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INFRARED SPECTROSCOPIC STUDIES ON METAL CARBONYL COMPOUNDS

XV*. ASSIGNMENTS OF THE C–O STRETCHING INFRARED SPECTRA AND FORCE CONSTANTS OF SOME (ARENE)$Co_4(CO)_9$ COMPLEXES

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SUMMARY

The preparation and the IR study of some compounds of the type (arene)$Co_4(CO)_9$ (where arene denotes toluene, tetrahydronaphthalene, or mesitylene) are reported. The C–O stretching bands in the spectra of the compounds have been assigned, and the force and interaction constants calculated. The relative band intensities have been used in a tentative determination of bond angles and relative dipole moment gradients. The "anomalously" high intensity of the $\nu_3(E)$ bands is discussed in detail, and an induced dipole moment mechanism is suggested to account for it.

There is still no satisfactory interpretation of the infrared spectra in the C–O stretching region of tetrametal dodecacarbonyls having C_{3v} molecular symmetry (*e.g.*, $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$, $Co_3FeH(CO)_{12}$), in spite of the considerable number of papers in this field[1–9]. Recently we have been reinvestigating this problem using the ^{13}CO-enriched spectra of $Co_4(CO)_{12}$[10,11]. In the initial stages of this study we found the analysis of the spectra of the compounds (arene)$Co_4(CO)_9$ (I)[12] to be very helpful in elucidating the assignment problems for $Co_4(CO)_{12}$, and clarifying, at least partially, the marked discrepancies between our preliminary force and interaction constants and those published recently by Cariati *et al.*[9].

The preparation of compounds (I) (where arene is C_6H_6, toluene, and mesitylene) was first reported by Pauson *et al.*[12], but they did not give details of the reaction conditions or of their IR spectra.

EXPERIMENTAL

Tetracobalt dodecacarbonyl was prepared by refluxing dicobalt octacarbonyl

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* For Part XIV see preceding paper.

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TABLE 1

REACTION CONDITIONS FOR THE PREPARATION OF SOME (ARENE)$Co_4(CO)_9$ COMPOUNDS

Arene	*Time (h)*	*Temperature (°C)*
Toluene	5–6	110
Tetrahydronaphthalene	2	100
Mesitylene	3	100

in petroleum ether (b.p. 50–60°, distilled from Na under nitrogen), and was recrystallized from the same solvent. Some of the cobalt octacarbonyl was a commercial product supplied by Alpha Inorganics, and the remainder was prepared and kindly donated by Prof. P. Chini of Milan. The aromatic hydrocarbons were analytical grade reagents and were used without further purification.

EXPERIMENTAL

Preparations of the (arene)$Co_4(CO)_9$ compounds were usually carried out by dissolving about 300 mg of $Co_4(CO)_{12}$ in 10–20 ml of the aromatic solvent, and heating the stirred solutions under nitrogen. Heating temperatures and reaction times are shown in Table 1.

The original brown colour of the solutions turned slowly to dark olive-green, and there was extensive decomposition. IR spectroscopic monitoring showed that the compounds of type (I) were the only soluble products formed in the reactions. After the reaction times shown the aromatic solvents were removed *in vacuo*, and the solid residue was dissolved in hexane, and purified by chromatography on a silica gel column using a 30/70 benzene/hexane mixture as eluant. Compounds (I) were eluted as dark olive-green zones. Evaporation of the solvent *in vacuo* gave dark green oily products which, after recrystallization from n-hexane, gave black crystals. Yields were not determined since our object was only to obtain good samples for spectroscopic studies.

One of the products, (tetrahydronaphthalene)$Co_4(CO)_9$, was identified by mass spectroscopy. The complete analogy of the IR spectra left no doubt about the identity of the other two compounds.

Infrared spectra were run in n-hexane solutions, with a Perkin–Elmer 621 spectrophotometer, using an expanded linear wave number scale ($1 \text{ cm} \equiv 10 \text{ cm}^{-1}$). Relative band intensities were determined from spectra scanned with a linear absorptivity scale.

