

Yamada & Hamaya (1983) have compared two groups of  $A_2BX_4$  compounds:  $A_2\text{ZnX}_4$  materials ( $A = \text{K, Rb, NH}_4$ ;  $X = \text{Cl, Br}$ ) and  $(\text{TMA})_2\text{MCl}_4$  materials [ $\text{TMA} = \text{N}(\text{CH}_3)_4$ ,  $M = \text{Zn, Cu, Co, Fe, Ni}$ ] which present different INC–C successive phase transitions. In the first group, the temperature range of the INC phase is relatively wide and the incommensurate wavevector decreases as the temperature decreases, and locks into  $q = 1/3$ . In the second group, the modulation wavevectors tend to increase with decreasing temperature, the lock-in wavevectors take several values ( $2/5, 1/2, 1/3$ ) and the temperature range of the INC phases is reduced. With an EXAFII model, Yamada & Hamaya (1983) have shown that  $A_2\text{ZnX}_4$  compounds are characterized by relatively small second- and third-neighbour interactions, opposite to observations of  $(\text{TMA})_2\text{MCl}_4$  compounds. These results are in agreement with the fact that Rb–Cl interatomic distances and their variations are very similar to the Rb–Br ones (Hogervorst & Helmholdt, 1988), given the difference between the ionic radii of Cl and Br atoms, and the INC phases of these two compounds are really isostructural. In contrast, the TMA–Cl distances and their variations are relatively stronger than the Rb–X ones, whereas the M–Cl distances in a tetrahedron are similar in both groups. These results may be related to the difference between the cell parameters of the two families and may explain the existence of two different types of INC structures and of two different INC–C phase-transition processes. From these considerations, the hypothesis can be made of two families of isostructural  $A_2BX_4$  compounds, which must be confirmed by further structural studies.

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## Molecular Volumes and Packing Efficiency. An Approach to Metal Cluster Properties in the Solid State

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### Abstract

Molecular volumes, surfaces and packing coefficients are calculated, starting from known crystal structures, for a number of neutral metal-carbonyl clusters by applying the method of intersecting caps widely used in organic solid-state chemistry. The problem of an appropriate atomic radius attribution is discussed. The

results of the packing analysis are used to investigate the relationship between packing efficiency and occurrence of dynamic processes in the solid state, as well as many structural properties of metal-carbonyl clusters.

### Introduction

Although the concept of molecular shape has been diffusely applied to the analysis of transition-metal

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cluster structures (Hitchcock, Mason & Textor, 1976; Benfield & Johnson, 1980; Johnson & Benfield, 1981; Mingos, 1982; Lauher, 1986), very little has been said on the relationship between quantities such as molecular volumes, surfaces and atomic radii and the way in which metal cluster molecules are distributed in the crystals. In most cases 'packing forces' and 'intermolecular interactions' are invoked only to account for unexpected molecular features or to cover a large variety of (poorly understood) steric and electronic factors which cooperatively control arrangements and properties of the molecules in the solid state. Moreover, the recent results obtained by MAS NMR in the investigation of dynamic processes occurring in the solid state for some organometallic compounds and metal clusters (Dorn, Hanson & Motell, 1981, 1982; Hanson, Sullivan & Davis, 1984; Hanson, Lisic, Petty & Iannacone, 1986; Hanson & Lisic, 1986; Aime, Botta, Gobetto, Osella & Milone, 1988) appear to require a more precise and, possibly, quantitative description of the molecular structures in terms of size and shape, and of the way in which the molecules are organized within the crystals. This paper presents some results obtained by applying a volume and packing analysis, of the kind largely used in organic solid-state chemistry (Kitaigorodsky, 1973; Bernstein & Hagler, 1978; Bar & Bernstein, 1984; Gavezzotti, 1982, 1983, 1985), to a number of 'fundamental' polynuclear metal carbonyls. Besides the problem of molecular volume evaluation, the concept of 'packing efficiency' and its relationship with the occurrence of dynamic processes in the solid state, and an analysis of the differences among packing arrangements of some neutral species are examined. The goal of this paper is to show that the method, though based on some crude (and sometimes simplistic) assumptions, provides a simple and straightforward means to approach many aspects of organometallic solid-state chemistry.

