-M-Co}$  system, which are expected to be small in the cases of C-O stretches and several of the  $\text{Co-C-O}$  bends, closely spaced infrared-Raman "pairs" of frequencies should be observed. Furthermore, the frequency separation of the two bands is a measure of these interactions.

**The  $\nu(\text{C-O})$  Region.**—The strongest infrared band, occurring at *ca.*  $2000 \text{ cm}^{-1}$  in each spectrum, is assigned as  $\nu_{26}$  of  $E_u$  symmetry. The two remaining infrared bands, observed at *ca.*  $2075$  and *ca.*  $2020 \text{ cm}^{-1}$  in the spectra of all three compounds, are assigned as the fundamentals  $\nu_{11}$  and  $\nu_{12}$ , respectively, both of  $A_{2u}$  symmetry. These assignments are in agreement with the previously assigned<sup>9-11</sup> infrared spectrum of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  in this region. The stretches of only the equatorial CO groups contribute to  $\nu_{26}$ , while  $\nu_{11}$  and  $\nu_{12}$  involve both axial and equatorial CO groups.

As discussed above, one expects to observe Raman-active, infrared-active "pairs" of vibrations in this region. That is, for a fundamental which is primarily an axial C-O stretching vibration, the form of the Raman-active ( $A_{1g}$ ) mode differs from the infrared-

(25) Only 13 middle-frequency modes were observed in the spectrum of  $\text{Cd}[\text{Co}(\text{CO})_4]_2$ .

TABLE I

OBSERVED AND ASSIGNED VIBRATIONAL BANDS AND CALCULATED VIBRATIONAL MODES FOR THE  
 $M[\text{Co}(\text{CO})_4]_2$  MOLECULES

