Dynamic Behaviour of Some Metal Carbonyl Clusters in the Solid State

Dario Braga *
Dipartimento di Chimica 'G. Ciamician,' Università di Bologna, Via F. Selmi 2, 40126 Bologna, Italy
Christopher E. Anson, Adrian Bott, and Brian F. G. Johnson *
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW
Elisabeth Marseglia
Department of Physics, Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE

The dynamic motion that the carbonyls $[Co_2(CO)_8]$, $[Fe_3(CO)_{12}]$, and $[Co_4(CO)_{12}]$ undergo in the solid and solution has been examined. Evidence is offered to suggest that the fluxional behaviour and the isomerisation the molecules undergo may be best understood in terms of the polyhedral model in which the metal unit librates within the CO polyhedron. Support for this approach comes from an examination of the anisotropic displacement parameters of the metal atoms and the usefulness of this method to the understanding of molecular motion in the solid is stressed.

The stereochemical changes, fluxionality and isomerisation, that many transition-metal carbonyl compounds exhibit have become one of the most widely studied phenomena in inorganic chemistry[1] and although the mechanisms of some examples may be conveniently explained using simple ideas of localised rotations or terminal-bridge interconversions, no simple coherent approach applicable to examples in both solid and solution appears to have evolved. In this paper we offer a possible solution to this problem which we believe provides a more unified view of these fascinating phenomena.

Although dynamic behaviour of this kind has been recognised for some time the detailed examination of it had to wait the advent of a suitable analytical tool and nuclear magnetic resonance has proven ideal for this purpose.[2] There were also early indications that *X*-ray analysis would provide support and complementary data to explain molecular rearrangements along well defined pathways.[3] In this case evidence derived for one physical state (*X*-ray crystal data) was initially employed to explain phenomena in another (solution n.m.r.). More recently magic-angle spinning (m.a.s.) ^{13}C n.m.r. spectrometry has been used to make detailed studies of molecular motions in the solid,[4] and in an earlier communication[5] we commented on the way in which information derived by this method could be used in conjunction with information from *X*-ray experiments to explain motion in the solid state.

When we consider fluxionality or isomerisation in simple co-ordination compounds, ML_n, we normally require that certain bond angles and bond distances in the parent compound change until the co-ordination shell of ligands, L, assumes its complementary geometry in what would constitute either the transition state or an intermediate. The relative movements of atoms or groups of atoms within the parent molecule depend upon the energy difference between the complementary geometries (the ground state and the transition state), the activation energy for the process, and on symmetry considerations. When the complementary geometries are energetically close, either because of the nature of the ligands or because of the inherent properties of certain co-ordination numbers, the barrier to motion will be small. In many cases the barrier will be increased by the need of the system to traverse an intermediate in which the ligand distribution or unfavourable bond angles and/or unfavourable bond distances lead to instability. The best examples of stereochemical non-rigidity will be found for those complexes in which the barrier between complementary geometries is significantly smaller than the free energy of activation for bond fission. The problem usually is on deciding upon the appropriate, accessible complementary geometry.[6]

For five-co-ordination, for example, the complementary geometries, the trigonal bipyramid, which for convenience we will refer to as {5}, and the square pyramid, are energetically close to one another. Their relationship is clear to see. Expansion of one of the three equatorial edges of the trigonal bipyramid leads directly to the square pyramid {6 − 1},† the complementary geometry, and further expansion along the same pathway leads to a new trigonal bipyramid, {5}. This expansion arises from a normal mode of the trigonal bipyramid which has gone 'soft' and does not demand an excessive extension of the M–L bonds. As a consequence, the tendency to undergo motion *via* the Berry twist mechanism[7] can be quite considerable. This mechanism also provides an example of the simple, single, diamond–square–diamond rearrangement process.

In contrast, the octahedron appears to be extremely rigid stereochemically. According to the Bailar twist mechanism[8] the most likely complementary geometry is the trigonal prism and a trigonal twist of 60° about one of the three-fold axes will convert an octahedron into a trigonal prism and *vice versa*. The energy barrier to this type of rotation is generally similar or greater than the activation energy for bond fission. The high barrier to this kind of rotation in octahedral systems even in solution is easy to understand. First, it requires a considerable movement of ligands L, secondly, there is a significant decrease in the number of L $\cdots$ L contacts, and finally and most importantly, the conversion to the trigonal prismatic intermediate may require a substantial increase in M–L bond lengths. In the case of the trigonal bipyramid we have an example of a relatively small movement of atoms or ligands leading to dynamic behaviour, and with the octahedron an example of a large movement requiring relatively major reorganisation of the molecular geometry. Clearly, the extent of these motions is dependent on the magnitude of the M–L bond strength (and to a much lesser extent on the L $\cdots$ L interactions), but most importantly on the physical state of the sample. First and foremost the complementary geometry must, obviously, be available by a low-energy process which also corresponds to a normal mode of the molecule. Secondly, and very importantly, the route to the proposed complementary geometry must not involve any unreasonable extension of the M–L bond length.

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† {6 − 1} Refers to an octahedron with one vertex removed.

Finally, the process should maintain as many L ··· L contacts as possible.[9]

The process in metal carbonyl clusters is much more complicated. Unlike the examples of simple homoleptic mononuclear complexes given above, complementary geometries are much harder to establish. The motions may involve at least three different processes. First, there is the intramolecular site exchange of CO ligands bonded to the metal cluster framework; this corresponds to the sort of ligand migration described above for five-co-ordination. Secondly, there may be a reorganisation of the metal framework itself, and thirdly, there exists the intriguing possibility of a reorientation of the metal unit within the ligand envelope. These motions cannot be totally independent, but until recently carbonyl fluxionality was regarded only as involving physical movement of the ligands about the metal cluster unit which, in general, was taken to be rigid. In an earlier report[5] we concentrated attention on motion of the third type which we believe to be of special significance to fluxionality of the metal carbonyls in the solid state. This followed from the alternative view of the dynamic motion of $[Fe_3(CO)_{12}]$ in solution.[10] Recognition of the fact that, in general terms, the cluster carbonyls may be viewed as consisting of one polyhedron, *viz.* the metal cluster unit, embraced within another, *viz.*, the CO envelope, led to the postulate that the libration of one polyhedron within another could lead to fluxionality and 'apparent' CO exchange.[10] This possibility of course is general and is certainly not restricted to the cluster carbonyls. The fundamental difference in this type of motion compared to the two others described above is that this process does not necessitate direct ligand interchange, which is what is usually meant by the term fluxionality. In other words the relative positions of ligands one to another within the CO envelope remain essentially constant although the type of bond they have with the central unit may change character, for example, from terminal to bridging. This type of motion, or libration, is particularly relevant to the solid state where the movement of ligands relative to one another is expected to be restricted by substantial intermolecular interactions. That is not to say that other motions of the ligands do not occur, merely that the librational motion is the one of lowest energy.

