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Application of the ligand polyhedral model to dicobalt octacarbonyl

Brian F. G. Johnson* and Emilio Parisini

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland (UK)

Abstract

Application of the ligand polyhedral model (LPM) to dicobalt octacarbonyl, $[Co_2(CO)_8]$, leads to an explanation of the μ_2-bridged structure that the molecule adopts in the solid state and also of the isomeric forms which co-exist in equilibrium in solution. It further provides a convenient explanation of both the observed low energy interconversion of these isomers and the fluxional behaviour they exhibit.

Introduction

On the basis of a comparatively early single crystal X-ray diffraction study [1], dicobalt octacarbonyl, $[Co_2(CO)_8]$, was shown to possess in the solid state the molecular structure shown in Fig. 1(a). In this, a classic amongst inorganic structures, two $Co(CO)_3$ units are linked through two μ_2-CO bridges and a cobalt–cobalt bond. The Co–Co distance of 252 pm is taken to represent a single cobalt–cobalt bond and accounts for the observed diamagnetism of the compound. As such, the molecule is 'bent' and has been frequently described as possessing a 'book-shaped' configuration. It is also clearly related to diiron enneacarbonyl, $[Fe_2(CO)_9]$ [2], possessing almost exactly the same geometric distribution of carbonyl groups except that one of the three μ_2-CO bridges of $[Fe_2(CO)_9]$ is missing (Fig. 1). Significantly, the Co–Co distance in $[Co_2(CO)_8]$ and the Fe–Fe distance in $[Fe_2(CO)_9]$ are the same. The relationship between these two structures has been explored in detail by Braga and Grepioni [3] who have examined this phenomenon not only on a molecular basis but also on the consequences of this site deficiency on the crystallographic lattice. The structure of $[Co_2(CO)_8]$ is not static on the NMR time scale in the solid and detailed studies of the ^{13}CO NMR spectrum of the solid reveal [4] that the molecule is fluxional over a wide temperature range.

In solution, the nature of $[Co_2(CO)_8]$ is far more difficult to establish. Although a carbonyl-bridged structure persists in solution**, the molecule is highly fluxional and only one singlet ^{13}CO resonance is observed over a wide temperature range [5]. Evidence for the existence of at least three isomeric forms (I, II and III) comes from a detailed examination of the IR spectrum [6] in a range of different solvents and at different temperatures. Isomer I contains CO bridges, whereas isomers II and III correspond to non-bridged forms (see below). The IR spectrum of isolated $[Co_2(CO)_8]$ molecules condensed from the gas phase into an argon matrix also shows the presence of the same three forms (I, II and III).

For temperatures <77 K the order of free energies has been given as I<II<III with an estimated ΔG for the conversion of II to I of 26 kJ mol^{-1}; conversion of III into II also occurs readily [7]. The IR spectra are also consistent with an increasing proportion of the non-bridged isomers II and III with increasing temperature.

Structure A, shown schematically in Fig. 2, corresponds to the solid state structure and has two bridging carbonyls and has been ascribed also to the bridged form I in solution. It approximates to C_{2v} symmetry very closely, which demands five IR active bands in the terminal C–O region and two in the μ_2-CO bridging region. This is more-or-less in agreement with experimental observation[†]. The structures of the two other non-bridged isomers II and III cannot be so easily established but, until now, there appears to be a general acceptance that they correspond to forms B and C. Form B, with D_{3d} symmetry, is observed for the closely related dianion $[Fe_2(CO)_8]^{2-}$ [8] and the bis-substituted species $[Co_2(CO)_6(PEt_3)_2]$ [9]. The D_{2d} structure reported [10] for $[Co_2(P(OR_3)_8)]$ and $[M_2(PF_3)_8]$ (M = Rh

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[*] Author to whom correspondence should be addressed.

[**] Usually taken to be the same as that in the solid (Fig. 1(a)).

