

From Molecule to Molecular Aggregation: Clusters and Crystals of Clusters

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1. Introduction

Crystallography is undoubtedly the most powerful method currently available for studying the structure of metal clusters at atomic resolution in widespread use. Over the years automated diffractometers and inexpensive computing have made X-ray analysis a method of election and yielded results of ever increasing accuracy even for complex systems such as transition metal clusters.¹ Considerable progress has been made in the understanding of interatomic bonding and of the relationship between molecular structure and chemical reactivity.² However, information on the molecular organization in a solid, as well as on the atomic and molecular dynamics, has, in many cases, appeared mainly as a "byproduct" of the primary analytical goal. For instance, very little is known about the factors responsible for intermolecular aggregation of clusters, crystal formation and crystal stability, although it has been shown that transition metal clusters have properties that are intermediate between those of dispersed and bulk metals.³ These properties depend on the complex interplay between the properties of the individual molecular entity and those of the *collection of molecules* present in the solid material.

Our main objective with this paper is to show that much can be learned about *both* molecular and "supramolecular" (crystal) structure by investigating how molecules interact and assemble, and how the assembling process alters the structure of the molecule at rest. We will provide evidence that, in the minimization of the *global energy* of a system formed by *flexible molecules in a crystal*, the environment is not simply a spectator but participates in the definition of the molecular features.

The basis of our reasoning is simple and yet complex at the same time: a crystal (any crystal) has to be regarded as a *most specialized molecular ensemble* whose construction (from the first crystalline nucleus to the final crystal) is based on fundamental processes of molecular recognition and self-organization. Crystal growth can be envisaged as a process of molecular

deposition over a surface with specific recognition requirements. The relationship between molecular recognition and crystal construction has never been properly addressed in organometallic chemistry, while substantial work has been done in the neighboring field of organic solid-state chemistry.⁴

Insights into the relationship between size, shape, and charge of the component molecules and the molecular organization in the crystal have initially been obtained by *decoding*⁵ observed crystal packings by means of empirical packing potential energy calculations⁶ and computer graphics.

More recently, direct *crystal generation* starting from molecular structures alone has been attempted.⁷ In this way the existence of alternative crystal packings for some fundamental carbonyl complexes, such as $\text{Co}_2(\text{CO})_8$, $\text{Fe}_2(\text{CO})_9$,⁸ $\text{Ni}(\text{CO})_4$, and $\text{Fe}(\text{CO})_5$,⁹ has been investigated.

In order to put our analysis into perspective we need to address first the steric–electronic *dualism* that controls the molecular geometry (or geometries) in the solid state. It is important to appreciate that this dualism pervades all aspects of structural chemistry and becomes especially intriguing with organometallic molecules, most of which possess internal degrees of structural freedom.¹⁰ Such a structural nonrigidity (or molecular flexibility) is responsible for the many stereochemical changes that are observed in solution and/or in the solid state on the time scale of spectroscopic techniques. The dynamic processes in the solid state (libration, diffusion, reorientation, *etc.*), besides depending on the temperature, are under direct *intermolecular control* and are strongly influenced by the actual molecular or ion organization.

(1) Albano, V. G.; Braga, D. *Accurate Molecular Structures*; Domenicano, A., Harghittai, I., Eds.; Oxford University Press: Oxford, U.K., 1991.

(2) See, for example: Mingos, D. P. M.; May, D. F. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990; p 11.

(3) Kharas, K. C. C.; Dahl, L. F. *Adv. Chem. Phys.* 1988, 70, 1. Johnson, D. C.; Benfield, R. E.; Edwards, P. P.; Nelson, W. J. H.; Vargas, M. D. *Nature* 1985, 314, 231. Teo, B. K.; DiSalvo, F. J.; Waszczak, J. V.; Longoni, G.; Ceriotti, A. *Inorg. Chem.* 1986, 25, 2265.

(4) Gavezzotti, A.; Simonetta, M. *Chem. Rev.* 1982, 82, 1. (b) Berkovitch-Yellin, Z.; Leiserowitz, L. *J. Am. Chem. Soc.* 1982, 104, 4052.

(5) (a) Braga, D.; Grepioni, F. *Organometallics* 1991, 10, 2563. (b) Braga, D.; Grepioni, F. *Organometallics* 1992, 11, 711. (c) Braga, D.; Grepioni, F.; Sabatino, P. *J. Chem. Soc., Dalton Trans.* 1990, 3137.

(6) Pertsin, A. J.; Kitaigorodsky, A. J. *The Atom-Atom Potential Method*; Springer-Verlag: Berlin, 1987.

(7) Gavezzotti, A. *J. Am. Chem. Soc.* 1991, 113, 4622.

(8) Braga, D.; Grepioni, F.; Sabatino, P.; Gavezzotti, A. *J. Chem. Soc., Dalton Trans.* 1992, 1185.

(9) Braga, D.; Grepioni, F.; Orpen, A. G. *J. Am. Chem. Soc.*, submitted.

(10) Braga, D. *Chem. Rev.* 1992, 92, 633 and references therein.