These librations, or small amplitude motions of the metal cluster within the CO framework, involve no direct bond breaking. They can occur in both the solid and in solution, and will be governed by clearly defined symmetry constraints. However, it is important to recognise that during this librational motion the CO-ligand envelope will also undergo a perturbation. This will be subject to the same symmetry constraints and the two motions will be concerted and synergic, but the extent to which it will occur will be phase dependent. The perturbation of the ligand envelope will be of the same type as that observed for mononuclear, homoleptic complexes of the type described above for five- and six-co-ordinate systems. Both motions, *i.e.* libration of the metal unit and CO movement, will lead eventually to the complementary geometry or transition state. As the temperature is increased the amplitude of these motions will increase leading eventually to bond breaking and more extensive CO rearrangements. The extent to which such processes occur will be governed by the extent of intermolecular bonding within the crystal and on the efficiency with which the CO groups are packed around the central cluster unit. It is thus very important to make a clear distinction between motion in the solid and in solution. That is not to say that the same basic motions cannot operate in both states. Rather it is to stress the fundamental differences between the forces experienced by a molecule surrounded by (rapidly moving) solvent molecules in solution and those experienced by a molecule embraced within the solid lattice, *i.e.* surrounded by identical entities, in well defined positions, distributed according to crystal symmetry. Therefore, whereas in solution it is necessary only to consider the symmetry of a single molecule in any appreciation of fluxional behaviour, this is not the case for the solid. In order to interpret spectroscopic properties of molecules in the solid it is necessary to study the organisation of the molecules within the crystal lattice and the number of (symmetry) independent molecules contained in the unit cell.[4,11] Further, the possibility of having the molecules randomly distributed in two (or more) different orientations ('static' disorder) or rapidly reorientating between them ('dynamic' disorder) is expected to have different effects on a spectroscopic experiment and must also be appreciated.[12] In this paper we shall consider further this dynamic or fluxional behaviour of some of the binary metal carbonyls in the solid state.

Relationship between Spectroscopic and Diffraction Experiments.—Coalescence phenomena are often observed in n.m.r. spectra and are routinely used for the investigation of exchange processes or fluxional behaviour. In vibrational spectroscopy, analogous temperature dependent changes in the band shapes are only observed when the processes responsible for these phenomena take place on a picosecond time-scale. Accordingly, the few examples known involve conformational changes or proton transfer in organic species.[13] The possibility that rapid intramolecular rearrangements in organometallic systems might also be observed by i.r. spectroscopy has been considered to explain the behaviour exhibited by $[Fe_3(CO)_{12}]$.[14] In our view this not the case, but as we explain later, changes are seen in the variable-temperature i.r. spectrum of $[Fe_3(CO)_{12}]$ which are related in a very special way to the fluxional behaviour of this molecule. The important distinction to be made is in the different time-scales of these various measurements,[15] and in the next section we try to clarify this issue.

A value of 10^{-18} s is often quoted for the time-scale associated with *X*-ray diffraction studies. However, it should be stressed that although this value is correct it can be misleading when one is considering the time-scale for a diffraction experiment.[16] In fact a measurement of a single *X*-ray observation (a 'reflection') takes, on the average $(1—2) \times 10^2$ s. This is equivalent to about 10^{21} 'snap-shots,' each picture recording the positions of atoms which have been displaced by a different distance from their mean positions. Thus the intensity pattern of the total number of reflections in an *X*-ray experiment represents a time average of all possible atomic displacements averaged again over the entire crystal, and thus contains information on all atomic motion (vibrations, rotations, librations, diffusion *etc.*) that is taking place in the solid (see, for example, ref. 17).

On the n.m.r. time-scale ($\approx 10^{-4}$ to 10^{-9} s), the environment of the individual molecule is still probed over a relatively long period, and so a time average of atomic positions can often be observed in the form of a coalesced spectrum. The i.r. time-scale ($\approx 10^{-15}$ s) is fast enough so that usually it 'captures' the atomic positions in a particular form. Sometimes a superposition of distinct forms is found if there is exchange between isomers, weighted according to the proportion of the total molecules adopting each isomer. Coalescence is not observed in the i.r., except in a very few cases. In this respect it probes the relative population of each potential minimum at a given temperature and so gives thermodynamic information on the energy ΔG between those minima. N.m.r. coalescence data give information on the rate of exchange of molecules between the minima, and thus give kinetic information *i.e.* height of the potential barrier between the minima.

The averaging process mentioned above for an *X*-ray diffraction experiment takes place *via* the Fourier transform of the diffraction intensities.[18] Large displacements, whether they are associated with motions about discrete positions within the

