

VIBRATIONAL AND ELECTRONIC SPECTRA OF TRANSITION METAL CARBONYL COMPLEXES

IV. INFRARED SPECTRA OF SOME COBALT COMPLEXES

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SUMMARY

The infrared spectra of the compounds $\text{Hg}[\text{Co}(\text{CO})_4]_2$, $\text{Hg}[\text{Co}(\text{CO})_3\text{PR}_3]_2$, and $\text{Co}_2(\text{CO})_6(\text{PR}_3)_2$, where $\text{R} = \text{OPh}$, Ph , Et , and Bu , have been measured in the 2000 cm^{-1} and 4000 cm^{-1} regions. Assignments in the fundamental C–O stretching region have been made according to D_{3d} selection rules and are consistent with binary combination data.

INTRODUCTION

Previously, the infrared spectra of the compound $\text{Mn}_2(\text{CO})_{10}$ and its *trans*-disubstituted derivatives $\text{Mn}_2(\text{CO})_8(\text{PR}_3)_2$ were reported^{1,2}. Here, we describe the spectra of some structurally related cobalt complexes $\text{Hg}[\text{Co}(\text{CO})_4]_2$, $\text{Hg}[\text{Co}(\text{CO})_3\text{PR}_3]_2$, and $\text{Co}_2(\text{CO})_6(\text{PR}_3)_2$.

RESULTS AND DISCUSSION

$\text{Hg}[\text{Co}(\text{CO})_4]_2$

An X-ray crystallographic investigation³ of the compound $\text{Hg}[\text{Co}(\text{CO})_4]_2$ has demonstrated that its molecular structure corresponds to that shown in Fig. 1.

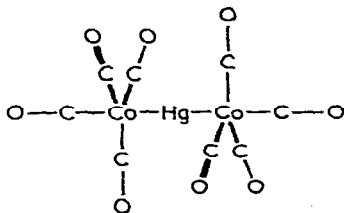


Fig. 1.

The molecule belongs, therefore, to the point group D_{3d} , and six fundamental C–O stretching modes are predicted: three ($2a_{2u} + e_u$) are infrared active and three ($2a_{1g} + e_g$) are Raman active. The corresponding symmetry coordinates are shown in Fig. 2 and the species of the nine infrared active overtones and combinations of the C–O stretching fundamentals are presented in Table 1. The infrared spectra in the 2000

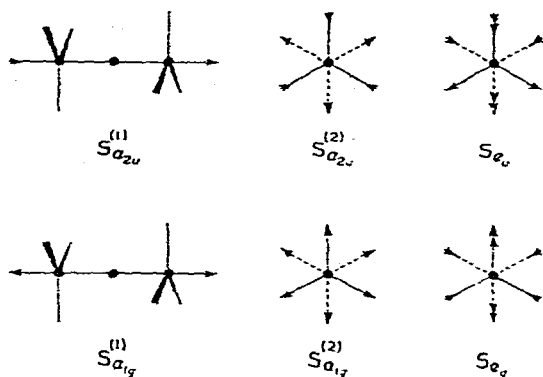


Fig. 2.

TABLE 1

INFRARED-ACTIVE BINARY COMBINATIONS AND OVERTONES FOR THE POINT GROUP D_{3d}

| | | | | |
|------------------------|-------------------|----------------|----------------|----------------|
| Fundamental components | $a_{1g} + a_{2u}$ | $a_{1g} + e_u$ | $e_g + a_{2u}$ | $e_g + e_u$ |
| Species of combination | A_{2u} | E_u | E_u | $A_{1u} + E_u$ |

and 4000 cm^{-1} regions together with previously reported vibrational data^{4,5} are given in Table 2. On the basis of the "method of oscillating dipoles", the band of