Ir freq, $\text{cm}^{-1}$	State (ir)	Raman freq, <sup>a</sup> $\text{cm}^{-1}$	$\nu_i$	$\Gamma_i$	$\nu_{\text{calcd}}, \text{cm}^{-1}$	Description
A. $\text{Zn}[\text{Co}(\text{CO})_4]_2$						
		2092	$\nu_1$	$A_{1g}$	2092	$\nu(R_{ax}) + \nu(R_{eq})$
2077	<i>b</i>		$\nu_{11}$	$A_{2u}$	2077	$\nu(R_{ax}) + \nu(R_{eq})$
2026	<i>b</i>		$\nu_{12}$	$A_{2u}$	2026	$\nu(R_{eq}) + \nu(R_{ax})$
		2028	$\nu_2$	$A_{1g}$	2028	$\nu(R_{eq}) + \nu(R_{ax})$
2003	<i>b</i>		$\nu_{26}$	$E_u$	2003	$\nu(R_{eq})$
		1976	$\nu_{18}$	$E_g$	1975	$\nu(R_{eq})$
		728	$2\nu_{30}$			
		561	$\nu_3$	$A_{1g}$	561	$\delta(\beta_{op}) + \delta(\gamma_{eq}) + \delta(\Delta_{op})$
548	<i>c</i>		$\nu_{13}$	$A_{2u}$	548	$\delta(\beta_{op}) + \delta(\Delta_{op}) + \delta(\gamma_{eq})$
		541	$\nu_{19}$	$E_g$	539	$\delta(\beta_{op}) + \delta(\beta_{ax}) + \delta(\Delta_{op})$
534	<i>c</i>		$\nu_{27}$	$E_u$	534	$\delta(\beta_{op}) + \delta(\beta_{ax}) + \delta(\Delta_{op})$
		513	$\nu_{20}$	$E_g$	513	$\delta(\beta_{ip}) + \delta(\Delta_{ip}) + \nu(r_{eq})$
512	<i>c</i>		$\nu_{28}$	$E_u$	512	$\delta(\beta_{ip}) + \delta(\Delta_{ip}) + \nu(r_{eq})$
		492	$\nu_{21}$	$E_g$	491	$\delta(\beta_{op}) + \delta(\beta_{ax})$
488	<i>c</i>		$\nu_{29}$	$E_u$	485	$\delta(\beta_{op}) + \delta(\beta_{ax})$
		463	$\nu_4$	$A_{1g}$	463	$\nu(r_{ax}) + \nu(r_{eq}) + \nu(L)$
		426	$\nu_5$	$A_{1g}$	426	$\nu(r_{eq}) + \nu(r_{ax})$
419	<i>d</i>		$\nu_{14}$	$A_{2u}$	419	$\nu(r_{ax}) + \nu(r_{eq}) + \nu(L)$
398	<i>d</i>		$\nu_{16}$	$A_{2u}$	398	$\nu(r_{eq}) + \nu(r_{ax})$
		369	$\nu_{22}$	$E_g$	368	$\nu(r_{eq}) + \delta(\beta_{ip})$
365	<i>d</i>		$\nu_{30}$	$E_u$	365	$\nu(r_{eq}) + \delta(\beta_{ip})$
284	<i>d</i>		$\nu_{16}$	$A_{2u}$	284	$\nu(L)$
		170	$\nu_6$	$A_{1g}$	170	$\nu(L) + \delta(\gamma_{eq}) + \delta(\beta_{op}) + \delta(\Delta_{op})$
			$\nu_{31}$	$E_u$	135	$\delta(\gamma) + \delta(\Delta) + \delta(\theta)$
			$\nu_{23}$	$E_g$	128	$\delta(\Delta) + \delta(\beta_{ip}) + \delta(\beta_{ax}) + \delta(\gamma_{ax})$
			$\nu_{17}$	$A_{2u}$	113	$\delta(\Delta_{op}) + \delta(\beta_{op}) + \delta(\gamma_{eq})$
			$\nu_{24}$	$E_g$	110	$\delta(\Delta)$
			$\nu_{32}$	$E_u$	109	$\delta(\Delta) + \delta(\gamma_{eq})$
			$\nu_{33}$	$E_u$	101	$\delta(\Delta_{ip}) + \delta(\theta) + \delta(\gamma_{eq}) + \delta(\beta_{ip})$
		92	$\nu_7$	$A_{1g}$	93	$\nu(L) + \delta(\gamma_{eq}) + \delta(\beta_{op}) + \delta(\Delta_{op})$
		61	$\nu_{25}$	$E_g$	65	$\delta(\gamma) + \delta(\Delta_{ip})$
			$\nu_{34}$	$E_u$	42	$\delta(\theta) + \delta(\gamma)$
$\epsilon = 0.60 \text{ cm}^{-1}$						
B. $\text{Cd}[\text{Co}(\text{CO})_4]_2$						
		2087	$\nu_1$	$A_{1g}$	2088	$\nu(R_{ax}) + \nu(R_{eq})$
2071	<i>b</i>		$\nu_{11}$	$A_{2u}$	2071	$\nu(R_{ax}) + \nu(R_{eq})$
2016	<i>b</i>		$\nu_{12}$	$A_{2u}$	2016	$\nu(R_{eq}) + \nu(R_{ax})$
		2020	$\nu_2$	$A_{1g}$	2020	$\nu(R_{eq}) + \nu(R_{ax})$
1995	<i>b</i>		$\nu_{26}$	$E_u$	1995	$\nu(R_{eq})$
		1976	$\nu_{18}$	$E_g$	1976	$\nu(R_{eq})$
		726	$2\nu_{30}$			
		561	$\nu_3$	$A_{1g}$	561	$\delta(\beta_{op}) + \delta(\gamma_{eq}) + \delta(\Delta_{op})$
548	<i>d, e</i>		$\nu_{13}$	$A_{2u}$	548	$\delta(\beta_{op}) + \delta(\gamma_{eq}) + \delta(\Delta_{op})$
		548	$\nu_{19}$	$E_g$	546	$\delta(\beta_{op}) + \delta(\beta_{ax}) + \delta(\Delta_{op})$
538	<i>d, e</i>		$\nu_{27}$	$E_u$	538	$\delta(\beta_{op}) + \delta(\beta_{ax}) + \delta(\Delta_{op})$
		520	$\nu_{20}$	$E_g$	516	$\delta(\beta_{ip}) + \delta(\Delta_{ip}) + \nu(r_{eq})$
511	<i>e</i>		$\nu_{28}$	$E_u$	509	$\delta(\beta_{ip}) + \delta(\Delta_{ip}) + \nu(r_{eq})$
487	<i>e</i>		$\nu_{29}$	$E_u$	484	$\delta(\beta_{ax}) + \delta(\beta_{op})$
		486	$\nu_{21}$	$E_g$	490	$\delta(\beta_{ax}) + \delta(\beta_{op}) + \delta(\beta_{ip})$
			$\nu_4$	$A_{1g}$	460	$\nu(r_{ax}) + \nu(r_{eq}) + \nu(L)$
		431	$\nu_5$	$A_{1g}$	431	$\nu(r_{eq}) + \nu(r_{ax})$
420	<i>d, e</i>		$\nu_{14}$	$A_{2u}$	420	$\nu(r_{ax}) + \nu(r_{eq}) + \nu(L)$
401	<i>e</i>		$\nu_{15}$	$A_{2u}$	401	$\nu(r_{eq}) + \nu(r_{ax})$
		372	$\nu_{22}$	$E_g$	372	$\nu(r_{eq}) + \delta(\beta_{ip})$
365	<i>d, e</i>		$\nu_{30}$	$E_u$	364	$\nu(r_{eq}) + \delta(\beta_{ip})$
218	<i>d, e</i>		$\nu_{16}$	$A_{2u}$	218	$\nu(L)$
		163	$\nu_6$	$A_{1g}$	163	$\nu(L) + \delta(\gamma_{eq}) + \delta(\beta_{op}) + \delta(\Delta_{op})$
		127	$\nu_{23}$	$E_g$	127	$\delta(\Delta) + \delta(\beta_{ip}) + \delta(\beta_{ax}) + \delta(\gamma_{ax})$
119	<i>e</i>		$\nu_{31}$	$E_u$	124	$\delta(\Delta) + \delta(\gamma_{ax}) + \delta(\beta_{ip}) + \delta(\beta_{ax})$
111	<i>e</i>		$\nu_{17}$	$A_{2u}$	111	$\delta(\Delta_{op}) + \delta(\gamma_{eq}) + \delta(\beta_{op})$
		108	$\nu_{24}$	$E_g$	109	$\delta(\Delta)$
			$\nu_{32}$	$E_u$	107	$\delta(\Delta)$
		100	$\nu_7$	$A_{1g}$	99	$\nu(L) + \delta(\gamma_{eq}) + \delta(\beta_{op}) + \delta(\Delta_{op})$
		73	$\nu_{25}$	$E_g$	70	$\delta(\gamma) + \delta(\Delta_{ip})$
			$\nu_{33}$	$E_u$	67	$\delta(\gamma) + \delta(\theta)$
51	<i>e</i>		$\nu_{34}$	$E_u$	48	$\delta(\theta)$
$\epsilon = 1.07 \text{ cm}^{-1}$						

TABLE I (Continued)