[†] Four bands are observed in the terminal region but the fifth, which is expected to be weak and appear around 2035 cm^{-1}, is not observed. This is not unusual; this band is not detectable in $[Fe_2(CO)_6Br_2]$ or some $[Fe_2(CO)_6(SR)_2]$ compounds of similar symmetry.

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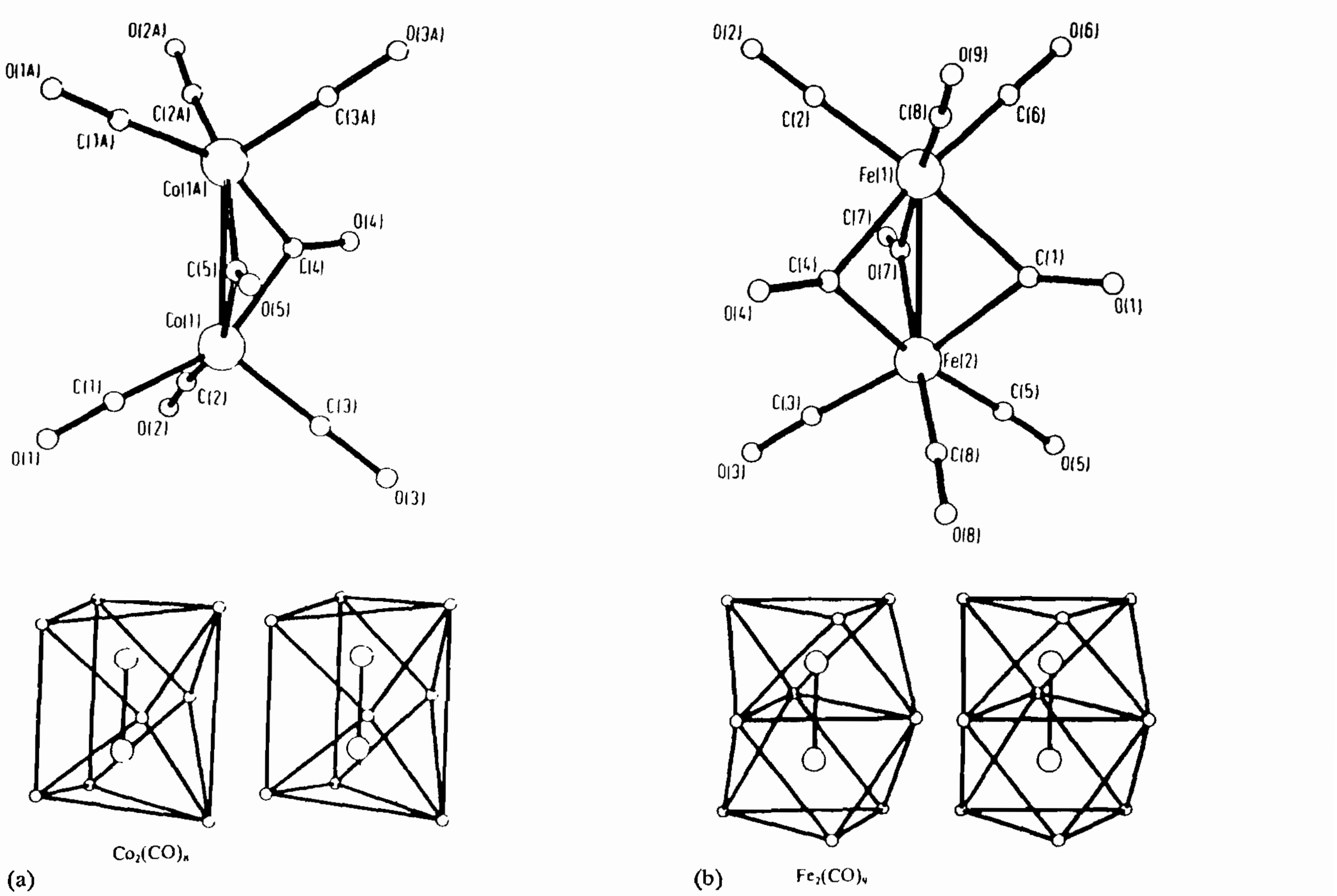


Fig. 1. Molecular structures of $Co_2(CO)_8$ (a) and $Fe_2(CO)_9$ (b).

