Inorganica Chimica Acta, 18 (1976) L18 - L20

A Correction to the Interpretation of the C–O Stretching Region of the Infrared Spectra of $Co_2(CO)_6(HC_2R)$ Complexes with Terminal Acetylenes as Bridging Ligands and an IR indication for the Distorted Molecular Geometry of $Co_2(CO)_6(C_6H_5C_2C_6H_5)$ in Solution

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Received February 9, 1976

Twelve years ago one of us published for the first time the "medium high resolution" IR spectra of a series of $Co_2(CO)_6(RC_2R')$ compounds.[1] These spectra were obtained with a spectral slit width of 2.1 cm^{-1}. Five C–O stretching bands, as expected for point group C_{2v}, were observed independently of the type of the bridging acetylene.

Molecules of the type $Co_2(CO)_6(HC_2R)$ may possess, at most, C_s symmetry, so that all six terminal C–O stretching modes would be expected to be IR active. However, the fact that this early work indicated that only five were observed, has been rationalised in the following way: "Diese Beobachtungen beweisen, dass für die Auswahlregel die Symmetrie des $Co_2(CO)_6C_2$-Skelettes massgebend ist, und dass die unsymmetrische Substitution gleichwertiger Kohlenstoffatome in den Brückenpositionen ohne Einfluss auf die Anzahl der IR-aktiven C–O Valenzschwingungen ist".

We now report that the sixth, $\nu_3^{CO}(A_2)$ mode which is inactive in terms of strict C_{2v} selection rules, *can* be observed in the spectra of several complexes formed with unsymmetrical substituted acetylenes, HC_2R, if a more efficacious instrument with a spectral slit width of at least 0.8–1.0 cm^{-1} is used.

Experimental

The complexes $Co_2(CO)_6(HC_2R)$ (where R = CH_3, n-C_4H_9, $tert$-C_4H_9, iso-C_5H_{11}, n-C_6H_{13}, C_6H_5) and $Co_2(CO)_6(C_6H_5C_2C_6H_5)$ were prepared by mixing equimolar amounts of $Co_2(CO)_8$ and the appropriate acetylene in n-hexane solution, under nitrogen, at room temperature. The reaction was complete within a few minutes. The raw reaction product contained in all cases small quantities of other metal carbonyl derivatives as impurities. As the simplest method of purification chromatography on a silica gel column was applied. With n-hexane as eluent only the $Co_2(CO)_6(HC_2R)$ complexes are eluted.

Spectra were scanned, in part in both Laboratories independently, on n-hexane solutions, using a Perkin Elmer 325 spectrophotometer.* Slit program 4.5, scale expansion 5X or 10X, and a scan speed of 5–10 cm^{-1}/minutes were applied. All compounds were studied in several concentrations to obtain optimal intensities for all C–O stretching bands, including natural ^{13}C isotopic satellites.

Results and Discussion

Figures 1 and 2 show the 2040–1990 cm^{-1} spectral region for the propyne and hexyne-1 com-

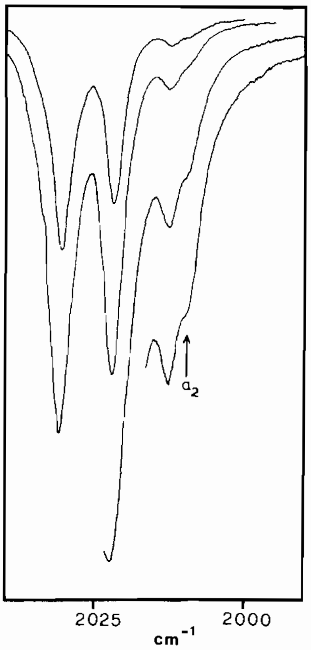

Figure 1. The high resolution infrared spectrum of $Co_2(CO)_6(CH_3C{\equiv}CH)$ of four solutions of different concentrations (transmittance scale).

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*Some spectra were also recorded on a Beckman IR 12 in Turin.

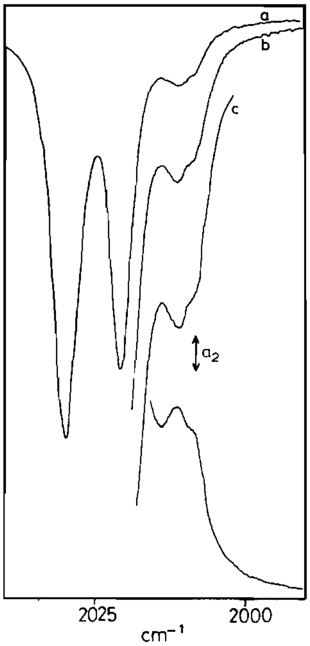

Figure 2. The high resolution infrared spectrum of $Co_2(CO)_6$-(hexyne-1). The series a–c are of solutions of increasing concentration (transmittance scale). Spectra d is of the same solution as for spectrum c but recorded in absorbance.

plexes. Table I gives the observed frequencies for six compounds of this type (in the case of the complex formed with propargyl alcohol the A_2 band could not be observed due to the broader form of the bands caused by the polar substituent).

The identity of the observed shoulder (in the low-frequency wing of $\nu_5^{CO}(B_1)$) with the A_2-species fundamental has been proven by calculations based on exactly determined ^{13}C–O isotopic bands.[2] As a matter of fact these shoulders were sought *after* their theoretical position had been ascertained by calculations, and they were then observed within ± 0.5 cm^{-1} at the predicted positions. The present report of the observation of this A_2 mode in the infrared is in agreement with that on the Raman spectra of derivatives of symmetrical acetylenes containing electronegative substitution.[3]

We suggest, therefore, to substitute for the sentence quoted above[1] the following statement: "With some asymmetric acetylenes as ligands the electronic asymmetry inside the Co_2C_2 entity can be sufficient to relieve the strict C_{2v} point group selection rules and to give a slight intensity to the $\nu_3^{CO}(A_2)$ C–O stretching mode".