SPECTRA AND STRUCTURE

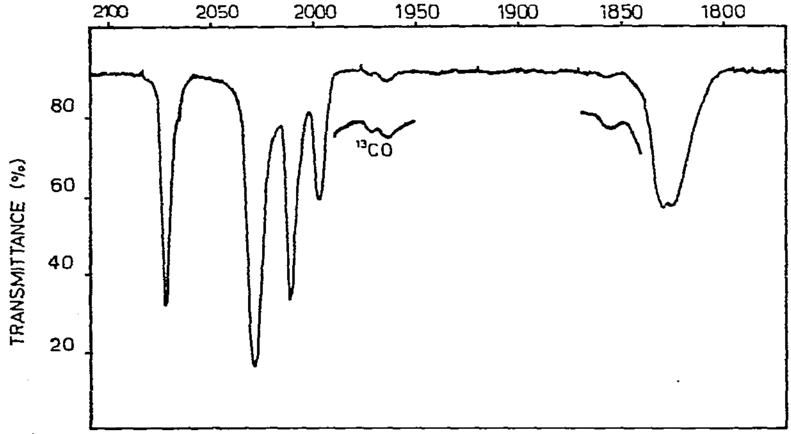
The three compounds have very similar IR spectra. In Table 2 we report the wave number values and the relative intensities of three of the terminal bands. The strongest band is labelled "vs"; the omission of this band from the quantitative intensity considerations is explained below. In Fig. 1 we show a representative spectrum.

TABLE 2

C–O STRETCHING FREQUENCIES[a] (in cm^{-1}) OF (ARENE)$Co_4(CO)_9$ COMPOUNDS

Arene	*Terminal* $\nu(^{12}C\text{–}O)$ *frequencies*[b]				$\nu(^{13}C\text{–}O)$ *bands*		*Bridging* $\nu(^{12}C\text{–}O)$ *frequencies*	
	$\nu_1(A_1)$	$\nu_3(E)$	$\nu_2(A_1)$	$\nu_4(E)$			(A_1)	(E)
Toluene	2074.5 (6.6)	2031.2 (vs)	2013.0 (10)	1999.8 (4.1)	1973.5	1966.5		1829.0
Tetrahydronaphthalene	2073.1 (7.6)	2029.4 (vs)	2011.8 (10)	1998.6 (4.1)	1972.0	1965.5	1856	1829–1825 (doublet)
Mesitylene	2072.0 (8.7)	2028.8 (vs)	2009.6 (10)	1996.8 (4.7)	1970.0	1962.0		1829.0

[a] The accuracy for the terminal bands is ±0.3 cm^{-1}, and for the isotopic and bridging bands is ±0.5 cm^{-1}. [b] The integrated intensities are in parentheses and are relative to the value of 10 assigned to band ν_2. For the strongest band, ν_3, no numerical value is given, for reasons discussed in the text.



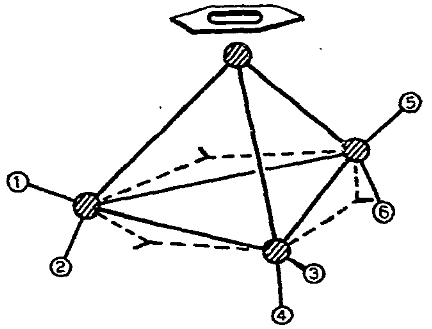


Fig. 1. IR spectrum of (tetralin)$Co_4(CO)_9$ in the C–O stretching region solvent: n-hexane. Insets correspond to higher concentration.

Fig. 2. Suggested structure[12] of the (arene)$Co_4(CO)_9$ compounds and the numbering scheme of the CO ligands.

The observed number (4 terminal + 1 or 2 bridging) of the ν(CO) bands is in agreement with the selection rules for compounds having the structure shown in Fig. 2[12], which is derived from that of $Co_4(CO)_{12}$ with the three apical CO groups replaced by a sandwich-bonded arene ligand. Neglecting the symmetry lowering effect of two of the aromatic ligands used, this structure belongs to point group C_{3v} (like $Co_4(CO)_{12}$ itself), requiring $2A_1+2E$ bands in the terminal and $1A_1+1E$ in the bridging region.

With mesitylene even the overall symmetry of the molecule is C_{3v}. We were curious to see the effect of the less symmetric arenes, mainly to determine whether they were capable of splitting the E bands and thus of facilitating the assignment. (This type of E-splitting has been reported, *e.g.*, for some (arene)$Cr(CO)_3$ compounds[13].)

We found evidence for this symmetry-lowering effect only with tetralin, and even in this case it is reflected only in the bridging region. The toluene derivative showed no such effect.