### Methodology

Molecular volumes ( $V_{\text{mol}}$ ), surfaces ( $S_{\text{mol}}$ ) and packing coefficients ( $C_p$ ) can be evaluated by applying the method of intersecting caps proposed by Kitaigorodsky (1973) and further developed by Gavezzotti (1983). The method considers a molecule as a collection of atomic spheres of given radii (usually van der Waals radii), centred at the atomic positions obtainable from X-ray crystallographic studies. Packing coefficients, which afford a quantitative evaluation of the packing efficiency in the crystal lattice, can then be obtained from the ratio  $(V_{\text{mol}}Z)/V_{\text{cell}}$ .

The very peculiar stereogeometry of most metal-carbonyl clusters (tight packing of CO ligands around the metallic cores) allows a fortunate simplification of the problem of atomic radius assignment, which would

otherwise constitute a major cause of dispute. In low-nuclearity metal clusters  $V_{\text{mol}}$  and  $S_{\text{mol}}$  are largely determined by the CO-ligand periphery, so that their values depend mainly on the dimensions of the O and C atoms, while the metal-atom size has little relevance as these atoms are almost completely enclosed within the carbonyl shell.

Van der Waals radii suitable for the calculations are not available for the metal atoms so they were given the van der Waals radii of the corresponding noble gases (Bondi, 1964; Gavezzotti, 1983). On the other hand, C- and O-atom van der Waals radii, though available, do not afford a satisfactory model for volume calculations. The O-atom radius of 1.40 Å is much smaller than the value obtainable from the average intermolecular O...O contacts (which are invariably found within the narrow range 3.00–3.05 Å), while the C-atom radius of 1.75 Å appears to be too large, leading to compression of non-bonded C-atom spheres of CO ligands. In order to assess a more sensible model a different criterion was adopted. The O atoms were given a 1.52 Å radius derived from the average *intermolecular* contact distance. The C atoms were instead allocated a 'tangential' radius ( $r_t$ ) defined as half of the average C...C contact distance between a C atom and the surrounding ones bound to the *same* metal atom. In such a way  $r_t$  represents a sort of limit for CO-ligand close packing over the cluster surface. Although  $r_t$  depends on the actual stereogeometry of the species under examination, its value falls within a fairly narrow range for terminal ligands (1.34–1.40 Å). Appropriate  $r_t$  values for the bridging ligands were also calculated by subtracting from the average  $C_t...C_b$  distance the  $r_t$  value obtained for terminal CO's only. The metal atoms were given the van der Waals radius of the corresponding noble gas (Bondi, 1964).

Results of the computations of  $V_{\text{mol}}$ ,  $S_{\text{mol}}$  and  $C_p$  for all the species under examination are reported in Table 1. Values in the first line of each entry were calculated by using van der Waals radii, while values in the second line were calculated by using an O-atom radius of 1.52 Å and  $r_t$  values for the C atoms; unless otherwise specified, distinct  $r_t$  values for bridging and terminal ligands were used for species containing  $\mu_2$ - or  $\mu_3$ -bridging CO's. It should be emphasized that the two approaches (van der Waals or 'tangential' radii) do not yield appreciably different results (see Table 1). What is more, despite the rather crude approximations illustrated above, the *relative ratios* of the quantities we are interested in are substantially independent from the model adopted for volume calculations. The use of other combinations of atomic radii was also checked confirming that the ratios between  $V_{\text{mol}}$ ,  $S_{\text{mol}}$  and  $C_p$  do not change, provided that a coherent choice is adopted. All calculations were performed by using a slightly modified version of the *OPEC* (organic packing energy calculations) computer program (Gavezzotti, 1983).