Ir freq, cm <sup>-1</sup>	State (ir)	Raman freq, <sup>a</sup> cm <sup>-1</sup>	$\nu_i$	$\Gamma_i$	$\nu_{\text{calc'd}}, \text{cm}^{-1}$	Description
C. Hg[Co(CO) <sub>4</sub> ] <sub>2</sub>						
		2090	$\nu_1$	A <sub>1g</sub>	2090	$\nu(R_{\text{ax}}) + \nu(R_{\text{eq}})$
2072	b		$\nu_{11}$	A <sub>2u</sub>	2072	$\nu(R_{\text{ax}}) + \nu(R_{\text{eq}})$
2022	b		$\nu_{12}$	A <sub>2u</sub>	2022	$\nu(R_{\text{eq}}) + \nu(R_{\text{ax}})$
		2027	$\nu_2$	A <sub>1g</sub>	2027	$\nu(R_{\text{eq}}) + \nu(R_{\text{ax}})$
2007	b		$\nu_{26}$	E <sub>u</sub>	2007	$\nu(R_{\text{eq}})$
		1982	$\nu_{18}$	E <sub>g</sub>	1983	$\nu(R_{\text{eq}})$
		720	2 $\nu_{30}$			
		580	$\nu_3$	A <sub>1g</sub>	580	$\delta(\beta_{\text{op}}) + \delta(\gamma_{\text{eq}}) + \delta(\Delta_{\text{op}})$
546	e		$\nu_{13}$	A <sub>2u</sub>	546	$\delta(\beta_{\text{op}}) + \delta(\Delta_{\text{op}}) + \delta(\gamma_{\text{eq}})$
		543	$\nu_{19}$	E <sub>g</sub>	542	$\delta(\beta_{\text{op}}) + \delta(\gamma_{\text{eq}})$
532	e		$\nu_{27}$	E <sub>u</sub>	530	$\delta(\beta_{\text{op}}) + \delta(\Delta_{\text{op}}) + \delta(\beta_{\text{ax}})$
499	e		$\nu_{28}$	E <sub>u</sub>	496	$\delta(\beta_{\text{ip}}) + \delta(\Delta_{\text{ip}}) + \nu(r_{\text{eq}})$
		498	$\nu_{20}$	E <sub>g</sub>	498	$\delta(\beta_{\text{ip}}) + \delta(\Delta_{\text{ip}}) + \nu(r_{\text{eq}})$
		477	$\nu_{21}$	E <sub>g</sub>	476	$\delta(\beta_{\text{ax}}) + \delta(\beta_{\text{eq}})$
476	e		$\nu_{29}$	E <sub>u</sub>	472	$\delta(\beta_{\text{ax}}) + \delta(\beta_{\text{eq}})$
		462	$\nu_4$	A <sub>1g</sub>	462	$\delta(r_{\text{ax}}) + \nu(L)$
		417	$\nu_5$	A <sub>1g</sub>	417	$\nu(r_{\text{eq}})$
416	e		$\nu_{14}$	A <sub>2u</sub>	416	$\nu(r_{\text{ax}}) + \nu(r_{\text{eq}}) + \nu(L)$
400 <sup>f</sup>			$\nu_{15}$	A <sub>2u</sub>	400	$\nu(r_{\text{eq}}) + \nu(r_{\text{ax}})$
		372	$\nu_{22}$	E <sub>g</sub>	371	$\nu(r_{\text{eq}}) + \delta(\beta_{\text{ip}}) + \delta(\beta_{\text{ax}})$
368	e		$\nu_{30}$	E <sub>u</sub>	367	$\nu(r_{\text{eq}}) + \delta(\beta_{\text{ip}}) + \delta(\beta_{\text{ax}})$
195	e		$\nu_{16}$	A <sub>2u</sub>	195	$\nu(L)$
		163	$\nu_6$	A <sub>1g</sub>	163	$\nu(L) + \delta(\gamma_{\text{eq}}) + \delta(\Delta_{\text{op}}) + \delta(\beta_{\text{op}})$
126	e		$\nu_{31}$	E <sub>u</sub>	127	$\delta(\Delta) + \delta(\gamma_{\text{ax}}) + \delta(\beta_{\text{ax}}) + \delta(\beta_{\text{ip}})$
			$\nu_{23}$	E <sub>g</sub>	124	$\delta(\Delta) + \delta(\beta_{\text{ax}}) + \delta(\gamma_{\text{ax}})$
109	e		$\nu_{17}$	A <sub>2u</sub>	109	$\delta(\gamma_{\text{eq}}) + \delta(\Delta_{\text{op}}) + \delta(\beta_{\text{op}})$
		101 <sup>g</sup>	$\nu_{24}$	E <sub>g</sub>	109	$\delta(\Delta)$
			$\nu_{32}$	E <sub>u</sub>	108	$\delta(\Delta)$
		101 <sup>g</sup>	$\nu_7$	A <sub>1g</sub>	92	$\nu(L) + \delta(\gamma_{\text{eq}}) + \delta(\Delta_{\text{op}}) + \delta(\beta_{\text{op}})$
			$\nu_{33}$	E <sub>u</sub>	78	$\delta(\gamma) + \delta(\theta) + \delta(\Delta_{\text{ip}})$
			$\nu_{25}$	E <sub>g</sub>	70	$\delta(\gamma) + \delta(\Delta_{\text{op}})$
45	e		$\nu_{34}$	E <sub>u</sub>	42	$\delta(\theta)$

$$\epsilon = 0.76 \text{ cm}^{-1}$$

<sup>a</sup> All Raman shifts measured on powdered samples. <sup>b</sup> Hexane solution. <sup>c</sup> Heptane solution. <sup>d</sup> Cyclohexane solution. <sup>e</sup> Nujol mull. <sup>f</sup> Frequency reported by Manning.<sup>11</sup> <sup>g</sup> The 101-cm<sup>-1</sup> band is very broad, including both  $\nu_7$  and  $\nu_{24}$ , but is not included in calculating  $\epsilon$ .

TABLE II  
SYMMETRIES OF VIBRATIONAL MODES FOR THE  
M[Co(CO)<sub>4</sub>]<sub>2</sub> MOLECULES (*D*<sub>3d</sub>)

Internal coordinate	Symbol	Representation
(C-O) <sub>ax</sub> str	R <sub>ax</sub>	1 A <sub>1g</sub> + 1 A <sub>2u</sub>
(C-O) <sub>eq</sub> str	R <sub>eq</sub>	1 A <sub>1g</sub> + 1 A <sub>2u</sub> + 1 E <sub>g</sub> + 1 E <sub>u</sub>
(Co-C) <sub>ax</sub> str	r <sub>ax</sub>	1 A <sub>1g</sub> + 1 A <sub>2u</sub>
(Co-C) <sub>eq</sub> str	r <sub>eq</sub>	1 A <sub>1g</sub> + 1 A <sub>2u</sub> + 1 E <sub>g</sub> + 1 E <sub>u</sub>
(M-Co) str	L	1 A <sub>1g</sub> + 1 A <sub>2u</sub>
(Co-C-O) <sub>eq,op</sub> bend	$\beta_{\text{op}}$	1 A <sub>1g</sub> + 1 A <sub>2u</sub> + 1 E <sub>g</sub> + 1 E <sub>u</sub>
(Co-C-O) <sub>eq,ip</sub> bend	$\beta_{\text{ip}}$	1 A <sub>1u</sub> + 1 A <sub>2g</sub> + 1 E <sub>g</sub> + 1 E <sub>u</sub>
(Co-C-O) <sub>ax</sub> bend	$\beta_{\text{ax}}$	1 E <sub>g</sub> + 1 E <sub>u</sub>
(C-Co-C) <sub>eq,ip</sub> bend <sup>a</sup>	$\Delta_{\text{ip}}$	1 A <sub>1g</sub> + 1 A <sub>2u</sub> + 1 E <sub>g</sub> + 1 E <sub>u</sub>
(C <sub>ax</sub> -Co-C <sub>eq,op</sub> ) def	$\Delta_{\text{op}}$	1 A <sub>1g</sub> + 1 A <sub>2u</sub> + 1 E <sub>g</sub> + 1 E <sub>u</sub>
(M-Co-C) <sub>eq</sub> def <sup>b</sup>	$\gamma_{\text{eq}}$	1 A <sub>1g</sub> + 1 A <sub>2u</sub> + 1 E <sub>g</sub> + 1 E <sub>u</sub>
(M-Co-C) <sub>ax</sub> def	$\gamma_{\text{ax}}$	1 E <sub>g</sub> + 1 E <sub>u</sub>
(Co-M-Co) def	$\theta$	1 E <sub>u</sub>
Torsion	$\tau$	1 A <sub>1u</sub>