There are several reasons which may be advanced for our observations, not necessarily mutually exclusive. Thus, Miller[4] has shown that molecular asymmetry may have a more pronounced effect on infrared intensities than on frequencies. Certainly, in the present case we do not believe that there is any substantial distortion of the C_{2v} symmetry of the $Co_2(CO)_6$ entity. This statement is based on the observation that such distortions in the geometry of the C–O ligand system are indicated by discrepancies between the observed and calculated positions of the ^{13}CO isotopic satellites. However, for the present species, the agreement between observed and calculated ^{13}CO frequencies is very good (the largest error is 0.8 cm^{-1}). It is, therefore, perhaps simplest to think of the distortion being electronic rather than geometric in nature.[5]

As an example for what is believed to be a real geometrical distortion we present a new feature observed in the spectrum of $Co_2(CO)_6(C_6H_5C_2C_6H_5)$. For this compound the A_2 mode has been calculated,[2] based on C_{2v} symmetry, to have the frequency of 2005 cm^{-1}. No intensity is to be expected for this mode on the argument presented above since the acetylenic ligand is symmetric. Surprisingly, however, the high resolution spectrum showed a new shoulder at 2010.2 (±0.5) cm^{-1} (Fig. 3). This value cannot be brought in accord with the frequencies of the observed isotopic bands.

We believe that the explanation of this observation lies in the strict inapplicability of C_{2v} symmetry and the existence of a substantial geometric distortion.

TABLE I. ^{12}C–O Stretching Frequencies (cm^{-1}) of some $Co_2(CO)_6(HC{\equiv}CR)$ Complexes with Assignments.

R	$\nu_1(a_1)$	$\nu_4(b_1)$	$\nu_6(b_2)$	$\nu_2(a_1)$	$\nu_5(b_1)$	$\nu_3(a_2)$
CH_3	2094.1	2053.7	2030.2	2021.6	2012.2	*2009.0*[a]
n-C_4H_9	2092.9	2052.7	2029.6	2020.4	2011.0	*2008.0*[a]
n-C_6H_{13}	2092.7	2052.7	2029.4	2020.2	2010.8	*2007.8*[a]
C_6H_5	2094.5	2057.7	2032.3	2027.9	2016.2	*~2011*[b]
t-C_4H_9	2092.2	2052.8	2029.4	2020.0	2010.2	*2008.9*[a]
2-C_5H_{11}	2091.7	2051.9	2028.8	2019.9	2010.3	*2007.9*[a]

[a] Shoulders, ± 0.5 cm^{-1}. [b] Poorly resolved, ± 1 cm^{-1}, All other frequencies: ± 0.2 cm^{-1}. Solvent: n-hexane.

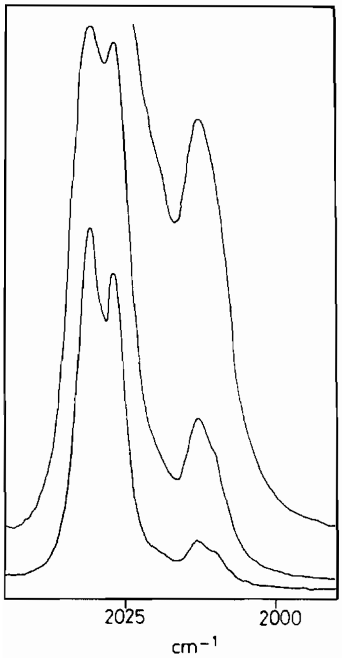

Figure 3. The high resolution infrared spectrum of $Co_2(CO)_6$-($C_6H_5C\equiv CC_6H_5$) of three solutions of different concentrations (transmittance scale).

Specifically, we believe that the orientation of the two aromatic rings of the ligand are not symmetry-related in the complex, so that the different interactions between these rings and the CO ligands on the two "sides" of the molecule result in a distortion of the geometry of the $Co_2(CO)_6$ framework. In this case at least three different CO sites should be present with, at least, nine different CO···C'O' interactions (instead of the two and six, respectively, of the C_{2v} geometry). However, we have no evidence that there is more than one conformer present in n-hexane solution.

In support of our explanation, the structure of the molecule determined in the solid state[6] shows two different orientations of the phenyl rings, resulting in different C(ring)···CO and CO···C'O' separations. Our ^{13}C NMR spectra were virtually identical to those published recently.[7] For differently twisted phenyl rings the *ortho* and *meta* carbon atoms are not equivalent in the two rings. However, no splitting of the appropriate peaks could be observed. This observation is presumably a consequence of a very low potential barrier between twisted isomeric forms combined with the small chemical shift between the *ortho* and *meta* carbon atoms.

A sixth band at the low frequency end of the terminal C–O stretching region, with higher separation from the lower B_1 band than here reported, has been found independently by Pályi *et al.* for $Co_2(CO)_6(RC_2R')$ derivatives, where, however, R and R' differ markedly in size as well as in electronegativity.[5] In these cases it is likely that both of the mechanisms considered above are effective.

Acknowledgements

G.B. thanks Professor P. Pino for the excellent working facilities, Dr. P. Skrabal for recording and discussing the ^{13}C NMR spectra and Dr. G. Pályi for the communication of their results prior to publication.

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