Dario Braga graduated in chemistry at the University of Bologna in 1977. He was a postdoctoral fellow first at the University of Bologna and then at the University of North London working on the solid-state structure of high-nuclearity transition metal clusters. He joined the Faculty of Science of the University of Bologna in 1982, where he is currently Associate Professor of General and Inorganic Chemistry. His research interests include the static and dynamic structure of organometallic molecules and clusters and the relationship between solid-state properties and molecular organization in organometallic crystals.

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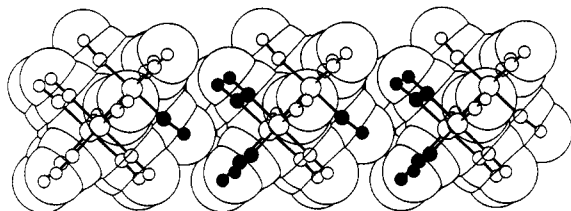


Figure 1. Crystal structure decoding: a one-dimensional crystal of $\text{Ru}_3(\text{CO})_{12}$ molecules forming the “backbone” of the observed crystal structure (filled atom spheres mark the atoms involved the “key-keyhole” interaction). Reprinted with permission from ref 14. Copyright 1991 American Chemical Society.

2. Packing Decoding

This section is devoted to an examination of the intermolecular interactions between transition metal clusters in which carbon monoxide is the only or principal ligand. The outer molecular shape of a carbonyl cluster is characterized by the presence of CO molecules protruding from the surface and by cavities formed between the CO ligands. It is important to appreciate that different molecular structures may result in extremely similar molecular shapes. Thus, for example, $\text{Fe}_3(\text{CO})_{12}$ ¹¹ and $\text{Co}_4(\text{CO})_{12}$ ¹² have approximately the same molecular shapes (*viz.*, icosahedral).¹³ In these cases, the metal cluster geometry can be considered an “internal property” only partly reflected on the outer shape of the molecule.

We have shown that a given crystal structure can be efficiently decoded by focusing on the molecular “enclosure shell” (ES), *i.e.*, on the number and distribution of the nearest neighbors around the reference molecule or ion.^{8,14} The ES approach avoids the strictness of the lattice translational and point symmetry and affords a direct appreciation of the most relevant intermolecular interactions. This facilitates the investigation of the effects that intermolecular interactions may have on the molecular structure observed in the solid state. We commence from the known molecular structure and study how the observed crystal can be reconstructed. We proceed by first preparing a “one-dimensional” crystal by linking molecules to form a molecular row, then a “two-dimensional” system by coupling molecular rows, and finally, a three-dimensional crystal by stacking molecular layers.¹⁴

In $\text{Ru}_3(\text{CO})_{12}$,¹⁵ for example, a row of molecules forming the crystal backbone is obtained by insertion of one axial CO ligand into a tetragonal cavity (formed by two axial and two radial CO's) on a next neighboring, equally oriented molecule (see Figure 1). This intermolecular interaction is responsible for the deviation of the molecular symmetry from idealized D_{3h} symmetry. Once a molecular row of $\text{Ru}_3(\text{CO})_{12}$ molecules is formed, a molecular layer is obtained by placing other

rows on both sides of the central one. The layer presents $(\text{CO})_3$ and $(\text{CO})_4$ units protruding from the surface. These units afford a “Velcro”-type interaction between molecular layers, which can then pile up, generating a three-dimensional stacking, *viz.*, the crystal.¹⁴

In $\text{Fe}_3(\text{CO})_{12}$,¹¹ the quasi-icosahedral geometry of the polyhedron described by the outer oxygen atoms is responsible for the well-known disorder shown by this molecule in its crystal. The quasi-centrosymmetry of the ligand coverage implies that the crystal packing does not discriminate between one orientation or its reversed one. The molecules form a close-packed cubooctahedral ES,¹⁴ *i.e.*, a ccp structure similar to that found in crystals of $\text{Fe}(\text{CO})_5$ and $\text{Mn}_2(\text{CO})_{10}$.^{5c} In the crystal of the almost isostructural species $\text{OsFe}_2(\text{CO})_{12}$,¹⁶ only 8% of the molecules are in the alternative centrosymmetric orientation. This difference has been tentatively explained by assuming that the contribution to crystal cohesion of the inner metal frame is more significant in $\text{OsFe}_2(\text{CO})_{12}$ than in $\text{Fe}_3(\text{CO})_{12}$ because of the presence of the heavier Os atom, thus decreasing the “centrosymmetric effect” of the CO coverage.