<sup>a</sup> A<sub>1g</sub> and A<sub>2u</sub> modes redundant with those of  $\Delta_{\text{op}}$ . <sup>b</sup> All modes redundant with those of  $\Delta_{\text{op}}$ .

active (A<sub>2u</sub>) mode only in the phase relationship of the stretching motion of the axial C-O group in one Co(CO)<sub>4</sub> unit to that in the other Co(CO)<sub>4</sub> unit. In the A<sub>1g</sub> mode, both axial C-O groups vibrate in phase while in the A<sub>2u</sub> mode one axial C-O group vibrates 180° out of phase with respect to the other. The same argument applies to the A<sub>1g</sub> and A<sub>2u</sub> modes which are predominantly equatorial C-O stretching vibrations.

The symmetry coordinates for these modes, when used in the Wilson *GF* matrix method<sup>26</sup> approach to

the solution of the vibrational secular equation, generate the diagonal elements of the symmetrized *F* (potential energy) matrix which, for the vibrations being considered here, have the forms.

$$F_{\text{ax}}(A_{1g}) = k_{\text{ax}} + k'_{\text{ax,ax}}$$

$$F_{\text{eq}}(A_{1g}) = k_{\text{eq}} + 2k_{\text{eq,eq}} + k'_{\text{eq,eq}} + 2k''_{\text{eq,eq}}$$

$$F_{\text{ax}}(A_{2u}) = k_{\text{ax}} - k'_{\text{ax,ax}}$$

$$F_{\text{eq}}(A_{2u}) = k_{\text{eq}} + 2k_{\text{eq,eq}} - k'_{\text{eq,eq}} - 2k''_{\text{eq,eq}}$$

The symbols  $k_{\text{ax}}$ ,  $k_{\text{eq}}$ , and  $k_{\text{eq,eq}}$  are the general notations for diagonal and interaction valence force constants; the symbols  $k'$  and  $k''$  refer to interaction forces between C-O groups that, in the *D*<sub>3d</sub> point group, are equivalent to one another under the symmetry operations *i* and *S*<sub>6</sub>, respectively. The coupling of the C-O groups in one Co(CO)<sub>4</sub> unit to those in the other Co(CO)<sub>4</sub> unit across the Co-M-Co bonding framework is not expected to be large, so the interaction force constant  $k'_{\text{ax,ax}}$  and the sum ( $k'_{\text{eq,eq}} + 2k''_{\text{eq,eq}}$ ) should be small and the A<sub>1g</sub>, A<sub>2u</sub> "pairs" are nearly degenerate.

In the absence of Raman polarization measurements which would have permitted unambiguous assignment of the Raman spectra of the three compounds in this spectral region, we have utilized the above argument to assign the three bands observed in the Raman spectra. Thus, the bands observed at *ca.* 2090 and *ca.* 2025 cm<sup>-1</sup> are assigned as  $\nu_1$  and  $\nu_2$ , respectively, the A<sub>1g</sub> analogs of  $\nu_{11}$  and  $\nu_{12}$ . The remaining band at *ca.*

(26) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955.

1975  $\text{cm}^{-1}$  is assigned as the fundamental  $\nu_{18}$  of  $E_g$  symmetry.

The relatively large frequency difference between the bands assigned as  $\nu_{18}$  and  $\nu_{26}$  is also explained by the above arguments. For these two modes, the diagonal elements in the symmetrized  $F$  matrix are  $F_{\text{eq}}(E_g) = k_{\text{eq}} - k'_{\text{eq,eq}} + k'_{\text{eq,eq}} - k''_{\text{eq,eq}}$  and  $F_{\text{eq}}(E_u) = k_{\text{eq}} - k'_{\text{eq,eq}} - k'_{\text{eq,eq}} + k''_{\text{eq,eq}}$ . Requiring the magnitude of the sum  $(k'_{\text{eq,eq}} + 2k''_{\text{eq,eq}})$  to be small imposes no other restrictions on the signs and magnitudes of  $k'_{\text{eq,eq}}$  and  $k''_{\text{eq,eq}}$ . It appears that their signs and magnitudes are such as to make the sum  $(k'_{\text{eq,eq}} - k''_{\text{eq,eq}})$  large enough to cause an appreciable separation between  $\nu_{18}$  and  $\nu_{26}$ .

**The Middle-Frequency Region.**—Observed bands in this region (300–800  $\text{cm}^{-1}$ ) are due primarily to Co–C stretching vibrations and Co–C–O bending vibrations and include seven Raman-active fundamentals (3  $A_{1g}$  and 4  $E_g$ ) and seven infrared-active fundamentals (3  $A_{2u}$  and 4  $E_u$ ).

The observed infrared spectra of the three compounds in the middle-frequency region are very similar, having one group of four bands between 475 and 550  $\text{cm}^{-1}$  and a second group of three bands between 365 and 425  $\text{cm}^{-1}$ . The former group is collectively assigned to the primarily Co–C–O bending vibrations (1  $A_{2u}$ , 3  $E_u$ ) and the latter to the primarily Co–C stretching vibrations (2  $A_{2u}$ , 1  $E_u$ ).

We employ the results of Manning's investigation<sup>11</sup> of the infrared spectrum of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  and its axially substituted derivatives,  $\text{Hg}[\text{Co}(\text{CO})_3\text{L}]_2$ , in assigning the band observed at *ca.* 547  $\text{cm}^{-1}$  in the infrared spectrum of all three compounds as the fundamental  $\nu_{13}$  of  $A_{2u}$  symmetry. The three remaining bands in this group are assigned as the fundamentals  $\nu_{27}$ ,  $\nu_{28}$ , and  $\nu_{29}$  of  $E_u$  symmetry.

