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INFRARED SPECTROSCOPIC STUDIES ON METAL CARBONYL COMPOUNDS

XVI*. ANALYSIS OF THE C–O STRETCHING REGION OF THE TRIMERIC THIOLATOCOBALT CARBONYL COMPLEXES $Co_3(CO)_4(SR)_5$. THE QUESTION OF TERMINAL–BRIDGING COUPLING IN FORCE CONSTANT CALCULATIONS

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SUMMARY

The analysis of the infrared spectrum of $Co_3(CO)_4(SCH_3)_5$ in the C–O stretching region shows that not even the use of the ^{13}C–O isotopic frequencies can provide proof that the interactions between terminal and bridging CO ligands have non-zero values. Thus the neglect of these interactions in force constant calculations is a justified procedure.

INTRODUCTION

In an earlier paper[1] we reported the values of force and interaction constants (in a factored C–O force field) for compounds of the type (π-arene)$Co_4(CO)_9$[2]. In that study we neglected all interactions between terminal and bridging CO groups, a procedure which could be criticized in the light of the fact that non-zero interaction constants were calculated for spatially more distant terminal CO groups in these (arene)$Co_4(CO)_9$ compounds and also, *e.g.*, in $Mn_2(CO)_{10}$[3], $HgCo_2(CO)_8$[4], and their axially disubstituted derivatives[5,6]. However, the isotopic frequencies of ^{13}CO-enriched $Co_4(CO)_{12}$[7,8] can be calculated accurately in the bridging region by assuming only bridge–bridge interactions[9]. We wished to obtain more direct evidence for the correctness of this assumption in the framework of a C–O factored model[10]. We have thus carried out an accurate determination of the ratio $\nu(^{13}CO)/\nu(^{12}CO)$

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in a compound that contains only one bridging CO group in addition to the terminal ones.

We chose as models compounds of the type $Co_3(CO)_4(SR)_5$, described for the first time by Klumpp *et al.**[12]. The structure of the $R=C_2H_5$ compound has been determined by Wei and Dahl[13].

EXPERIMENTAL

Preparation of $Co_3(CO)_4(SCH_3)_5$

To a stirred solution of 214 μl (2.33 mmol) of $(CH_3)_2S_2$ in 4 ml of n-heptane was added dropwise, under nitrogen, about 7 ml of a solution of $Co_2(CO)_8$ (400 mg, 1.16 mmol, in 7.5 ml of n-heptane). The reaction was taken to be complete when the bridging band of $Co_2(CO)_8$ at 1857 cm^{-1} did not disappear within a few minutes. The slight excess decomposes during chromatography. The solution was then concentrated to 2–3 ml *in vacuo* and chromatographed on a silica gel column (30 × 1.5 cm) with 50 v/v per cent mixture of benzene and n-heptane as eluant. The first zone of dark brown colour contained $Co_4(CO)_{12}$, and the next, deep red, fraction was $Co_3(CO)_4(SCH_3)_5$, which was identified by its IR spectrum, which, apart from a small shift towards higher frequencies, is identical with that reported for the compound with $R=C_2H_5$[11].

Infrared spectra

The spectra were recorded on a Perkin–Elmer 621 spectrophotometer using very low scanning speeds (2–5 sec/cm^{-1}). Wave numbers were calibrated against carbon monoxide and water vapour spectra.

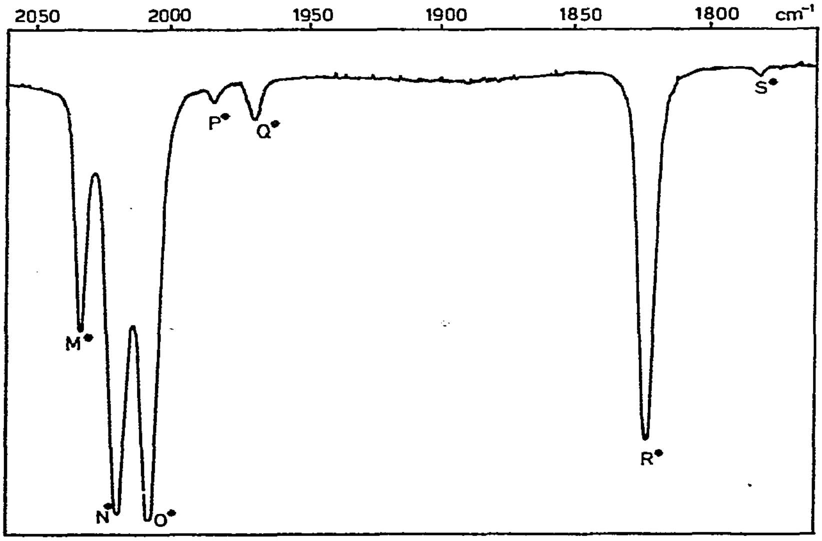

Fig. 1. Infrared spectrum of $Co_3(CO)_4(SCH_3)_5$ in the C–O stretching region (n-hexane solution).