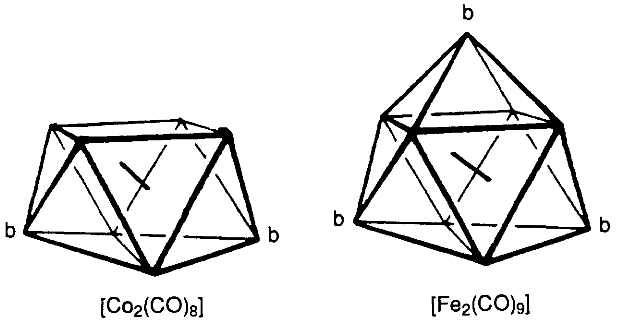

Figure 1. Peripheral CO polyhedra in $[Co_2(CO)_8]$ and $[Fe_2(CO)_9]$, b = bridging carbonyl

harmonic approximation, or with freely rotating groups, or with some intermediate type of situation, cause a decrease of long-range order and, *via* interference in diffraction from neighbouring unit cells, cause a decrease of the Bragg peak intensities (Debye–Waller effect) and a consequent increase of the diffuse background scattering.[19] However, part of the information on the dynamic aspects of the diffraction experiment can be extracted in the form of anisotropic displacement parameters (a.d.p.s) for individual atoms.[17,20] Relatively large values for particular a.d.p. may indicate a dominance of contributions from low-frequency motion along those particular displacement directions. This motion can arise, for example, from bond-bending vibrational modes, from 'rigid body' motion or indeed from any motion which involves relatively weak restoring forces. It is important to emphasise, however, that a discrimination between genuine atomic motions and some kind of static disorder, which also will affect the atomic a.d.p., requires either variable-temperature diffraction experiments or 'external' sources of spectroscopic information on the dynamic nature of the phenomenon under investigation. It is not unreasonable, then, to seek correlation between the low activation energy dynamic processes that are observed by n.m.r. spectroscopy and the a.d.p. obtained from *X*-ray and neutron diffraction: or, at least, to expect some of these dynamic processes to be revealed in the extent and preferential orientations of the mean square displacement amplitudes (m.s.d.a.s) of the atoms involved. In some cases indications of atomic motions or low-energy rearrangements have been indirectly provided by an analysis of these 'thermal' parameters obtained from *X*-ray and neutron diffraction data (although, when dealing with metal carbonyl clusters, the data must be treated with some caution because the C-atom a.d.p.s are substantially affected by bonding electron density deformation).[21] Methods based on this approach have been recently used to investigate the occurrence of dynamic Jahn–Teller distortions in solid complexes of Cu^{II} and Fe^{III},[22] and the relationship between *X*-ray solid-state data and CO-migrational pathways found by multinuclear n.m.r. techniques in solution.[23] Thermal motion analysis and potential-energy calculations have also provided information on the reorientational motions of unsaturated organic molecules bound to metal centres in the solid state.[24] Moreover variable temperature *X*-ray studies on both organic and organometallic species have shown that the temperature dependence of the atomic displacement parameters has physical significance and contains information on true atomic motions.[25]

Discussion

In the following we provide three examples in which the solid state dynamic behaviour has been investigated by a combination of some or all of these techniques *i.e.* *X*-ray diffraction, solid-state i.r. and ^{13}C m.a.s. n.m.r. spectroscopy. We also offer a general model, based on the polyhedral model for metal carbonyls, by which this fascinating phenomenon may be easily appreciated.

$[Co_2(CO)_8]$.—*Structure and the existence of isomers.* In the solid the structure of $[Co_2(CO)_8]$, established by single crystal *X*-ray analysis, possesses two bridging CO groups and three terminal ligands on each Co atom.[26,27] The molecular symmetry is C_s/m and is coincident with the crystallographic symmetry (a mirror plane bisecting the Co–Co bond and comprising the two bridging ligands). Two independent crystallographic studies have been carried out, the more recent one at 100 K in order to investigate the experimental charge density of the metal–metal bond.[27] Unlike $[Fe_3(CO)_{12}]$ and $[Co_4(CO)_{12}]$ no disorder is present in the crystal. Studies of the i.r. spectra of samples both in solution and in frozen matrices have revealed that $[Co_2(CO)_8]$ exists in several different isomeric forms.[28] Although suggestions of possible structural forms have been made it is difficult to visualise simply the relationship they bear one to another. It is clear however, on the basis of these same i.r. spectroscopic studies, that one or more of these isomeric forms do not contain CO bridges.

In the alternative polyhedral description of the structure in the solid[29] the CO arrangement may be considered to be the bicapped trigonal prism, $\{9 - 1\}$. This is shown in Figure 1 where the relationship to $[Fe_2(CO)_9]$ with a tricapped trigonal-prismatic CO arrangement is easily seen. For eight CO ligands however we may also consider two other likely, closely related polyhedra, *viz.*, the dodecahedron $\{8\}$, and the square antiprism $\{10 - 2\}$. The relationship between these three polyhedra is clear to see. The parent or lowest-energy polyhedron is the dodecahedron $\{8\}$, single edge-cleavage takes us to the bicapped trigonal prism $\{9 - 1\}$ and cleavage of a second appropriate edge brings us to the square antiprism $\{10 - 2\}$. As we progress across the series $\{8\}$, $\{9 - 1\}$, $\{10 - 2\}$ the polyhedra become increasingly more open and the interstitial site more spacious (Figure 2). As a consequence an increase in both the Co–Co and the Co–CO bond distances might be expected, although the latter may be offset by a corresponding decrease in the C–O bond lengths. It is these factors which provide the barrier to stereochemical rearrangement whether it be low-energy fluxionality or high(er) energy isomerisation. We can thus immediately visualise three isomeric forms of $[Co_2(CO)_8]$ corresponding to the insertion of the linear Co–Co unit into each of these three possible polyhedra, *viz.* $\{8\}$, $\{9 - 1\}$, and $\{10 - 2\}$ or more if we consider even more spacious polyhedra such as the cube $\{14 - 6\}$. These are shown in Figure 2. However, other isomers also based on these same CO polyhedra are possible. The linear Co–Co unit may adopt at least two different orientations within each polyhedron as shown in Figure 2. For example, the two possibilities for the bicapped trigonal prism are shown in (**2a**) and (**2b**). Form (**2a**) corresponds to the observed geometry in the solid state as described above in which there are three terminal CO groups per Co atom and two CO bridges, the two bridging CO's corresponding to the two polyhedral caps in the bicapped trigonal prism $\{9 - 1\}$. In contrast, isomer (**2b**), which may be derived from (**2a**) by a small rotation of the Co–Co vector, corresponds to a structure which contains only terminally bonded CO's, four per cobalt. A similar result is found in examples (**1a**) and (**1b**) where the arrangement of carbonyls is $\{8\}$, and in (**3a**) and (**3b**) where the CO polyhedron is $\{10 - 2\}$. Interconversion from one isomer to another is thus easy to see, and involves both a libration of the Co_2 vector and stereochemical exchange of the CO groups in a manner closely related to that discussed above for five-co-ordinate compounds. Clearly interconversion between the various ligand polyhedra

