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ON THE INFRARED SPECTRUM OF DICOBALT OCTACARBONYL. RESULTS OF ^{13}CO ENRICHMENT STUDIES

GYÖRGY BOR
*Laboratorio di Chimica e Tecnologia dei Radioelementi del C.N.R., Padova (Italy)**

KLAUS NOACK
*F. Hoffmann—La Roche Ltd., Basel (Switzerland)**

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Summary

Studies of the infrared spectra in the 2000 cm^{-1} region of $Co_2(CO)_8$ enriched with ^{13}CO have permitted the distinction between the weak bands due to fundamental C—O stretching vibrations of the all-^{12}CO compound and the satellites due to the naturally abundant ^{13}C compound. Thus it has been possible to resolve the discrepancy between earlier proposals for the structure of the non-bridged form which exists in solution in equilibrium with the bridged form. Two weak bands could not be assigned, and indicate the presence of a small amount of yet a third form, of unknown structure.

Introduction

About 10 years ago we independently reported the existence of two isomers of $Co_2(CO)_8$ in solution [1,2]. We agreed that the geometry of the bridged form (I) (or "low temperature form", LTF) was that first proposed by Mills [3], and confirmed later for the crystalline compound by Sumner, Alexander, and Klug [4]. However, for the second isomer ("high temperature form", HTF), although agreeing that it did not contain bridging groups, and that the two halves of the molecule are linked only by a single cobalt—cobalt bond, we proposed different geometries. One of us (K.N.) proposed structure (IIa), mainly on the basis of analogies with the spectra of $CdCo_2(CO)_8$ and $HgCo_2(CO)_8$, especially in the far infrared region [1c]. The other of us (G.B.)

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* Present addresses. The studies reported here were carried out independently by one of the authors (G.B.) in the "Hungarian Oil and Gas Research Institute, M.Á.F.K.I.", Veszprém (Hungary), and the other (K.N.) in the (now defunct) "Cyanamide European Research Institute" Cologny/Geneva (Switzerland). Since both authors had left these respective laboratories, it seemed appropriate to publish the available results jointly. Correspondence to G.B. should be addressed to: Technisch-chemisches Laboratorium der ETH, CH 8006 Zürich, Universitätstrasse 6 (Switzerland).

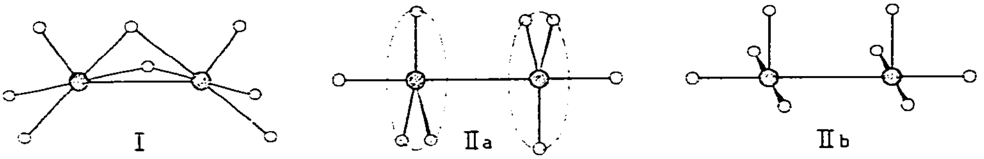

Fig. 1. Structure of the "low temperature form" (I), and the two earlier suggestions for the "high temperature form" [(IIa) [1] and IIb [2]] of dicobalt octacarbonyl in solution.

attributed special importance to the doublet form of the very weak fundamental belonging to the totally symmetric in-phase vibration [2a,b] (maxima at 2111 and 2107 cm^{-1}), and regarded as a fundamental the weak band at 2058 cm^{-1} (regarded as a ^{13}CO satellite by K.N.) which did not fit into the spectrum of either form (I) or of form (IIa), and so proposed a structure (IIb) of lower symmetry [2c].

To clarify the problem of isomer (II) (HTF) and to propose an unequivocal assignment of all of the C—O stretching bands of dicobalt octacarbonyl we subsequently agreed on two different approaches: (*a*) the study of the spectra of analogous Rh and Ir carbonyls, and (*b*) isotopic enrichment to facilitate a decision on the origin of the weak bands present in the spectrum.

The study (*a*) was unsuccesful, since all efforts to prepare the compounds $M_2(CO)_8$ (with M = Rh or Ir) failed [5]. From the recent studies by Whyman [6], we now know that these species can exist only under high CO pressure and low temperature, and the original reports of their preparation [7,8] must be considered erroneous. Since the spectra of $Rh_2(CO)_8$ taken by Whyman under 490 atm pressure of CO are considerably obscured by the broad absorption of dissolved carbon monoxide they cannot be used for detailed stuctural analysis.

Isotopic enrichment, however, furnished important new data for the interpretation of the spectrum, and the results are described below.