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* For the $R=C_2H_5$ compound the composition was previously incorrectly given as $Co_4(CO)_5(SEt)_7$[11].

RESULTS

For the compound having $R=C_2H_5$ we calculated the force and interaction constants only for the terminal region, using the published frequencies[11], since for this compound the isotopic satellite of the bridging band was not available in the literature. For the exact study, taking into account the bridging region, we prepared the hitherto unreported derivative with $R=CH_3$ by a modification of the published method[11]. The $Co_3(CO)_4(SR)_5$ compounds are formed in better yield and in higher purity if the solution of dicobalt octacarbonyl is added to the solution of the disulfide, so that an excess of this latter is present throughout. Under these conditions other tri-, penta-, or hexa-nuclear Co–CO–SR compounds[11–14] are not formed and the only by-product is $Co_4(CO)_{12}$, from which the $Co_3(CO)_4(SR)_5$ compounds can readily be separated.

For $Co_3(CO)_4(SCH_3)_5$ we determined all the fundamental ^{12}C–O and natural ^{13}C–O frequencies with high precision. The spectrum is shown in Fig. 1, and the frequencies are given in Table 1.

TABLE 1

FUNDAMENTAL AND ISOTOPIC C–O STRETCHING FREQUENCIES OF $Co_3(CO)_4(SCH_3)_5$

Label[a]	*Wave number*[b] (*cm*$^{-1}$)	*Assignment*
M*	2033.3	A'
N*	2020.1	A''
O*	2008.5	A'
P*	1982.8	^{13}C–O
Q*	1968.6	^{13}C–O
R*	1821.3	A' (bridge)
S*	1778.6	^{13}C–O (bridge)

[a] Labels refer to Fig. 1. [b] Solvent n-hexane; accuracy ±0.4 cm^{-1}.

THE QUESTION OF THE CO_{bridge}–$CO_{terminal}$ COUPLING

The structure of the compound and the numbering scheme for the CO groups are shown in Fig. 2. If we neglect the non-planarity of the sulphur atoms the $Co_3(CO)_4S_5$-skeleton of the molecule belongs to point group C_s. The molecule mono-substituted isotopically in the bridging position possesses the same symmetry, and has 3 vibrations of species A' (2 terminal + 1 bridging) and one of species A'' in the C–O stretching region.

The frequency ratios of the isotopic bands are determined by the factor $\sqrt{(\mu_i/\mu)}$, where μ_i and μ are the isotopic (^{13}CO) and ^{12}CO reduced masses, respectively. In the case of monocarbonyls, in which the isotopic effect influences just one C–O stretching mode, ν_i/ν ratios of 0.9772–0.9774 have been observed for $(h^5\text{-}C_5H_5)CoI_2(CO)$[15] and $(Et_3P)_2CoCl_2(CO)$[15,16]. The actual value of this factor is lower than the theoretical value of 0.9778 because of coupling with the M–C stretching modes[16], which is neglected in the Cotton–Kraihanzel types of force field[17].

In the presence of effective coupling between various CO groups of polycarbonyls, the isotopic effect is distributed among all the roots of an *n*th order equation (in the case of an *n*th order species); consequently the separation $\Delta\nu$ between the lowest ν(C–O) fundamental and its satellite (which is usually the most easily recognizable isotopic band) decreases, and hence their ratio increases.

In the case of $Co_3(CO)_4(SCH_3)_5$, the ratio of the bridging isotopic frequency S* (see Fig. 1) and its parent band R*, is $\nu_S/\nu_R = 0.9766$, which proves unequivocally that the bridging carbonyl group behaves as if it were a simple monocarbonyl, without any influence from interactions. This ν_i/ν ratio is even lower than those reported in ref. 16, which points to higher K_{MC} and/or a lower K_i [between ν(C–O) and ν(M–C)] values than are usual for terminal CO groups.