The infrared bands due to primarily Co–C stretching vibrations are assigned, in decreasing frequency order, to the fundamentals  $\nu_{14}(A_{2u})$ ,  $\nu_{15}(A_{2u})$ , and  $\nu_{30}(E_u)$ , respectively. The very weak band assigned as  $\nu_{15}$  was not observed in the infrared spectrum of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ . Manning,<sup>11</sup> however, did observe this band and we include in Table I his reported frequency.

We expect the same near degeneracy of infrared- and Raman-active band "pairs" in this region as was observed in the  $\nu(\text{C}-\text{O})$  region. For bands of  $E$  symmetry, this near degeneracy is observed with, for example, the bands in the Raman spectrum of  $\text{Zn}[\text{Co}(\text{CO})_4]_2$  observed at 541, 513, 492, and 369  $\text{cm}^{-1}$  and assigned as the fundamentals  $\nu_{19}-\nu_{22}$  of  $E_g$  type correlating with the observed infrared bands at 534, 512, 488, and 365  $\text{cm}^{-1}$  of  $E_u$  symmetry.

For bands of  $A$  symmetry in this region, increased coupling with Co–M distortions and consequent interactions across the Co–M–Co framework is expected to cause rather large separations of the ir and Raman "pairs." Thus, we assign the Raman bands at 561 (Zn, Cd) and 580  $\text{cm}^{-1}$  (Hg) as  $\nu_3$ , at 463 (Zn) and 462  $\text{cm}^{-1}$  (Hg) as  $\nu_4$ , and at 426 (Zn), 431 (Cd), and 417  $\text{cm}^{-1}$  (Hg) as  $\nu_5$ , all of  $A_{1g}$  symmetry. No band assignable as  $\nu_4$  was observed for  $\text{Cd}[\text{Co}(\text{CO})_4]_2$ .

The Raman frequencies reported by Stammreich, *et al.*,<sup>7</sup> for  $\text{Cd}[\text{Co}(\text{CO})_4]_2$  in methanol solution deviate significantly from the data, obtained from powdered samples, that we report. Because of the similarity of

the Raman powder spectrum of the Cd compound to those of the Zn and Hg compounds, because of the similarity of the Raman spectra of all three compounds to their respective infrared spectra, and because of the changes observed in the  $\nu(\text{C}-\text{O})$  region of the infrared spectrum of these compounds on dissolution in more polar solvents such as methanol, we conclude that they exist in methanol, not as  $\text{M}[\text{Co}(\text{CO})_4]_2$  molecules, but as partially dissociated or solvent-complexed species.<sup>27-29</sup> Support for this conclusion comes from Stammreich's data. Stammreich<sup>30</sup> observed Raman bands at 532 and 619  $\text{cm}^{-1}$  in the spectrum of an aqueous solution of  $\text{NaCo}(\text{CO})_4$  and Edgell and Lyford<sup>31</sup> observed a band at 558  $\text{cm}^{-1}$  in the Raman spectrum of the same system. All three frequencies agree, within experimental error, with bands reported by Stammreich in the Raman spectrum of  $\text{Cd}[\text{Co}(\text{CO})_4]_2$  at 530, 560, and 619  $\text{cm}^{-1}$  and may be due to  $\text{Co}(\text{CO})_4^-$ . However, recent 5- $\mu$  spectra and conductance measurements<sup>28</sup> indicate relatively low  $\text{Co}(\text{CO})_4^-$  concentrations in methanol, so the origin of the extra bands observed by Stammreich in this solvent is not unequivocally established.

**The Low-Frequency Region.**—This spectral region is characterized by a strong Raman-active band ( $\nu_6$ ,  $A_{1g}$ ) and a strong infrared-active band ( $\nu_{16}$ ,  $A_{2u}$ ) due primarily to the symmetric and asymmetric stretching motions, respectively, of the M–Co bonds. These bands, shown in Figure 1, are easily identifiable in the observed spectra of the three compounds. The Raman-active symmetric stretching motion should be insensitive to the mass of the central metal atom; the band observed at *ca.* 165  $\text{cm}^{-1}$  in all three molecules is accordingly assigned as the fundamental  $\nu_6$ . For reasons discussed above, Stammreich's<sup>7</sup> observed value of 152  $\text{cm}^{-1}$  for  $\nu_6$  in the Cd compound is considered erroneous. The infrared-active bands assigned as  $\nu_{16}$  exhibit the expected strong dependence on the mass of M and are observed at 284, 218, and 195  $\text{cm}^{-1}$ , respectively, for the Zn, Cd, and Hg compounds.

The remainder of the bands observed in this region are due to C–Co–C and skeletal bending deformations. Four such bands are expected in the Raman (1  $A_{1g}$  + 3  $E_g$ ) and five are expected in the infrared spectrum (1  $A_{2u}$  + 4  $E_u$ ), with the "extra" infrared band being due to a bending vibration of the Co–M–Co unit which has no Raman counterpart because the M atom occupies the center of symmetry.

The spectrum of the Cd compound, in which seven of the nine predicted modes were observed, is used as the basis for assigning these low-frequency bands. The Raman band at 100  $\text{cm}^{-1}$  and the infrared band at 111  $\text{cm}^{-1}$  are assigned as  $\nu_7(A_{1g})$  and  $\nu_{17}(A_{2u})$ , respectively, and are due primarily to M–Co–C<sub>eq</sub> and C–Co–C<sub>op</sub> deformations. The remaining Raman bands at 127, 108, and 73  $\text{cm}^{-1}$  are  $\nu_{23}$ ,  $\nu_{24}$ , and  $\nu_{25}$  of  $E_g$  type; the in-

(27) In contrast to  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  which exhibits  $\nu(\text{C}-\text{O})$  at 2066 (m) and 1998 (s)  $\text{cm}^{-1}$  in methanol, the infrared spectrum of  $\text{Cd}[\text{Co}(\text{CO})_4]_2$  in this solvent contains bands at 2065 (w), 2048 (m), 1981 (s, sh), 1967 (s), 1954 (s, sh), and 1916 (vw)  $\text{cm}^{-1}$ .<sup>28</sup> The presence of solvated three- or four-coordinated cadmium species is strongly indicated by the complexity of the spectrum and by the shift of the principal bands to lower frequencies. Mays and Robb<sup>29</sup> have noted similar shifts in complexes of  $\text{Cd}[\text{M}(\text{CO})_3\text{C}_2\text{H}_5]_2$  (M = Mo, W) with nitrogen bases.