Experimental part

The ^{13}CO exchange was performed by shaking appropriate solutions of $Co_2(CO)_8$ with enriched CO gas. The ^{13}CO content was in some cases determined mass spectrometrically.

The spectra were taken either on a Zeiss Model UR 10 or a Perkin - Elmer Model 521 spectrophotometer. The conditions were identical to those used in our earlier studies on cobalt carbonyl [1,2]. The variable temperature cell used has been described [1a].

Results

The ^{13}CO enrichment studies were performed in the two laboratories independently, and gave substantially identical results. One of us (K.N.) also carried out variable temperature studies down to -40° with the ^{13}CO-enriched sample. These studies did not, however, furnish immediate answers to the assignment problems in the spectrum of $Co_2(CO)_8$, and enrichment studies (^{13}CO and $C^{18}O$) with simpler systems were needed [9 - 14] to facilitate the understanding of the enriched spectra.

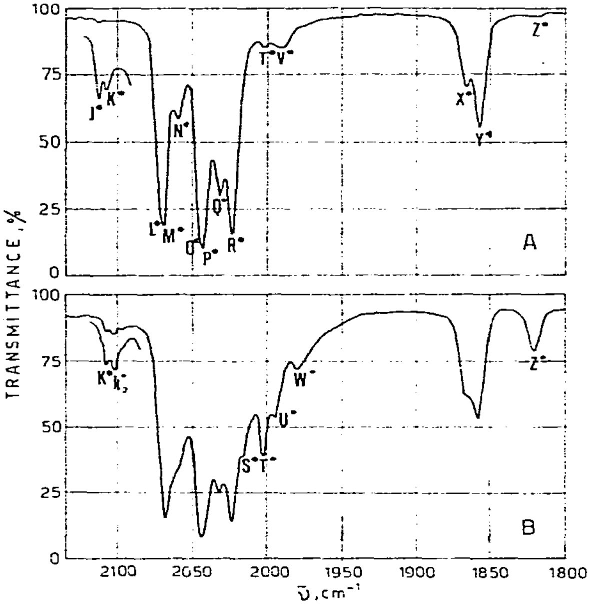

Fig. 2. Comparison between the infrared spectra of (A) "natural" (^{13}C 1.1%) and (B) isotopically enriched (^{13}C 22.5%) dicobalt octacarbonyl in the C—O stretching region (solvent n-hexane). Band labels refer to points (*a*) - (*h*) in the Discussion. The band labelled k_2^*, not mentioned in the text, belongs to the bis-^{13}C-substituted molecular species which are present in about the same concentration as the mono-^{13}C-substituted species at this concentration of ^{13}CO (cf. Fig. 2 of ref. 14b). Insets correspond to higher concentrations.

The spectra are shown in Figs. 2, 3, and 4. In the case of some bands, spectra of less enriched samples were more useful for unambiguous assignments. The results can be summarized as follows, beginning at the high energy end of the spectrum:

(*a*). The weak band K* at 2107 cm^{-1}, considered previously [2b,c] as the ν_1(CO) band of form (IIb) (HTF) *increases* in intensity with increasing ^{13}CO concentration, and thus it is clearly an isotopic band. Spectra taken at —40° make it very probable that the band belongs to the LTF (I), and hence is a satellite of band J*.

(*b*). The strong doublet L*—M* broadens in its low-energy wing as the isotopic concentration increases. With higher enrichment (Fig. 2B) the band maximum is shifted by 2 - 3 cm^{-1} to lower values. This is clearly due to satellite bands invisible in the original spectrum, as confirmed by calculations.

(*c*). The band N* at 2058 cm^{-1} *does not increase* with isotopic enrichment, only the minimum-gap between N* and the doublet L*—M* is filled up by the satellites of these strong bands, of which L* was shown previously [1a] to belong to the LTF and M* to the HTF.

(*d*). A shoulder, S*, appears at about 2011 cm^{-1} in the low energy wing of band R*. By analogy to $HgCo_2(CO)_8$ [14b] we assign it to the high temperature form.