The molecular and crystal structure of a number of ruthenium and osmium clusters of nuclearity between 3 and 6 containing arene fragments such as C_6H_6 , $\text{C}_6\text{H}_3\text{Me}_3$, $\text{C}_6\text{H}_4\text{Me}_2$, and $\text{C}_6\text{H}_5\text{Me}$ has also been investigated,¹⁷ showing that the arene fragments tend to group together in the lattice, establishing graphitic-like interactions or forming ribbons.¹⁸ In crystalline $\text{H}_2\text{Os}_4(\text{CO})_{10}(\eta^6\text{-C}_6\text{H}_6)$ and $\text{H}_2\text{Os}_4(\text{CO})_{10}(\eta^6\text{-C}_6\text{H}_5\text{Me})$, for instance, the arene fragments interlock in a chevron-like fashion.^{17a} The most interesting molecular arrangement is shown by the pair of isomeric bis-arene clusters $\text{Ru}_6\text{C}(\text{CO})_{11}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)(\eta^6\text{-C}_6\text{H}_6)$ ^{19a} and $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_6)_2$.^{19b} In both crystals the benzene ligands face each other in graphitic arrangements, causing the formation of molecular “snakes” and “rows”, respectively (see Figure 2).¹⁸ Intermolecular arene-arene association is also present in crystals of $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)(\eta^6\text{-C}_6\text{H}_6)$ and $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)_2$.^{19c} The tendency to group together the arene fragments and to establish preferential arene-arene interactions is, therefore, maintained on changing the mode of coordination of the arenes as well as the type of ligand.

Packing decoding has also allowed us to rationalize the difference in molecular and crystal structures between $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$ ²⁰ and $\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$.^{19a} In the former species the face-capping benzene fragment, besides showing C-C bond length alternation and out-of-plane bending of the H atoms, is rotated *ca.* 5° away from exact eclipsing of the double bond midpoints over the Ru atoms. This distortion originates from the torsion of the tricarbonyl units,

(11) (a) Wei, C. H.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 1351. (b) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4155. (c) Braga, D.; Farrugia, L.; Grepioni, F.; Johnson, B. F. G. *J. Organomet. Chem.*, in press.

(12) (a) Wei, C. H. *Inorg. Chem.* **1969**, *8*, 2384. (b) Carré, F. H.; Cotton, F. A.; Frenz, B. A. *Inorg. Chem.* **1976**, *15*, 380.

(13) Johnson, B. F. G.; Benfield, R. E. *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: New York, 1980; p 471 and references therein.

(14) Braga, D.; Grepioni, F. *Organometallics* **1991**, *10*, 1254.

(15) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

(16) Churchill, M. R.; Fettinger, J. C. *Organometallics* **1990**, *9*, 752.

(17) (a) Braga, D.; Grepioni, F.; Johnson, B. F. G.; Parisini, E.; Martinelli, M.; Gallop, M. A.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1992**, 807. (b) Braga, D.; Grepioni, F.; Righi, S.; Johnson, B. F. G.; Bailey, P. J.; Dyson, P. J.; Lewis, J.; Martinelli, M. *J. Chem. Soc., Dalton Trans.* **1992**, 2121.

(18) Braga, D.; Grepioni, F.; Johnson, B. F. G.; Chen, H.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1991**, 2559.

(19) (a) Gomez-Sal, M. P.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Wright, A. H. *J. Chem. Soc., Chem. Commun.* **1985**, 1682. (b) Adams, R. D.; Wu, W. *Polyhedron* **1992**, *21*, 23. (c) Braga, D.; Grepioni, F.; Righi, S.; Dyson, P. J.; Johnson, B. F. G.; Bailey, P. J.; Lewis, J. *Organometallics* **1992**, *11*, 4042.

(20) Braga, D.; Grepioni, F.; Johnson, B. F. G.; Lewis, J.; Housecroft, C. E.; Martinelli, M. *Organometallics* **1991**, *10*, 1260.

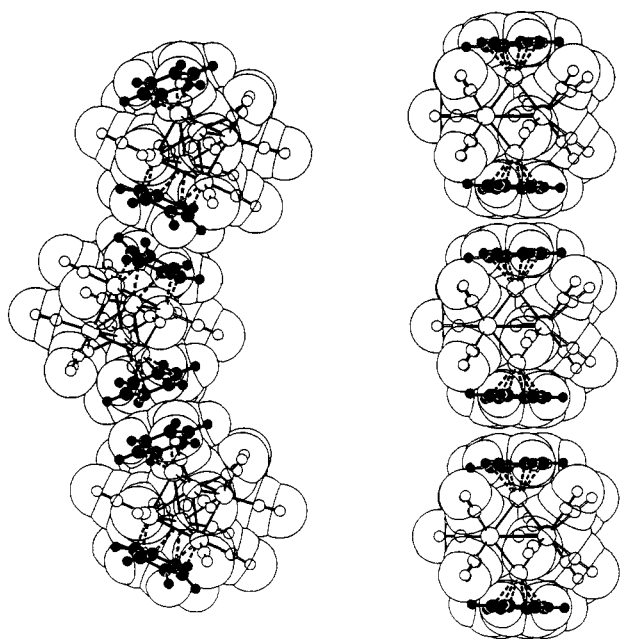


Figure 2. Crystal structure decoding: molecular organization in crystalline $\text{Ru}_6\text{C}(\text{CO})_{11}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)(\eta^6\text{-C}_6\text{H}_6)$ and $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_6)_2$. Note how the benzene ligands belonging to next neighboring molecules face each other in graphitic arrangements resulting in molecular "snakes" (left) and "columns" (right), respectively.

