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CLUSTER CHEMISTRY

XIV*. CRYSTALLOGRAPHIC DISORDER AS STRUCTURAL EVIDENCE FOR THE CONSTANCY OF PERIPHERAL ATOM POLYHEDRA AROUND CLUSTERS OF METAL ATOMS

MICHAEL I. BRUCE, BRIAN K. NICHOLSON,
Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, S.A. 5001 (Australia)
and ALLAN H. WHITE
Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, W.A. 6009 (Australia)

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Summary

The observed disorder in solid-state structures of several substituted cluster complexes $M_3(CO)_{12-n}(L)_n$ (M = Fe, Ru, n = 1—3) is explained by a model in which peripheral atoms (O for CO, N for CNR, P for PR_3) occupy the same sites, while the M_3 triangle takes up one of two orientations, related by a 60° rotation about a vector normal to the M_3 plane.

Much recent work has suggested that the structural and fluxional properties of metal cluster carbonyls can be rationalised by a simple approximation of the CO ligands to spheres of radius 3.02 Å, and packing these to leave a sufficiently large polyhedral cavity to accommodate the metal core [1]. Later calculations of inter-CO repulsions have refined these conclusions. Fluxionality is the result of a reorientation of the metal cluster within the ligand polyhedron; only minimal rearrangements, usually small changes in M—M bond lengths or ligand separations, are necessary. To date, however, these studies have largely relied upon the interpretation of variable temperature NMR data, and on relationships between the low-temperature, low-energy structures so deduced to be present in solution and the solid-state structures determined by X-ray or neutron diffraction methods. Relatively few asymmetric systems (usually containing mixed-metal clusters) have been studied [2].

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*For Part XIII, see ref. 13.

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Many early structural investigations of iron group cluster carbonyl derivatives include reference to disorder giving a 'Star-of-David' arrangement of partially occupied metal-atom sites. Most examples had one of the partial occupancy factors considerably less than 0.5, and it was assumed that if ligand occupancy was similar, the resulting atom peaks for the minor component in the final electron density map would be at the limits of resolution. While detailed calculations of the geometries of complexes $M_m(CO)_n$ are possible, introduction of other ligands reduces the overall symmetry, and gross structural changes have generally been considered in terms of simple terminal-to-bridging transformations (cf. $Ir_4(CO)_{12}$ vs. $Ir_4(CO)_9(PPh_3)_3$ [3]), or if present, of differing degrees of symmetry of the μ-CO groups (cf. $Fe_3(CO)_{11}(L)$, L = CO or PPh_3 (two isomers), and $Fe_3(CO)_9(PMe_2Ph)_3$ [4]).

The disorder referred to above is formally a 60° rotation of the cluster about a vector normal to the M_3 triangle, and requires only a small rearrangement of the M—L vectors for the peripheral atom polyhedron to remain unchanged. We wish to draw attention to the importance of peripheral atom packing in these structures. The icosahedral shape of $Fe_3(CO)_{12}$ was noted as early as 1966 [5], and the report included the comment: "It is clear, however, that whatever the molecular structure of $Fe_3(CO)_{12}$, the oxygen atoms must be at nearly identical positions in the crystal for the two possible orientations of the triangle of iron atoms, since they determine the mode of packing of the molecules, as found in the case of $Co_4(CO)_{12}$."

We also note that the later refinement of $Fe_3(CO)_{12}$ described 12 ellipsoidal peaks, which were subsequently refined in terms of half-weighted C and O atoms which lie 'very close together' in the superimposed half-molecules; the separations of a number of such parts were comparable to the nominal resolution [4b].