(*e*). The weak band T* at 2001 cm^{-1} gains considerable intensity with

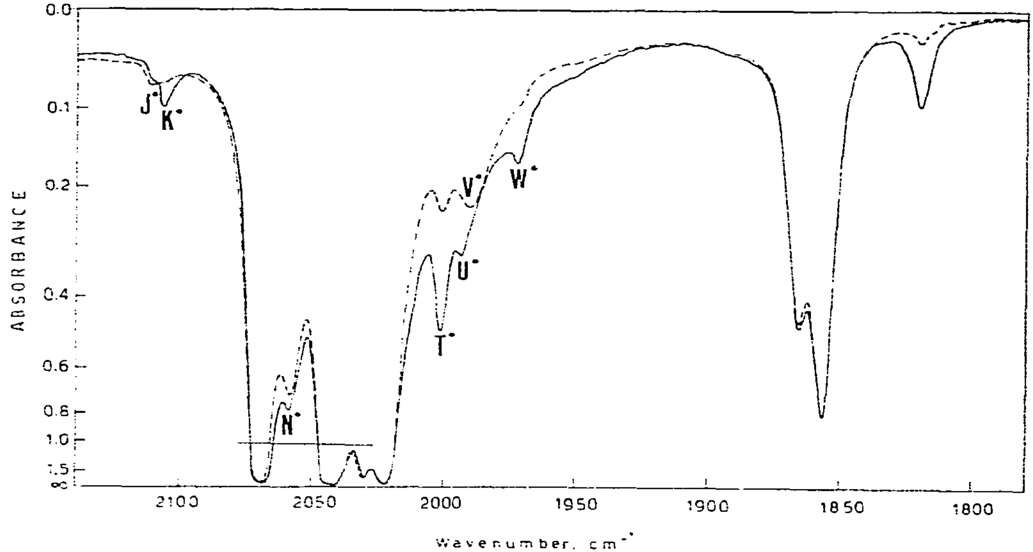

Fig. 3. Spectra of $Co_2(CO)_8$ with natural abundance of ^{13}C (broken line) and of a sample enriched to ≈ 7.5 per cent of ^{13}C (solid line) at room temperature in n-heptane.

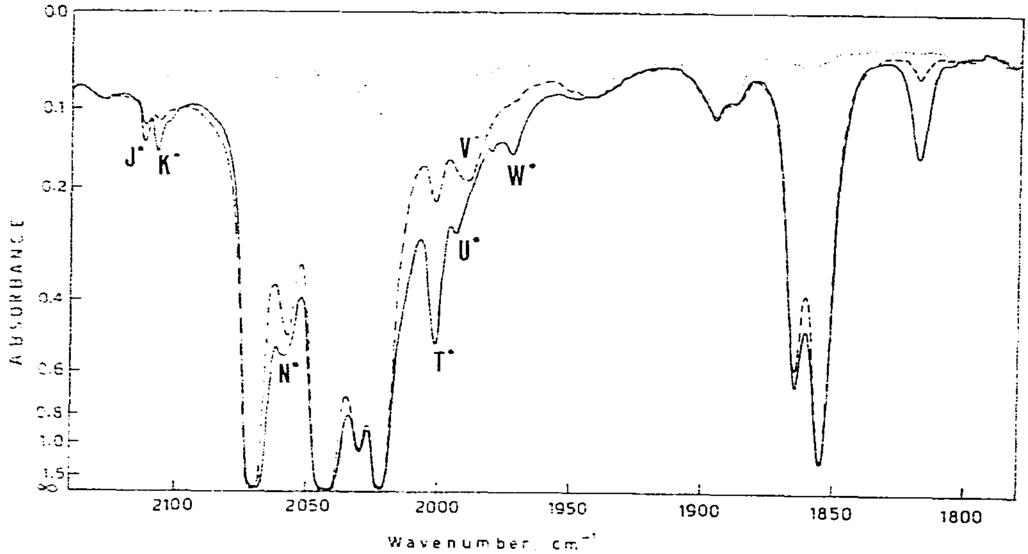

Fig. 4. Spectra of $Co_2(CO)_8$ with natural abundance of ^{13}C (broken line) and of a sample enriched to ≈ 7.5% of ^{13}C (solid line) at —40° in n-heptane. The dotted line shows the spectrum of the solvent at —40°.

enrichment; it is clearly an isotopic band. Calculations showed that belongs to the bridged LTF.

(*f*). In contrast, the equally weak neighbouring band V* at 1990 cm^{-1} does not increase with isotopic enrichment; instead a new maximum U* emerges at 1994 cm^{-1}. It behaves as if it belongs to the HTF, since it decreases at —40°.