In the tetralin compound we observed not only the splitting of the bridging *E* band (of 3 cm^{-1}), but also found that the other band (A_1) gains some intensity. This absorption cannot be observed in the spectra of the other two compounds, presumably because of the planarity of the basal $Co_3(CO_{\text{bridge}})_3$ entity. This higher "sensitivity" of the bridging region to asymmetry, as compared with the terminal section of the spectrum, is reflected also in the ^{13}CO-enriched spectra of $Co_4(CO)_{12}$[10,11], and in the spectrum of $Co_2Rh_2(CO)_{12}$[14].

In Table 2 we also show the low-frequency ^{13}CO satellites of the terminal region. These were obtained from the spectra of highly concentrated solutions, without isotopic enrichment. One of these bands belongs to the "equatorially", the other one to the "axially" ^{13}C-substituted molecules.

ASSIGNMENTS AND METHOD OF CALCULATION

The numbering scheme of the terminal ligands is shown in Fig. 2. As far as the interactions between terminal and bridging CO ligands are concerned, we were able to show[15] in the case of $Co_3(CO)_4(SCH_3)_5$ and $Co_4(CO)_{12}$ that it is effectively impossible to prove, even using the isotopic frequencies, that these interactions have non-zero values. However, values arbitrarily chosen for these types of interaction constants between 0 and 0.20 mdyn/Å influenced the terminal force and interaction constants only in the third decimal place, and thus their effect can be neglected. Thus we have set equal to zero all the terminal-bridge interactions in the present study also. Moreover, we limited ourselves to the terminal part of the spectrum, since the bridging A_1 band did not show up for the toluene and mesitylene compound even in highly concentrated solutions.

After neglecting the bridging interactions, we have only two sets of equivalent CO ligands; those labelled 1, 3, and 5 we shall refer to as "equatorial", and those labelled 2, 4, and 6 as "axial" ones.

The terminal C–O stretching symmetry coordinates were defined as follows:

$$\begin{aligned}
&\text{Species } A_1 \begin{cases} R_1 = 3^{-2}(\Delta r_1 + \Delta r_3 + \Delta r_5) \\ R_2 = 3^{-2}(\Delta r_2 + \Delta r_4 + \Delta r_6) \end{cases} \\
&\text{Species } E \begin{cases} R_{3a} = 6^{-2}(2\Delta r_1 - \Delta r_3 - \Delta r_5) \\ R_{3b} = 2^{-2}(\Delta r_3 - \Delta r_5) \\ R_{4a} = 6^{-2}(2\Delta r_2 - \Delta r_4 - \Delta r_6) \\ R_{4b} = 2^{-2}(\Delta r_4 - \Delta r_6) \end{cases}
\end{aligned} \qquad (1)$$

The force and interaction constants in a CO-factored model are listed in Table 3. It will be seen that there are 6 constants to be determined from the 4 frequencies, but with the use of the two isotopic frequencies as additional data, the problem is soluble.

Having two second order species, we found it convenient to use our[16] "cos *β*

TABLE 3

THE MATRIX OF THE FORCE AND INTERACTION CONSTANTS

Ligand number	1	2	3	4	5	6
1	K_{eq}	i_{cis}	i_{ee}	i_{ea}	i_{ee}	i_{ea}
2		K_{ax}	i_{ea}	i_{aa}	i_{ea}	i_{aa}
3			K_{eq}	i_{cis}	i_{ee}	i_{ea}
4				K_{ax}	i_{ea}	i_{aa}
5	(symmetrical)				K_{eq}	i_{cis}
6						K_{ax}

parameter method"* for the calculations, in the way we used with success for the dinuclear carbonyls $Hg[Co(CO)_4]_2$[20a] and $Mn_2(CO)_{10}$[20b]. The excellent agreement of our results on $Mn_2(CO)_{10}$ with those subsequently obtained by Adams *et al.*[21] by direct laser Raman measurements provides additional evidence of the validity of the use of the same numerical value of the parameter $\cos\beta$ in both species of second order (*cf.* eqn. (2) in ref. 20a).

This assumption seems to be justified in all cases where the *local* way of symmetrical and antisymmetrical couplings, *i.e.*, within one $M(CO)_n$ entity, is the same for both species of second order, and the resulting modes differ only in the different types (symmetric, antisymmetric, or degenerate, respectively) of coupling of the local ν(C–O) modes.

