93. Infrared Spectroscopic Studies on Metal Carbonyl Compounds

Part XIX.¹)

Analysis of the Terminal C–O Stretching Region of the Infrared Spectra of Tetracobalt and Tetrarhodium Dodecacarbonyl by ^{13}C Isotopic Enrichment and of Hydridoirontricobalt Dodecacarbonyl. Calculation of C–O Stretching Force and Interaction Constants

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Summary. Based on ^{13}C-enriched spectra the assignment of the terminal C—O stretching bands of $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$, and $HFeCo_3(CO)_{12}$ is presented. This corresponds in all three cases to the scheme $A_1 > A_1 > E > E > A_1 > E$. For the calculation of the 'non-rigorous' C—O stretching force and interaction constants a parametric method is described. On the basis of the extremely low C—O stretching force constant of the ligands bonded to the iron atom in $HFeCo_3(CO)_{12}$ a considerable polarization of the Fe-H bond in the sense Fe(δ^{-})––––H(δ^{+}) is suggested, and the position of the H-ligand is supposed 'in the cage' near, or on the Co_3 plane.

Introduction. – In continuation of the studies aiming at the interpretation of the vibrational spectra of polynuclear metal carbonyls we have recently presented the IR. spectra and the C–O stretching force and interaction constants of some compounds of the type (arene)$Co_4(CO)_9$ [2]. We now report the results of the studies performed with the related unsubstituted tetranuclear cluster complexes $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$ and with $HFeCo_3(CO)_{12}$.

The first structural study on $Co_4(CO)_{12}$ was that of *Corradini* [3] who proposed a C_{3v} structure composed of an apical $Co(CO)_3$ group and of three equivalent $Co(CO)_2$ groups on the basis face of a trigonal pyramide, connected also by three edge-bridging CO ligands. Subsequent X-ray work of *Wei* & *Dahl* [4a, c] refined this structure, and these authors confirmed the same structural type also for $Rh_4(CO)_{12}$ [4b, c]⁴).

Recently the structure of disordered $Co_4(CO)_{12}$ has been reexamined by *Frenz* & *Cotton* [5] and the C_{3v} structure has been definitely confirmed.

Lucken et al. [6], and independently *Haas* & *Sheline* [7] have shown by ^{59}Co NMR. measurements on dodecacarbonyl tetracobalt the presence of the same structure also

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⁴) A detailed chronological survey of the conflicting ideas on the structures and spectra of the compounds $M_4(CO)_{12}$ is given in the introduction of [4c].

in solution, since they have found one Co atom in a different environment than the three others which are identical to each other. (A numerical discrepancy is due to a misprint in Table I of *Haas & Sheline*'s paper: The chemical shifts must be multiplied by 10).

Table 1. *Explanation of the symbols of the terminal (MC)—O stretching force and interaction constants of the compounds $M_4(CO)_{12}$ with C_{3v} symmetry* (for the numbering of the ligands see Fig. 1)

Constants	Symbols	Number of the ligands
Equatorial...	K_1	1, 3, 5
Axial...	K_2	2, 4, 6
Apical...	K_3	7, 8, 9
Geminal interactions	i_1	1–2, 3–4, 5–6
	i_2	7–8, 8–9, 9–7
Basal indirect interactions	j_1	1–3, 3–5, 5–1
	j_2	2–4, 4–6, 6–2
	j_3	1–4, 1–6, 3–6, 3–2, 5–2, 5–4
Apical-basal indirect interactions	j_4	1–7, 3–8, 5–9
	j_5	2–7, 4–8, 6–9
	j_6	1–8, 1–9, 3–7, 3–9, 5–7, 5–8
	j_7	2–8, 2–9, 4–7, 4–9, 6–7, 6–8

A ^{13}C-NMR. study of isotopically enriched (~16% ^{13}CO) $Rh_4(CO)_{12}$ from about 0° to +60° showed that rapid intramolecular scrambling of the carbonyl groups occurs [8]. In a more recent low-temperature study of similar character (~70% ^{13}CO), the limiting low-temperature spectrum was observed at −65° (in CD_2Cl_2), where $Rh_4(CO)_{12}$ exhibits four resonances of equal intensity. This NMR. spectrum is in agreement with the solid state structure which must be present also in solution. The coalescence temperature was reported at $-5 \pm 5°$ [9]. No site-selectivity was found in the high-temperature scrambling process, confirming thus the previously suggested mechanism [8].

On the IR. spectroscopic time-scale we can hence assume the presence of the solid-state structure of $Rh_4(CO)_{12}$ also in solution, even at higher temperatures. The complete analogy of the spectra leaves no doubt that the same is true also for $Co_4(CO)_{12}$.

For $FeHCo_3(CO)_{12}$ no X-ray study is known, but on the basis of the analogy of the IR. [10] and mass spectra [11] as well as inelastic neutron scattering measurements [12], there are no doubts about the analogous pyramidal cluster structure of this compound, with the iron atom on the apex. The position of the hydrogen is uncertain, but it is very probably located in the threefold axis of the molecule [12].

The IR. spectra of these compounds have been discussed by different authors [10] [13–21], however always in an approximate and incomplete way. No assignment of the C–O stretching frequencies supported by spectra of isotopically enriched compounds of this family is known. There exists only one oversimplificated study of the C–O stretching force and interaction constants [21] of Co_4- and $Rh_4(CO)_{12}$.

In this paper we discuss the spectra of isotopically enriched tetracobalt and tetrarhodium dodecacarbonyl, and the first high-resolution spectrum of $HFeCo_3(CO)_{12}$. We present the assignment of all of their C–O stretching modes and the C–O factored non rigorous' force and interaction constants derived thereof[5]).

Experimental Part

Tetracobalt dodecacarbonyl was prepared from commercial (*Alpha Inorganics*) dicobalt octacarbonyl by heating in benzene solution. Tetrarhodium dodecacarbonyl and hydridoiron-tricobalt dodecacarbonyl were kindly donated by Professor *P. Chini*, Milan.

Isotopically enriched $Co_4(CO)_{12}$ was prepared from enriched dicobalt octacarbonyl of a previous study [24], or by shaking a heptane solution of tetracobalt dodecacarbonyl in the presence of a gas phase of 50% enriched ^{13}CO for 15 to 30 min at room temperature.

Isotopically enriched (about 16% ^{13}CO) $Rh_4(CO)_{12}$ was prepared by *Cotton et al.* for ^{13}C-NMR. studies [8], and a sample of it was kindly donated to us by Professor *F. A. Cotton.*

Spectra were recorded on *n*-hexane or *n*-heptane solutions with a *Perkin-Elmer* Model 621 spectrophotometer. Spectral slit width in the region 2200–1800 cm^{-1} was between 1.0 and 1.4 cm^{-1} (slit program 700). The spectra were obtained on an expanded abscissa scale (10 cm^{-1} = 1, 2, or 4 cm), and calibrated against carbon monoxide and water vapour bands. The frequencies are accurate within ± 0.5 to 1.0 cm^{-1}.

The spectra of isotopically enriched $Co_4(CO)_{12}$ were recorded with a *Perkin-Elmer* model 521 spectrophotometer modified in such a way that the grating order change was at 2200 cm^{-1} rather than at 2000 cm^{-1}.

A special technique was employed to render weak and strongly overlapped ^{13}CO bands visible: The solution containing the partly enriched $Co_4(CO)_{12}$ was placed in the sample beam and a solution of natural $Co_4(CO)_{12}$ in the reference beam. The concentration of this latter solution was varied in order to obtain a series of spectra ranging from undercompensated to slightly over-compensated natural $Co_4(CO)_{12}$ content.