There is thus direct evidence for the absence of terminal–bridging interactions, at least in the framework of the CO-factored model. Further indirect evidence is given by force constant calculations, as follows.

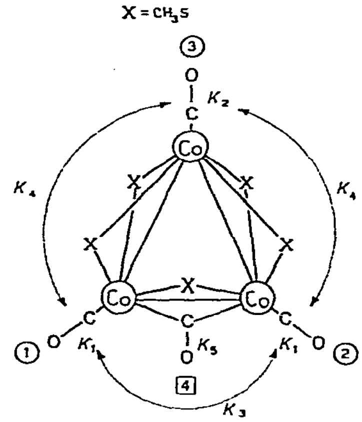

Fig. 2. Schematic structure of the $Co_3(CO)_4S_5$ core of the molecule, with the numbering scheme for the ligands and for the principal C–O stretching force and interaction constants.

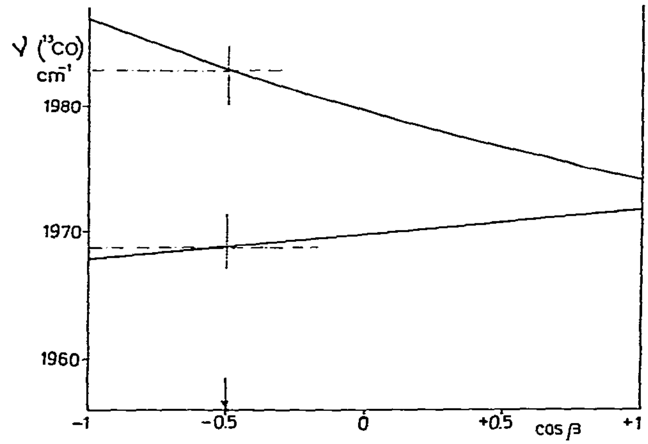

Fig. 3. Comparison between calculated (solid line) and observed (-·-·-·-) lower isotopic frequencies *vs.* cos β for assignment (*i*).

FORCE CONSTANTS

We first calculated the terminal force and interaction constants, and separately, the uncoupled bridging force constant. We then inserted arbitrary but reasonable values into the force constant matrix for the terminal–bridging interactions, and observed their effect on the isotopic frequencies and on the force and interaction constants. The numbering of the force constants K_1–K_5 is shown in Fig. 2.

The assignment of band M* (see Fig. 1) to species *A′* is straightforward[18], but we cannot predict *a priori* the distribution of bands N* and O* among the two species. Therefore we performed calculations with two assignments:

(*i*): *A′*...M* and O*; *A″*...N*

(*ii*): *A′*...M* and N*; *A″*...O*

using our "cos β parameter method"[19] for obtaining the force constants, and the principle of the transfer of the isotopic effect from the G^{-1} to the F matrix[20] for the determination of the isotopic frequencies *vs.* cos β.

The results are shown in Fig. 3–5. With assignment (*ii*) we have agreement between measured and calculated isotopic frequencies only for cos β -0.81 (Fig. 4), and this value of the parameter implies a negative K_3 (Fig. 5B), which is in conflict with the Cotton–Kraihanzel[17] and Bullitt–Cotton[25] principles of CO–C′O′ interactions.

With assignment (*ii*) even the calculated intensities of the isotopic satellites P* and Q* are inverted compared with the observed ratio. Thus we decided in favour of assignment (*i*), which leads to agreement between calculated and observed isotopic frequencies for cos β -0.5 (Fig. 3), and a reasonable set of force and interaction constants (Fig. 5A and Table 2). Moreover, we obtained nearly equal relative intensities

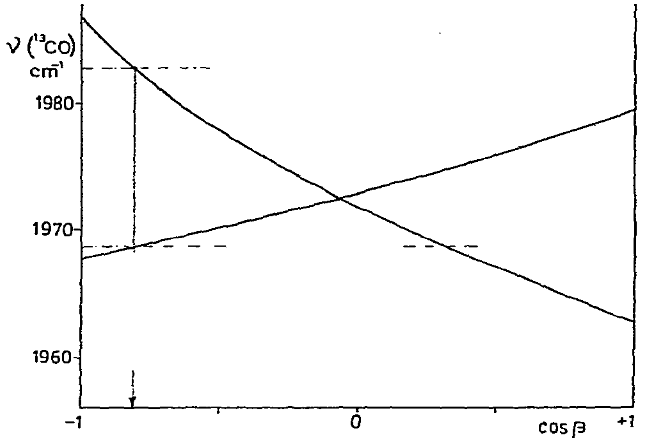

Fig. 4. Comparison between calculated (solid line) and observed (-·-·-·-) lower isotopic frequencies *vs.* cos β for assignment (*ii*).