TABLE 2

THE INFRARED SPECTRUM^a OF THE COMPOUND $\text{Hg}[\text{Co}(\text{CO})_4]_2$ IN THE 2000 cm^{-1} AND 4000 cm^{-1} REGIONS

| Observed ^b (cm^{-1}) | Assignment | Calculated (cm^{-1}) |
|---|---------------------------------------|------------------------------------|
| 2005.8 | e_u | |
| 2007.3 ^c | e_u | |
| 2019.8 | $a_{2u}^{*(1)}$ | |
| 2021.7 ^c | $a_{2u}^{*(1)}$ | |
| 2071.6 | $a_{2u}^{*(2)}$ | |
| 2072.3 ^c | $a_{2u}^{*(2)}$ | |
| 1990 ^d | e_g | |
| 2030 ^d | $a_{1g}^{*(1)}$ | |
| 2107 ^d | $a_{1g}^{*(2)}$ | |
| 3978 s | $e_g + e_u$ | 3996 |
| 3994 (sh) | $e_g + a_{2u}^{*(1)}$ | 4010 |
| 4034 m | $\{ a_{1g}^{*(1)} + e_u \}$ | 4036 |
| | $\{ a_{1g}^{*(1)} + a_{2u}^{*(1)} \}$ | 4050 |
| 4059 m | $e_g + a_{2u}^{*(2)}$ | 4062 |
| 4089 s | $\{ a_{1g}^{*(1)} + a_{2u}^{*(2)} \}$ | 4102 |
| | $\{ a_{1g}^{*(2)} + e_u \}$ | 4113 |
| | $\{ a_{1g}^{*(2)} + a_{2u}^{*(1)} \}$ | 4127 |
| 4157 s | $\{ a_{1g}^{*(2)} + a_{2u}^{*(2)} \}$ | 4179 |

^a Measured in CCl_4 . ^b s=strong; m=medium; (sh)=shoulder. ^c Measured in n-heptane⁵. ^d Raman spectrum⁴.

highest intensity in the C–O stretching region is attributed to the e_u vibration; this is analogous to the assignment of the e band in the spectrum of $\text{Mn}_2(\text{CO})_{10}$. The two remaining bands at 2071.6 and 2019.8 cm^{-1} are assigned respectively to the $a_{2u}^{(2)}$ and

$a_{2u}^{(1)}$ modes. The ratio of the intensities of these bands is approximately 10. This large ratio suggests that normal coordinates associated with these vibrations cannot be equated with the isolated $a_{2u}^{(2)}$ and $a_{2u}^{(1)}$ symmetry coordinates. In this sense, the assignment has only a formal significance; we designate these modes, therefore, $a_{2u}^{*(2)}$ and $a_{2u}^{*(1)}$. The Raman active mode of highest frequency would clearly be that termed $a_{1g}^{(2)}$, but again it is preferable to emphasise that this vibration is probably not described by $S(a_{1g})^{(2)}$. Hence it is labelled $a_{1g}^{*(2)}$. Polarisation measurements were only reported for the derivative $Cd[Co(CO)_4]_2$, but by analogy, the Raman line observed at 2030 cm^{-1} in the spectrum of the mercury compound may be assigned to the other a_{1g} mode, designated $a_{1g}^{*(1)}$; the remaining band then corresponds to the e_g vibration. In the 4000 cm^{-1} region, the six bands may be tentatively assigned according to the scheme given in Table 2. A convincing assignment is impaired by anharmonicity and the absence of certain expected bands.

$Hg[Co(CO)_3PR_3]_2$ and $Co_2(CO)_6(PR_3)_2$

The infrared spectra of the compounds $Hg[Co(CO)_3PR_3]_2$ and $Co_2(CO)_6(PR_3)_2$ ($R = OPh, Ph, Et, \text{ and } Bu$) in the 2000 cm^{-1} region and of the compounds $Hg[Co(CO)_3PR_3]$ ($R = OPh, Et, \text{ and } Bu$) and $Co_2(CO)_6(PR_3)_2$ ($R = Et \text{ and } Bu$) in the 4000 cm^{-1} region are given in Tables 3 and 4. The simplicity of the spectra of

