The Structures of Simple Binary Carbonyls†

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Summary A model for the rationalisation of the structures of simple binary carbonyls is presented.

IN recent years there has been considerable speculation on the presence of bridging carbonyl groups in polynuclear transition-metal carbonyl complexes. Cotton[1] has put forward proposals to account for the formation of CO-bridges in a variety of systems; in particular he has stressed the importance of the length of the metal–metal bond supporting the bridge and the need to maintain electronic neutrality throughout the metal unit. However, although Cotton's arguments account for the formation of bridges in many simple systems they do not, for example, account for bridge formation in $[Co_4(CO)_{12}]$ and $[Rh_4(CO)_{12}]$;[2] nor do they explain the unusual arrangement of the two bridges in

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$[Fe_3(CO)_{12}]$.[2,3] Much of the early discussion of this subject was concerned with CO bridges in the solid but more recent studies have emphasised the stability of such bridges and their persistence in solution.[4] This account is an attempt to provide a general explanation for the formation of CO bridges and to offer a simple mechanistic viewpoint for the non-rigid behaviour observed for many polynuclear carbonyls.

It may be taken that the numbers and distribution of bridging[5] and terminal CO groups in a polynuclear species $[M_m(CO)_n]$ reflect: (i) the polyhedral arrangement of the *n* carbonyl groups and (ii) the orientation of the M_m unit within this polyhedron.

The problem is to discover why for a given M_m geometry[6] one particular CO arrangement is preferred to others. I propose that the polyhedron (i) may be predicted from simple packing arguments and that it is possible to deduce the orientation of the M_m unit from a consideration of the space and sites available within the CO polyhedron and the sizes of the atoms M. The adopted polyhedral shape (i) will vary (within those available for polyhedra based on *n* groups) according to the size and shape of the M_m unit such that all metal atoms maintain close contact with the surrounding CO ligands. It is assumed that metal–metal distances will correspond to the sum of the metallic radii and that this sum will be exceeded only when necessary to maintain close contact between the metal atoms and the surrounding CO ligands. Implicit in these arguments is the idea that the CO ligand has a fixed *effective* radius.[7]

polyhedron from an icosahedron to a cubo-octahedron (thereby enlarging the polyhedral hole) the larger Ru_3 or Os_3 unit may be accommodated.[10] A similar relationship exists between the structures of $[Co_4(CO)_{12}]$ and $[Ir_4(CO)_{12}]$.[2] In $[Co_4(CO)_{12}]$ the CO arrangement approximates to an icosahedron and in $[Ir_4(CO)_{12}]$ to a cubo-octahedron.[11] It is apparent (Table) that the Co_4 tetrahedron is small enough to be accommodated within the icosahedron whereas the larger Ir_4 requires the more spacious cubo-octahedral arrangement. Thus for both $[M_3(CO)_{12}]$ and $[M_4(CO)_{12}]$ the transformation from a CO-bridged to a non-bridged structure is largely brought about by an increase in size of the M_m unit. The Ni_5 (trigonal bipyramidal) unit[12] will also pack into the cubo-octahedron (Table) but in order to accommodate larger metal clusters, *e.g.* Ni_6[13] or Pt_6,[14] the twelve CO groups must adopt less efficient packing arrangements. If the M_m unit is sufficiently large, *e.g.* Pt_6, an eclipsed bihexagonal (6:6) arrangement is anticipated. Thus, the icosahedral $\{[Fe_3(CO)_{12}]$ and $[Co_4(CO)_{12}]\}$, the cubo-octahedral $\{[Ru_3(CO)_{12}]$, $[Os_3(CO)_{12}]$, $[Ir_4(CO)_{12}]$, and $[Ni_5(CO)_{12}]^{2-}\}$, the puckered bihexagonal $\{[Ni_6(CO)_{12}]^{2-}\}$, and finally the eclipsed bihexagonal $\{[Pt_6(CO)_{12}]^{2-}\}$ illustrate the stages in the transition from the icosahedral to bihexagonal packing of twelve CO groups as the spatial demands of the M_m unit increase. This transition from one CO polyhedron to another may be predicted on the basis of simple radius ratio arguments.[15]

Having established the CO polyhedron the next problem is to decide on the orientation of the interstitial M_m unit.