Method of calculation. – The compounds under study have three different sets of terminal CO ligands (equatorial, axial and apical), and one set of bridging groups. Since in a previous study we have shown [25] that the interaction constants between terminal and bridging CO groups can be considered zero, we deal only with the $M_4(CO)_9$ core of these molecules.

The structure of this $M_4(CO)_9$ core and the numbering scheme of the ligands is shown in Fig. 1. The symbols of the force and interaction constants are explained in Table 1. The C–O stretching symmetry coordinates are given in Table 2, and the relationships connecting symmetrized F_{ij} elements with valence force constants are compiled in Table 3.

General theory. – Due to the presence of two third order species (A_1 and E) the eigenvalue problem of these compounds is highly underdetermined even in a factored-off C–O stretching force field. The approach applied is an extension of our second order parameter method [26], related to some extent to the method developed independently by *Braterman, Bau & Kaesz* [27].

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[5]) The C—O factored force field for the determination of the nonrigorous C—O stretching force and interaction constants has been proposed for the first time in a detailed form by *Cotton & Kraihanzel* [22] and it is often referred to as CKFF. However, by including the isotopic frequencies into the analysis of the spectra some of the *a priori* constraints of the CKFF have proved unnecessary. The non-rigorous force and interaction constants are here interpreted according to the 'local normal coordinate' idea of *Miller* [23] as composite properties of the MCO units.

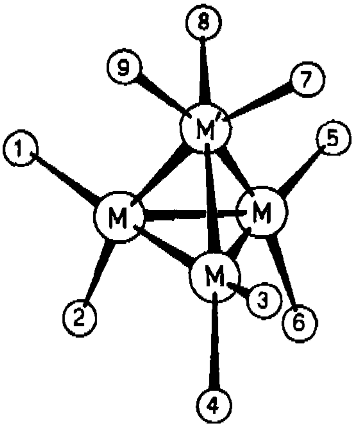

Fig. 1. *The structure of the $M_4(CO)_9$ core of the tetrametal dodecacarbonyls of C_{3v} structure, and the numbering scheme of the CO ligands*

Table 2. *Terminal (MC)—O stretching symmetry coordinates of the $M_4(CO)_{12}$ compounds.* (For the numbering of the ligands see Fig. 1)

Species A_1	$\mathbf{R}_1 = 3^{-2}(\Delta r_1 + \Delta r_3 + \Delta r_5)$ $\mathbf{R}_2 = 3^{-2}(\Delta r_2 + \Delta r_4 + \Delta r_6)$ $\mathbf{R}_3 = 3^{-2}(\Delta r_7 + \Delta r_8 + \Delta r_9)$
Species E	$\mathbf{R}_{4a} = 6^{-2}(2\Delta r_1 - \Delta r_3 - \Delta r_5)$ $\mathbf{R}_{4b} = 2^{-2}(\Delta r_3 - \Delta r_5)$ $\mathbf{R}_{5a} = 6^{-2}(2\Delta r_2 - \Delta r_4 - \Delta r_6)$ $\mathbf{R}_{5b} = 2^{-2}(\Delta r_4 - \Delta r_6)$ $\mathbf{R}_{6a} = 6^{-2}(-2\Delta r_7 + \Delta r_8 + \Delta r_9)$ $\mathbf{R}_{6b} = 2^{-2}(\Delta r_9 - \Delta r_8)$

Table 3. *Relationships connecting symmetry-factored* F_{ij} *elements and valence force constants*

Species A_1	$F_{11} = K_1 + 2j_1$ $F_{22} = K_2 + 2j_2$ $F_{33} = K_3 + 2i_2$ $F_{12} = i_1 + 2j_3$ $F_{13} = j_4 + 2j_6$ $F_{23} = j_5 + 2j_7$	Species E	$F_{44} = K_1 - j_1$ $F_{55} = K_2 - j_2$ $F_{66} = K_3 - i_2$ $F_{45} = i_1 - j_3$ $F_{46} = j_6 - j_4$ $F_{56} = j_7 - j_5$

The third and higher order parametric approach is based on the principles of *Taylor* [28], *Pulay & Török* [29], and of *Toman & Pliva* [30].

The force and interaction constants are expressed as functions of the eigenvalues y_i:

$$y_i = \lambda_i/\mu_{CO} = 0.40407 \times 10^{-5} \times \nu_i^2 \tag{1}$$

by the use of certain parameters which permit to cover the complete region of the mathematically allowed real solutions. This region is then narrowed down by the use of isotopic frequencies and by the transfer of known relationships between interaction constants.

According to *Taylor* [28] there exists a real orthogonal matrix **B** such that

$$\tilde{\mathbf{B}}\, \Gamma^{1/2}\, \tilde{\mathbf{A}}\, \mathbf{F}\, \mathbf{A}\, \Gamma^{1/2}\, \mathbf{B} = \Lambda \tag{2}$$

where Γ is a diagonal matrix obtained from the kinematic matrix **G** by the orthogonal transformation (3), where **A** contains the eigenvectors of **G**:

$$\tilde{\mathbf{A}}\, \mathbf{G}\, \mathbf{A} = \Gamma \tag{3}$$

From the approximation of *Cotton & Kraihanzel* [22] the inverse kinematic matrix of the factored C–O stretching force field of metal carbonyls is constant and diagonal:

$$\mathbf{G}^{-1} = \mu_{CO}^{-1}\, \mathbf{E} \tag{4}$$

(where **E** is the unit matrix of n-th order and $\mu_{CO} = 1/m_C + 1/m_O$) thus we have

$$\mathbf{A} = \tilde{\mathbf{A}} = \mathbf{E}, \qquad \Gamma = \mathbf{G}, \text{ and } \qquad \Gamma^{1/2} = \mu_{CO}^{1/2}\, \mathbf{E}. \tag{5}$$

Hence Eq. (2) simplifies to (6):

$$\tilde{\mathbf{B}}\, \mathbf{F}\, \mathbf{B} = \mu^{-1} \Lambda \tag{6}$$

Equation (6) is identical to (7) introduced independently by us in the study dealing with the second order problem of metal carbonyl spectra [26]:

$$\tilde{\mathbf{N}}\, \mathbf{F}\, \mathbf{N} = \mathbf{Y} \tag{7}$$

where **Y** is a diagonal matrix containing the values y_i defined by Eq. (1)[6].

Applied in the form of (8):

$$\mathbf{N}\, \mathbf{Y}\, \tilde{\mathbf{N}} = \mathbf{F} \tag{8}$$

it is matrix **N** by the use of which we can sweep over the entire range of the mathematically allowed real solutions. Matrix **N** is obtained as a product of m = n (n – 1)/2 two-dimensional rotational matrices $\mathbf{R}^{(i,j)}$ (where n = the order of the matrix) each of which contains one angular parameter ϕ_q (q = 1,2,..., m) in the following way [29] [30]. Matrices $\mathbf{R}^{(i,j)}$ are unit matrices except for four elements: two diagonal elements $R_{ii} = R_{jj} = \cos\phi_q$, and two off-diagonal elements $R_{ij} = -R_{ji} = \sin\phi_q$.

In the second order case m = 1, and hence there is just one angular parameter. The previously obtained [26] second order matrix **N** contained $\cos(\beta/2)$ in the diagonal, and $\pm\sin(\beta/2)$ in the off-diagonal positions, which, for reasons of easier graphical representation, were expressed in terms of $\pm[(1 \pm \cos\beta)/2]^{1/2}$, and $\cos\beta$ was used as parameter in the expressions for the force and interaction constants.

Since $\beta/2$ by its definition is identical with ϕ used by *Braterman et al.* [27], we maintain the symbols ϕ_q for the angular parameters of our present treatment.