The force constants *vs.* $\cos\beta$ equations in terms of the $y_i = \lambda_i/\mu(\text{CO})$ values are thus as follows:

$$\begin{aligned}
K_{eq} &= (y_1+y_2+2y_3+2y_4+(y_1-y_2+2y_3-2y_4)\cdot\cos\beta)/6\\
K_{ax} &= (y_1+y_2+2y_3+2y_4-(y_1-y_2+2y_3-2y_4)\cdot\cos\beta)/6\\
i_{cis} &= (y_1-y_2+2y_3-2y_4)\cdot\sin\beta/6\\
i_{ee} &= (y_1+y_2-y_3-y_4+(y_1-y_2-y_3+y_4)\cdot\cos\beta)/6\\
i_{aa} &= (y_1+y_2-y_3-y_4-(y_1-y_2-y_3+y_4)\cdot\cos\beta)/6\\
i_{ea} &= (y_1-y_2-y_3+y_4)\cdot\sin\beta/6
\end{aligned} \tag{2}$$

The definition of the symmetry coordinates, and our usual choice of the numbering of the frequencies according to which $\nu_1 > \nu_2$ (species A_1) and $\nu_3 > \nu_4$ (species E), would mean assigning ν_1 and ν_3 to the equatorial, and ν_2 and ν_4 to the axial types of C–O vibrations, if there were no coupling between these symmetry coordinates (*i.e.*, $\cos\beta = +1.0$ or $\phi = 0°$ [16,18]).

In the assignment of the four terminal bands there were only two possibilities to be considered, since the highest frequency always belongs to the in-phase vibration of the totally symmetric species (in this case A_1), and the strongest band is always of the type E in rotational type point groups. The assignment of the two lower bands

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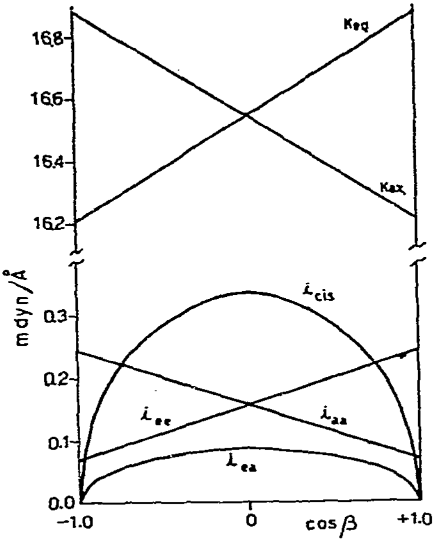
* As indicated by Haines and Stiddard[17] this method of calculation is closely related to methods published independently by Bau, Braterman and Kaesz[18], and by Manning and Miller[19]; the following relationships being valid between our parameter β[16], the ϕ-value of Bau *et al.*[18], and the ρ and p values of Manning and Miller[19]: $\beta = 2\phi$, $\rho = \tan\phi$ and $p = \tan 2\phi = \tan\beta$.



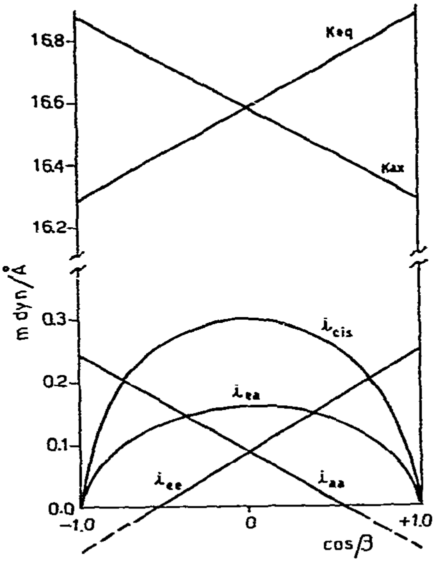


Fig. 3. Force constants *vs.* cos β diagram for assignment (*i*) (arene = tetralin).

Fig. 4. Force constants *vs.* cos β diagram for assignment (*ii*) (arene = tetralin).