(*g*). The very weak shoulder W* at about 1975 cm^{-1}, hardly observable in the natural spectrum, gains in intensity with enrichment; it is an isotopic satellite, and calculations show that it belongs to the HTF (IIa).

(*h*). In the bridging region we see the two changes expected: viz. the increase of the weak isotopic band Z* at 1820 cm^{-1}* (^{13}CO bridging), and the filling up of the minimum between bands X* and Y* by a new isotopic band to give rise to a composite broad band.

Discussion

Observation (*a*) invalidates the main argument [2c] for a lower symmetry of the HTF, and thus the possibility of structure (IIb) must be abandoned.

On the other hand, the *non-isotopic*, i.e. fundamental $^{12}C—O$ origin of the two weak bands N* and V* is proved by the enrichment studies. In the spectra of compounds which have either exclusively the geometry (I), e.g. compounds of the type $Co_2(CO)_6(RC\equiv CR')$ [15,16] and $Co_2(CO)_6(As_2)$ [16], or solely structure (IIa), e.g. $HgCo_2(CO)_8$ [14b], no weak bands are present which were not in accord with the selection rules for their respective point groups, or which were not proved definitely to be ^{13}CO satellites; thus the two bands concerned cannot be explained by the superposition of the "theoretical" spectra of the LTF (I) and HTF (IIa) of $Co_2(CO)_8$ only.

At present we cannot suggest a better explanation for these two bands than postulating that a *third* form of the compound is present in low concentration. A monomeric nature for this species must be excluded on the basis of absence of paramagnetism in solution [1a] (in contrast to the sublimed and frozen-out solid as found by Keller and Wawersik [17] at liquid nitrogen temperature). The presence of a coordinatively unsaturated species, e.g. $Co_2(CO)_7$ must also be ruled out, since recent kinetic studies by Ungváry [18] have shown that a concentration of such a species cannot exceed 0.1%.

From the low-temperature spectra it can be seen that the intensities of bands N* and V* decrease at lower temperatures, and thus they behave as though they belong to form (II). From this observation we conclude that these bands should belong to another "high temperature form", related in some way to form (II).

The absence of anomalies in the bridging region, (it being assumed that the unknown species of $Co_2(CO)_8$ has *only* these two bands) suggests a structure without CO bridges, analogous to that of $Mn_2(CO)_{10}$ but without the two axial ligands, i.e. two nearly square planar $Co(CO)_4$ entities linked together by an apical cobalt—cobalt bond [Form (III), Fig. 5]. This structure would imply two C—O stretching bands (B_2 + E). In the case of the $Mn_2(CO)_8L_2$ complexes [19], where the phosphinic ligands L occupy the axial positions, the higher band (B_2) is much less intense than the very strong E band. In the absence of the ligands L, however, the B_2 mode could gain additional intensity by an induced dipole moment mechanism, as suggested for the intensity anomaly of the higher B_2 band of $Mn_2(CO)_{10}$ by Cotton and Wing [20] and considered more quantitatively recently [21]. The observed separation of 67

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*As a result of a printing error this was reported previously [2c] as lying 1832 cm^{-1}.

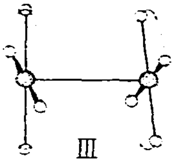

Fig. 5. Possible structure for the third isomer of $Co_2(CO)_8$, giving two C - O stretching bands.

cm^{-1} between these two bands, however, is much larger than the B_2-E separation for the compounds $Mn_2(CO)_8L_2$ which was reported [19,22] to be between 20 and 40 cm^{-1}. More specifically, in the case of $Mn_2(CO)_8(PF_3)_2$ which can be regarded as a model for form III, the frequencies 2036.4 (B_2) and 2011.9 (E) cm^{-1} have been reported [22], corresponding to a separation of 24.5 cm^{-1}. However, there are very considerable differences between the CO—CO interaction constants of the carbonyls of cobalt and manganese, respectively, which may markedly influence the band separations. Hence, although unlikely, model (III) can not be definitively excluded.

If we assume that there are other weak bands present, possibly in the bridging region also, but that these are overlapped by the strong bands of the two principal isomers, other structures can be suggested which may play a role in the fast interconversion between structures (I) and (II). More detailed discussion of this possibility would be too speculative, however.

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