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[6] We prefer to maintain the symbol **N** for the real orthogonal eigenvector matrix which diagonalizes **F** to $\mathbf{Y} = \mu^{-1}\Lambda$ since the matrix symbol **B**, used by *Taylor* [28], has previously been used in the classical paper of *Wilson* [31] to denote a matrix which transforms cartesian coordinates into internal valence coordinates. The symbol **U** is used by *Pulay & Török* [29] for the same type of matrix, a symbol previously reserved by *Wilson* [32] and by *Meister & Cleveland* [33] for the matrix which connects internal coordinates with symmetry coordinates. *Toman & Pliva* [30] used the symbol **C** for the same matrix, which symbol, in turn, has been introduced previously for the compliance matrix [34] [35].

For the third and higher order cases we must define the order in which the rotational matrices are multiplied. This is a matter of convention, and we define it for the transposed forms according to increasing index q, which is related to the indices i and j by (9) [30]:

$$q = n\,(i-1) + j - i\,(i+1)/2 \tag{9}$$

Consequently

$$\tilde{\mathbf{N}} = \tilde{\mathbf{R}}^{(1,2)} \cdot \tilde{\mathbf{R}}^{(1,3)} \cdot \tilde{\mathbf{R}}^{(2,3)} \tag{10}$$

where *e.g.*

$$\tilde{\mathbf{R}}^{(1,2)} = \begin{pmatrix} \cos\phi_1 & \sin\phi_1 & 0 \\ -\sin\phi_1 & \cos\phi_1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \textit{etc.} \tag{11}$$

The explicit expressions of the nine elements of matrix **N** are given in Table 4.

Table 4. *Explicit expressions of the* N_{ij} *elements for the third order case* (c_i stands for $\cos\phi_i$ and s_i for $\sin\phi_i$)

$N_{11} = c_1c_2$
$N_{21} = -c_1 s_2 s_3 + s_1 c_3$
$N_{31} = c_1 s_2 c_3 + s_1 s_3$

$N_{12} = -s_1c_2$
$N_{22} = s_1 s_2 s_3 + c_1 c_3$
$N_{32} = -s_1 s_2 c_3 + c_1 s_3$

$N_{13} = -s_2$
$N_{23} = -c_2 s_3$
$N_{33} = c_2 c_3$

By using these expressions the individual F_{ij} elements of matrix **F** are constructed by (12):

$$F_{ij} = \sum_{k=1}^{n} N_{ik}N_{jk}\,y_k \qquad (n = 3) \tag{12}$$

and then the individual valence force and interaction constants are expressed by the relationships existing between these and the F_{ij} elements (Table 3).

Limitation of the range of combinations. – Some limitations in the above outlined scheme of calculation have now to be introduced, since the 'rotation' of all three parameters (*i.e.* 6 for both symmetry species) over the entire range of 360°, with all possible combinations, would yield a hardly evaluable quantity of data, and in the same time it would mean an unnecessarily long computation time. Therefore the hitherto explained approach is used only as a refinement procedure, and it is preceded by a limited number of orienting approximations to establish the sign distribution in the eigenvector matrix **N**, and the rough magnitude of its elements. With a given sign distribution each parameter can be limited within one quadrant, and the allowed combination of quadrants reduces to 1/64 the range to be covered.

The orienting approximations are performed as follows. Different values are assigned to the C–O stretching force and interaction constants by transferring them from already studied models; these approximate constants are arranged to matrix $\mathbf{F}^{(a)}$, which is then diagonalized by a computer procedure. From the eigenvalues $y_i^{(a)}$ the calculated approximate frequencies, $\nu_i^{(a)}$ are obtained by the inverse application of Eq. (1). The corresponding approximate eigenvalue matrix $\mathbf{N}^{(a)}$ is also obtained in the diagonalization step. This matrix is now applied to the $y_i^{(t)}$ values of the true observed frequencies (completed, if necessary, with the estimated frequencies of IR.-inactive modes), arranged according to one or more possible assignments:

$$\mathbf{N}^{(a)}\,\mathbf{Y}^{(t)}\,\tilde{\mathbf{N}}^{(a)} = \mathbf{F}^{(c)} \qquad (13)$$

The matrix $\mathbf{F}^{(c)}$ contains the 'corrected' force and interaction constants. By comparing the $F_{ij}^{(c)}$ elements with starting input constants one can correct some obviously erroneous assumptions in the starting constants or/and in the assignment of the frequencies.

Different matrices $\mathbf{N}^{(a)}$ are obtained in this way, and some representative examples of them serve then as basis for obtaining the starting set of the ϕ_q parameters for the refinement procedure.

First one obtains ϕ_2 from element N_{13}. Due to the sine function, this angle can belong to two quadrants. We proceed with both possibilities to elements N_{23} and N_{33} to obtain ϕ_3. The quadrant of ϕ_3 is fixed by that of ϕ_2. To determine ϕ_1 one has more possibilities, and N_{11} is preferred for the simpler form of its explicit expression (see Table 4). From N_{11} one obtains two possible solutions of ϕ_1 for each pair of ϕ_2 and ϕ_3, however, only one of the solutions is compatible with the numerical values of the other elements of this column.

The set of parameters ϕ_1, ϕ_2, ϕ_3, determined in this way satisfies only one form of the second column: either the original one, or the one with opposite signs.

In addition to the two combinations of quadrants obtained as outlined above, other six can be calculated by starting from a matrix where two of the columns are multiplied by -1. (The multiplication of only one column, or all three columns by -1 is not allowed, since these do not yield equivalent solutions.)

Thus only 8 of the possible 64 quadrant combinations are valid, and it is sufficient to perform the calculations just with one of them since the other seven give identical results.

For the species A_1 and E of the compounds in question the quadrant distributions are usually different, and any of the eight combinations for A_1 can be coupled with any of the eight E combinations. (The parameters in species E were labelled ϕ_4, ϕ_5, and ϕ_6.)

We have written a computer program in FORTRAN IV for the refinement cycle outlined above. It calculates from the assigned frequencies the following values in the function of the six parameters ϕ_q ($q = 1 \ldots 6$), which can be 'rotated' between optional limits and with various steps: C–O stretching force and interaction constants, isotopic frequencies (by the procedure given previously [36] [37]), and intensities (calculated on the local oscillating dipole concept [2] [27]) of the fundamental and isotopic bands.

The analogous fourth order method has been also developed and applied to the analysis of the spectrum of $MnRe(CO)_{10}$ [38].

Assignment of the C–O stretching bands. – The following criteria were chosen for finding the correct assignment and the final set of parameters: (*i*) a 'reasonable' set of force and interaction constants, based on the results obtained previously for the compounds (arene)$Co_4(CO)_9$; (*ii*) an agreement (within ± 1 cm^{-1}) with the isotopic frequencies measured on the enriched spectra.

A third criterion could have been that of the band intensities, used by other authors [21]. This criterion, however, can be applied only limitedly with severe restrictions and reserves. First of all the two very strong twin bands must be excluded from the comparison of intensities since the analysis of the form of these vibrations shows that both of these two modes must be influenced by a strong 'molecular induced dipole moment contribution' [39] postulated previously for vibration ν_3^{CO} of the compounds (arene)$Co_4(CO)_9$ [2], which add to the vectorial sum of the 'local' intensities. In the case of the compounds $M_4(CO)_{12}$ we can foresee one A_1 C–O stretching fundamental with a strong 'induced dipole moment' along the z-axis (Fig. 2), and another of species *E*, with components in directions x-y (*cf.* Fig. 8 in [2]). Hence for these bands the relative intensity calculated on the basis of local oscillating dipoles only, is much lower than the observed one.