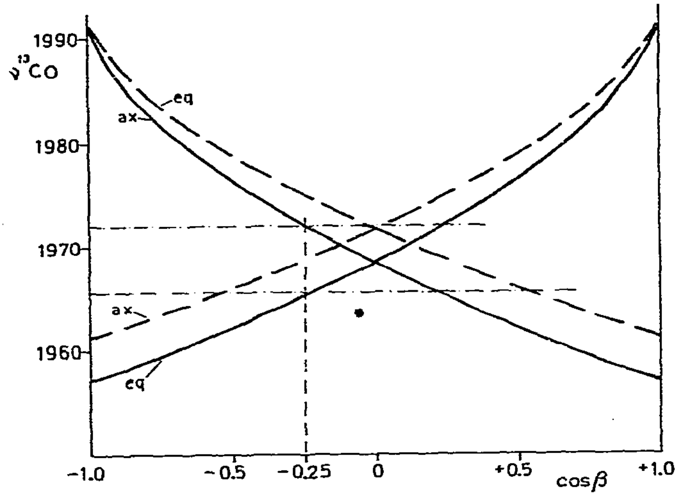


Fig. 5. The calculated lowest ^{13}CO isotopic frequencies *vs.* cos β (solid lines: assignment (*i*); broken lines: assignment (*ii*); the horizontal –·–·– lines correspond to the observed values).

was decided on the basis of calculations. The results obtained with the two possible assignments:

(*i*): A_1(i.p.) $>E$(i.p.) $>A_1$(o.p.) $>E$(o.p.) and

(*ii*): A_1(i.p.) $>E$(i.p.) $>E$(o.p.) $>A_1$(o.p.)

are shown graphically in Figs. 3, 4, and 5. (The labels (i.p.) and (o.p.) stand for *in-phase* and *out-of-phase* coupling of the equatorial and axial type symmetry coordinates, respectively.) It will be seen that assignment (*ii*) gives no agreement with the observed isotopic frequencies (Fig. 5), and also that the relative values of the interaction constants i_{ee}, i_{aa}, and i_{ea} are much less reasonable than those with assignment (*i*). This assignment, in which the band around 2010 cm^{-1} belongs to species A_1 and the lowest band at about 1998 cm^{-1} to species *E*, gave acceptable interaction constants and complete agreement with both observed isotopic bands.

RESULTS

The calculations for all three compounds gave $\cos\beta = \pm 0.25$ (± 0.05), and a negative sign was selected on the basis of the band intensities (see next section). Using this value we obtained agreement within ± 1 cm^{-1} with the observed $^{13}C-O$ frequencies. The higher of these frequencies (1970–1973 cm^{-1}) belongs to the axially-, and the lower (1962–1966 cm^{-1}) to the equatorially-^{13}C-substituted molecular species. This latter band is the more intense (see Fig. 1).

The negative value of the parameter $\cos\beta$ means that the contribution of the axial symmetry coordinates in the higher frequency modes is stronger than that of the equatorial ones, in contrast to the original assignment between R_i's and ν_i's, *i.e.*, L_{12} becomes greater than L_{11} ($=L_{22}$). In quantitative terms, for species A_1, using eqn. (38) of ref. 16, we obtain:

$$\begin{aligned} Q_1 &= 0.61\,R_1 + 0.79\,R_2 \\ Q_2 &= -0.79\,R_1 + 0.61\,R_2 \end{aligned} \tag{3}$$

The force and interaction constants obtained with $\cos\beta = -0.25$ from eqns. (2) for the three compounds investigated are shown in Table 4. There is a relatively small difference (~0.17 mdyn/Å) between the K_{eq} and K_{ax} values, the latter being higher. We do not wish to comment on these values until the final force constants of $Co_4(CO)_{12}$ have been determined.

The interaction constants, however, merit some comment. The "direct" interaction, i_{cis}, between geminal axial and equatorial CO groups has a value of 0.33 mdyn/Å, which is in the usual range for this type of constant. (For comparison the CO–CO interaction in $(C_6H_6)Cr(CO)_3$ has the value of 0.35 mdyn/Å.) Keeping in mind that as the values of *K*(CO) decrease under the influence of a ligand which is a poorer π-acceptor than CO, the interaction constants increase[22], we can predict a "normal" value of 0.24–0.32 mdyn/Å for this interaction in the unsubstituted $Co_4(CO)_{12}$. This is in sharp contrast to the value of 0.0939 mdyn/Å, reported by Cariati *et al.*[9].

TABLE 4

C–O FACTORED FORCE AND INTERACTION CONSTANTS (mdyn/Å) OF (ARENE)$Co_4(CO)_9$ COMPOUNDS

Arene	K_{eq}	K_{ax}	i_{cis}	i_{ee}	i_{aa}	i_{ea}
Toluene	16.47	16.65	0.33	0.13	0.17	0.08
Tetralin	16.46	16.63	0.33	0.13	0.18	0.08
Mesitylene	16.44	16.61	0.33	0.13	0.18	0.08

The three types of "indirect" interactions, CO–C′O′, between CO groups bonded to different metal atoms, have distinctly different values, and it would be a very rough approximation to suppose them to be *a priori* equal. This simplification has been applied by some authors[23] to this type of indirect interaction (or perturbation[23]) constants in some binuclear iron carbonyl derivatives. The values obtained are again within the usual range. The through-space mechanism for this type of interaction[24–26], at least in the CO-factored approximation*, is correctly reflected by their relative magnitudes: the larger the distance between the interacting groups the lower is their (still positive) value.