which, in turn, is caused by the interpenetration of molecular layers in the crystal. Fenske–Hall calculations²⁰ have shown that if the $(\text{CO})_3$ torsion is accompanied by benzene rotation, the overall ligand-to-cluster bonding is unaffected; hence optimization of the intermolecular interactions if the primary origin of the deformations. The difference in intermolecular cohesion caused by substitution of Os for Ru has been invoked to explain the different crystal structure possessed by the analogous Os cluster and, therefore, the different effect of the crystal packing on the molecular structure.²⁰

3. Crystal Packing Generation

The idea of predicting the crystal structure of a given compound is both fascinating and intriguing to structural chemists and crystallographers. The first attempts of this kind in the organometallic field have been made recently by studying the relationship between the molecular and crystal structures of $\text{Co}_2(\text{CO})_8$ and $\text{Fe}_2(\text{CO})_9$.⁸ In spite of the differences in space group symmetry and in molecular geometry, the crystal structures of $\text{Co}_2(\text{CO})_8$ and $\text{Fe}_2(\text{CO})_9$ are very similar.^{5c} The absence of the ninth CO in $\text{Co}_2(\text{CO})_8$ with respect to $\text{Fe}_2(\text{CO})_9$ results in the formation of large continuous channels in the crystal.

Alternative ways to pack $\text{Co}_2(\text{CO})_8$ and $\text{Fe}_2(\text{CO})_9$ molecules in the solid state have been explored by generating dimolecular nuclei (DMN) that optimize the interactions between the two component molecules.⁸ The three-dimensional distribution of the best DMN is optimized via cell variation procedures and the calculated structures compared with the observed crystal structures. We have shown that $\text{Co}_2(\text{CO})_8$ molecules can indeed be arranged in a way that uses the empty bridging sites and, thus, yields a crystal without channels. For example, in the monoclinic

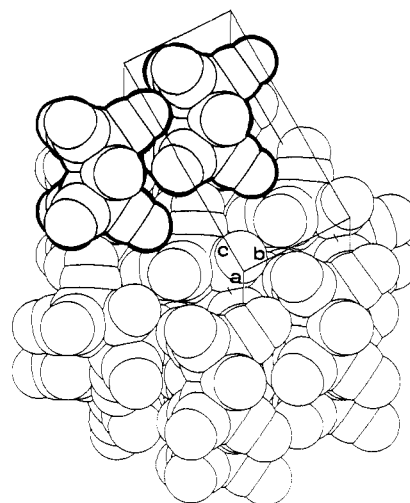


Figure 3. Crystal structure generation: the alternative monoclinic crystal structure obtained by the nucleus search and packing optimization procedure for $\text{Co}_2(\text{CO})_8$; thickened space-filling outlines mark the fundamental DMN used in the crystal structure generation procedure.

crystal shown in Figure 3, one terminal ligand of one $\text{Co}_2(\text{CO})_8$ molecule is inserted between the four terminal ligands surrounding the empty bridging site of an adjacent molecule, resulting in a crystal without channels or cavities. This packing arrangement is competitive with the observed one in terms of efficiency of space occupation and of cohesive energy. The reliability of the method and of the potential parameters was confirmed by the structure generation procedure on $\text{Fe}_2(\text{CO})_9$ that retraced directly the experimental crystal structure.

4. Organometallic Crystal Isomerism

In this section the term *crystal isomerism* is used to identify the case of flexible polynuclear molecules possessing extensive structural freedom that crystallize in different crystal systems.

$\text{Ru}_6\text{C}(\text{CO})_{17}$ can be crystallized in two different crystal forms,²¹ one of which contains one and one-half crystallographically independent molecular units, for a total of three molecular units. At the molecular level the three units differ essentially in the rotameric conformation of the tricarbonyl units above and below the equatorial plane containing the bridging ligands, and in the pattern of terminal, bridging, and semibridging CO's around the molecular equator. The resulting average structure is shown in Figure 4. The presence of three different rotameric conformations indicates that the apical $(\text{CO})_3$ units lie on a rather flat potential energy well. The conformational choice is then controlled primarily at the intermolecular level. This result is in agreement with recent molecular mechanics calculations on octahedral carbonyl clusters.²²

The difference in molecular and crystal structure between the two forms of $\text{HRu}_6\text{B}(\text{CO})_{17}$ ²³ and of Ir_6

(21) Braga, D.; Grepioni, F.; Johnson, B. F. G.; Dyson, P. J.; Frediani, P.; Bianchi, M.; Piacenti, F.; Lewis, J. J. *J. Chem. Soc., Dalton Trans.* **1992**, 2565.

(22) Sironi, A. *Inorg. Chem.* **1992**, *31*, 2467.

(23) (a) Hong, F. E.; Coffy, T. J.; McCarthy, D. A.; Shore, S. G. *Inorg. Chem.* **1989**, *28*, 3284. (b) Draper, S. M.; Housecroft, C. E.; Keep, A. K.; Matthews, D. M.; Song, X.; Rheingold, A. L. *J. Organomet. Chem.* **1992**, *423*, 241.