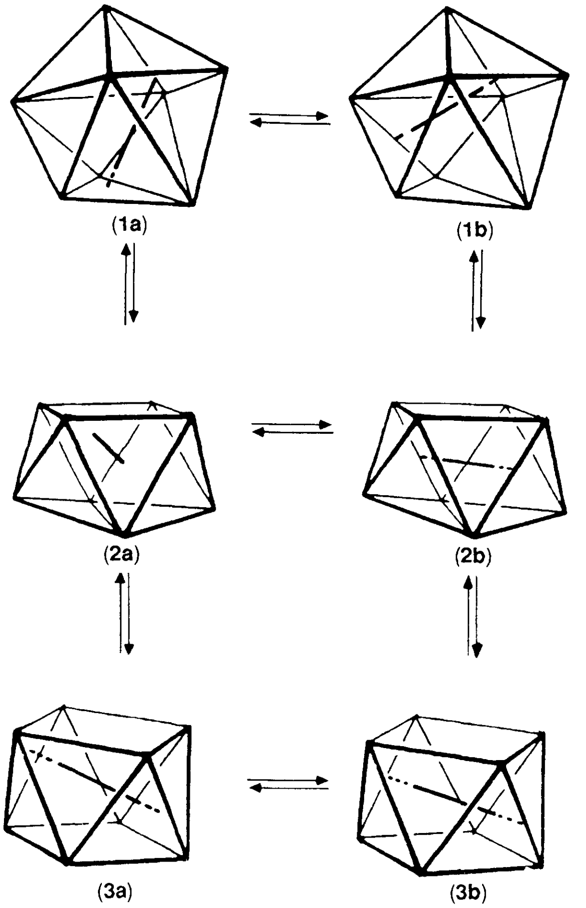

Figure 2. Alternative CO polyhedra available for $[Co_2(CO)_8]$: dodecahedron {8}, bicapped trigonal prism {9 − 1}, and square antiprism {10 − 2}

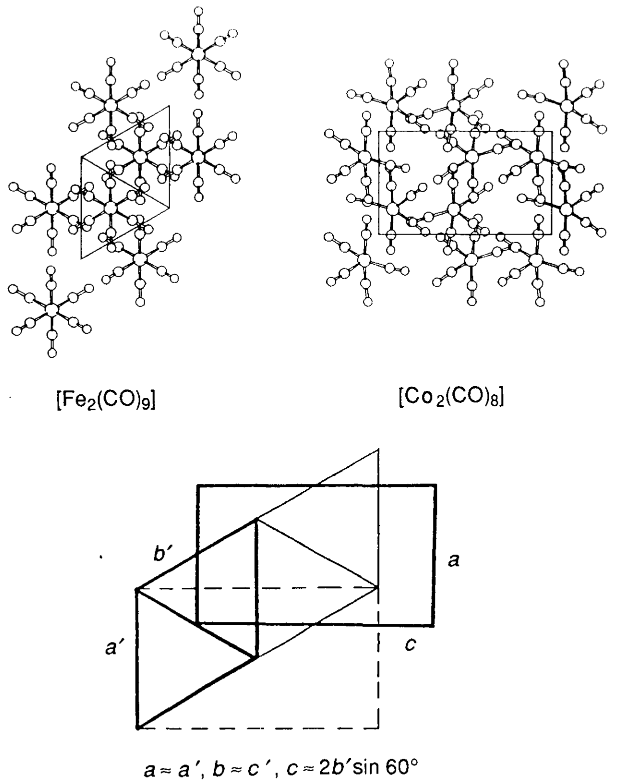

Figure 3. Relationship between the crystal packing of $[Co_2(CO)_8]$ (space group $P2_1/m$, 010 projection) and of $[Fe_2(CO)_9]$ (space group $P6_3/m$, 110 projection) (from ref. 31). Primed cell axes refer to the latter species. The unit cell of $[Co_2(CO)_8]$ is represented by broken lines

may more easily occur in solution than in the solid, nevertheless, exchange between isomers (**1a**) and (**1b**) could occur.

Fluxional behaviour. ^{13}C M.a.s. n.m.r. spectra for $[Co_2(CO)_8]$ have been recorded over a large temperature range (−134 to +40 °C) showing only one resonance at high temperature (>20 °C) which separates out into an increasingly complex system of signals as the temperature is decreased.[30] The low-temperature spectra reveal the presence of two signals in the intensity ratio 4:1, whose chemical shift has been attributed to terminal and bridging C atoms, respectively. The difference from the expected ratio of 3:1 has been attributed to large experimental errors. The exchange process was attributed to CO_t—CO_b interchange by carbonyl migration which, if it occurs, must involve exchange between crystallographically defined positions with concerted jumps of 3 Å or more. These jumps would involve the simultaneous movement of all ligands, and follow a well defined pathway. Examination of the crystal structure reveals that the molecular packing of $[Co_2(CO)_8]$ very closely resembles that of $[Fe_2(CO)_9]$[31] (which, incidentally, is 'static' in the solid state)[32] although the two species crystallise in two rather different space groups ($P2_1/m$, $P6_3/m$[33]) (see Figure 3). The 'hole' left by the 'missing ligand' {with respect to $[Fe_2(CO)_9]$} causes loss of packing efficiency, though not at the expense of the intermolecular O ••• O interactions which are fairly short [range 2.97 ••• 3.15 Å at room temperature].[31] Consequently, while more space is left for localised librational motions, full-scale migration of the CO ligands around one molecule will affect the CO ligands around other molecules adjacent to it (*i.e.* ligands cannot 'get through' the molecular packing without pushing away surrounding ligands). This has been demonstrated by recent potential energy calculations.[34] For this reason we regard this mechanism as unlikely. We would argue for an alternative mechanism which involves only a limited (a few degrees) librational motion of the Co–Co axis about its centre of mass (see Figure 2) to bring about the partial interchange between forms (**1a**) and (**1b**) and lead to apparent CO equilibration. An average displacement of 0.2—0.3 Å around the equilibrium position of the Co atom can be achieved by a tilting of *ca.* 10°. This motion is enough to cause an extensive degree of asymmetry of the bridging CO's (Co–C_b in the range 2.09—1.78 Å). This motion is also expected to be accompanied by a slight displacement of the CO ligands towards their complementary geometry, most probably a square antiprism {10 − 2} (see below). By this means equilibration can be achieved without major reorganisation of the CO ligands throughout the crystal lattice and by a method which would only instantaneously break the crystallographic symmetry. Within the limits of the harmonic approximation for small displacements about discrete positions the a.d.p. for $[Co_2(CO)_8]$ at room temperature should be able to convolute in their averaging process this dynamic behaviour.