Table 1. *Molecular volumes ( $V_{\text{mol}}$ ), packing coefficients ( $C_p$ ) and surfaces ( $S_{\text{mol}}$ ) for some neutral metal-carbonyl clusters*

	$V_{\text{cell}}(\text{\AA}^3)$	$r_{\text{O}}(\text{\AA})$	$r_{\text{C}}(\text{\AA})$	$V_{\text{mol}}(\text{\AA}^3)$	$C_p$	$S_{\text{mol}}(\text{\AA}^2)$	X-ray ref.
$\text{Co}_2(\text{CO})_8$	1167.3	1.40	1.75	191	0.65	245	(1)
r.t.		1.52	1.37	181	0.62	258	
$\text{Co}_2(\text{CO})_8$	1116.9	1.40	1.75	186	0.66	228	(2)
100 K		1.52	1.37 <sup>a</sup>	177	0.64	244	
$\text{Fe}_2(\text{CO})_9$	578.4	1.40	1.75	195	0.68	237	(3)
		1.52	1.36 <sup>a</sup>	189	0.66	260	
$\text{Fe}_3(\text{CO})_{12}$	831.5	1.40	1.75	276	0.66	302	(4)
		1.52	1.36 <sup>a</sup>	261	0.63	347	
$\text{Co}_4(\text{CO})_{12}$	1817.1	1.40	1.75	277	0.61	310	(5)
		1.52	1.40 <sup>a</sup>	264	0.60	351	
$\text{Rh}_4(\text{CO})_{12}$	1970.3	1.40	1.75	296	0.60	346	(6)
		1.52	1.40 <sup>a</sup>	291	0.59	373	
$\text{Ru}_3(\text{CO})_{12}$	1732.6	1.40	1.75	305	0.71	320	(7)
		1.52	1.40	292	0.67	362	
$\text{Os}_3(\text{CO})_{12}$	1710.4	1.40	1.75	306	0.72	323	(8)
		1.52	1.40	293	0.69	363	
$\text{Ir}_4(\text{CO})_{12}$	1373.7	1.40	1.75	324	0.72	364	(9)
		1.52	1.46	310	0.69	388	
$\text{Ir}_6(\text{CO})_{16}$	2406.2	1.40	1.75	359	0.60	419	(10)
'red'		1.52	1.35	366	0.61	470	
( $\mu_3$ -CO's)		1.52	1.34/1.70 <sup>b</sup>	381	0.63	456	(10)
$\text{Ir}_6(\text{CO})_{16}$	2385.2	1.40	1.75	387	0.65	417	
'black'		1.52	1.35	381	0.64	476	
( $\mu_2$ -CO's)		1.52	1.34/1.64 <sup>b</sup>	400	0.68	460	

Notes: (a) No appreciable differences were detected in C-atom 'tangential radii' between terminal and bridging CO's. (b) Radial attributed to  $\mu_3$ -CO's or  $\mu_2$ -CO's were calculated as described in the text.

References: (1) Summer *et al.* (1964); (2) Leung & Coppens (1983); (3) Cotton & Troup (1974a); (4) Wei & Dahl (1969); Cotton & Troup (1974b); (5) Wei (1969) and Carré *et al.* (1976); (6) Wei (1969); (7) Churchill, Hollander & Hutchinson (1977); (8) Churchill & De Boer (1977); (9) Churchill & Hutchinson (1978); (10) Garlaschelli *et al.* (1984).

## Results and discussion

Although the following discussion will be devoted to a comparative analysis of the quantities reported in Table 1, a preliminary consideration is necessary with respect to the  $C_p$  values. The packing coefficients calculated for the neutral species listed in Table 1 fall in the range 0.60–0.72 observed for most organic molecules (Gavezzotti, 1983, 1985). This fact provides an indication that the treatment of neutral transition-metal cluster crystals as pure molecular crystals, similar to those of most organic molecules, is substantially correct. However, the aim of this study is not the calculation of the absolute values of the quantities under examination. The use of the information obtainable by comparing closely related species will be illustrated through a number of (non-exhaustive) examples in the following.