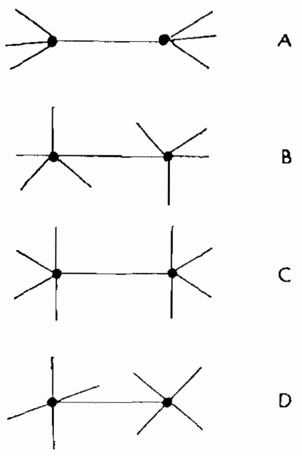


Fig. 2. Possible structures for the isomers I, II and III of $Co_2(CO)_8$ in solution.

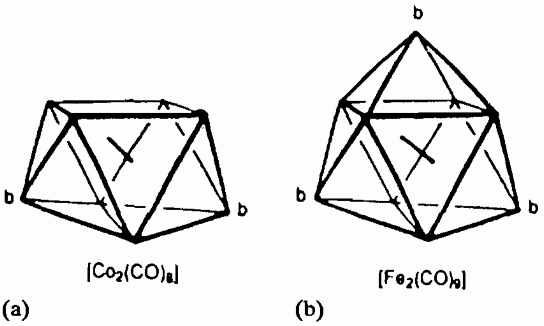
or Ir) may exemplify form C. Extended Hückel calculations [11] have been carried out on the three structures A, B, and C to determine optimised geometries and investigate reaction pathways between the three different forms. Estimated cobalt–cobalt bond distances are 256 (I), 265 (II) and 265 (III) pm.

Other possibilities have been suggested, e.g. structure D with D_{2d} symmetry similar to that observed for the rhodium dication $[Rh_2(CNPh)_8]^{2+}$ [12] and structure of C_s symmetry observed for the monanion $[CoFe(CO)_8]^-$ and which contains a single CO bridge [8].

In this paper we wish to offer an alternative explanation of these phenomena based on the ligand polyhedral model [13], which we believe not only gives a satisfactory explanation of the C_{2v}-bridge in the solid state and its relationship to the structure of $[Fe_2(CO)_9]$ but also offers a clearer understanding of the nature of isomers I, II and III and the mechanism of their interconversion in solution. Some details of this work have been given elsewhere [13, 14].

A number of researchers working on the structures of binary metal carbonyls have commented on the fact that the CO ligands tend to occupy positions which, to a fair approximation, define the vertices of regular of semi-regular polyhedra. In 1966, Dahl and Blount [16] observed a *nido*-icosahedron of carbonyl groups in the triangulo-iron anion $[Fe_3(CO)_{11}H]^-$ and concluded that the 'missing vertex' was occupied by the H ligand. On the basis of this conclusion, Dahl and Blount were able to correctly deduce the molecular structure of $[Fe_3(CO)_{12}]$ at a time when crystal disorder prevented a detailed X-ray structural analysis. Later, when many other molecular structures of binary carbonyls and related derivatives had been established, we proposed [13] that these CO-polyhedral geometries might be of more fundamental importance. Close examination of a wide range of CO arrangements led to the conclusion that the CO polyhedron was governed by primarily steric effects and a 'radius' of 302 pm was attributed to the CO ligand*.