(28) J. M. Burlitch and T. Blackmore, unpublished observations.

(29) M. J. Mays and J. D. Robb, *J. Chem. Soc. A*, 561 (1969).

(30) H. Stammreich, K. Kawai, Y. Tavares, P. Krumholz, J. Behmoiras, and S. Brill, *J. Chem. Phys.*, **32**, 1482 (1960).

(31) W. F. Edgell and J. Lyford, *ibid.*, **52**, 4329 (1970).

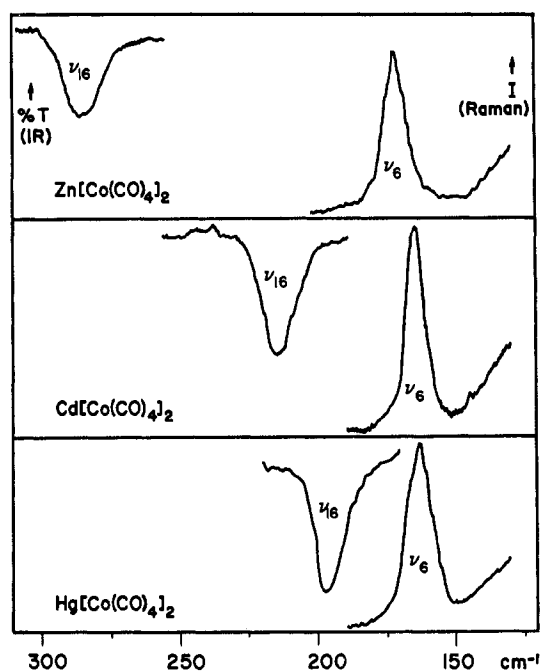


Figure 1.—Spectral comparison of the predominantly metal-metal stretching modes  $\nu_{16}(A_{2u})$ , infrared) and  $\nu_6(A_{1g})$ , Raman) in the  $M[\text{Co}(\text{CO})_4]_2$  series.

frared band at  $119\text{ cm}^{-1}$  is  $\nu_{31}$  of  $E_u$  type. These four bands and the unobserved  $\nu_{32}$  and  $\nu_{33}$  are expected to be complex mixtures of the C-Co-C<sub>ip</sub>, C-Co-C<sub>op</sub>, M-Co-C<sub>eq</sub>, and M-Co-C<sub>ax</sub> bending vibrations. The lowest frequency infrared band at  $51\text{ cm}^{-1}$  is assigned as  $\nu_{34}(E_u)$  and is primarily a Co-M-Co bending deformation.

Although fewer bands have been observed in this region for the Zn and Cd compounds, the similarities of the observed band positions to those in the Cd compound lead to the assignments given in Table I.

#### Vibrational Analysis and Molecular Force Fields

The complete infrared and Raman spectra, taken together with the similarity of these compounds, our reported work on  $M\text{Co}(\text{CO})_4$ -containing systems,<sup>32,33</sup> and the energy factoring that is observed for metal carbonyls, provide a basis for evaluating a valence force field for each of the closely related compounds in the  $M[\text{Co}(\text{CO})_4]_2$  series. The spectra of each compound were found to be independent of the physical (mull, solution) state of the sample in all regions, except for broadening of mull spectra in the  $5\text{-}\mu$  region. The similarity of solid and solution spectra is not surprising for a nonpolar, nonionic system. In the  $5\text{-}\mu$  region, data on dilute solutions in nonpolar solvents have been used since they are most free of intermolecular perturbations on intramolecular modes. The force field evaluation has been done as discussed below.

The vibrational spectrum of each molecule was computed employing the normal-coordinate analysis programs GMAT and VSBC.<sup>34</sup> The symmetry coordinates, based on valence-type internal coordinates,

were generated in the conventional manner.<sup>26,35</sup> The vibrational analysis program of Edgell and Yantis<sup>36</sup> was employed in initial force field definition.

The force fields reported here were obtained by the following procedure. First, approximate values for the  $k(\text{CO})$ 's and associated interaction constants were calculated for one  $\text{Co}(\text{CO})_4$  moiety, assumed uncoupled from the rest of the molecule, by solving the energy-factored eigenvalue problem with the average frequency of each ir-Raman spectral "pair." These values were refined and coupling across the Co-M-Co system was introduced by approximately solving the similar problem for the case of the entire C-O oscillator system uncoupled from the remainder of the molecule. At this point the values of the calculated constants for the molecule  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  were in reasonable agreement with those resorted to by Bor<sup>10</sup> based on the  $^{13}\text{C}$ O isotope absorption bands observed in the infrared spectrum. Bor's procedure, however, does not consider coupling of the C-O oscillator system with the remainder of the molecule and, as such, does not include contributions of Co-CO stretching motions to the  $\nu(\text{CO})$  modes. We have found that such motions contribute 5-10% to the total energy of the  $\nu(\text{CO})$  modes; the effect of this contribution is substantially to lower the values of several of the CO interaction force constants from the values reported by Bor.<sup>10</sup>

Next, the middle- and low-frequency spectra were computed in a perturbed localized mode calculation to approximate agreement with the observed spectra using the Edgell-Yantis program<sup>36</sup> using force field elements transferred from work on  $X_3M\text{Co}(\text{CO})_4$  compounds<sup>32,33</sup> as a starting point. The Co-M and Co-M, Co-M constants were approximated from  $\nu_6$  and  $\nu_{16}$  using a pseudotriatomic model by assigning the Co atoms an effective mass of 87 amu, which corresponds to that of Co and the axial C-O. On this basis, the initial values of  $k(\text{M-Co})$  were 1.30, 1.16, and 1.19 mdyn/Å for Zn-Co, Cd-Co, and Hg-Co, respectively. These are closer in magnitude to the final values than those based on any other approximation reported to date, but they are not sufficiently good since they do not give the correct ordering or an indication of just how similar the values actually are. We will deal with the problem of formulating more accurate localized model approximations for metal-metal stretching modes in a future paper.<sup>37</sup>

Finally, coupling between the C-O oscillator system and the remainder of the molecule was introduced and the force field refinement was carried out by first adjusting the main diagonal elements,  $F_{ii}$ , to obtain a common force field that gave an approximately correct calculated spectrum for the three compounds. This approach is suggested by the similarity of their spectra. However, the observed spectra require the three force fields to differ. Thus, analogous  $A_{1g}$  and  $E_g$  type bands in the three compounds do not coincide despite the symmetry-required exclusion of any dependence of these frequencies on the mass of the central metal. Therefore, the initial force field was perturbed sepa-

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

(33) K. L. Watters, W. M. Butler, and W. M. Risen, Jr., *ibid.*, **10**, 1970 (1971).