Our results, summarised below, indicate that one form of disorder can be explained in terms of differing orientations of a metal core within a fixed peripheral ligand atom polyhedron. Structures solved on this basis include several whose polyhedra are far from regular. We have recently been able to obtain pure crystalline samples of a variety of complexes $M_3(CO)_{12-n}(L)_n$ (M = Fe or Ru, n = 1,2 or 3, L = C-, N-, P-, As- or Sb-donor ligands) [6]. Structural studies of some of these complexes revealed disorder which was refined using an atom polyhedron which is identical to that of its inversion image so that the two possible dispositions of the M_3 core can be accommodated. The polyhedron is constructed from the peripheral atoms (O) of the CO groups, the N atom of an isocyanide ligand, or the P atom of a tertiary phosphine or phosphite. Thus, we find crystals belonging to space groups such as $P\bar{1}$, which has an inversion centre, also have $Z = 1$. This condition can only be satisfied for a molecule based on the M_3 cluster if the 'Star-of-David' disorder results in no change to the peripheral atom polyhedron defined as above.

The examples* shown in Fig. 1 illustrate the point in more detail, and the salient points are summarised below.

1. $Ru_3(CO)_{11}(CNBu^t)$ (I) ($P2_1/c$, $Z = 4$): as noted earlier, the disorder (population 0.139, 0.861) in this molecule is also accompanied by a significant twisting of one of the $Ru(CO)_4$ groups relative to the other about a vector joining the

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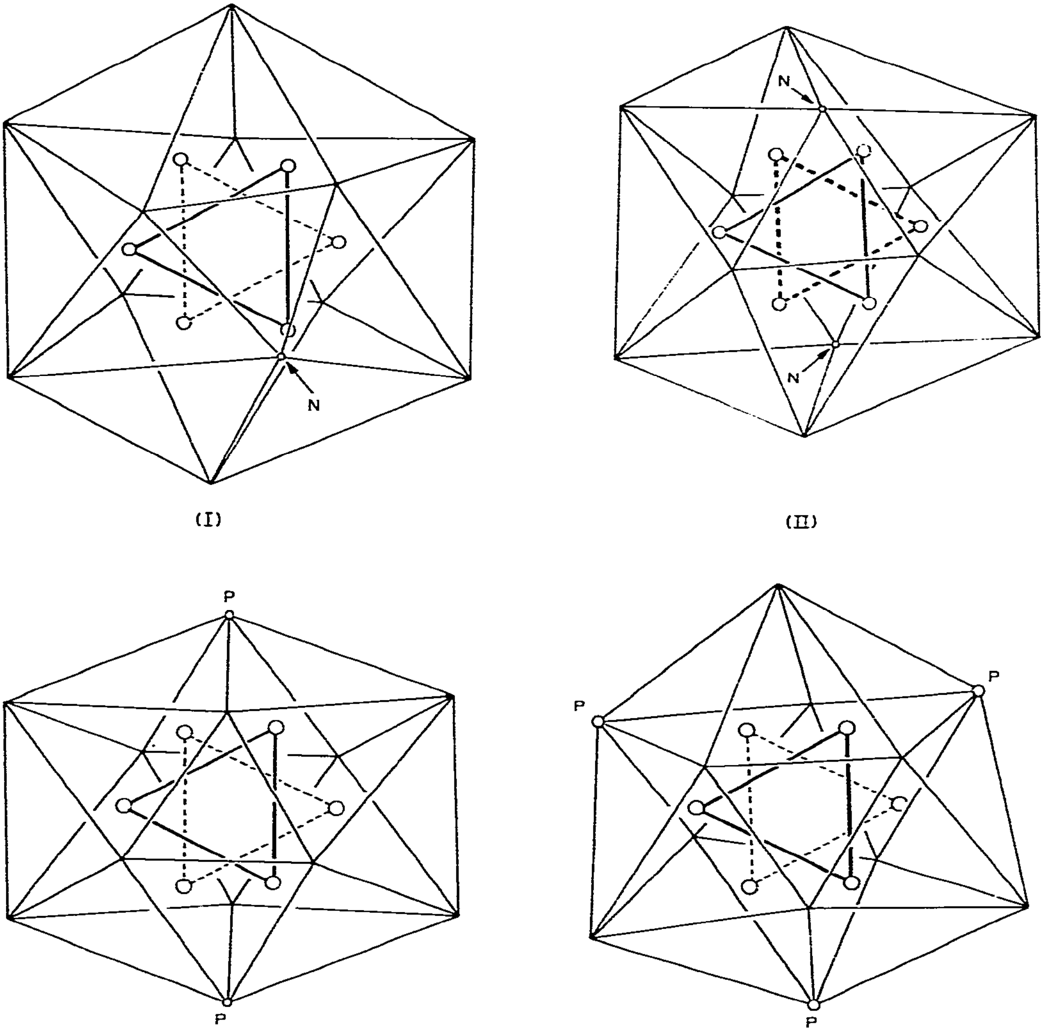
*Full details of the structural studies on which these observations are based will be given elsewhere.