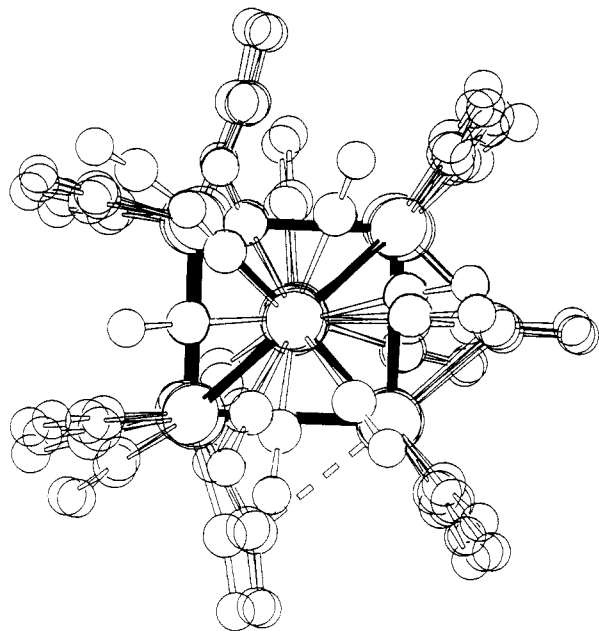


Figure 4. Crystal isomerism: the “average” molecular structure of $\text{Ru}_6\text{C}(\text{CO})_{17}$ obtained by overlapping the three structures observed in the two different crystalline modifications. Note how the apical CO's adopt different conformations with respect to the bridging equatorial ligand.

$(\text{CO})_{16}$,²⁴ or between the two independent molecules of $\text{Ru}_5\text{S}(\text{CO})_{15}$ ²⁵ (just to mention a few examples), can be rationalized similarly.²⁶

The solid-state *merry-go-round* isomerism is related to the crystal isomerism discussed above. The neutral derivatives $\text{Ir}_4(\text{CO})_9(\mu_3\text{-}1,3,5\text{-trithiane})$ and $\text{Ir}_4(\text{CO})_6(\mu\text{-CO})_3(\mu_3\text{-}1,3,5\text{-trithiane})$ [trithiane = 1,3,5-(SCH_2)₃]²⁷ and the ionic species $[\text{Ir}_4(\text{CO})_{11}(\text{SCN})][\text{NMe}_2(\text{CH}_2\text{Ph})_2]$ and $[\text{Ir}_4(\text{CO})_8(\mu\text{-CO})_3(\text{SCN})][(\text{Ph}_3\text{P})_2\text{N}]$ ²⁸ are present with two main structural forms in solution: the “all-terminal” with no bridging CO ligands and the “bridged” form with three edge-bridging CO ligands. Packing potential energy calculations^{27a} have shown that the most cohesive packing is associated with the bridged form, which also possesses a smaller volume and a higher molecular density than the unbridged one. This is in agreement with the positive activation volume obtained by variable-pressure NMR for the bridged–unbridged interconversion process.^{27b} Interestingly, a network of C–H...O hydrogen-bonding interactions is present in these crystals. In the bridged isomer only the bridging CO ligands are involved in short hydrogen bonds (see Figure 5). These interactions affect the molecular geometry to a great extent and are responsible for the asymmetry of the CO bridges, *i.e.*, for the deviation of the molecular geometry from idealized C_{3v} symmetry.^{27a}

In the crystalline salts $[\text{Ir}_4(\text{CO})_{11}(\text{SCN})][\text{NMe}_2(\text{CH}_2\text{Ph})_2]$ ^{28a} and $[\text{Ir}_4(\text{CO})_8(\mu\text{-CO})_3(\text{SCN})][(\text{Ph}_3\text{P})_2\text{N}]$ ^{28b} there is clear evidence that the negative charge is carried by

(24) Garlaschelli, L.; Martinengo, S.; Bellon, P. L.; Demartin, F.; Manassero, M.; Chiang, M. Y.; Wei, C. H.; Bau, R. *J. Am. Chem. Soc.* 1984, 106, 6664.

(25) Adams, R. D.; Babin, J. E.; Tasi, M. *Organometallics* 1988, 7, 503.

(26) Braga, D.; Grepioni, F. *Acta Crystallogr.* 1989, B45, 378.

(27) (a) Braga, D.; Grepioni, F. *J. Chem. Soc., Dalton Trans.* 1993, 1223. (b) Orlandi, A.; Frey, U.; Suardi, G.; Merbach, A. E.; Roulet, R. *Inorg. Chem.* 1992, 31, 1304.

(28) (a) Della Pergola, R.; Garlaschelli, L.; Martinengo, S.; DeMartin, F.; Manassero, M.; Sansoni, M. *Gazz. Chim. Ital.* 1987, 117, 245. (b) Brown, M. P.; Burns, D.; Harding, M. M.; Maginn, S.; Smith, A. K. *Inorg. Chim. Acta* 1989, 162, 287.