TABLE 3

INFRARED SPECTRA^a OF TERTIARY PHOSPHINE DERIVATIVES (cm^{-1})

| Compound | Assignment | | |
|--------------------------|------------|--------|---------------------------|
| | a_{2u} | e_u | |
| $Co_2(CO)_6[P(OPh)_3]_2$ | 2000.8 | 1981.2 | |
| $Co_2(CO)_6(PPh_3)_2^b$ | 1968.1 | 1946.3 | |
| $Co_2(CO)_6(PEt_3)_2$ | 1969.1 | 1948.8 | |
| $Co_2(CO)_6(PBu_3)_2$ | 1968.5 | 1948.0 | |
| $Hg[Co(CO)_3P(OPh)_3]_2$ | 2022.5 | 1972.5 | 1900 (sh), 2012.1, 2049.6 |
| $Hg[Co(CO)_3PPh_3]_2^b$ | 1990.0 | 1935.8 | |
| $Hg[Co(CO)_3PEt_3]_2$ | 1985.6 | 1943.3 | |
| $Hg[Co(CO)_3PBu_3]_2$ | 1948.8 | 1942.3 | |

^a Measured in CCl_4 . ^b Measured in nujol.

the mercury compounds in the fundamental C–O stretching region suggests strongly that the substituent ligands are symmetrically disposed. Indeed, if it is assumed that the staggered configuration of the parent is retained then the C–O stretching vibrations may be assigned according to the D_{3d} point group. The spectra of compounds of the type $Co_2(CO)_6(PR_3)_2$ are very similar and it may be assumed that they have

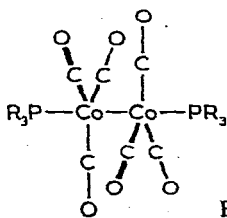


Fig. 3.

TABLE 4

INFRARED SPECTRA^a OF THE COMPOUNDS $\text{Co}_2(\text{CO})_6(\text{PR}_3)_2$ AND $\text{Hg}[\text{Co}(\text{CO})_3\text{PR}_3]_2$ IN THE 4000 cm^{-1} REGION

| Compound | Observed (cm^{-1}) | Assignment | Calcd. Raman-active component (cm^{-1}) |
|---|----------------------------------|---|--|
| $\text{Co}_2(\text{CO})_6(\text{PEt}_3)_2$ | 3859 s | $e_u + e_g$ | 1910 |
| | 3878 (sh) | $a_{2u} + e_g$ | 1909 |
| | 3967 s | $e_u + a_{1g}$ $a_{2u} + a_{1g}$ | 2018 |
| $\text{Co}_2(\text{CO})_6(\text{PBu}_3)_2$ | 3855 s | $e_u + e_g$ | 1907 |
| | 3881 (sh) | $a_{2u} + e_g$ | 1912 |
| | 3965 s | $e_u + a_{1g}$ $a_{2u} + a_{1g}$ | 2017 |
| $\text{Hg}[\text{Co}(\text{CO})_3\text{P}(\text{OPh})_3]_2$ | 3903 s | $e_u + e_g$ | 1930 |
| | 3964 s | $a_{2u} + e_g$ | 1941 |
| | 4005 s | $e_u + a_{1g}$ | 2032 |
| | 4069 s | $\text{P}(\text{OPh})_3$ $a_{2u} + a_{1g}$ | |
| $\text{Hg}[\text{Co}(\text{CO})_3\text{PEt}_3]_2$ | 3860 s | $e_u + e_g$ | 1917 |
| | 3907 s | $a_{2u} + e_g$ | 1921 |
| | 3958 s | $e_u + a_{1g}$ | 2015 |
| | 3991 w | $a_{2u} + a_{1g}$ | 2015 |
| $\text{Hg}[\text{Co}(\text{CO})_3\text{PBu}_3]_2$ | 3854 s | $e_u + e_g$ | 1912 |
| | 3906 s | $a_{2u} + e_g$ | 1921 |
| | 3946 s | $e_u + a_{1g}$ $a_{2u} + a_{1g}$ | 2004 |

^a Measured in CCl_4 .