TABLE. Predicted polyhedra for 12 CO groups

Carbonyl	R/Å[a]	Predicted CO[b] arrangement	Calc. M–M[c] Distance/Å	Observed M–M[d] Distance/Å
$[Fe_3(CO)_{12}]$	2·69	Icosahedron (Limiting radius 2·86 Å)	2·50 2·64 2·64 (2·60)	2·56 2·68 2·68 (2·62)
$[Co_4(CO)_{12}]$	2·78		2·56	2·52
$[Ru_3(CO)_{12}]$	2·91	Cubo-octahedron[11] (Limiting radius 3·02 Å)	2·80	2·85
$[Os_3(CO)_{12}]$	2·91		2·80	2·88
$[Rh_4(CO)_{12}]$	3·02		2·72	2·73
$[Ir_4(CO)_{12}]$	3·02		2·72	2·68
$[Ni_5(CO)_{12}]^{2-}$	3·02[e]		[f]	—
$[Ni_6(CO)_{12}]^{2-}$	3·10[e]	Bihexagon (puckered)	[f]	—
$[Pt_6(CO)_{12}]^{2-}$	3·36	Bihexagon (eclipsed)	[f]	—

[a] R = radius sphere which *just* embraces M_m unit (employing metallic radii). [b] Using *effective* radius CO 3·02 Å. [c] Assuming M_m unit expands so that M and CO contact. [d] Average values, unless otherwise stated. [e] Estimated. [f] These species cannot be dealt with from such a simplistic viewpoint. A detailed account of these molecules will be given elsewhere.

Consider the three dodecacarbonyls $[Fe_3(CO)_{12}]$, $[Ru_3(CO)_{12}]$, and $[Os_3(CO)_{12}]$. Only the Fe molecule is based on the favourable icosahedral arrangement of CO groups,[2] the others possessing the slightly less favourable cubo-octahedral disposition.[8] Thus the essential difference between the structures of the Fe and the Ru or Os dodecacarbonyls is that the Fe_3 triangle can be accommodated within the icosahedron whereas the larger Ru_3 or Os_3 cannot (see Table).[9] It may be supposed that by modifying the CO

Since we suppose that the M_m unit is surrounded by a close-packed array of CO groups the M atoms can be imagined as occupying the various interstices of such a CO arrangement and provided the criteria outlined above are followed the molecular structure may be correctly predicted. This is clearly illustrated by $[Fe_3(CO)_{12}]$.[3,16] The variation in M–M distances observed for the binary carbonyls also follows from this idea of site occupancy. Thus the deviation from an *idealised* triangular Fe_3 arrangement in $[Fe_3(CO)_{12}]$ and an *idealised* trigonal bipyramidal Os_5 arrangement in $[Os_5(CO)_{16}]$ may be accounted for on this basis.[17]

An increase in cluster size does not necessarily lead to a change in the CO polyhedron. Larger M_m clusters can occasionally be accommodated by changing their orientation within given polyhedron. Thus the variation in geometry along the isoelectronic series $[Co_2(CO)_8]$ (two bridges), $[CoFe(CO)_8]^-$ (one bridge), and $[Fe_2(CO)_8]^{2-}$ (no bridges), which has been described as remarkable,[18] merely reflects the change in orientation of the M_2 unit within the $(CO)_8$ polyhedron with increase in the M–M distance.[19]

The most favourable arrangement of eight carbonyl groups which can effectively accommodate two metal ions can be shown to be the bicapped trigonal prism.[20] For this arrangement two limiting orientations of the M_2 unit can be envisaged. In the first the metal atoms occupy interstitial positions between the two triangular (CO) faces of the trigonal prism. This leads to a predicted M–M distance of 2·50 Å and two CO bridges (capped positions) and corresponds closely to the known structure of $[Co_2(CO)_8]$ (Co–Co 2·52 Å). In the second, the metal atoms occupy the two square-pyramidal holes and since these are larger, a longer M–M distance (3·02 Å) is required. Thus, as the M–M distance increases the M_2 unit is expected to migrate away from the first orientation towards the second and for octacarbonyls with M–M distances between 2·50 and 3·02 Å the M_2 unit will arrange itself somewhere between these two extremes. Migration may occur in two ways. (i) Rotation about a C_2 axis (not through a CO-bridge) will lead to exchange of two CO bridges with two terminal CO groups. During this process an intermediate geometry will be reached in which all CO groups are terminally bonded; this approximates to the structure of $[Fe_2(CO)_8]^{2-}$ {or the alternative, high energy form of $[Co_2(CO)_8]$}. (ii) Rotation about the C_2 axis (involving a CO bridge) will lead first to a single-bridged geometry as observed with $[CoFe(CO)_8]^-$ and finally to a triple-bridged arrangement.

Rotations (i) and (ii) also offer a simple view of the fluxional behaviour of $[Co_2(CO)_8]$;[22] (i) corresponds to total bridge–terminal exchange and (ii) to interchange with the maintenance of a single CO bridge.

Similar arguments may be applied to account for the structures of $[Fe_2(CO)_9]$[21] and $[Os_2(CO)_9]$.[22,23] Both are expected to be based on tricapped trigonal prismatic CO arrangements and rotation about any one of the three C_2 axes (as M–M distance increases) would lead to a single-bridged situation and eventually to bridge–terminal exchange. For $[Fe_2(CO)_9]$ (Fe–Fe 2·52 Å) three bridges are predicted and for Os_2 (sum of metallic radii 2·70 Å) migration towards a single-bridged arrangement.