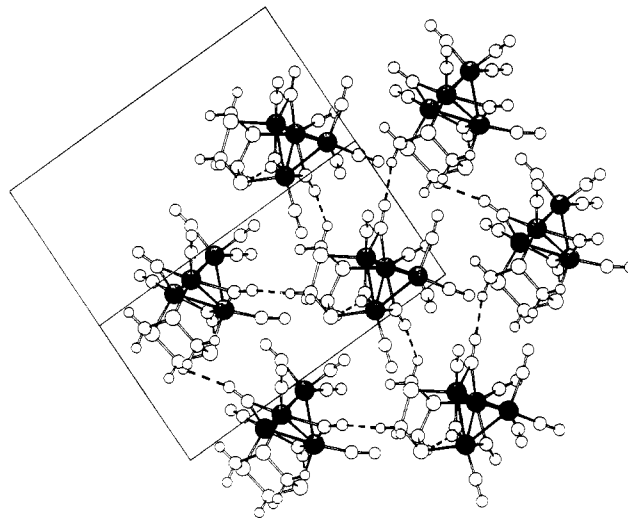


Figure 5. CH...O hydrogen-bonding network (broken lines) in crystalline $\text{Ir}_4(\text{CO})_6(\mu\text{-CO})_3(\mu_3\text{-}1,3,5\text{-trithiane})$.

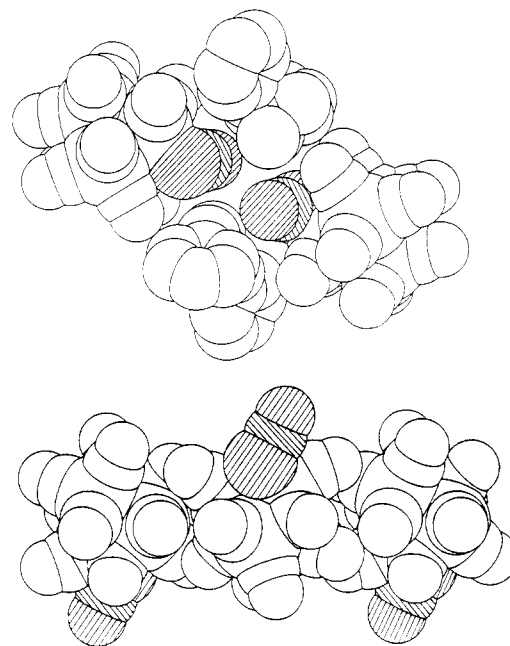


Figure 6. “Merry-go-round” isomers in the solid state: (a, top) in crystalline $[\text{Ir}_4(\text{CO})_{11}(\text{SCN})][\text{NMe}_2(\text{CH}_2\text{Ph})_2]$, the SCN ligands (shaded atoms) of two molecules are segregated within a “cage” generated by the surrounding $\text{NMe}_2(\text{CH}_2\text{Ph})_2^+$ cations; (b, bottom) in crystalline $[\text{Ir}_4(\text{CO})_8(\mu\text{-CO})_3(\text{SCN})][(\text{Ph}_3\text{P})_2\text{N}]$, the anions form an anionic pile with the SCN ligands pointing externally.

the SCN groups and not delocalized over the whole cluster molecule as in most carbonyl anions (see below). In the former crystal the ligands are segregated within a “cage” generated by four surrounding $[\text{NMe}_2(\text{CH}_2\text{Ph})_2]^+$ cations (see Figure 6a), while in the bridged form the crystal contains anionic piles (see Figure 6b) embraced by the $[\text{PPN}]^+$ cations.

5. Molecular Salts of High-Nuclearity Clusters

Neutral transition metal clusters form typical molecular crystals in which the cluster molecules are held together by interactions of the van der Waals type among tightly interlocked CO ligands. Molecular salts containing large cluster anions and large organic cations show similar features, with very little effect due to the

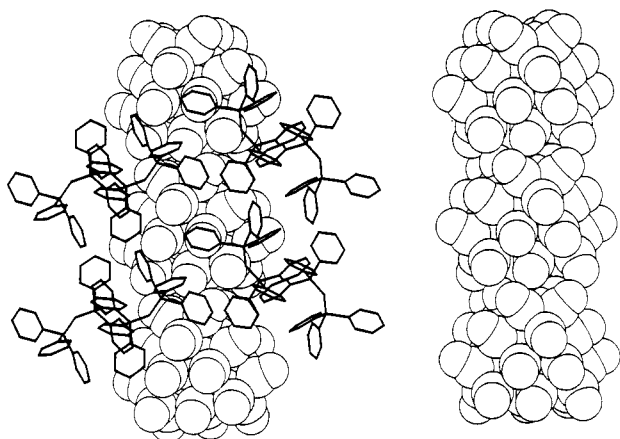


Figure 7. Analogy between neutral crystals and salts: (a, left) space-filling representation of a "coaxial cable" formed by $[M_{10}C(CO)_{24}]^{2-}$ ($M = Ru, Os$) dianions and surrounded by $[PPN]^+$ cations; (b, right) an identical pile present in crystalline $H_2Os_{10}C(CO)_{24}$. Reprinted with permission from ref 29a. Copyright 1992 American Chemical Society.

presence of ionic charges, although the specific shape requirements of the component ions impose additional intermolecular constraints on the crystalline organization.