BAND INTENSITIES

In the present study the relative band intensities not only served for the tentative determination of bond angles and relative dipole moment gradients of the two different types of CO ligands, but also established the sign of cos β, and thus served to decide between two equally acceptable sets of force constants. In all cases of metal carbonyls in which the number of CO ligands belonging to the two different sets is equal, we have the same ambiguity in the force constant calculations: we obtain equal but interchanged numerical values for the force constants and for certain pairs of interaction constants, and also the assignment of the isotopic satellites interchanges if the symmetry coordinates are assigned in the opposite way to the frequencies of the same species. In terms of our parameter method, this means that in these cases, even by the use of the isotopic frequencies, one can obtain only the absolute value of cos β (*i.e.*, one cannot distinguish between ϕ and $90^\circ - \phi$ by the method of Bau *et al.*[18]). Changing the sign of the determined numerical value (see Fig. 5) has the effect of interchanging the L_{ij} coefficients in the Q_j *vs.* R_i equations; interchanging K_{ax} with K_{eq}, and i_{ee} with i_{aa}; and of attributing the higher isotopic satellite to the equatorially substituted molecule**.

This ambiguous "symmetry" in the mathematical solution (reflected also in Figs. 3, 4, and 5) does not, however, extend to the band intensities: the calculated values for the positive or negative cos β values are distinctly different, as shown in Fig. 6. In that Figure we show the band intensities *vs.* cos β calculated with one final set of bond angles and of the μ'_{eq}/μ'_{ax} ratio of the tetralin derivative.

Although the bond angles α_1 and α_2 (see Fig. 7) and the dipole moment gradients μ'_{eq} and μ'_{ax} have a considerable influence on the calculated values of the intensities, the trend of these "intensity *vs.* cos β" curves is the same for all three arene compounds and for a given choice of the symmetry coordinates: I_1 and I_4 become very low, even zero, in the positive part of the cos β scale, and I_2 and I_3 there attain their highest values (where I_i stands for the intensity of the ν_i band). The sum of two calculated

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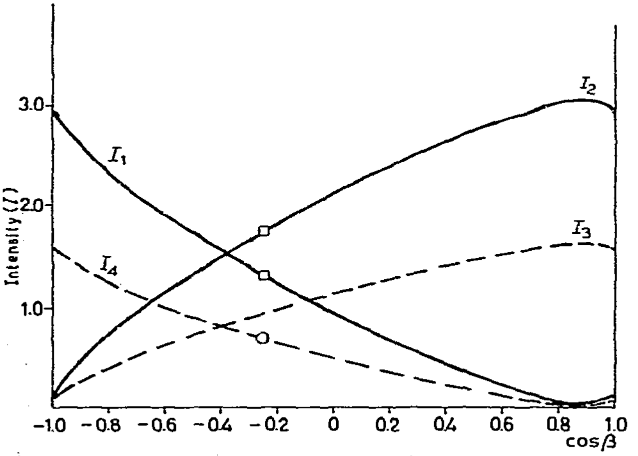
* We are, of course, aware of the justified criticism[24,27,28] of assumption of simplified force fields from the strict physical point of view. In metal carbonyl spectroscopy, however, their application has proved to be very useful[29]. We consider these force and interaction constants from the practical point of view as quantities analogous to the chemical shifts and coupling constants, respectively, in nuclear magnetic resonance spectroscopy.

** Another example of a molecule with this type of ambiguous solution is presented by the $X_2Fe(CO)_4$ compounds also studied, after isotopic enrichment, by Johnson *et al.*[30]. These compounds also have equal numbers of equatorial and axial CO groups.

intensities within a species, *i.e.*, I_1+I_2 and I_3+I_4, respectively, remains constant for a given geometry and μ' values.