The nature of the fluxional behaviour in solution may be similarly visualised. Consider form (**2a**) in Figure 2. Rotation of the Co–Co vector about its two-fold axis with a concomitant Co–Co bond stretch will lead initially to the formation of two asymmetric bridges and eventually to the non-bridged form (**2b**), hence, to the apparent equilibration of bridging and terminal groups. In reality, at no point do the CO ligands actually migrate from one metal atom to the other within the dimeric unit. In turn, as the temperature is raised the amplitude of the same librational motion will increase, and the CO polyhedron will undergo an even larger perturbation, and it would not seem unreasonable to associate this with the

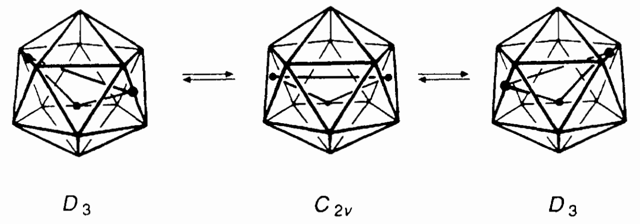

Figure 4. Schematic representation of the $C_2 \longleftrightarrow D_3$ ligand distribution interconversion in $[Fe_3(CO)_{12}]$ *via* libration of the iron triangle around the molecular C_2 axis

distortion of the bicapped trigonal prism {9 − 1} towards the square antiprism {10 − 2}. Eventually, as the temperature is increased, and the amplitude of the libration becomes sufficiently large a new isomer with the square antiprismatic geometry will be reached. Thus there would be a systematic change in the process, motion leading naturally first to fluxional behaviour and apparent ligand interconversion and then to isomerisation and real ligand interconversion *via* polyhedral rearrangement. Importantly, the same processes could occur in both solid and solution phase, but in the solid movement would be restricted by strong intermolecular forces and isomerisation obviously would lead to the breakdown of the crystal lattice. In this case, however, and unlike the other examples discussed below, the available, room-temperature, *X*-ray data[26] on $[Co_2(CO)_8]$ are very poor and no information about the vibrational motion of the Co or C, O atoms can be obtained from them. The high quality, low temperature *X*-ray data refer to a molecule which is no longer fluxional (−173 °C).[27] We trust that a full assessment of the phenomenon will be made possible by the collection of accurate data sets at room temperature and just below coalescence (< −4 °C) which is presently under way.

$[Fe_3(CO)_{12}]$.—*Structure and the existence of isomers.* Single crystal *X*-ray studies have shown that $[Fe_3(CO)_{12}]$ shows orientational disorder in the solid state.[35,36] In the molecular structure two carbonyls are in asymmetric bridging positions along one edge of an iron triangle, which is shorter than the other two. The molecule possesses formal C_1 site symmetry, but is very close to C_2 symmetry with a pseudo two-fold axis passing through the middle of the bridged Fe–Fe bond and the opposite Fe atom and will be referred to as the 'C_2 form.' Random occupancy of one or other of two possible molecular orientations in the crystal lattice results in the presence of an inversion centre within the unit cell statistically relating two crystallographic 'half molecules' in each of the two orientations. In the more recent and more precise of the two independent structure determinations[36] the almost superposed C- and O-atom images were distinguished, showing that the O···O and C···C image pairs are separated, on average, by 0.43 and 0.50 Å respectively. The disorder is due to the high regularity of the outer, almost icosahedral, peripheral polyhedron described by the O atoms, which does not appreciably differ whether the iron triangle is in one orientation or its inverse.[35] According to the polyhedral model[10] the iron triangle may be considered to occupy the interstitial site within an idealised but slightly flattened icosahedron which corresponds to the optimum geometry for twelve CO ligands.

The cluster $[Fe_3(CO)_{12}]$ crystallises in the space group $P2_1/n$ with $Z = 2$, so factor-group analysis indicates that the solid-state i.r. spectrum should have the same number of bands as that of the isolated C_2 molecule. Although disorder is present it is not thought that this will greatly affect the spectrum. Poliakoff and Turner[37] have shown that in an argon matrix at 20 K, $[Fe_3(CO)_{12}]$ has an i.r. spectrum consistent with C_2 or C_{2v} geometry. There is a weak band at 2 110 cm^{-1}, weak and medium intensity bands at *ca.* 1 867 and 1 830 cm^{-1}, and six medium-to-strong bands in the region 2 060—2 000 cm^{-1}. On this basis, it would appear that unlike $[Co_2(CO)_8]$, only one isomeric form exists in the solid at this temperature. However, we have carried out an examination of the manner in which the i.r. spectrum of this carbonyl in the solid state varies as a function of temperature. Infrared spectra were recorded for solid samples from room temperature down to 118 K in the region 1 500 to 2 500 cm^{-1}. At 118 K the spectrum appeared almost identical to that of $[Fe_3(CO)_{12}]$ in an argon matrix at 20 K, consistent with the presence of only one isomer and agreeing well with the reported *X*-ray structure. Thus, at 118 K a large majority of the molecules must be in the C_2 form. However, as the temperature was increased, new bands appeared at 2 107vw, 2 050vs, 2 039m, 2 026mw, 2 016(sh), 2 013s, and 1 997w cm^{-1}, and at the same time the bands corresponding to the C_2 form decreased in intensity. All the new bands are in the terminal region which is consistent with an increasing population of a new isomeric species. The CO bands (particularly those in the bridging region) broaden on warming but there is no evidence for a continuum of structures. These changes with temperature are completely reversible.