The relationship between 'dynamic' behaviour in the solid and molecular packing can be approached first.  $^{13}\text{C}$  MAS NMR experiments have afforded a wealth of information on the occurrence of dynamic processes for a number of organometallic compounds. Among these, solid  $\text{Co}_2(\text{CO})_8$  (Hanson *et al.*, 1984),  $\text{Fe}_3(\text{CO})_{12}$  (Dorn *et al.*, 1981; Hanson, Lisic, Petty & Innacone, 1986) and  $\text{Co}_4(\text{CO})_{12}$  (Hanson & Lisic, 1986) have been investigated, showing that terminal and bridging CO

ligands are equilibrated at room temperature on the NMR time scale. The averaging mechanisms proposed for  $\text{Co}_2(\text{CO})_8$  (migration of the CO ligands between crystallographically observed positions) and  $\text{Fe}_3(\text{CO})_{12}$  and  $\text{Co}_4(\text{CO})_{12}$  (metal-frame reorientation within the CO envelope) have been recently questioned. In the case of  $\text{Fe}_3(\text{CO})_{12}$ , it has been proposed (Anson, Benfield, Bott, Johnson, Braga & Marseglia, 1988) that the observed dynamic behaviour can be interpreted on the basis of small internal librations of both the metal frames and the CO ligands around their equilibrium positions in accord with the molecular symmetry. Regardless of the interpretation adopted, such dynamic behaviour is logically related to (and depends on) the way in which the molecules are held together in the crystal lattice. It seems reasonable to expect that either small- or large-amplitude atomic displacements, let alone full-scale ligand migrations, require 'free space' in the crystal to allow smooth potential-energy pathways compatible with low activation energy barriers. On these premises, it is worth noting that the  $C_p$  values for the 'dynamic' species show a clear tendency towards lower limits compared with the values of species such as  $\text{Fe}_2(\text{CO})_9$  (Dorn *et al.*, 1982),  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Os}_3(\text{CO})_{12}$  (Aime *et al.*, 1988) which have been ascertained as 'static' in the solid state. This is an indication that dynamic processes in the solid state for metal carbonyls

are favoured by a loose molecular packing. Unfortunately, no discriminating criterion between large-amplitude and small-amplitude atomic motions can be afforded by an analysis confined to packing coefficients. However, it is worth noting that the  $C_p$  values calculated for the *cis* and *trans* isomers of  $[(C_5H_5)_2Fe_2(CO)_4]$ , which undergo facile reorientation of the  $C_5H_5$  ligands in the solid as evidenced by both MAS NMR (Dorn *et al.*, 1982) and potential-energy calculations (Braga, Grepioni & Gradella, 1989), are much smaller (0.53 and 0.55, respectively) than the values calculated for  $Co_2(CO)_8$ ,  $Fe_3(CO)_{12}$  and  $Co_4(CO)_{12}$ .

Let us examine  $Co_2(CO)_8$  in more detail. A comparison of the  $C_p$  values calculated for the room-temperature (Summer, Klug & Alexander, 1964) and low-temperature (100 K) (Leung & Coppens, 1983) determinations affords, *inter alia*, a direct test of the sensitivity of the molecular volume analysis method. On decreasing the temperature to 100 K the cell volume shrinks more than the molecular volume, leading to an increase in packing efficiency and, consequently, to freezing of the molecular motions in keeping with the observation of a static structure below 296 K (Hanson *et al.*, 1984).