According to the LPM the CO arrangement observed in crystalline samples of $[Co_2(CO)_8]$ corresponds to a bicapped trigonal prism $\{9-1\}$**. Using the established radius of CO as 302 pm, the calculated cobalt–cobalt distance, 250 pm, corresponds almost exactly to that observed experimentally. For $[Fe_2(CO)_9]$, the CO polyhedron is a perfect tricapped trigonal prism; the 'best' low energy arrangement for nine ligands [13]. Here the iron–iron distance is, as expected for two such related polyhedra, viz. $\{9-1\}$ and $\{9\}$, the same value of 250 pm (Fig. 3). Thus, the relationship between the two dimetal carbonyls is clear to understand. On these grounds, the observation that the dicobalt octacarbonyl molecule is 'bent' is also understandable. This follows naturally from the $\{9-1\}$ polyhedron, just as the pyramidal structure of NH_3 follows from the $\{4-1\}$ polyhedron. There is nothing unusual about *nido* polyhedra in coordination chemistry, although its significance has not previously been appreciated in systems such as $[Co_2(CO)_8]$ which is by no means uncommon. More recently, Lauher [15] has re-examined many of these carbonyl clusters and the steric factors which influence their structures. Significantly, he has stressed the relative importance of the CO steric interactions and the need to sustain 'good' metal–metal bonds.



(Fig. 3. The polyhedral arrangement of (a) eight CO ligands in $Co_2(CO)_8$ and (b) nine CO ligands in $Fe_2(CO)_9$.

For eight CO ligands we should also consider other likely, closely related polyhedra, viz. the fully triangulated dodecahedron $\{8\}$, and the square antiprism $\{10-2\}$. According to the LPM, the order of stabilities is $\{8\}>\{9-1\}>\{10-2\}$. The differs from the VSEPR theory which regards the square antiprism as the only stable arrangement, although many MX_8 molecules do adopt the triangular dodecahedral arrangement $\{8\}$. Assuming a hard sphere model for CO, progress across the series $\{8\}$ to $\{9-1\}$ to $\{10-2\}$ would lead to an increase in the cobalt–cobalt distance which, depending on the orientation of the Co–Co vector within the given polyhedron (see below) would range from *c.* 240 pm in $\{8\}$ to a maximum of *c.* 300 pm in $\{10-2\}$[†].

Given the relatively short Co–Co distance required if $\{8\}$ is adopted, this possible geometry for the eight CO groups may be excluded, although its role has been investigated by us elsewhere [14]. Polyhedron $\{9-1\}$ is observed in the solid; within this polyhedron the Co–Co vector lies along the principal axis of the trigonal prism and the two polyhedral caps correspond to the two μ_2-CO bridges. There is, however, an alternative orientation available. This is illustrated in Scheme 1 (1b). The shift from orientation 1a to 1b may be achieved by a low amplitude libration of the Co–Co vector about the C_2 axis orthogonal to it. Configuration 1b would lead to a new form of $[Co_2(CO)_8]$ in which two $Co(CO)_4$ units are linked solely by a Co–Co bond.

Within each $Co(CO)_4$ unit two carbonyls are axially bonded and two equatorially bonded but the symmetry is C_s. Libration of the CO_2 unit in this fashion to produce 1b (and 1b′) would have the effect of more-or-less equilibrating all CO groups. But it is of the utmost importance to recognise that at no time do the carbonyl groups undergo actual interchange of positions and the effect of this pulsating motion would not be expected to cause undue stress on the crystallographic lattice. However, if the libration were accompanied by elongation of the prismatic edge to generate a square antiprism of CO groups (as shown in Scheme 1), followed by closure of the alternative square face to generate a 'new' form 1a′, then all COs would truly equilibrate. Continuation of both libration and polyhedral rearrangement $[\{9-1\}\rightarrow\{10-2\}\rightarrow\{9-1\}']$ would lead to total CO scrambling. If such motion were restricted about the same two square faces, the motion experienced by the CO groups would be small and if the motion was concerted, i.e. as one square face formed the other returned to a diamond, then only one ^{13}CO signal would be observed in the ^{13}C NMR. Thus, equivalence would