(I) (II) (III) (IV)

Fig. 1. Polyhedra constructed using peripheral atoms (O of CO, N of CNR, P of PR$_3$) of ligands in several complexes $M_3(CO)_{12-n}(L)_n$, showing location of disordered M_3 clusters. The projection chosen has the plane of the M_3 triangle in the plane of the paper. (I) $Ru_3(CO)_{11}(CNBu^t)$ (populations 0.14, 0.86); (II) $Ru_3(CO)_{10}(CNBu^t)_2$ (0.5, 0.5); (III) $Ru_3(CO)_{10}[P(OMe)_3]_2$ (0.5, 0.5); (IV) $Ru_3(CO)_9(PMe_3)_3$ (0.06, 0.94).

Ru to the mid-point of the opposite Ru—Ru bond [7]. The resulting polyhedron is intermediate between the anticuboctahedron found for $Ru_3(CO)_{12}$, and the icosahedron.

2. $Ru_3(CO)_{10}(CNBu^t)_2$ (II) ($P2_1/a$, $Z = 2$): the crystallographic requirement for a centrosymmetric molecule is met by equal populations of the disordered pair. Each $CNBu^t$ ligand has a population of 1, i.e. the ligand position, or more specifically the ligand N atom, is insensitive to the rotation of the Ru_3 core.

3. $Ru_3(CO)_{10}[P(OMe)_3]_2$ (III) ($P\bar{1}$, $Z = 1$): the tertiary phosphite ligands occupy equatorial positions on different Ru atoms of the disordered pair (popula-

tions 0.5, 0.5). The ligands are necessarily in two different orientations as required by the two directions of coordination to the Ru_3 cores, but the positions of peripheral O atoms, and phosphite P atom, are common to both molecules. In this case, two disordered arrangements of the OMe groups are also found. Figure 2 illustrates the oscillation of the equatorial ligand-to-metal bonds about the O or P atoms required to accommodate the two orientations of the Ru_3 core.

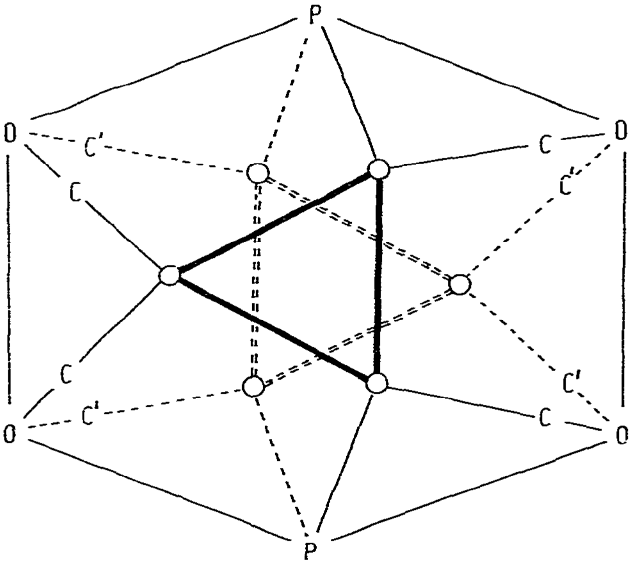


Fig. 2. Plot of Ru_3 core and equatorial ligands in $Ru_3(CO)_{10}[P(OMe)_3]_2$ (II), showing how the two different orientations of the Ru_3 core are accommodated within the same peripheral ligand atom polyhedron by an appropriate oscillation of the ligand-to-metal bonds about the peripheral atoms.