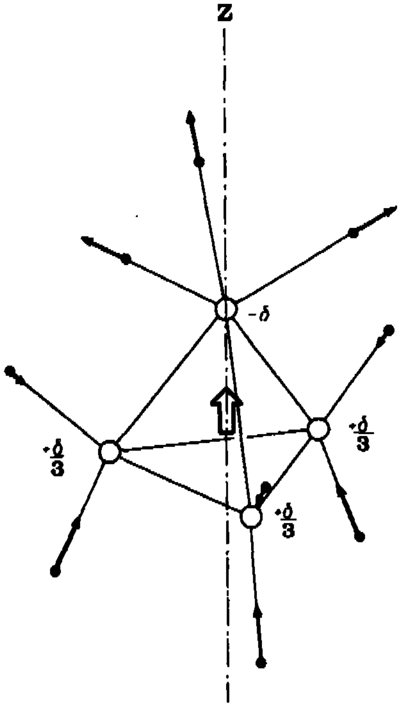

Fig. 2. *Origin of the 'induced dipole moment contribution' along axis z which enhances strongly the intensity of band* $\nu_2(A_1)$. The arrows representing the relative vibrational amplitudes of the local C–O dipoles correspond to the values obtained for $Co_4(CO)_{12}$.

Another limitation is due to the fact that the integrated intensities of the bands are not known and it was outside the scope of this study to measure these values. The ε_{max} values are considerably sensitive to the spectral slit width due to the narrow band forms, and hence the data reported earlier [14] [17] cannot be used to spectra obtained with more efficient instruments.

Finally, it was shown for the (arene)$Co_4(CO)_9$ complexes that the dipole moment gradients of the two types of CO ligands had a ratio of 0.7–0.85 [2]. For the apical ligands of the $M_4(CO)_{12}$ compounds even a more different $\partial\mu/\partial r$ can be expected.

Hence the 'calculated' intensities obtained

(a) with the assumption that the $\partial\mu/\partial r$ values of all three types of CO ligands are equal, and
(b) with the neglection of the 'molecular induced dipole moment'

have little diagnostic value. Therefore we limited our conditions as to obtaining an agreement with the relative orders of magnitude for the two very weak (ν_1 and ν_6) and two medium intensity (ν_3 and ν_5) bands.

$Co_4(CO)_{12}$. – The spectra are shown in Fig. 3. Five of the expected six terminal C–O stretching bands are easily located: Two very strong and two medium-strong bands were recognized already in the first medium-high resolution spectra [13–17]. Subsequently the very weak band at 2104.4 cm^{-1} has been identified as the in-phase totally symmetric C–O fundamental [18]. This assignment has found an additional confirmation in a study of the spectra of the substituted $Co_4(CO)_{12-n}L_n$ derivatives [40]. So far no unequivocal assignment was, however, reported for the sixth C–O stretching fundamental. The two frequencies suggested earlier, *i.e.* 2048 [18] and 2059.3 cm^{-1} [21] are now found to be in error.

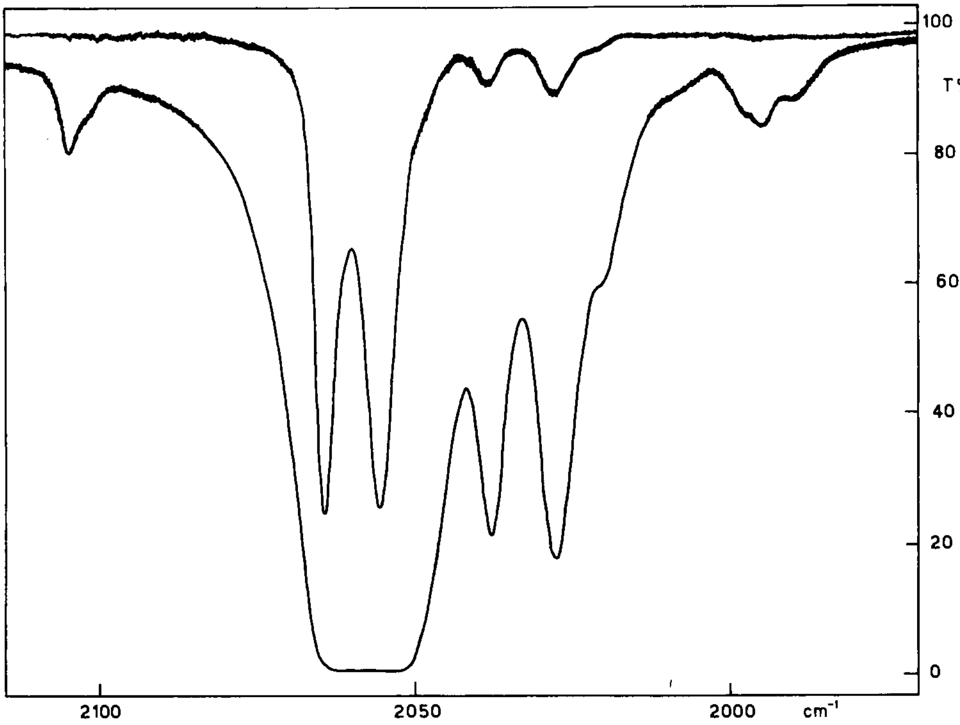

Fig. 3. *The terminal C—O region of the spectrum of $Co_4(CO)_{12}$ with natural abundance of ^{13}C* (two concentrations)

The calculations led us to locate the 6th fundamental at a frequency lower than all the other five, and accordingly it could be observed as a shoulder at 2020.5 cm^{-1} in the wing of the band at 2027.5 cm^{-1}. One can detect this shoulder also in earlier published spectra [17] [18].

This band at 2020.5 cm^{-1} must be assigned to an *E* mode, since its assignment to species A_1 would result in a disagreement between observed and calculated isotopic frequencies.

The results of the ^{13}CO enrichment experiments can be summarized as follows:

a) The intensity of the isotopic band centred at 1992 cm^{-1} increases and its composite band form containing three individual components (1997, 1993 and 1987 cm^{-1}) becomes more evident. These components belong to the equatorially, axially and apically substituted $Co_4(^{12}CO)_8(^{13}CO)$ molecular cores, respectively.

b) The shoulder at 2048 cm^{-1} increases with isotopic enrichment proving its ^{13}C-satellite origin, as proposed recently by *Cariati et al.* [21].

c) Difference spectra (where the all-^{12}CO bands were compensated by a non-enriched sample) have shown the presence of a strong isotopic band at 2062 cm^{-1}, overlapped in the non-compensated spectra by the strong doublet 2063–2054 cm^{-1}.

d) Additional isotopic bands were detected at 2101, 2052 and 2025 cm^{-1}.