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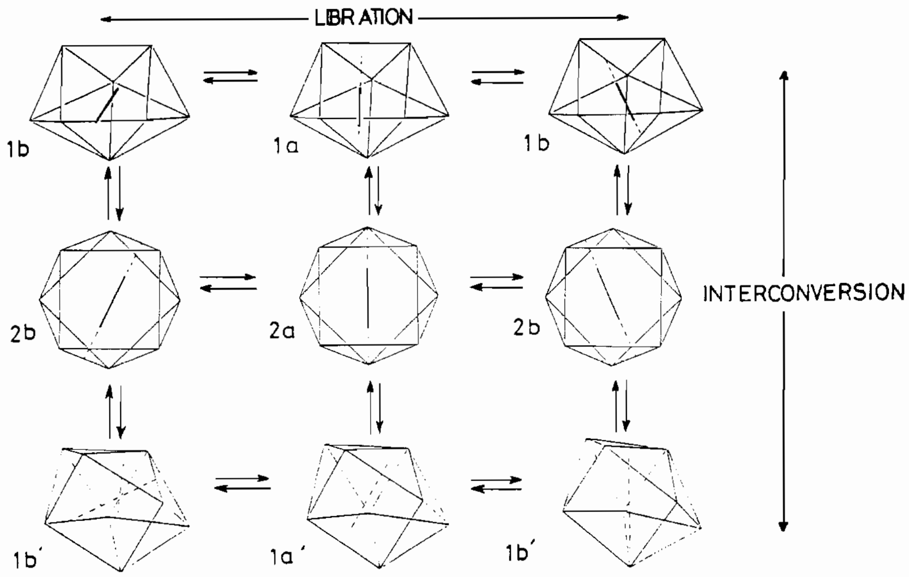
*This value was derived empirically from an examination of many carbonyl systems.

**A polyhedron with *n* vertices is designated $\{n\}$; a *nido*-polyhedron is designated $\{n-1\}$; an *arachno*-polyhedron $\{n-2\}$, etc. These *nido, arachno* etc. polyhedra do not necessarily correspond to those described for the central unit in clusters.

[†] For this arrangement, $\{10-2\}$, there is a clear relationship to $[Mn_2(CO)_{10}]$, for which an Mn–Mn distance of 302 pm is observed and the CO ligands adopt the 'best' $\{10\}$ configuration, viz. a bicapped square antiprism.



Scheme 1. Libration of Co_2 unit with bicapped trigonal prism and square antiprism; interconversion of bicapped trigonal prism ⇄ square antiprism.

be achieved with comparatively little motion of the CO ligands and certainly would not be expected to unduly disturb the crystallographic lattice.

Thus, within this new scheme we have the possibility of a bridged (1a) and non-bridged (1b) structure in which the observed capped trigonal prismatic arrangement of CO groups is maintained. There is also the possibility of a bridged (2a) and non-bridged (2b) structure in which the eight CO ligands adopt a square antiprismatic geometry, {10−2}. Each of these possibilities (1a, 2a, 1b and 2b) may sit in a well defined potential energy well, although we would expect, given our knowledge of eight coordinate complexes in general, that the barrier one to another will be relatively small. Thus, for $[Co_2(CO)_8]$ in solution we may consider that isomer I will possess either structure 1a, as previously suggested (Fig. 2 A), or 2a. For 2a the calculated cobalt–cobalt distance is slightly longer and for this reason is regarded as the less likely alternative. For isomers II and III, structures 1b and 2b are the preferred possibilities. They are clearly closely related, differing only in the relative orientation of the two $(Co(CO)_4$ units, and very similar to the previously postulated structure C (Fig. 2).

For structure 2a with C_{2v} symmetry, terminal CO IR active bonds are predicted. For structure 1b and 2b, three and two CO IR active bonds are predicted, respectively. An increase in the Co–Co distance in progressing from 1a to 2a or from 1b to 2b is in line with the values of ν(Co–Co) (hexane) of 236, 185 and 157 cm^{-1} recorded for isomers I, II and III, respectively.