In the families of crystalline salts based on the clusters $[M_{10}C(CO)_{24}]^{2-}$ ($M = Ru, Os$) and $[M_6C(CO)_{15}]^{2-}$ ($M = Rh, Co$) the anions show a clear tendency toward formation of *monodimensional anionic crystals* (rows or piles of anions) surrounded by counterions.^{29a} All $[PPN]^+$ salts of $[M_{10}C(CO)_{24}]^{2-}$ ($M = Ru, Os$) are isomorphous. These crystals share the same basic packing motif: piles of dianions parallel to the c -axis (see Figure 7a). The $[PPN]^+$ cations form a tight belt around each dianion pile as in a sort of coaxial cable. Identical piles constitute the crystal backbone in crystals of the neutral dihydride $H_2Os_{10}C(CO)_{24}$ ^{29b} (see Figure 7b), thus offering a strict structural analogy between crystals of neutral and ionic high-nuclearity clusters.

In order that these initial observations may be generalized, the family of hexanuclear cluster anions of general formula $[M_6(CO)_n]^{m-}$ or $[M_6X(CO)_n]^{m-}$ (where $X = C, N, H,$ or B , $n = 12-19$, and $m = 1-4$) has been investigated recently.³⁰ Anion sublattices are observed depending on the ratio between the van der Waals volume of the cluster anion and that of the *entire* formula unit [volume of the anion plus that of the cation(s) and of solvent molecules which may be present], *viz.*, the volume ratio: $VR = V_{anion}/V_{formula}$. In general, the VR value increases as the degree of anion organization in the crystal structure increases with the formation of piles or "snakes" (one-dimensional organization) and of anionic layers (two-dimensional organization). Small cations usually drive toward one-dimensional aggregation of the anions, while large cations lead to partial association (as in anionic "pairing") or to complete separation of the anions. In

(29) (a) Braga, D.; Grepioni, F. *Organometallics* 1992, 11, 1256. (b) Braga, D.; Grepioni, F.; Righi, S.; Johnson, B. F. G.; Frediani, P.; Bianchi, M.; Piacenti, F.; Lewis, J. *Organometallics* 1991, 10, 706.

(30) Braga, D.; Grepioni, F.; Milne, P.; Parisini, E. *J. Am. Chem. Soc.* 1993, 115, 5115.

(31) (a) Kitaigorodsky, A. I. *Mixed Crystals*, Springer-Verlag, Berlin 1984; (b) Sarma, J. A. R. P.; Desiraju, G. R. *J. Am. Chem. Soc.* 1986, 108, 2791.

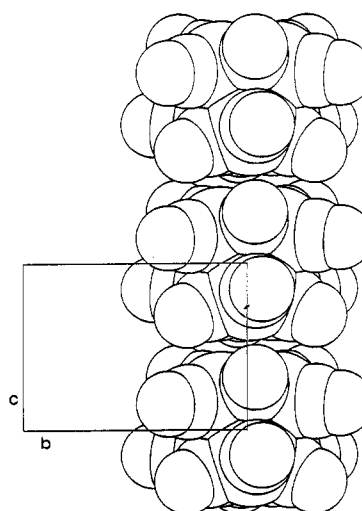


Figure 8. One-dimensional anion aggregation: space-filling representation of a columnar substructure formed by $[Ni_6(CO)_{12}]^{2-}$ anions in crystalline $[Ni_6(CO)_{12}][NMe_4]_2$.

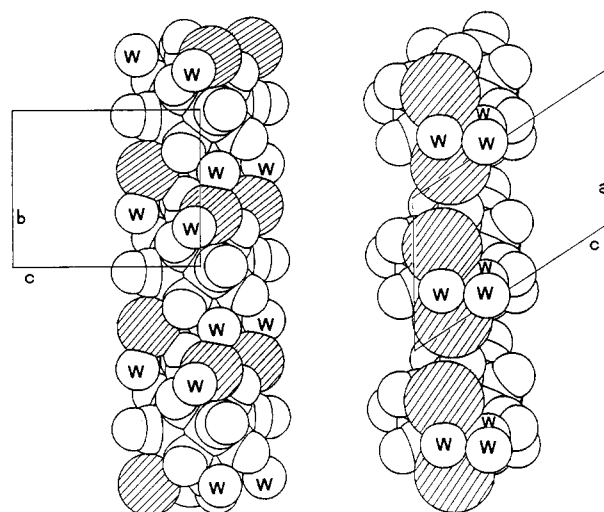


Figure 9. Anion aggregation in alkali salts: anion columns in crystalline (left) $[Co_6(CO)_{14}]K_4 \cdot 6H_2O$ and (right) $[Co_6(CO)_{15}]Cs_2 \cdot 3H_2O$. Note how the alkali metal atoms (shaded spheres) are embedded within the CO coverage. The coordinated water molecules (marked W) participate in a network of $CO \cdots HOH$ and $M \cdots OH_2$ interactions. Reprinted with permission from ref 30. Copyright 1993 American Chemical Society.

these cases the packing pattern is essentially that of molecular *mixed crystals*.³¹

The dianion $[Ni_6(CO)_{12}]^{2-}$ in its NMe_4^+ salt affords a striking example of a one-dimensional substructure. Anionic columns are formed *via* direct $Ni \cdots Ni$ van der Waals contacts between the triangular bases of the octahedral core (see Figure 8). The anionic columns are surrounded by six columns of $[NMe_4]^+$ cations.