According to the polyhedral model, several isomeric possibilities may exist.[5,10] The simplest corresponds to the reorientation of the iron triangle within the icosahedron of CO groups. Rotation of the iron triangle about the molecular C_2 axis by about 15° produces a second isomeric form of the molecule with D_3 symmetry (Figure 4). This is also based on an icosahedron of CO groups, but in contrast to the solid-state structure all CO groups are terminally bonded and all Fe–Fe distances are the same (2.60 Å). This rotation of the iron triangle will also cause the slightly flattened icosahedron of CO groups to become regular. It is interesting to note that for $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ which possess D_{3h} symmetry four CO vibrations are infrared active. Lowering the symmetry from D_{3h} to D_3 would result in further modes becoming i.r. active. For a distortion of the magnitude proposed here however, the i.r. spectrum should still be dominated by four bands, with the additional modes giving rise to weaker features. This is indeed the case in the spectrum of the high temperature isomer, supporting our proposal that it is of D_3 symmetry. In this case reduction of the molecular symmetry from D_{3h} to D_3 is expected to lead to additional bands. Arguably therefore the new isomer is that with D_3 symmetry. Other isomers based on alternative CO polyhedra are also possible, the most obvious probably being that based on the less compact anti-cuboctahedron of CO groups giving a pseudo-$[Os_3(CO)_{12}]$ structure. Other possibilities exist but these will be described in a later paper.

A plot of ln *K versus* $1/T$ gives the free energy ΔG for the interconversion $C_2 \longleftrightarrow D_3$. In deriving ΔG it is assumed that the relative intensities of bridging and terminal bands for the C_2 species remain constant with temperature. Given this, the intensity of the bridging bands (I_m) is proportional to the population of the C_2 species. A plot of I_m *vs.* T shows a decrease with temperature down to 118 K and a limiting 'pure C_2' spectrum had not been obtained at this temperature. It would be necessary to go to even lower temperatures to obtain a pure C_2 spectrum. However, it is still possible to obtain an estimate for ΔG. I_m varies from 53.6 at 118 K to 27.2 at 323 K; we may postulate limiting values of I_m of 60, 70, and 80. At high temperatures, all three minima (the C_2 and the D_3 structures obtained by clockwise and anticlockwise libration) are equally occupied, so that the limiting low temperature value of I_m is probably three times that at high temperature giving 80 as an upper estimate (3 × 27.2 = 81.6). Plots of ln *K vs.* $1/T$ assuming limiting low temperature values give values for ΔG of +1.1, +1.2, and +1.6 kJ mol^{-1} respectively for I_m = 60, 70, and

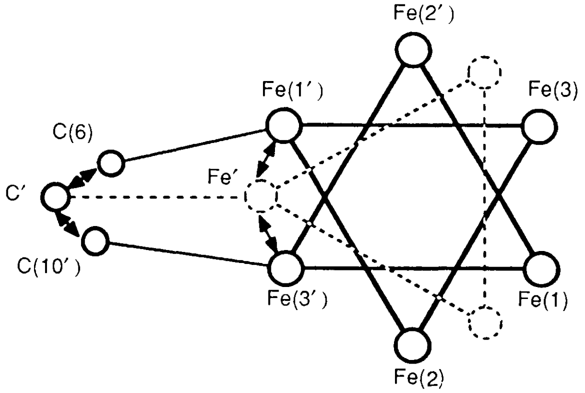

Figure 5. Effect of the iron triangle rotation on the Fe–C distances in solid $[Fe_3(CO)_{12}]$

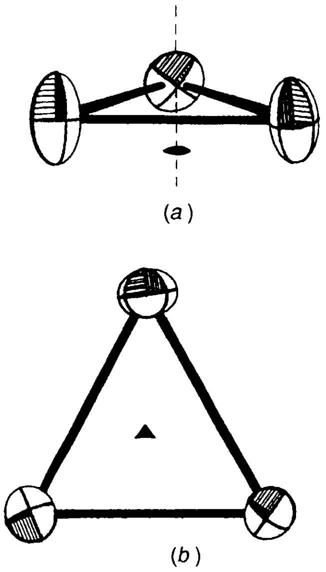

Figure 6. Iron-atom anisotropic displacement parameters (from ref. 36) in $[Fe_3(CO)_{12}]$ projected along the pseudo two-fold axis (*a*) and the pseudo three-fold axis (*b*)

80. This is comparable in magnitude and sign to Lauher's calculated value.[38]

If we turn now to the infrared spectrum of $[Fe_3(CO)_{12}]$ in solution we find that it is basically similar to that of the solid except in this case the isomeric distribution is markedly solvent dependent.[39] Thus, in n-hexane there are three bands of variable intensity in the region 2 000—2 050 cm^{-1} but only weak, broad bands at *ca.* 1 867 and 1 838 cm^{-1}. This change in the infrared spectrum was the first indication of the presence of different isomeric forms, and it would appear from the general similarities of the spectra in the solid and solution that the new isomer is probably the same in each case.