This leaves us with the previous suggestion that one of the isomers possessed structure B (Fig. 2). This suggestion was made on the very reasonable grounds that a similar structure is observed for the dianion $[Fe_2(CO)_8]^{2-}$. A plot of the O atom positions for this diiron dianion reveals that the carbonyl polyhedron corresponds to a slightly distorted cube with the Fe–Fe vector lying across a diagonal as shown (Fig. 4). The cube is, as far as the LPM is concerned, the least favourable CO polyhedron, but will be expected for a

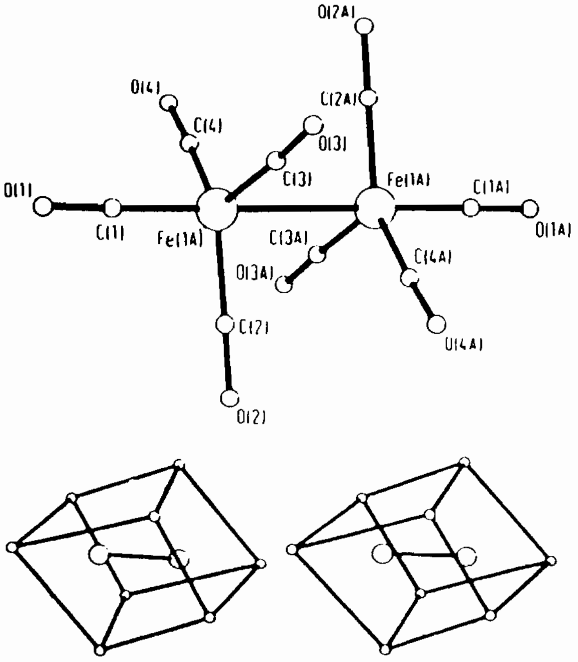


Fig. 4. The structure and polyhedral arrangement of eight CO ligands in the dianion $[Fe_2(CO)_8]^{2-}$.

'longer' metal–metal distance as anticipated for an Fe^{-I}–Fe^{-I} bond (relative to $Co^{(0)}$–$Co^{(0)}$). The relationship between $[Co_2(CO)_8]$ and $[Co_2(CO)_6(PEt_3)_2]$ should not be drawn too closely. The PEt_3 ligand will have a profound effect on the ligand polyhedron*.

Conclusions

We believe that the LPM provides a far more convenient way of looking at carbonyl structures. It follows naturally from our views of coordination polyhedra which came from simple coordination geometry and clearly establishes possible relationships between closely related isomeric forms. Mechanisms for isomer interconversion and for carbonyl fluxionality, both in the solid and in solution, clearly follow easily from these relationships, depending on the libration of the metal unit within the ligand polyhedron and polyhedral interconversion of the ligand polyhedron. However, the most attractive feature of this approach must be the way in which it allows the connections of carbonyl structures of different nuclearities to be demonstrated, e.g. $[Co_2(CO)_8]$, $[Fe_2(CO)_9]$ and $[Mn_2(CO)_{10}]$. That is not to say that the conclusions reached are necessarily correct. At best the method provides an easily understandable model. The true test must await more detailed information about the nature of $[Co_2(CO)_8]$ in solution; at present it is difficult to design experiments to make such measurements.

Finally, a comment on the recent paper by Lauher [15]. Clearly the approach adopted is more sophisticated than that reported here. Nevertheless, Lauher appears to have missed the significance of the relationship between the various polyhedral forms that the ligands in $M_2(CO)_8$ systems may adopt and which has been developed in some detail in an earlier paper [16]. We feel that the LPM approach has the distinct advantage of simplicity and permits a clear and logical view of the variety of available polyhedral forms. Furthermore, its application to ligand fluxionality is unprecedented.

Acknowledgements

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*This aspect of the LPM will be developed in detail in a forthcoming paper.