Anionic columns are also present in the alkali salts $[Co_6(CO)_{14}]K_4 \cdot 6H_2O$ and $[Co_6(CO)_{15}]Cs_2 \cdot 3H_2O$ (see Figure 9). The counterions are deeply embedded in the cluster carbonyl envelope and carry the H_2O solvate molecules. These molecules participate in the stabilization of the crystal structures by linking the anions throughout the lattice *via* $C=O \cdots HOH$ hydrogen bonding and $CO \cdots K/CO \cdots Cs$ interactions. Similarly, the halogen atoms appear to play an important part in crystalline carbonyl halide cluster salts such as $[Ir_6(CO)_{14}Br][PPh_4]$ and $[Ir_6(CO)_{14}I][PPN]$, where the halogen atoms establish intermolecular "bridges" *via*

preferential I...I and Br...Br interactions of the kind formed by halogenated organic compounds.^{31b}

6. Conclusions and Outlook

The *crystal structure* of transition metal clusters has been given very little attention in the field of organometallic chemistry while some useful design criteria have been developed in the neighboring organic chemistry field.³²

In this Account we have addressed the intimate interplay between *molecular and crystal structure*. This is of special relevance when the molecule is flexible. In such a case the structure in the solid state is influenced by the surroundings; *i.e.*, the structural choice is largely controlled by intermolecular interactions.

We have argued that the formation of a crystalline material is a process of molecular aggregation which depends basically on the number and type of atoms, overall volume and shape, and charge distribution in the molecule, irrespective of the interatomic bonding skeleton. Structurally nonrigid molecules can be expected to form *crystal isomers* quite easily as long as the energy difference between the various ligand distributions is comparable to the energy difference between the crystalline forms. In the case of carbonyl clusters it is also evident that the CO ligand distributions, frozen out in the solid state, are related to low-energy migration pathways. The comparison of structures in different crystal environments relates to the structural correlation method put forward by Dunitz and Bürgi.^{33a} With a similar approach the interconversion trajectory from linear-terminal to symmetric bridging of CO ligands bound to polymetallic systems has been studied.^{33b} In a more recent extension of the structural correlation approach, the CO migration across triangular clusters as well as the rearrangement pathways of Ru₃Au₂ clusters has been investigated.^{33c}

In mono- and bis-arene cluster species the packing choices appear to be dictated by the need to optimize

the interlocking of flat arene fragments with the cavities and bumps of the carbonyl coverage. In general, this problem is dealt with by grouping together in the lattice the fragments with the same shape requirements. Arene ribbons organized in "herringbone" patterns, or molecular "snakes" linked *via* graphitic-like interactions, are then established.

The formation of anisotropic arrangements in *molecular salts* appears to be governed by the *relative* sizes of the component ions. When the anion is large with respect to the cation or cations, one- and two-dimensional aggregation is produced. When cations and anions have comparable sizes, the lattice organization recalls that of molecular *mixed crystals*³¹ whose structure is governed mainly by the steric similarity between the anions on one side, and between the cations on the other.

C-H...O interactions have a far from negligible role in organometallic crystals, where a large number of CO groups are present. These interactions, though weak, can drive the crystallization process and select a particular molecular structure favoring, for instance, isomers with bridging CO's over those with only terminal ligands. The participation of these weak hydrogen bonds in the cohesion of organic solids has recently been discussed by Desiraju.³⁴

All these aspects point to the importance of intermolecular interactions. The way molecules self-recognize and interact, self-assemble, and interlock to generate extended molecular arrays and crystals has just begun to be explored in the area of surface and solid-state organometallic chemistry. The two typical features of transition metal clusters, namely, the presence of soft metal skeletons and of ligands able to migrate on the cluster surface with little energy cost, yield *plastic* molecular systems whose collective properties in the solid state differ from those of the single molecule or ion. Material chemistry, for example, has much to gain from the study of the relationship between molecular assemblage and physical properties of organometallic and inorganic solids.

(32) Desiraju, G. R. *Crystal Engineering, The Design of Organic Solids*; Elsevier: Amsterdam, 1989; p 47.

(33) (a) Bürgi, H. B.; Dunitz, J. D. *Acc. Chem. Res.* 1983, 16, 153. (b) Crabtree, R. H.; Lavin, M. *Inorg. Chem.* 1986, 25, 805. (c) Orpen, A. G.; Salter, I. D. *Organometallics* 1991, 10, 111.

(34) Desiraju, G. R. *Acc. Chem. Res.* 1991, 24, 290.