(34) J. H. Schachtschneider, Technical Reports No. 231-64 and 57-65, Shell Development Co., Emeryville, Calif.

(35) For a partial tabulation of the symmetry coordinates employed, see ref 11.

(36) W. F. Edgell and R. L. Yantis, unpublished work; R. L. Yantis, Sc.M. Thesis, Purdue University, 1964.

(37) K. L. Watters, J. R. Johnson, and W. M. Risen, Jr., to be submitted for publication.

TABLE III  
 M[Co(CO)<sub>4</sub>]<sub>2</sub> MOLECULAR FORCE FIELDS<sup>a</sup>

Force Field Elements <sup>b,c</sup> Constant for the Series							
$k_{r,R}$	0.735		$k_{r_{ax},\beta_{op}}$	0.15	$k_{\theta}$		0.085 <sup>d</sup>
$k_{R_{ax},R_{eq}}$	0.17		$k_{\Delta}$	0.157 <sup>d</sup>	$k_{\beta_{ip},\beta_{ip}}$		0.03
$k_{r_{ax},r_{eq}}$	0.1		$k_{\gamma_{eq}}$	0.10 <sup>d</sup>	$k_{\Delta,\Delta}$		0.007
$k'_{L,r_{ax}}$	-0.05		$k_{\gamma_{ax}}$	0.075 <sup>d</sup>			
Force Field Elements <sup>b,c</sup> Which Vary for the Series							
	Zn	Cd	Hg		Zn	Cd	Hg
$k_L^d$	1.30	1.28	1.26	$k_{L,r_{ax}}$	0.27	0.25	0.24
$k_{L,L}$	0.10	0.14	0.08	$k_{L,\gamma_{eq}}$			
				$-k_{L,\Delta_{op}}$	0.04	0.07	0.045
$k_{R_{ax}}^d$	17.47	17.38	17.40	$k_{\beta_{ax}}^d$	0.272	0.274	0.236
$k'_{R_{ax},R_{ax}}$	0.108	0.118	0.126	$k_{\beta_{ip}}^d$	0.273	0.267	0.244
$k_{R_{eq}}^d$	16.45	16.35	16.48	$k_{\beta_{op}}^d$	0.31	0.32	0.33
$k_{R_{eq},R_{eq}}$	0.100	0.061	0.078	$k_{\beta_{op},\beta_{op}}$	0.00	0.00	0.00
$k'_{R_{eq},R_{eq}}$	-0.179	-0.130	-0.149	$k'_{\beta_{op},\beta_{op}}$	0.00	0.00	0.01
$k''_{R_{eq},R_{eq}}$	0.049	0.034	0.061	$k''_{\beta_{op},\beta_{op}}$	-0.004	-0.006	-0.00
$k_{r_{ax}}^d$	2.30	2.33	2.30	$k_{\beta_{ax},\beta_{ip}}$	-0.027	-0.019	-0.027
$k'_{r_{ax},r_{ax}}$	0.130	0.098	0.155	$k_{\gamma_{eq},\gamma_{eq}}$	0.023	0.029	0.017
$k_{r_{eq}}^d$	1.90	1.93	1.94	$k'_{\gamma_{eq},\gamma_{eq}}$	0.021	0.028	0.014
$k_{r_{eq},r_{eq}}$	0.47	0.48	0.41	$k''_{\gamma_{eq},\gamma_{eq}}$	0.019	0.018	0.007
$k'_{r_{eq},r_{eq}}$	0.08	0.10	0.06	$k_{\theta,\gamma_{ax}}$	-0.012	-0.023	-0.012
$k''_{r_{eq},r_{eq}}$	0.065	0.064	0.031	$k_{\theta,\gamma_{ax}}$	-0.01	-0.02	-0.01

<sup>a</sup> The numerical values reported here are those used in calculating the spectra reported in Table I. They have been rounded off to the limits of physical significance, but for no element did the roundoff involve more than 0.005 mdyn/Å. <sup>b</sup> All force field elements in millidynes per ångström. <sup>c</sup> All internal valence coordinates are defined as positive for bond stretching or angle opening; thus all force field elements have unique signs. Internal coordinate symbols are defined in Table II, columns 1 and 2. <sup>d</sup> Diagonal element; corresponds to  $k_{\xi\xi}$  for internal valence coordinate  $\xi_i$ .

rately in each case to bring the calculated spectrum into agreement with the observed spectrum.

Numerically, the extent of calculated-observed agreement is given commonly by  $\epsilon = (\sum_i |\nu_i(\text{calcd}) - \nu_i(\text{obsd})|)/n$ , where  $n$  is the number of observed fundamentals. The  $\epsilon$  values in this work are given in Table I. However, requiring  $\epsilon$  to approach zero, once it is less than about 3 or 4 cm<sup>-1</sup>, is not a particularly meaningful measure of force field validity, because of isotopic distribution, anharmonicity, and experimental effects. At that point, more meaningful criteria include requiring that the calculated eigenvectors and potential energy contributions for each mode correspond to the character of the vibrational mode to which the observed band is assigned. Each of these criteria has been applied here.

The force fields with which the calculated frequencies given in Table I were obtained are given in Table III. As can be seen, the force fields for the three molecules are very similar, and, in fact, many of their elements are identical. Only a few elements differ significantly, and in most of these cases the differences are within the inaccuracy with which the values reported there are known. There are, however, three characteristics of the force field evaluation that require comment. First, the spectra clearly require that certain relationships exist between equivalent force constants for the series of compounds. For example, the  $\nu(\text{C-O})$  bands in the Cd[Co(CO)<sub>4</sub>]<sub>2</sub> spectra are lower in frequency than analogous bands in the Zn[Co(CO)<sub>4</sub>]<sub>2</sub> spectra, so it is to be expected that the C-O stretching force constants for the Cd molecule would be a bit lower than those for the Zn molecule. We have examined each of the trends in force constants, including the interaction constants, and find that they are consistent with the observed spectral variations. It must be reemphasized, however, that the variations in both the spectra and the force constants are relatively small.