4. $Ru_3(CO)_9(PMe_3)_3$ (IV) ($P2_1/n$, $Z = 4$): a much lower degree of disorder (populations 0.068, 0.932) is accompanied by twist distortions in the Ru environments.

5. $Fe_3(CO)_{12}$: as mentioned above, this structure was resolved in terms of a rotationally disordered pair (populations 0.5, 0.5); the ligand polyhedra of both second components were not refined [4b].

6. $Fe_3(CO)_{11}(CNBu^t)$ ($P2_1/n$, $Z = 4$): in contrast with the Ru complex, the iron analogue is not disordered, the isocyanide ligand occupying an axial site on the unique Fe of an $Fe_3(CO)_{12}$-derived structure. A possible explanation for this difference is that the usual 60° rotation of the Fe_3 triangle would result in the isocyanide occupying a bridging position. Although complexes containing bridging isocyanide ligands are known, there is a significant preference for terminal sites for ligands with bulky substituents*.

Several other complexes are reported to have disordered structures, and these can be similarly explained; they include $[H_6Re_4(CO)_{12}]^{2-}$ [9], $Fe_3(\mu_3\text{-As})_2(CO)_9$ [10], the recently determined $Os_3(\mu\text{-CH}_2)(\mu\text{-CO})(CO)_{10}$ [11], and $Ir_4(CO)_{12}$ [3a]. However, we believe that this is the first occasion that this disorder has been resolved in cluster complexes containing such disparate ligands.

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*An investigation of $Fe_2(CO)_3(CNBu^t)(\eta\text{-}C_5H_5)_2$ gave a value of ca. 12.5 kJ mol^{-1} for the preference of the $(\mu\text{-CO})_2$ isomer over the $(\mu\text{-CO})(\mu\text{-CNBu}^t)$ isomer [8].

The rationale for these observations is that the particular crystalline form of a molecule which can exist in two or more conformations is largely determined by crystal packing interactions. In general, one form is more stable than the other(s), and an ordered lattice results from all molecules having the same conformation. Crystal packing interactions are determined by intermolecular contacts of the peripheral atoms of the molecule, so that if the two or more conformations have the same arrangement of peripheral atoms, random occupation of lattice sites will result. In the special instance of symmetry-related sites in the polyhedron, half-occupancy of $M_3(CO)_{10}(L)_2$, for example, may occur.

In summary, the solid-state structures of the above-mentioned complexes are consistent with a model in which the peripheral atoms (O for CO, N for CNR, P for PR_3 or $P(OR)_3$) occupy the same sites, while the M_3 triangle takes up one of two orientations, related by a 60° rotation through its centre of symmetry. The other ligand atoms refine separately with the appropriate relative populations. One form is related to the other by a oscillation of the M—C—X (X = O or NR) or M—P bonds about the X or P atoms. We also suggest that the observed twisting of ML_4 moieties relative to one another, which has no obvious theoretical (electronic) justification, occurs to accommodate distortions in the peripheral atom polyhedron arising from the presence of non-carbonyl ligands.

It is clear that the X-ray diffraction experiment (time scale ca. 10^{-18} sec) which shows all instantaneous structures superimposed on one another enables a determination of the preferred geometry(ies) of the ligand polyhedron and cluster core at the temperature of the determination. This is relevant to the recent observation of fluxional behaviour in crystalline $Fe_3(CO)_{12}$, consistent with the presence of the two forms observed crystallographically [12]. In cases where non-equal populations of conformers are found, it will be instructive to carry out variable temperature X-ray diffraction and NMR experiments on the solid.

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