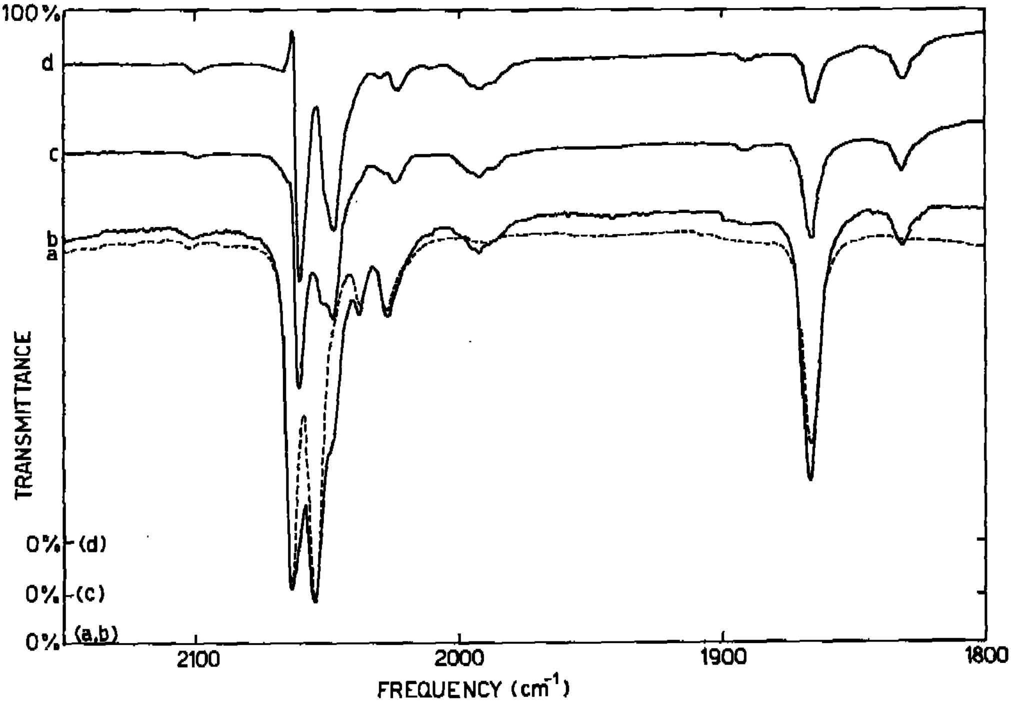

Fig. 4. *The IR. spectrum of isotopically enriched (^{13}C ≈ 50%) $Co_4(CO)_{12}$ in the C—O stretching region* a) spectrum with natural ^{13}C-abundance (-·---); b) spectrum of the ^{13}C-enriched complex; c) the enriched spectrum, with nearly compensated all-^{12}C bands; d) the enriched spectrum, slightly overcompensated by a 'natural' sample.

We checked systematically all possible assignments (keeping 2104.4 cm^{-1} as A_1 and 2020.5 cm^{-1} as *E* constant) and found that the assignments where the two stronger bands (at 2063.2 and 2054.5 cm^{-1}), and the two weaker ones (at 2037.9 and 2027.5 cm^{-1}), respectively, belong to the same species, (*i.e.* the assignments A_1A_1EE, or

EEA_1A_1 for these four bands) give rise to inacceptable results. The two very intense bands must be assigned to different symmetry species, also because the induced dipolar contribution only can account for the extremely high intensities, and as outlined earlier, there is one vibrational form in species A_1 (Fig. 2) and one for species E [2] which can give rise to this effect.

There remained 4 assignments, as shown in Table 5. Assignments III and IV are eliminated because they are in conflict with the above outlined criteria. The assignment of the higher-frequency component of the characteristically intense band pair to species A_1 and the lower one two species E is in agreement with the proposal of *Labroue & Poilblanc* [40] based on analogies with the spectra of $Co_4(CO)_{11}L$ derivatives.

Table 5. *The 4 discussed assignments of the terminal C–O stretching bands of $Co_4(CO)_{12}$*

Assignment	Frequencies, cm^{-1}					
	2104.4	2063.2	2054.5	2037.9	2027.5	2020.5
I	$\nu_1\ (A_1)$	$\nu_2\ (A_1)$	$\nu_4\ (E)$	$\nu_3\ (A_1)$	$\nu_5\ (E)$	$\nu_6\ (E)$
II	$\nu_1\ (A_1)$	$\nu_2\ (A_1)$	$\nu_4\ (E)$	$\nu_5\ (E)$	$\nu_3\ (A_1)$	$\nu_6\ (E)$
III	$\nu_1\ (A_1)$	$\nu_4\ (E)$	$\nu_2\ (A_1)$	$\nu_3\ (A_1)$	$\nu_5\ (E)$	$\nu_6\ (E)$
IV	$\nu_1\ (A_1)$	$\nu_4\ (E)$	$\nu_2\ (A_1)$	$\nu_5\ (E)$	$\nu_3\ (A_1)$	$\nu_6\ (E)$

The thus remaining two possibilities (assignment I and II) give results which do not differ drastically and one cannot exclude decisively either of these assignments.

We prefer assignment II, for the following reasons:

a) Although in I the constants have reasonable values, however, with a difference $K_{ax} - K_{eq} = 0.05$ mdyn/Å, whereas for the compounds (arene)$Co_4(CO)_9$ we obtained 0.17 mdyn/Å, and one can expect at least the same value also for $Co_4(CO)_{12}$;

b) with assignment I one obtains a calculated isotopic band at about 2035 cm^{-1} with a very high intensity, which is not observed in the spectrum.

Assignment II does not lead to these contradictions, hence it is to be preferred to assignment I. The final calculations have been performed with this assignment, and the results are presented in Tables 6 (assignment and isotopic frequencies), 7 (force and interaction constants), and 8 (eigenvector matrices and ϕ_q parameters).

$Rh_4(CO)_{12}$. – The spectrum in the C–O stretching region shows only three strong well-resolved bands [15]. Scanning with expanded scale, however, and with a spectral slit width lower than 1.7 cm^{-1} reveals that the band at 2043 cm^{-1} [15] is rather broad, composed of a sharp stronger component at 2044.6 cm^{-1} and a shoulder at 2042 cm^{-1}. The very weak band of the totally symmetric in-phase vibration $\nu_1(A_1)$ can be found at 2106.6 cm^{-1}. The sixth C–O fundamental is more difficult to locate. We assigned it to the weak shoulder at 2035 cm^{-1}.

Previously *Cariati et al.* [21] calculated for this sixth fundamental a frequency of 2072.7 cm^{-1}, almost coincident with the very strong band observed by them at 2074.5 cm^{-1}. Furthermore these authors assigned it to the species A_1.

The shoulder at ~2061 cm^{-1}, reported also by *Beck & Lottes* [15], which could be another candidate for the sixth fundamental, is somewhat increased in the spectra

Table 6. *Assignment of the C—O stretching frequencies of $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$ and $HFeCo_3(CO)_{12}$ with the observed and calculated frequencies of their ^{13}CO-mono-substituted derivatives*

		$Co_4(CO)_{12}$			$Rh_4(CO)_{12}$			$HFeCo_3(CO)_{12}$		
Species A_1	ν_1	2104.4			2106.6			2099.8		
	ν_2	2063.2			2074.9			2058.2		
	ν_3	2027.5			2044.6			2014.0 (sh)		
Species E	ν_4	2054.5			2069.5			2049.4		
	ν_5	2037.9			2042.0			2026.0		
	ν_6	2020.5 (sh)			2035.0 (sh)			1988.4		
^{13}CO-subst.:		eq	ax	ap	eq	ax	ap	eq	ax	ap
a)		2101.7	2102.8	2099.3	2104.4	2105.4	2101.2	2095.9	2096.1	2097.9
b)		2101.5	*	*	2104.0	*	*	2096.0	*	*
a)		2062.8	2061.0	2060.9	2074.4	2073.4	2072.0	2057.7	2056.3	2054.3
b)		2062.0[c]	*	*	2073.0[c]	*	*	**	**	**
a)		2048.6	2046.4	2052.4	2061.6	2060.0	2068.5	2044.4	2036.8	2048.7
b)		2048.0	*	2052.0	2061.0	*	**	**	**	**
a)		2037.8	2032.6	2028.3	2043.1	2043.8	2044.5	2018.5	2015.5	2025.0
b)		**	**	**	**	**	**	**	**	**
a)		2025.2	2024.7	2023.5	2038.6	2037.0	2038.8	1996.4	1996.4	2010.8
b)		2025.0[c]	*	*	**	**	**	1997.0	*	**
a)		1985.5	1994.1	1997.2	2003.8	2006.4	2000.8	1976.8	1988.2	1953.5
b)		1987.0	1993.5	1997.0	2003.0	2005.0	2001.0	(**)	**	1954.0

N.B.: Only the A' modes of the isotopic frequencies are given, since the A'' modes occure at the same frequencies as the parent all-^{12}CO E modes.