The second characteristic of this calculation is that the diagonal force field elements for the skeletal deformations have been held to constant values while the low-frequency modes which depend on them have been fit with their interaction force constants. Since the metal-metal stretching modes, especially  $\nu_6$ , mix significantly with these deformations (the contribution of the M-Co stretching motion to the potential energy of modes  $\nu_6$ ,  $\nu_7$ ,  $\nu_{16}$ , and  $\nu_{17}$  was calculated to be, on the average, 65, 33, 100, and 5%, respectively), the validity of  $k(\text{M-M})$  values depends upon the deformation modes being accurately calculated. Thus, the fit of these modes with identical diagonal deformation force constants and small variations in interaction deformation force constants supports the calculated magnitudes of the metal-metal force constants reported here.

The third characteristic of the calculation concerns the interaction force constants. There are two types of interaction constants of interest: those of the metal-metal system with the Co(CO)<sub>4</sub> moieties and those between these moieties across the Co-M-Co system. Those of the latter type are small and are required by the observed nondegeneracy of the infrared-Raman "pairs" discussed earlier. Their required non-zero values prevent the force field from having fewer elements than that reported in Table III. Interaction constants of the former type were varied as necessary to fit the calculated spectra. For example, the value for the Co-M, Co-C<sub>ax</sub> interaction was initially set to 0.25 mdyn/Å for all three molecules on the basis of preliminary calculations and the similarity of the observed spectra. It was varied within the constraints placed by the axial Co-C stretching mode and the greatly different extents of its involvement in the Co-M stretching modes.

Interaction force constants within the Co(CO)<sub>4</sub> moieties are, for the most part, typical of those found in previous publications. Thus, the Co-C, C-O inter-

actions involving a common carbon atom have been set to 0.735 mdyne/Å, the value employed in earlier calculations for metal carbonyls.<sup>32,33,38</sup>

### Discussion

The most intriguing result of the vibrational analysis is that the three metal-metal force constants are so nearly equal. We have found that the loci of possible  $k(\text{M-Co})$  values are sufficiently closely restricted to a small region about the reported values that the trend in them, which is also supported by the experimental spectra, is probably real. However, within strictly numerical criteria for the absolute accuracy of such force constants at this level, they may be considered identical. In any event, there are not the 10-25% differences between the three  $k(\text{M-Co})$  values previously reported.<sup>7,20</sup>

The simplest description of Co-M bond in these molecules is, of course, that of a single  $\sigma$ -type covalent bond which is formally the result of  $(\text{CO})_4\text{Co} \rightarrow \text{M}$  electron-pair donation. On this basis alone and the naive assumption that the bond strengths depend only on the difference of Co and M electronegativities, one would expect the Zn-Co bond to be a bit stronger than the Cd-Co or Hg-Co bonds. Although this expectation appears to be borne out by the  $k(\text{M-Co})$  values, it is too facile.

It is straightforward to show that Co-M  $\pi$ -type bonding can exist in addition to  $\sigma$  bonding and that it may be significant. Thus, with conventional coordinate system definitions, the M  $ns$  and M  $np_z$  orbitals transform as  $A_{1g}$  and  $A_{2u}$  and form the primary M atom basis for M-Co(CO)<sub>4</sub>  $\sigma$  bonding, since  $\Gamma_\sigma(\text{Co-M-Co}) = A_{1g} + A_{2u}$ . Symmetry-proper combinations of either Co atomic orbitals or "molecular orbitals" of a pseudomolecular  $C_{3v}$  Co(CO)<sub>4</sub><sup>-</sup> construct are readily formed to complete the  $\sigma$ -bonding theory. With either description of the Co(CO)<sub>4</sub><sup>-</sup> ligand orbitals, *i.e.*, Co atomic orbitals or  $C_{3v}$  Co(CO)<sub>4</sub><sup>-</sup> pseudomolecular orbitals, there are based on this moiety orbitals which transform as  $E_u$  in the whole-molecule point group and have the proper spatial properties to overlap with the  $E_u(\text{M } np_x, np_y)$  orbital pair. Since these Co(CO)<sub>4</sub><sup>-</sup>

based  $E_u$  orbitals are formally filled and the M  $np_x, np_y$  pair is formally empty,  $\pi$ -type bonding is feasible. The resulting symmetrized basis orbitals will mix, in the eigenvalue solution, with the other  $E_u$  basis functions. From overlap considerations it is estimated that the greatest mixing will be with those generated from both axial and equatorial CO  $\pi^*$  orbitals. Since the resulting  $E_u$  molecular  $\pi$ -type orbitals extend over the entire molecule, the possible importance of  $\pi$ -type bonding in determining the  $k(\text{M-Co})$  values is seen, and the necessity for significant interaction force constants across the Co-M-Co system, such as  $k'_{7,7}$  or  $k'_{R,R}$ , is understood. The extent of  $\pi$ -type overlap is expected to be greater in the Zn compound, because of its size relationship to Co, than in the Hg compound.

The 70-eV mass spectra of the M[Co(CO)<sub>4</sub>]<sub>2</sub> compounds have been interpreted to indicate that the Zn-Co and Cd-Co bonds are substantially stronger than the Hg-Co bond, with respect to fragmentation by electron impact.<sup>22</sup> However, such a conclusion does not derive simply from the 70-eV spectra alone. Thus, the higher normalized mass spectral intensities for MCO<sub>2</sub>-containing fragments in the Zn and Cd cases than in the Hg case do not necessarily result only from relative resistance to M-Co cleavage in the three unperturbed molecules and may result, for example, from the greater ability of the Zn and Cd to stabilize, through  $\pi$  bonding, metastable polymetallic species in the mass spectrometer. We do not accept a great difference in the M-Co bond dissociation energies of the ground-state molecules as being firmly established by the mass spectral measurements reported to date. It is clear that the M-Co bond strengths, as given by  $k(\text{M-Co})$ , in the three ground-state molecules are very similar.

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