Fluxional behaviour. Variable-temperature ^{13}C m.a.s. n.m.r. solid-state measurements on $[Fe_3(CO)_{12}]$ show that at temperatures below −95 °C the observed spectrum is consistent with the crystal structure, indicating two bridging and ten terminal carbonyls.[40] At 24 °C there are three pairs of resonances of similar integrated intensities, but none of the observed chemical shifts is consistent with either bridging or semi-bridging carbonyls. In order to explain this equivalence of terminal and bridging carbonyls and the temperature dependence of the n.m.r. spectra, it has been postulated that the Fe_3 triangle undergoes a fast rotational motion about the pseudo three-fold axis which passes through the iron triangle, bringing about the interchange between the two crystallographically determined orientations.[40] Provided the 60° jumps between the contiguous positions are rapid on the n.m.r. time-scale the spectrum of an averaged structure would be seen. An activation energy of 50 kJ mol^{-1} for the process has been estimated from the coalescence temperature of −55 °C.[40] However, an examination of this motion in more detail leads us to suppose that the existence of crystallographically separated images of the nearly superposed carbonyls implies that C and O atoms would have to follow the motion of the Fe_3 triangle. As a result the overall carbonyl motion has to be more complicated than a simple 'jump' because during the rotation of the triangle some Fe–C interactions would become extremely short [computed separations after a 30° rotation (half-way through) are: Fe(1) ··· C(6) 1.49, Fe(2) ··· C(2) 1.61, Fe(3) ··· C(11) 1.56, Fe(3) ··· C(12) 1.58 Å]. For example, to pass from C(6) to C(10′) [C(6) ··· C(10′) 0.61 Å] a C atom cannot simply switch from one position to the other and keep, at the same time, a reasonable distance from the Fe atom, which is switching from Fe(1) to Fe(3′), but has to move outwards and then inwards, describing an arc as shown in Figure 5. Therefore the peripheral ligand polyhedron has to expand and contract continuously in order to follow the triangle rotation. Although such a 'breathing' motion will almost certainly occur for any process, in this case it is especially extensive and an unreasonably high activation energy would be required in the solid state where the molecules are packed together in three-dimensional long range order. A possible contraction of the metal frame (say Fe–Fe bonds stretching between *ca.* 2.6 and 2.7 Å on passing from bridged to unbridged situation) would only slightly alleviate these packing constraints, so that any expansion would have to occur against strong packing forces dominated by intermolecular O ··· O interactions.[34]

Evidence that motion about a pseudo three-fold axis may not be responsible for the n.m.r. results comes from the a.d.p.s which have been reported for this molecule.[36] Analysis of these parameters shows that there is no indication of preferential motion about the pseudo three-fold axis, rather, the thermal ellipsoids for the iron atoms (shown in Figure 6) indicate a preferred libration of the Fe_3 triangle about the molecular pseudo two-fold axis. This corresponds to the librational motion described above which, provided the amplitude is sufficiently large, brings about isomerisation. Such a libration between the limiting C_2 (from C_1) and D_3 molecular conformations will explain the pattern of bands observed in the room-temperature ^{13}C m.a.s. n.m.r. spectrum. Confirmation that the Fe-atom a.d.p.s represent true metal-frame librational motion and not some sort of artifact arising from the data treatment and/or disorder comes from the recent structural determination of $[Fe_2Os(CO)_{12}]$, which retains the 'C_2 form' of $[Fe_3(CO)_{12}]$.[41] This molecule is only slightly affected by disorder (a 12:1 'star-of-David') while the Fe-atom a.d.p.s show a clear preferential orientation along the molecular C_2 axis which closely resembles that of $[Fe_3(CO)_{12}]$.

In solution, the molecule is known to be highly fluxional.[14,42] In this case the same mechanism may operate as in the solid. However, just as with $[Co_2(CO)_8]$, the CO ligands may also undergo a concerted polyhedral rearrangement to produce a new complementary geometry. For polyhedra with twelve vertices the mechanism for interconversion and the nature of the complementary geometry are not easy to establish. However, given that $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ possess anticubeoctahedral CO arrangements[43,44] and that the same polyhedron has been previously regarded as an appropriate intermediate in such polyhedral rearrangements we believe it reasonable to assume this complementary geometry here. The same assumption was made in our earlier work on the fluxionality of $[Co_4(CO)_{12}]$ (see below and ref. 29). We would

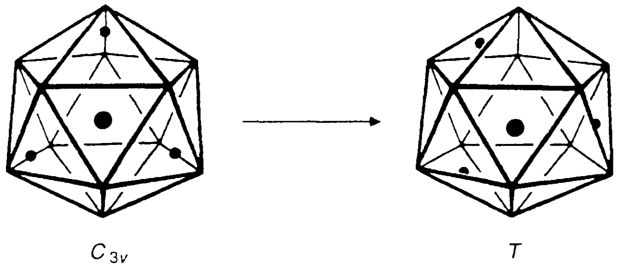

Figure 7. Different orientations of the Co_4 tetrahedron of $[Co_4(CO)_{12}]$ within the CO-ligand icosahedron

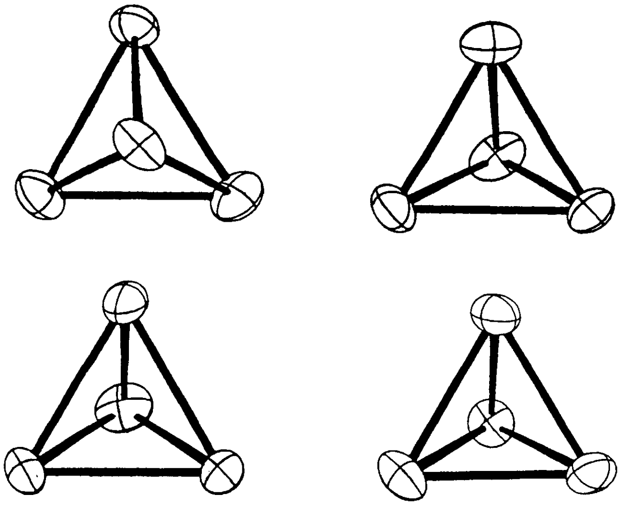

Figure 8. Orientations of the Co atoms anisotropic displacement parameters in $[Co_4(CO)_{12}]$ (from ref. 45*c*)

emphasise, however that other possibilities, *e.g.* the bicapped pentagonal bipyramid, do exist and will be discussed in a subsequent paper. We would suggest, therefore, that during the fluxional process the molecule first acquires the D_3 structure *via* libration of the Fe_3 triangle about its pseudo two-fold axes; this will also bring about the formation of a regular icosahedron of CO groups as discussed above, then libration may occur about any one of the now equivalent two-fold axes resulting in complete equilibration of the carbonyls. In the crystal, of course, libration of the metal framework seems to be confined to motion about one of these three axes (that coincident with the molecular C_2 axis) and so only partial equilibration of the carbonyls is observed. As the temperature is raised the amplitudes of both the libration of the iron triangle and of the CO rearrangement (towards the cubeoctahedron) will increase ultimately leading to a quasi-$[Os_3(CO)_{12}]$ structure.