The ideas outlined in this paper may be employed to account for the structures of all binary carbonyl species. They are not restricted to the prediction of CO bridges but may also be used to account for distortions and anomalous bond lengths as, *e.g.* in $[Mn_2(CO)_{10}]$.[24] The limitations of this, a hard-sphere approach, which depends on fixed radii for CO and the metal must be emphasised.[25] It is meant to be nothing more than a structural model. It is of use in predicting the structures of polynuclear carbonyls and, together with the Wade theory,[26] offers a means of predicting the formulae of new polynuclear carbonyls.

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[1] F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, 1974, **96**, 1234; and references therein.

[2] C. M. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, 1966, **88**, 1821; 1969, **91**, 1351; C. M. Wei, G. R. Wilkins, and L. F. Dahl, *ibid.*, 1967, **89**, 4792.

[3] F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, 1974, **96**, 4155.

[4] See *e.g.* J. Evans, B. F. G. Johnson, J. R. Norton, and F. A. Cotton, *J.C.S. Chem. Comm.*, 1973, 807 and references therein.

[5] Of any description, *i.e.*, symmetrically or asymmetrically bonded to two metals or triply bonded to three.

[6] The *idealised* geometry of this unit may be derived by Wade's method.[26] Deviations from ideality may be accounted for on the basis of the packing arguments presented here.

[7] It is convenient to regard the CO ligand as spherical. It should be appreciated that it is egg-shaped (packing more closely laterally than longitudinally) but since the close packing involves a minimum packing distance (which may be derived as 3·02 Å from simple radius ratio considerations or from a consideration of *both* the C · · · · C and O · · · · O non-bonding distances) a hard-sphere model is adequate. This concept and its limitations will be discussed in a full report.

[8] R. Mason and A. J. M. Rae, *J. Chem. Soc.* (*A*), 1968, 778; E. R. Carey and L. F. Dahl, *Inorg. Chem.*, 1962, **1**, 521.

[9] Employing metallic radii, see *ref.* 25, p. 984.

[10] There is a *comparatively* small change in the effective radius of CO in going from the 1st to the 2nd and 3rd transition-metal series. Obviously the Fe_3 unit may be placed in a cubo-octahedron; however, this would lead to longer Fe–Fe distances combined with a less favourable CO arrangement.

[11] The difference between $[Rh_4(CO)_{12}]$ and $[Ir_4(CO)_{12}]$ may reflect the two types of polyhedron available, see ref. 25, p. 115.

[12] G. Longoni, P. Chini, L. D. Lower, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1975, **97**, 5034.

[13] J. C. Calabrese, L. F. Dahl, A. Cavalieri, P. Chini, G. Longoni, and S. Martinengo, *J. Amer. Chem. Soc.*, 1974, **96**, 2616.

[14] J. C. Calabrese, L. F. Dahl, P. Chini, G. Longoni, and S. Martinengo, *J. Amer. Chem. Soc.*, 1974, **96**, 2614.

[15] Such arguments are intended merely as a convenient illustration and are not readily applied to polyhedra which do not possess a spherical hole. Much more important are the sites available for occupancy by metal atoms.

[16] There is an alternative packing arrangement of Fe_3 in the icosahedron which would lead to a non-bridged structure with three equivalent Fe–Fe distances of 2·64 Å. This does *not* correspond to the $[Os_3(CO)_{12}]$ structure and is regarded as less favourable since all three Fe–Fe distances exceed the sum of the metallic radii.

[17] At present there is no alternative way of predicting such deviations. M–M distances vary from the sum of the metallic radii to very large values {*e.g.* as with $[Mn_2(CO)_{10}]$}.

[18] H. B. Chin, M. B. Smith, R. D. Wilson, and R. Bau, *J. Amer. Chem. Soc.*, 1974, **96**, 5285.

[19] The M–M distance is expected to increase in progressing from the (formally) Co^0–Co^0 to the Fe^{-1}–Fe^{-1} system.

[20] The dodecahedral hole is too small and packing inside a cube or square antiprism would lead to unreasonably long M–M distances.

[21] F. A. Cotton and J. M. Troup, *J.C.S. Dalton*, 1974, 800; and references cited therein.

[22] See *e.g.* F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, 1974, **96**, 4422; and references therein.

[23] J. R. Moss and W. A. G. Graham, *Chem. Comm.*, 1970, 835.

[24] L. F. Dahl and R. E. Rundle, *Acta. Cryst.*, 1963, **16**, 419.

[25] A. F. Wells, 'Structural Inorganic Chemistry, 2nd edn., Clarendon, Oxford, 1962.

[26] K. Wade, *Chem. in Britain*, 1975, **11**, 177.