A further consideration arises from a comparison of the crystal packings of  $Co_2(CO)_8$  and  $Fe_2(CO)_9$ , which turn out to be very similar, despite the fact that the two species crystallize in two very different space groups ( $P2_1/m$  and  $P6_3/m$ , respectively) (Summer *et al.*, 1964; Leung & Coppens, 1983; Cotton & Troup, 1974a). The relationship between the [010] and [100] planes of  $Co_2(CO)_8$  and  $Fe_2(CO)_9$ , respectively, is sketched in Fig. 1; space-filling packing diagrams of the [100] and [110] planes are shown in Fig. 2. The important point is that the two molecular packings differ *only* for the 'missing ligand' of  $Co_2(CO)_8$  with respect to  $Fe_2(CO)_9$ . This fact may account for the different dynamic behaviour shown by the two species in the solid state: more room for molecular motion is available for  $Co_2(CO)_8$  than for  $Fe_2(CO)_9$ , in agreement with their respective  $C_p$  values.

The orientational disorder shown by  $Fe_3(CO)_{12}$  and  $Co_4(CO)_{12}$  also deserves some attention. The disorder in both cases arises from random occupation of the crystal sites by the molecules in two *almost* equivalent orientations due to the quasi-icosahedral ligand polyhedra (Wei & Dahl, 1969; Cotton & Troup, 1974b; Wei, 1969; Carré, Cotton & Frenz, 1976). Therefore

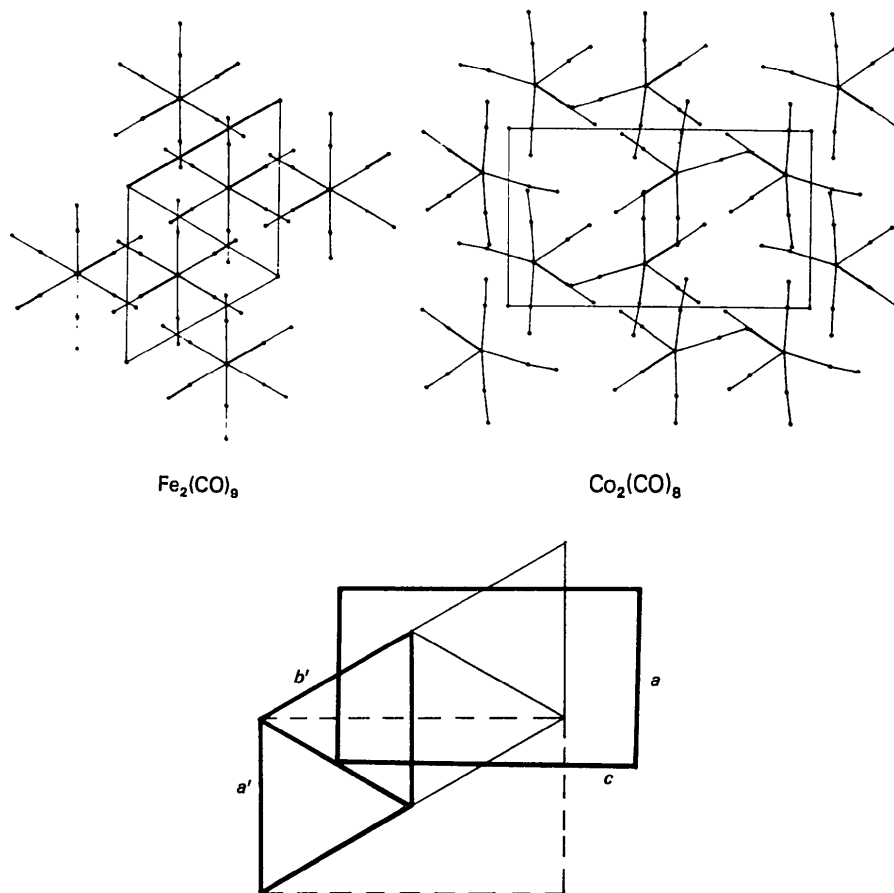


Fig. 1. Projections in the [001] and [010] planes of the crystal packings of  $Fe_2(CO)_9$  and  $Co_2(CO)_8$ , and the relationship between the two unit cells ( $a \simeq a'$ ,  $b \simeq c'$ ,  $c \simeq 2b' \sin 60^\circ$ ; primed axes refer to the former species). The unit cell of  $Co_2(CO)_8$  before origin translation is represented by broken lines.

the misfitting among the molecules in the lattice may determine a poorer packing efficiency with respect to species without disorder problems and can thus account for the lower  $C_p$  values.