[a] Calculated isotopic frequencies.

[b] Observed isotopic frequencies.

[c] Observed only in the spectra of isotopically enriched samples.

*) Due to the very small separation between the related frequencies calculated for the different isotopic-isomers no resolution of the components can be expected. In these cases the value given in the column 'eq' refers to the whole triplet (or doublet) of isotopic satellites. In all these cases the equatorial component had the highest calculated intensity.

**) Overlapped by bands of the all-^{12}CO molecules.

of the enriched sample, and its isotopic origin was confirmed also by our calculations, in accordance with the suggestion of *Cariati et al.* [21]. Assigning this frequency to the sixth fundamental would lead to serious inconsistencies:

a) no calculated isotopic frequency falls in the neighbourhood of 2035 cm^{-1}, hence there would be no explanation for this shoulder;

b) the calculated force and interaction constants would differ too much from the reasonable combinations observed for the C.-K. force field.

We assign the sixth terminal fundamental at 2035 cm^{-1} to species E in analogy with $Co_4(CO)_{12}$, since an assignment to A_1 would be in conflict with force constant arguments.

For the assignment of the other bands we used arguments analogous to those given for $Co_4(CO)_{12}$. The only important new information obtained from the isotopic enrichment was that the relative intensity of the band at 2073 cm^{-1} increases with

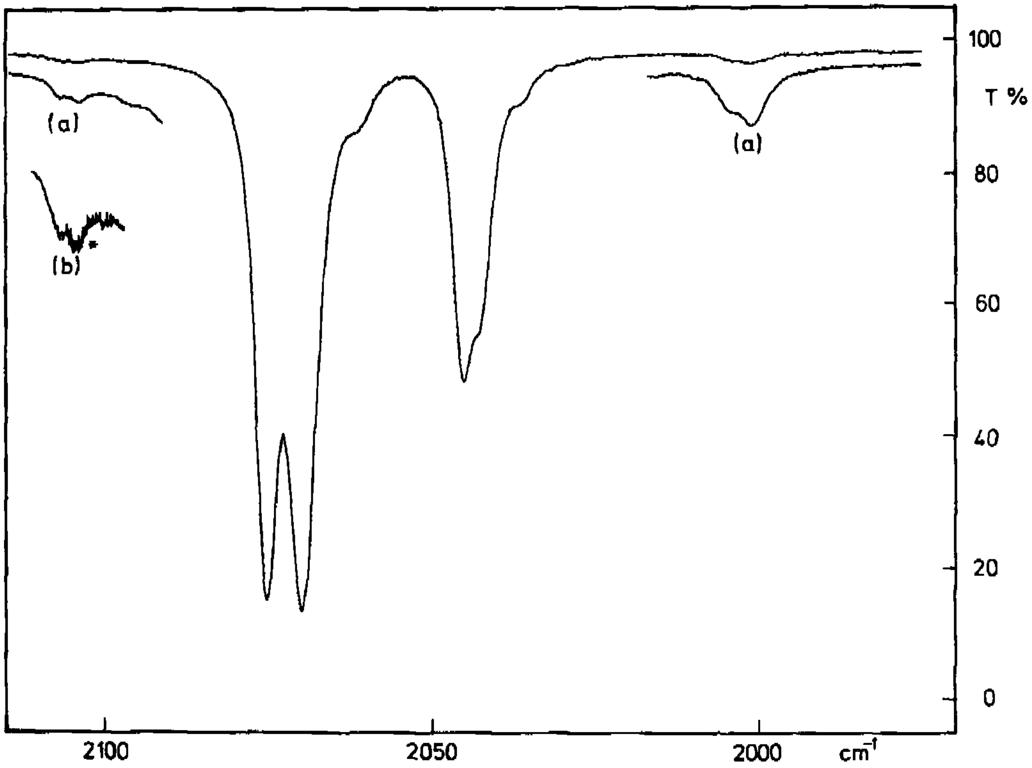

Fig. 5. *The IR. spectrum of $Rh_4(CO)_{12}$ in the terminal C—O stretching region* a) more concentrated solution; b) *idem*, with 5-fold ordinate expansion. – Note that the ^{13}C-isotopic satellite labelled with * has an intensity higher than its parent band even without isotopic enrichment.

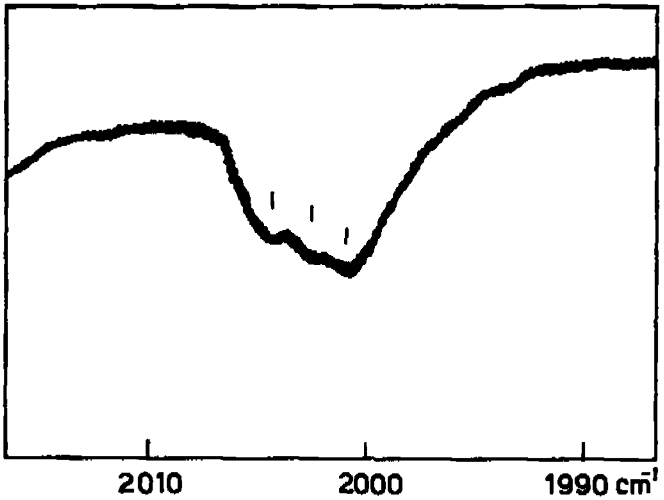

Fig. 6. *The lower terminal isotopic band triplet in the spectrum of ^{13}C-enriched $Rh_4(CO)_{12}$*, scanned with expanded wave number scale

enrichment proving that there is an isotopic band overlapped by this strong fundamental, and that the isotopic band at ~2002 cm^{-1} is a triplet, like in $Co_4(CO)_{12}$, with components at 2005, 2003, and 2001 cm^{-1} (Fig. 6).

In the case of $Rh_4(CO)_{12}$ the closeness of the two components of the band at 2043 cm^{-1} renders a distinction between the assignment $A_1 > E$ and $E > A_1$ immaterial since the small difference between the two component frequencies leads to results which differ insignificantly for these two assignments. Also the decision between the remaining two possible assignments

$$\text{I: } \nu_2(A_1) > \nu_4(E) \quad \text{and} \quad \text{II: } \nu_2(A_1) < \nu_4(E),$$

is not straightforward, due to the small (5 cm^{-1}) separation between these two bands, which leads to acceptable results with both assignments. We prefer assignment I, since it is analogous to the one of the cobalt compound.

The numerical results for this assignment are compiled in Tables 6, 7 and 8.