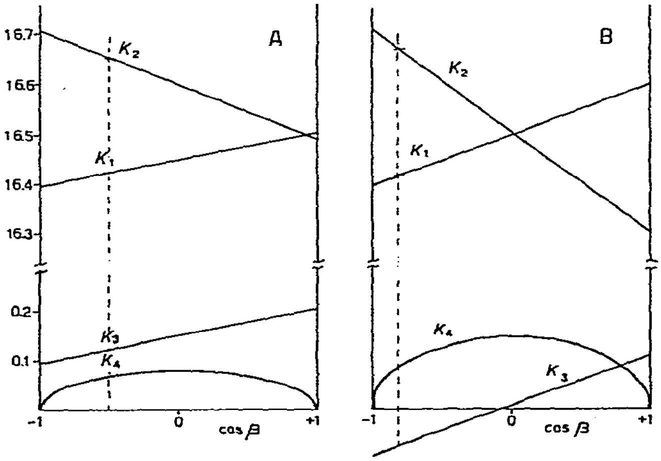

Fig. 5. Force constants *vs.* cos β diagrams[23]: A, for assignment (*i*); B, for assignment (*ii*).

TABLE 2

C–O STRETCHING FORCE AND INTERACTION CONSTANTS FOR $Co_3(CO)_4(SR)_5$ COMPOUNDS ($R=C_2H_5, CH_3$)

R	K_1	K_2	K_3	K_4	K_5	K_6	K_7
C_2H_5[a]	16.35	16.58	0.124	0.065	13.38		
CH_3[b]	16.422	16.651	0.121_4	0.066_2	13.403	0.0	0.0
CH_3[c]	16.418	16.644	0.117_7	0.066_5	13.418	0.148_9	0.049_7

[a] Calculated from frequencies given in ref. 12. [b] Values obtained with neglect of terminal–bridge interactions. [c] Values obtained with terminal–bridge interaction constants arbitrarily chosen as $K_6=0.15$ and $K_7=0.05$ mdyn/Å; these are slightly changed to give the above values by the refinement cycle of the calculation.

TABLE 3

COMPARISON OF CALCULATED AND OBSERVED ISOTOPIC FREQUENCIES OF $Co_3(CO)_4(SCH_3)_5$

		$1-[^{13}CO]$	$3-[^{13}CO]$	$4-[^{13}CO]$
Calculated	(i)	1968.65	1982.93	1779.77
	(ii)	1968.88	1982.49	1779.93
Found (±0.4 cm^{-1})		1968.6	1982.8	1778.6

(i), Without terminal–bridge interactions; (ii), with terminal–bridge interactions; *cf.* case CH_3[c] in Table 2.

for the isotopic bands with band Q* belonging to ^{13}CO-substitution in position "1". Since the concentration of this latter type is twice as high as that of the other mono-^{13}CO species (in position "3"), this result is in agreement with the observed relative intensities of these two bands (Fig. 1).

To examine the effect of non-zero terminal–bridge interactions we introduced into the force field the interaction, K_6, between CO "1" or "2" and the bridge, and the interaction, K_7, between ligand "3" and the bridging CO group. We increased K_6 gradually to 0.15 and K_7 to 0.05 mdyn/Å, values which are in accord with the observed values of K_3 and K_4. The final result is shown in the third row of Table 2. The comparison of the isotopic satellite frequencies calculated with and without these interactions is shown in Table 3.

We see that the effect of the introduction of K_6 and K_7 on the calculated isotopic frequencies is not greater than 0.45 cm^{-1}, *i.e.* it is at about the limit of the accuracy of the measurements. Hence not even inclusion of the isotopic frequencies into the calculations can prove or disprove the existence of terminal–bridging CO–C′O′ interactions in metal carbonyls.

But we see also from the data of Table 2 that this problem has no significance, since none of the terminal force or interaction constants vary by more than the uncertainty (0.01 mdyn/Å) due to the complete neglect of these interactions, and even the change in the bridging force constant is extremely low, *viz.* 0.015 mdyn/Å. Thus we conclude that neglect of the terminal–bridging CO–CO interactions in force constant calculations for metal carbonyls is justified.

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