the related structure shown in Figure 3. The eclipsed configuration D_{3h} cannot be excluded⁶, but is less likely when the overtone and combination data are considered also; for this point group, six infrared-active binary combinations would be expected. Although the absence of bands is not a good structural criterion, it is clear that the spectra in the 4000 cm^{-1} region is more readily assigned if the staggered configuration is accepted. The D_{3d} symmetry species ($a_{1g} + a_{2u} + e_g + e_u$) of the fundamental C–O stretching frequencies, the corresponding symmetry coordinates and the activity of the binary combinations may be derived from those of the compound $\text{Hg}[\text{Co}(\text{CO})_4]_2$ by neglecting the axial C–O groups. From considerations analogous to those used in the discussion of the spectrum of the compound $\text{Hg}[\text{Co}(\text{CO})_4]_2$, the band of higher intensity has been assigned to the e_u vibration. The low intensity band at higher frequency may be clearly assigned to the a_{2u} mode. The overtone and combination data for all of the compounds investigated are similar. Their profile suggests that the two bands of lowest energy may be attributed to a combination of the a_{2u} and e_u vibrations with another common fundamental vibration. If it is assumed that the C–O stretching frequency of highest energy is the totally symmetric a_{1g} mode, then these combination bands may be assigned to $(a_{1g} + e_u)$ and $(a_{1g} + a_{2u})$. The third combination band is readily assigned, but the binary combination $(a_{1g} + a_{2u})$ was not observed. Neglecting anharmonicity effects, some Raman-active fundamental C–O

stretching frequencies may be estimated from these data and are also listed in Table 4. In particular, the overtone and combination spectrum of the compound $\text{Hg}[\text{Co}(\text{CO})_3\text{-P}(\text{OPh})_3]_2$ is consistent with the assignment of the weak band at 2049.6 cm^{-1} to the a_{1g} vibration. Clearly, the D_{3d} selection rules are not wholly appropriate to this molecule and no explanation can be offered for the other weak absorptions.

EXPERIMENTAL

Preparation of complexes

The compounds $\text{Hg}[\text{Co}(\text{CO})_4]_2$, $\text{Hg}[\text{Co}(\text{CO})_3\text{PR}_3]_2$, and $\text{Co}_2(\text{CO})_6(\text{PR}_3)_2$ were prepared by established methods⁷⁻¹². Analyses are presented in Table 5.

TABLE 5

ANALYTICAL DATA

| Compound | Analysis (%) | | | | | |
|--|--------------|-----|------|-------|-----|------|
| | Calcd. | | | Found | | |
| | C | H | P | C | H | P |
| $\text{C}_8\text{Co}_2\text{HgO}_8$ | 17.7 | 0.0 | | 17.9 | 0.0 | |
| $\text{C}_{42}\text{H}_{30}\text{Co}_2\text{HgO}_{12}\text{P}_2$ | 45.6 | 2.7 | 5.6 | 45.7 | 2.6 | 5.6 |
| $\text{C}_{42}\text{H}_{30}\text{Co}_2\text{HgO}_6\text{P}_2$ | 49.9 | 3.0 | 6.1 | 49.7 | 3.3 | 6.0 |
| $\text{C}_{30}\text{H}_{54}\text{Co}_2\text{HgO}_6\text{P}_2$ | 40.4 | 6.1 | 7.0 | 40.1 | 6.0 | 6.9 |
| $\text{C}_{18}\text{H}_{30}\text{Co}_2\text{HgO}_6\text{P}_2$ | 29.9 | 4.2 | 8.6 | 30.1 | 4.2 | 8.7 |
| $\text{C}_{42}\text{H}_{30}\text{Co}_2\text{O}_{12}\text{P}_2$ | 55.6 | 3.3 | 6.8 | 55.5 | 3.5 | 6.9 |
| $\text{C}_{42}\text{H}_{30}\text{Co}_2\text{O}_6\text{P}_2$ | 62.2 | 3.7 | 7.6 | 62.1 | 3.9 | 7.4 |
| $\text{C}_{30}\text{H}_{54}\text{Co}_2\text{O}_6\text{P}_2$ | 52.2 | 7.9 | 9.0 | 51.9 | 7.9 | 8.8 |
| $\text{C}_{18}\text{H}_{30}\text{Co}_2\text{O}_6\text{P}_2$ | 41.4 | 5.8 | 11.9 | 41.5 | 6.7 | 11.8 |

Infrared spectra

Spectra were recorded using a Unicam SP100 spectrometer according to methods described previously^{2,13}.

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