$[Co_4(CO)_{12}]$.—*Structure and the existence of isomers.* As in $[Fe_3(CO)_{12}]$ the structure of $[Co_4(CO)_{12}]$ has been studied independently by different groups[45] and has been shown to be disordered in the solid state. Random occupancy of one or other of two possible molecular orientations in the crystal lattice results in the presence of a two-fold axis within the unit cell which passes through one basal Co atom and the centre of the opposite triangular face. The molecule itself has only C_1 symmetry with three carbonyl groups in edge bridging positions around a tetrahedral face, the remaining carbonyls being terminally bound. However, the peripheral polyhedron described by the O atoms is again approximately icosahedral, and the molecular symmetry is only slightly distorted from C_{3v}.

Although several alternative forms have been described in attempts to explain the fluxionality this molecule undergoes, *e.g.* one with D_{2d} and two with T_d symmetry,[10] there have been no reports of experimental evidence for the existence of other isomeric forms of this compound. We have recorded the infrared spectrum of $[Co_4(CO)_{12}]$ in the solid over a range of temperatures (20—80 °C) and have found evidence for a second isomeric form. At low temperatures, apart from some increase in the band mutiplicity, the spectrum is similar to that observed for solutions in cyclohexane, and as expected for a molecule with C_{3v} symmetry. As the temperature is raised, however, the spectrum changes and simplifies until at ≈ 80 °C it is clear that a new isomer which also contains CO bridges is present. The changes that occur in the variable-temperature i.r. are completely reversible. Although the precise nature of the high-temperature isomer cannot be established on the basis of these data alone the small number of bands indicate relatively high symmetry, and is compatible with the symmetry D_{2d}.

We have previously described that according to the polyhedral model the tetrahedral Co_4 unit occupies the interstitial site within an icosahedral arrangement of the twelve CO ligands.[29] Within the same icosahedron of carbonyl ligands at least two other orientations of the tetrahedron are possible (Figure 7). Rotation of the Co_4 tetrahedron about the unique C_3 molecular axis which passes through the apical Co atom and the centre of the basal Co_3 face produces a new form (**II**) which is also based on the icosahedron of carbonyl groups, but in contrast to isomer (**I**) all CO groups are now equivalent and terminal. This isomer has T symmetry. Alternatively, rotation of the Co_4 tetrahedron about any one of the three C_3 molecular axes which pass through a basal Co atom and the opposite Co_3 face produces a third isomeric form which also contains CO bridges and is of D_{2d} symmetry.[10] This agrees with the high-temperature i.r. studies and consequently we consider the second isomer to be of type (**III**).

Fluxional behaviour. The ^{13}C m.a.s. n.m.r. spectrum of $[Co_4(CO)_{12}]$ has been recorded over a wide temperature range (-62 to $+63$ °C).[46] Above 35 °C only one broad signal can be seen but below 24 °C four peaks appear. No other changes occur on cooling down to -62 °C. If we now look at the a.d.p. reported for $[Co_4(CO)_{12}]$[45] we see that there is a preferred librational motion of the Co_4 tetrahedron about its three pseudo three-fold axes. This motion and small concerted motions of the carbonyl polyhedron could lead to the time-averaged C_{3v} structure observed in the n.m.r. experiment below 24 °C. In particular, libration about one of the three pseudo three-fold axes, that coincident with the crystallographic two-fold axis, results in the observed partial equilibration of bridging and terminal carbonyls. At temperatures above 35 °C larger amplitude librations result in equilibration of all the carbonyls on the n.m.r. time-scale. Analysis of the a.d.p. of the Co atoms indicates that, despite disorder, the Co a.d.p.s are fairly trustworthy and the cluster frame is substantially rigid, *i.e.*, its librational motion can be approximated with a rigid-body motion of an almost regular tetrahedron.[17] On the contrary, no good use can be made of the a.d.p. of the poorly defined C and O atoms (as mentioned before, atoms of the two images are superposed). The a.d.p.s of the Co atoms appear to be preferentially oriented tangential to the pseudo three-fold axis of the tetrahedron (Figure 8) one of which is coincident with the crystallographic two-fold axis generated by the disorder model. No preferred motion around this latter with respect to the other three can be detected, nor is it necessary because libration around any one of the four axes results in extensive asymmetry of the bridging ligands which may lead to CO_t and CO_b equilibration on the n.m.r. time-scale. In fact the major components of Co a.d.p. range from 0.032 to 0.055 Å,^{2} implying displacements around the equilibrium positions in the range 0.18—0.23 Å. Such displacements can be achieved through librations of 9—10° around the three-fold axes, and cause lengthening and shortening (in the range 1.7—2.4 Å) of all Co–C interactions. Obviously some concerted motion of the CO's must also occur. This latter motion is difficult to quantify, though it should be well within the a.d.p. for the C and O atoms. As in the case of $[Fe_3(CO)_{12}]$, the temperature dependence of the ^{13}C m.a.s. n.m.r. spectra is a clear indication that the amplitudes of these librations decrease as the temperature is decreased to the point where equilibration no longer takes place.

Conclusion

We have shown that for the solid state the n.m.r. data for $[Fe_3(CO)_{12}]$ and $[Co_4(CO)_{12}]$ can be explained in terms of small internal librations of the metal unit within the CO polyhedron that do not involve the higher energy processes of CO interchange and of metal atoms 'pushing past' carbonyl ligands. In a similar manner the dynamic behaviour of $[Co_2(CO)_8]$ in the solid requires only small amplitude localised oscillations of both ligands and Co atoms, with no need for extensive and concerted ligand reorganisation in the lattice. We have also shown that evidence for these librations is found in the preferential orientation of the a.d.p. of the metal atoms in both $[Fe_3(CO)_{12}]$ and $[Co_4(CO)_{12}]$. Further experiments combining solid-state n.m.r. spectroscopy with analysis of accurate mean square displacement parameters from variable-temperature *X*-ray diffraction are expected to reveal more examples of this type of correlated motion.

In solution the same processes may also operate. However in this phase where the restraints of the crystalline lattice have been removed more extensive movement of the CO ligands may also occur. This movement which is similar to that normally found for homoleptic complexes containing one metal atom will be concerted with the libration of the internal metal unit and will lead eventually to complete CO scrambling.

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