The intensity calculations were performed by summarizing vectorially the local oscillating dipoles[31,32] along the coordinate axes, taking their squares, and summarizing the three intensity components. The equations are given in Table 5. The C_{ij} values are the terms of the eigenmatrix (where the index i stands for the column, *i.e.*, for a vibrational mode, and j stands for the row, *i.e.*, for the ordinal number of the ligands) and the final values are listed in Table 6. Of course, in the case of the A_1 modes only I_z, and with the E modes only $I_{x,y}$ had non-zero values.



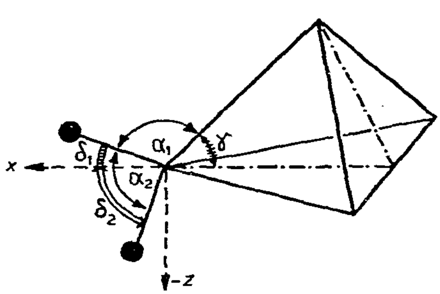


Fig. 6. Calculated intensities *vs*. cos β (arene = tetralin).

Fig. 7. Definition of bond angles.

TABLE 5

INTENSITY EQUATIONS OF THE (ARENE)$Co_3(CO)_9$ TYPE COMPOUNDS[a]

$$I_{ix}=\{[C_{i1}-0.5(C_{i3}+C_{i5})]\cos\delta_1\cdot\mu'_{rel}+[C_{i2}-0.5(C_{i4}+C_{i6})]\cos\delta_2\}^2$$
$$I_{iy}=0.75[(C_{i3}-C_{i5})\cos\delta_1\cdot\mu'_{rel}+(C_{i4}-C_{i6})\cos\delta_2]^2$$
$$I_{iz}=[(C_{i1}+C_{i3}+C_{i5})\sin\delta_1\cdot\mu'_{rel}-(C_{i2}+C_{i4}+C_{i6})\sin\delta_2]^2$$
$$I_i=I_{ix}+I_{iy}+I_{iz}$$

[a] δ_1 and δ_2 are the angles between the equatorial (or axial, respectively) ligands and the Co_3 basal plane, as shown in Fig. 7.

As mentioned earlier, the intensity of the strongest band, I_3, which belongs to an in-phase coupled E mode, was not considered. We suggest, as an explanation of the anomalously high intensity of this band, that in this type of vibration a strong dipole moment is generated in the extreme positions of the stretching vibrations, as indicated in Fig. 8. In the case of the dinuclear $M_2(CO)_{10}$ compounds (M = Mn, Tc, Re), the higher B_2 mode (ν_3) has an anomalously high intensity, and Cotton and Wing[33] were the first authors to explain this phenomenon by postulating an induced dipole moment in the direction of the M–M bond (z axis of the $M_2(CO)_{10}$ compounds).

TABLE 6

NUMERICAL VALUES FOR THE TERMS C_{ij} OF THE EIGENMATRIX OF $\cos\beta = -0.25$

	j					
	1	2	3*a*	3*b*	4*a*	4*b*
C_{i1}	0.3535	0.4664	−0.2500	0.4330	−0.3228	0.5590
C_{i2}	0.4664	−0.3535	−0.3227	0.5590	0.2500	1330
C_{i3}	0.3535	0.4664	−0.2500	−0.4330	−0.3228	−0.5590
C_{i4}	0.4664	−0.3535	−0.3228	−0.5590	0.2500	0.4330
C_{i5}	0.3535	0.4664	0.5000	0.0000	0.6455	0.0000
C_{i6}	0.4664	−0.3535	0.6455	0.0000	−0.5000	0.0000

In our experience this effect is observed for all pure di- and polynuclear metal carbonyls, and also in a considerable proportion of their substituted derivatives, and we think that the Cotton–Wing explanation is qualitatively valid*.

It is clear that in the case of the (arene)$Co_4(CO)_9$ compounds the direction of the dipole moment induced in vibration ν_3 is not bound to a direction coinciding with a metal–metal bond, but it proceeds in the x, y plane exactly as an ordinary doubly degenerate vibration. The form given in Fig. 8 represents one arbitrary choice. Comparing the calculated and measured values for the intensity of the band ν_3, for the case in which there is satisfactory accord for the I_1, I_2, and I_4 values, we find that only about 27% of the intensity of the ν_3 band has its origin in the vibration of the C–O dipoles, and 73% of its intensity is due to the intermetallic dipolar contribution. We can summarize the cases in which this dipolar contribution is not present as follows: (*a*), with vibrations for which there is an out-of-phase coupling of the C–O vibrations within one $M(CO)_x$ entity, so that the effects of the expanding and contracting C–O bonds cancel each other; and (*b*), with the totally symmetric in-phase vibration ν_1 (always having the highest frequency), if there are no hetero-ligands present which are good π-acceptors.