Table 7. Cotton-Kraihanzel-Miller *type MC—O stretching force and interaction constants of* $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$ *and* $HFeCo_3(CO)_{12}$ (in mdynes/Å), corresponding with the parameter values shown in Table 8

Constant	$Co_4(CO)_{12}$	$Rh_4(CO)_{12}$	$HFeCo_3(CO)_{12}$
K_1	16.806	17.102	16.782
K_2	16.949	17.133	17.005
K_3	17.034	17.097	16.343
i_1	0.289	0.279	0.270
i_2	0.250	0.293	0.306
j_1	0.099	0.066	0.120
j_2	0.108	0.085	0.170
j_3	0.056	0.030	0.085
j_4	0.041	0.033	0.037
j_5	0.031	0.018	0.001
j_6	0.180	0.133	0.240
j_7	0.051	0.037	0.028

Table 8. *Eigenvector matrices* **N** *of the species* A_1 *and* E *of the MC–O stretching modes of* $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$ *and* $HFeCo_3(CO)_{12}$, *and the corresponding parameter values* ϕ_i (i = 1...6)

Compound		A_1			E			A_1			E		
		ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6
$Co_4(CO)_{12}$	eq	0.5238	0.2669	−0.8090	0.6133	−0.0536	−0.7880	−27	54	−62	5	52	−56
	ax	0.4233	0.7425	0.5191	0.6996	0.5000	0.5105						
	ap	0.7392	−0.6144	0.2759	0.3666	−0.8648	0.3441						
$Rh_4(CO)_{12}$	eq	0.5155	0.3611	−0.7770	0.7022	−0.4209	0.5743	−35	51	−69	31	35	−30
	ax	0.3885	0.7098	0.5875	0.6918	0.5940	0.4105						
	ap	0.7638	−0.6048	0.2255	0.1684	−0.6856	0.7082						
$HFeCo_3(CO)_{12}$	eq	0.6346	−0.2823	−0.7191	0.5759	−0.7633	−0.2922	24	46	−25	53	17	−2
	ax	0.6462	0.7046	0.2936	0.8038	0.5937	0.0334						
	ap	0.4238	−0.6511	0.6296	0.1481	−0.2541	0.9557						

$HFeCo_3(CO)_{12}$. – The spectrum is shown in Fig. 7. In the spectrum there is a very weak absorption band at about 2000 cm^{-1} the intensity of which often increased during repeated scannings. After repeated purification the presence of a genuine very weak band at 1997 cm^{-1} (of isotopic origin) could be ascertained, which is then overlapped by a band of $Fe(CO)_5$ at 2001 cm^{-1} formed during a decomposition of $HFeCo_3(CO)_{12}$ in solution.

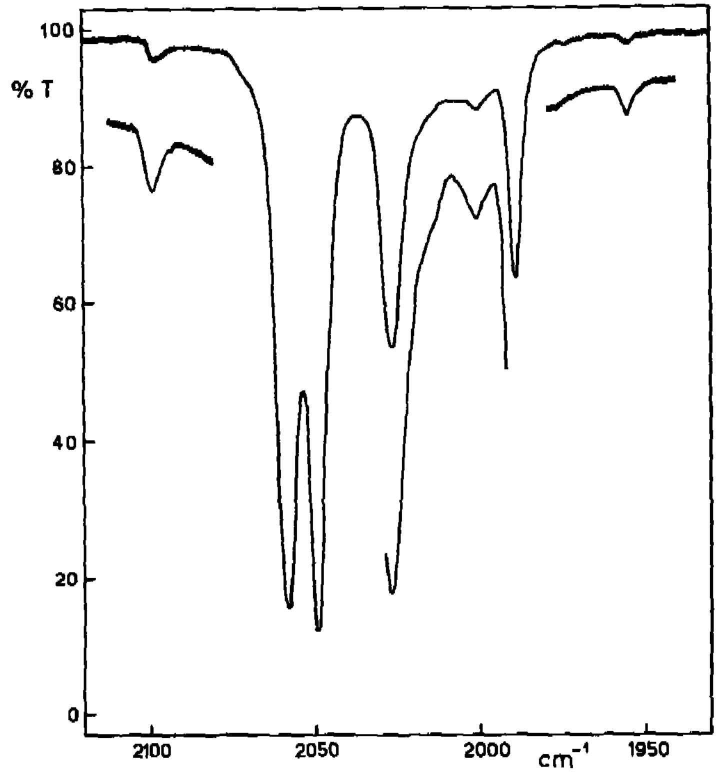

Fig. 7. *Spectrum of $HFeCo_3(CO)_{12}$ in the terminal C–O stretching region* (insets correspond to more concentrated solution)

Five terminal C–O fundamentals are easily located. We suggest the shoulder at 2014 cm^{-1} to be considered as the sixth fundamental, and assign it to species A_1. Thus one has a coherent trend in the assignments of the spectra of these compounds, as shown in Fig. 8.

The substitution of the $HFe(CO)_3$ group for the $Co(CO)_3$ fragment in the structure of $Co_4(CO)_{12}$ should have the effect that the frequencies of vibrations with strong participation of the $Fe(CO)_3$ group be decreased. This is due to the fact that the iron-bonded CO groups have lower C–O force constants than the analogous cobalt-bonded CO groups [26] [37]. One frequency of species A_1 and one of E are expected to show this effect.

One of these bands is easily identified at 1988 cm^{-1}. Its intensity and position clearly suggest its assignment to species $E(\nu_6)$. The corresponding A_1 mode is expected

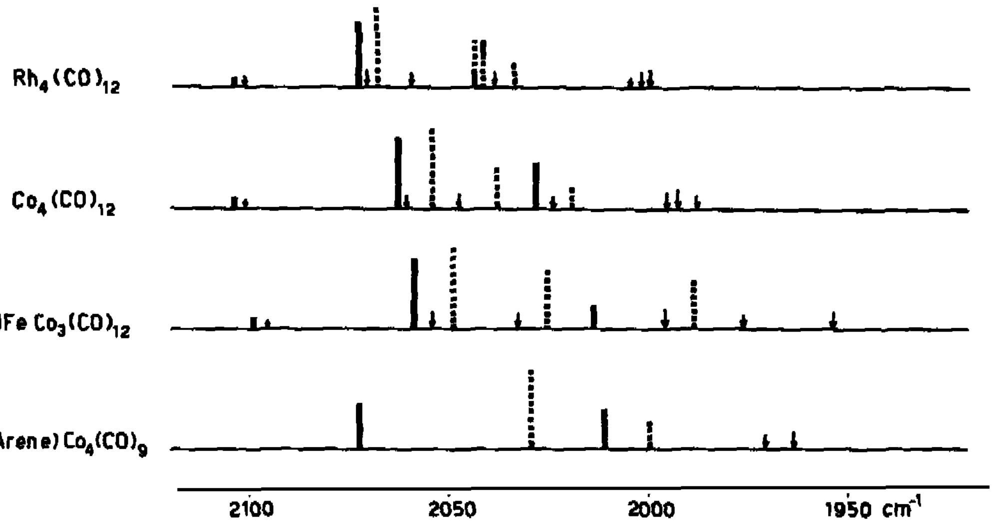

Fig. 8. *Graphical comparison of the terminal C—O stretching frequencies of $M_4(CO)_{12}$ (M=Co, Rh), $HFeCo_3(CO)_{12}$, and (arene)$Co_4(CO)_9$* [2] (full bars represent species A_1, broken bars species E, and arrows indicate the observed ^{13}C-isotopic band positions)

to give rise to a considerably weaker band at a frequency higher by 20–40 cm^{-1}. This leads to the assignment of the shoulder at 2014 cm^{-1} vibration $\nu_3(A_1)$.

Another possibility for $\nu_3(A_1)$ could have been the band at 1997 cm^{-1}, however, this assignment yields unreasonably low K_3 and i_2 constants. The suggestion that $\nu_3(A_1)$ = 2014 cm^{-1} not only fits well into the overall scheme of our assignments, but demands a strong isotopic band calculated at 1996.4 cm^{-1} both for the equatorial and for the axial ^{13}CO substitution (found at 1997 cm^{-1}), this band being the satellite of just the vibration $\nu_3(A_1)$.

The third possibility for $\nu_3(A_1)$, *i.e.* that it is nearly coinciding with the band at 2026 cm^{-1} like in the case of $Rh_4(CO)_{12}$, leaves both the shoulder at 2014 and the band at 1997 cm^{-1} without satifactory explanation.