Let us now compare species which possess approximately icosahedral ligand polyhedra [ $\text{Fe}_3(\text{CO})_{12}$  (Wei

& Dahl, 1969; Cotton & Troup, 1974b),  $\text{Co}_4(\text{CO})_{12}$ ,  $\text{Rh}_4(\text{CO})_{12}$  (Wei, 1969; Carré *et al.*, 1976)] with those with cubooctahedral [ $\text{Ir}_4(\text{CO})_{12}$  (Churchill & Hutchinson, 1978)] or anticubooctahedral [ $\text{Ru}_3(\text{CO})_{12}$  (Churchill, Hollander & Hutchinson, 1977),  $\text{Os}_3(\text{CO})_{12}$  (Churchill & De Boer, 1977)] ligand polyhedra. Packing of the latter polyhedra invariably leads to much higher  $C_p$  values than for the former ones, thus indicating that the packing of icosahedra is much less efficient (*ca* 10% less) than that of cubo- and anticubooctahedra (see Fig. 3) which may well be the cause of the commonly encountered disorder mentioned above. It can also be seen that the volume of  $\text{Ir}_4(\text{CO})_{12}$  is larger than that of  $\text{Rh}_4(\text{CO})_{12}$  even though the former possesses a smaller metal core [mean Ir—Ir 2.69 (1), Rh—Rh 2.72 (1) Å], thus indicating that the icosahedral distribution represents a more efficient way of packing ligands around the metal core. Altogether, it can be said that while the icosahedral envelope optimizes ligand packing around the molecule, the cubooctahedral one optimizes the molecular packing in the crystal.

Finally, the unusual case of ligand isomerism shown by  $\text{Ir}_6(\text{CO})_{16}$  can be examined. The face-bridged 'red' isomer possesses idealized  $T_d$  symmetry, while the edge-bridged 'black' isomer possesses  $D_{2d}$  idealized symmetry (Garlaschelli, Martinengo, Bellon, Demartin, Manassero, Chiang, Wei & Bau, 1984). Although the difference in energy between the two ligand distributions is certainly very small, interconversion of the two isomers was not detected (Garlaschelli *et al.*, 1984). Our calculations show that the 'red' isomer, which has a smaller  $V_{\text{mol}}$ , is less efficiently packed in the crystal than the 'black' isomer. On the basis of the close-packing

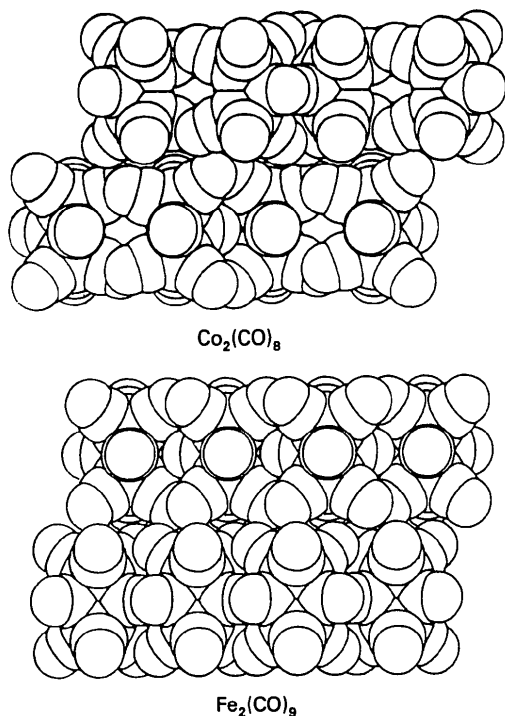


Fig. 2. Comparison of space-filling packing diagrams of  $\text{Co}_2(\text{CO})_8$  and  $\text{Fe}_2(\text{CO})_9$ .