In the case of the monomeric $LM(CO)_x$ complexes Darensbourg recently described a quantitative treatment of the band intensities also taking into account the "vibronic contribution" of the electrons of the L–M π-bond[35], which influences solely the ν_1(CO) vibration in a way somewhat analogous to the dipolar contribution of the ν_3-type vibrations of the polynuclear carbonyls.

On this basis one could not exclude *a priori* a "vibronic interaction" of the electrons of the ring—Co_{apical} bond, which would influence the intensity of the totally symmetric in-phase (ν_1) vibration. However, the studies of Fischer[36] and of Beck *et al.*[37] on the band intensities of (arene)$Cr(CO)_3$ compounds resulted in a perfect agreement between calculated and measured bond angles, thus proving the absence

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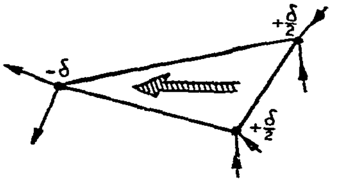
* Parker and Stiddard[34] expressed their doubts about this interpretation since they did not observe this unexpectedly high intensity for the corresponding B_2 band in the case of $Mn_2(CO)_8(PF_3)_2$. In the case of the substituted derivatives, however, with good π-acceptor ligands, there is the possibility of the cancellation of the partial charges formed on the metal atoms during the vibrations, through the heteroligands by a "vibronic contribution"[35]. We shall discuss this phenomenon in greater detail in a separate paper.



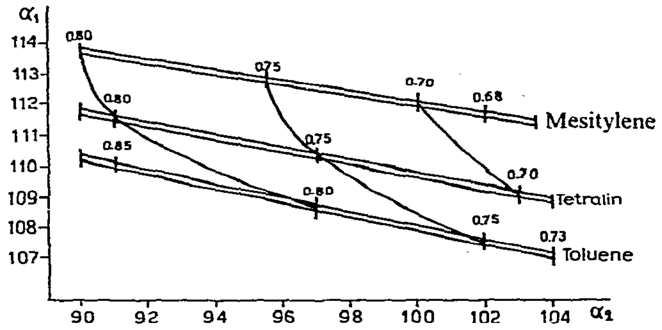


Fig. 8. The induced dipole moment component of the intensity of vibration ν_3.

Fig. 9. The calculated regions of the allowed α_1–α_2–μ'_{rel} combinations; the numbers above the lines indicate the $\mu'_{rel}=\mu'_{eq}/\mu'_{ax}$ values.

of any anomaly in the intensities in these spectra. More recently Darensbourg[38] also concluded that there is very little back-bonding in the (h^5-C_5H_5)–M bonds, and thus no vibronic interaction is present in the sandwich-bonded ligand. Hence we can assume, with high probability, the absence of vibronic contribution in the case of the $\nu_1(A_1)$ vibration of the (arene)$Co_4(CO)_9$ compounds also, and include the intensity of this band in the calculations.

Since we did not determine the absolute intensities of the bands, but only the relative integrated intensities in arbitrary units, we have just two intensity ratios, defined as I_1/I_2 and I_4/I_2, in determining the range of the possible solutions for α_1, α_2, and of the ratio of the two dipole moment gradients, $\mu'_{rel}=\mu'_{eq}/\mu'_{ax}$. We have set two reasonable constraints for limiting the possible values of α_1 and α_2: (*a*), we suppose that α_2 cannot be larger than the value determined by X-ray study[39] for $Co_4(CO)_{12}$, *i.e.* 104° and cannot be smaller than 90°; and (*b*), the sum $(\alpha_1+\alpha_2+\gamma)$ cannot exceed 270°, because of the mutual repulsion of the axial ligands. The value of γ is calculated as 54.7°, supposing that the Co_4 cluster forms a regular tetrahedron, thus giving the upper limit of 215.3° for $\alpha_1+\alpha_2$.

The results obtained are shown in Fig. 9, where each straight line corresponds to one of the three compounds studied. The numbers on these lines are the corresponding μ'_{rel} values. As we see, for the entire region of acceptable solutions this has a value of less than one, which means that $\mu'_{eq}<\mu'_{ax}$. In spite of the incomplete solution of the problem we see that there is an increase in the angle α_1 in the order toluene < tetralin < mesitylene, which is logical on steric grounds.

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