Also in this case it must be excluded that the two strongest bands belong to the same species. There remain again two possible assignments as in the case of the rhodium compound. This ambiguity cannot be eliminated, since both assignments give reasonable results in all respect. By analogy with the tetracobalt compound, we suggest, as more likely, the same order of assignment also for the mixed cluster compound.

The numerical results are given also for this compound in Tables 6, 7, and 8.

Discussion of the force and interaction constants. – The interaction constants i_1 and i_2 (Table 8) fall in the range of 0.24–0.32 mdyn/Å, as predicted in our previous study [2]. This is the usual range found for the values of geminal interactions [22]. Although the i_2 values reported by *Cariati et al.* [21] are also acceptable (0.307 and 0.224 mdyn/Å for Co_4- and $Rh_4(CO)_{12}$, resp.), the i_1 values obtained by these authors (0.094 and 0.177 mdyn/Å, resp.) are unlikely.

Our 'indirect' interaction constants are in accordance with a 'through space' mechanism of these interactions [41]: j_1, j_2, and especially j_6 refer to interactions between sterically close lying CO groups (see Table 1). Both the angle C^1-M-C^2 and the C^7-M'-C^8 one (Table 9) are smaller for the Rh_4-compound than for $Co_4(CO)_{12}$, and on the other hand, M'-M-C^1 is greater [4c], in accordance with the trends obtained with the j_i values.

Table 9. *Characteristic bond angles in the molecules of the $M_4(CO)_{12}$ complexes (M = Co, Rh) in the crystalline state*, obtained as averages of the values reported by *Wei* [4c] (in degrees)

M	M'–M–C^1	C^1–M–C^2	C^7–M'–C^8
Co	92.8	104.8	101.7
Rh	95.0	98.5	98.5

No X-ray structural data are known for $HFeCo_3(CO)_{12}$. On the basis of the extremely high value of j_6 obtained for this compound we tentatively suggest a more widely 'open' $Fe(CO)_3$ entity on the apex, as compared with the $M(CO)_3$ groups of the other two compounds. One could interpret this suggestion in favour of the hydrogen atom outside the cluster, with a terminal Fe-H bond along the z-axis. However, both the mass spectral [11] and the inelastic neutron scattering data [12] are too convincing in favour of the 'hydrogen inside the metal-atom cage' structure, to allow serious doubts as for its correctness.

The very low K_3 value of the mixed cluster hydride is somewhat surprising. It is considerably lower than both K_{CO} values of $Fe(CO)_5$: $K_{eq} = 16.57$, and $K_{ax} = 16.95$ mdyn/Å [37]. This K_3 value shows a decrease by 0.38 mdyn/Å, as compared with the K_{CO}^{mean} value of $Fe(CO)_5$, whereas for the monomeric hydridoiron carbonyl $H_2Fe(CO)_4$ a $K_{CO} = 17.096$ mdyn/Å can be calculated [43] from the ν (C–O) values [42], *i.e.* a value 0.38 mdyn/Å ***higher*** than that of $Fe(CO)_5$.

This implies that in contrast to the mononuclear hydride, where a partial positive charge on the metal atom and hydridic δ^- charge on the H-ligands should be responsible for the high K_{CO} value, in the tetranuclear mixed hydride a partial negative charge must be present on the iron atom, and the iron-hydrogen 'bond' should be polarized in the sense

$$Fe^{\delta-} - \cdots - H^{\delta+}$$

The finding that the cobalt-bound terminal C–O groups are practically not affected, as compared with $Co_4(CO)_{12}$, indicates that there can be only a slight transfer of the positive charge from the proton to the cobalt atoms. However, the force constants of the bridging C–O groups which are more sensitive on substitution effects as terminal C–O constants, indicate by an increase some positive charge on the cobalt atoms of the mixed compound: the bridging C–O stretching force constant of $Co_4(CO)_{12}$ is 14.23 mdyn/Å to be compared with the corresponding value of $HFeCo_3(CO)_{12}$, *i.e.* 14.55 mdyn/Å [44]. This fact favours the location of the proton near the center of the basal Co_3 face, as proposed by *Chini* [45], rather than near the iron atom inside of the cluster [12]. Indeed, the mass spectrum showed the presence of Co_3H^+ and Co_2FeH^+ fragments, but no FeH^+ fragments were reported to occur [11].

We suppose that the Fe-H 'bond' pointing towards the basal Co_3 face should influence the geometry of the hybrid orbitals of the iron atom in the way to result in a larger OC-Fe-CO angle. At the same time it is likely that also the C^1-Co-C^2 angles are increased as one can infer from the higher values of the interaction constants j_1, and especially j_2, this latter indicating that the 'axial' CO ligands form a smaller angle with the z-axis than in $Co_4(CO)_{12}$.

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94. Reaktionen von Tetracyanoäthylen mit Polyenen

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(6. II. 75)

Summary Reactions of tetracyanoethylene with polyenes have been studied. With vitamin A derivatives **7**,10- and 11,14-cycloadducts were formed. Starting with the unsaturated dihydroxy compound **13** tetracyanoethylene first catalyzed the ring closure to give the dihydrofuran **14** which then was dehydrogenated to the corresponding furan **15**.

Bei der Einwirkung von Tetracyanoäthylen auf Vitamin A-Derivate und auf Zwischenprodukte der Vitamin A-Synthese beobachteten wir folgende Reaktionstypen: Cycloaddition, Dehydrierung unter Bildung von Tetracyanoäthan sowie beim β-Jonon die von *Middleton et al.* [1] an anderen Beispielen beschriebene *Michael*-Addition unter Bildung eines substituierten Tetracyanoäthans.

1. Cycloaddition. – Aus der Analyse der Lichtabsorptionsspektren der *all-trans* Vitamin-A-Derivate folgt, dass der Polyen-Chromophor planar ist und dass die Einfachbindungen s-*trans*- oder annähernd s-*trans*-Konformation besitzen [2]. Bei der $({}_{\pi}4_s + {}_{\pi}2_s)$-Cycloaddition muss daher in einem gewissen Stadium der Reaktion die betreffende s-*trans*- in eine s-*cis*-Konformation umgewandelt werden. Soviel man bis jetzt darüber weiss, kann die Anwesenheit des Dienophils die zur Umwandlung notwendige Energie verringern [3]. Die Cycloaddition von Maleinsäureanhydrid an Retinolacetat wird mit einem 140fachen Überschuss an Dienophil durchgeführt [4], und die Reaktion ist bei Raumtemperatur erst nach 40 Std. beendet. Hierbei erfolgt Addition des Maleinsäureanhydrids am Ende der Kette in 11,14-Stellung.

Tetracyanoäthylen ist ausgeprägt elektrophil und bildet mit dem Reaktionspartner *Charge-Transfer*-Komplexe, welche den Übergang der s-*trans*- in die s-*cis*-Konformation erleichtern. Daher läuft die von uns untersuchte Cycloaddition des Tetracyanoäthylens an Polyene auch ohne Überschuss an Dienophil wesentlich schneller ab als diejenige des Maleinsäureanhydrids. Ausserdem erhielten wir nicht nur 11,14-Addukte, sondern in zwei Fällen zusätzlich noch 7,10-Addukte. Es wurde aber immer nur ein Mol Tetracyanoäthylen addiert, d.h. beim Versuch, die isolierten Primäraddukte ein zweites Mal mit Tetracyanoäthylen umzusetzen, fand keine Reaktion mehr statt.

Vitamin-A_1-Säure **1** liefert sowohl ein 7,10-Cycloaddukt **2** als auch ein 11,14-Cycloaddukt **3**. Da die Doppelbindung des neu entstandenen Cyclohexen-Ringes im