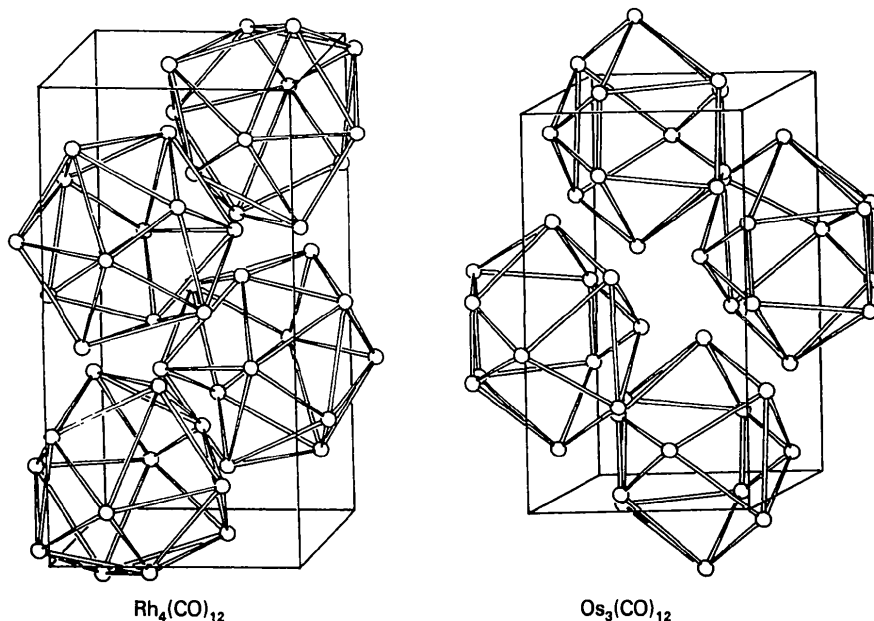


Fig. 3. Comparison between the packing arrangements of icosahedral ligand polyhedra [ $\text{Rh}_4(\text{CO})_{12}$ ] and of anticubooctahedral ligand polyhedra [ $\text{Os}_3(\text{CO})_{12}$ ].

principle (or density rule) (Kitaigorodsky, 1973) this latter isomer is expected to be the more stable form. It should be pointed out, however, that the density rule holds, in principle, only for small hydrocarbon species. It seems that the only conclusion one can draw to explain the existence of both isomers is that the differences in molecular and packing energies for the two forms must cancel (*i.e.* be approximately equal and of opposite sign). This behaviour leads to the role played by the aforementioned 'crystal forces', which appear to be in competition with ligand-packing optimization around the metal frame. Slightly different crystallization conditions may suffice in altering the subtle energy balance between these two factors in determining the final stereogeometry.

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## Interpretation of Atomic Displacement Parameters: Intramolecular Translational Oscillation and Rigid-Body Motion

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#### Abstract

An extension of the rigid-body model which includes intramolecular translational oscillations is presented. Some symmetry aspects are discussed, especially for cases where several symmetrically equivalent groups in a molecule perform coupled translational oscillations. The relationship between the general model and difference displacement parameters  $\Delta U$  between pairs of atoms along their internuclear vector is elaborated.

Some examples in the field of transition-metal complexes are given.

#### Introduction

Atomic displacement parameters, determined routinely with almost every crystal structure analysis, contain information on *atomic motion* and on *atomic disorder* in the crystal. A picture of *molecular motion* (and disorder) would, in many instances, be more informa-