On the Factors controlling the Crystal Packing of First-row Transition-metal Binary Carbonyls†

Dario Braga,* Fabrizia Grepioni, and Piera Sabatino
Dipartimento di Chimica 'G. Ciamician,' Universitá di Bologna, Via F. Selmi 2, 40126 Bologna, Italy

The crystal packings of $[V(CO)_6]$, $[Cr(CO)_6]$, $[Mn_2(CO)_{10}]$, $[Fe(CO)_5]$, $[Fe_2(CO)_9]$, $[Co_2(CO)_8]$, and $[Ni(CO)_4]$ have been examined. It is shown that each molecule except $[Ni(CO)_4]$ is enclosed in a 12-molecule shell. Two basic packing motives are recognized, namely the cubo-octahedron and the anti-cubo-octahedron. Crystal and molecular qualifiers, such as molecular volumes, and packing coefficients have been calculated. The atom–atom pairwise potential-energy method has been used to estimate the separate contributions to the total packing potential energy (p.p.e.) of each kind of intermolecular interaction; given the same number of metal atoms, a CO group contributes a fairly constant amount to the p.p.e. The CO-group intermolecular mutual orientations have also been examined, showing that the CO axes are preferentially orthogonal in projection.

A common view held by chemists (and crystallographers) working in the organometallic chemistry field is that the aim and ultimate result of a *crystal* structure analysis is the investigation of a *molecular* structure. A crystal is often regarded as a mere container of countless identical entities, the molecules, repeated in the three directions of space. This approach leads to a loss of a relevant portion of the structural information already contained, it is important to stress, in the results of any conventional single-crystal diffraction experiment. The development of suitable spectroscopic techniques for the investigation of the solid state [cross-polarization (c.p.) magic-angle-spinning (m.a.s.) n.m.r. spectroscopy, Raman spectroscopy, quasi-inelastic neutron scattering, *etc.*][1] has created new interest in the properties of the condensed state of matter also in the organometallic chemistry area. Phenomena such as small- and large-amplitude motions, molecular-fragment reorientations, solid-state fluxionality, and phase transition are the subject of current studies.[2–5] These studies require a detailed knowledge of the factors controlling the molecular environment in the crystal and of the forces at work among the molecules.

In this paper we focus our attention on the first-row-mono- and di-nuclear neutral binary carbonyls $[V(CO)_6]$, $[Cr(CO)_6]$, $[Mn_2(CO)_{10}]$, $[Fe(CO)_5]$, $[Fe_2(CO)_9]$, $[Co_2(CO)_8]$, and $[Ni(CO)_4]$. These are prototypical species on which much experimental and theoretical work has been done, and whose structural bonding and spectroscopic characteristics are still a matter of debate in the scientific community.

We will attempt to answer the following questions: (*i*) do molecules of neutral binary carbonyls pack in their solids according to the same close-packing principles as organic molecules?; (*ii*) if they do so, is there a preferential packing motif which can be recognized?; (*iii*) is there a preferential mutual orientation of the CO groups belonging to neighbouring molecules in the crystal? (and, consequently, is there any unfavourable 'forbidden' orientation?); and (*iv*) is it possible to relate some physical properties (melting points, sublimation enthalpies, *etc.*) and spectroscopic properties (static or dynamic solid-state behaviour) to some basic features of their solids?

For this purpose we have chosen to apply to these systems methods and procedures developed in the neighbouring field of organic solid-state chemistry, where solid-state properties have been the subject of much work over the last two decades and of continuing investigations.[6]

Methodology

A mono- or poly-nuclear metal carbonyl can be regarded as a metallic core from which the CO groups are disposed more or less radially, so that the outermost surface is covered by the oxygen terminations, while the metal atom(s) is encapsulated within the CO coverage. The intermolecular interactions are, therefore, controlled primarily by the $O\cdots O$ contacts, although interlocking of CO ligands is also possible depending on the molecular geometry. The crystals of neutral binary carbonyls fulfil the two basic requirements of the (rather broad) definition of a molecular crystal,[7] namely absence of net ionic charge and presence in the lattice of discrete molecular entities (which can be recognized purely on the basis of the intermolecular separations). What is more, both theoretical and experimental studies[8] have shown that the charge separation on the C and O atoms of a metal-bound CO is very small so that dipolar interactions can, to a first approximation, be neglected. Consequently the working hypothesis on which this paper is based is that the crystal packing of these species is determined primarily by van der Waals interactions.

On these premises, the methods widely used to treat molecular crystals of organic substances can be transferred (with some further, far from trivial, approximation) to study the properties of solid metal carbonyls. The correctness of this approach will have to be judged heuristically from the results. The following crystals and molecular 'qualifiers' will be examined.

(*a*) *Molecular Volumes* (V_{mol}) *and Surfaces* (S_{mol}).—These can be obtained by the Kitaigorodsky method of intersecting caps.[7,9] The method considers a molecule as a collection of atomic spheres of given radii centred at the crystallographically determined atomic positions. Van der Waals radii taken from the literature[10a] are used for the C and O atoms (1.75 and 1.40 Å, respectively), while the metal atoms are attributed a constant radius of 2.15 Å. The choice of atomic radii in transition-metal complexes has already been discussed, and it was found that, as long as the analysis is carried out on a *relative basis* and a coherent choice is made for all species under investigation, the results of volume and surface calculations are substantially independent of the model adopted.[10b]

(*b*) *Packing Coefficients* (*p.c.s*).—These are obtained from the ratio $V_{mol}Z/V_{cell}$. This quantity gives a rough indication of the efficiency of molecular packing in the crystal.[7] Being based on the calculation of V_{mol}, the p.c. values are useful, once again, only on a relative basis.

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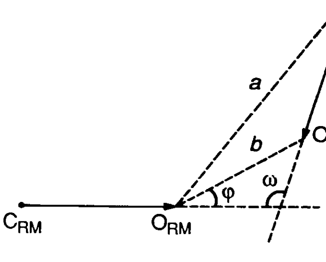
† *Non-S.I. unit employed:* cal = 4.184 J.

Table 1. Parameters for the atom–atom potential-energy calculations *

	A/kcal mol^{-1}	B/Å^{-1}	C/kcal mol^{-1} Å^{-6}
C $\cdots$ C	71 600	3.68	421.0
O $\cdots$ O	77 700	4.18	259.4
M $\cdots$ M	270 600	3.28	3 628.0

* For crossed interactions: $A = (A_xA_y)^{\frac{1}{2}}$, $B = (B_x + B_y)/2$, and $C = (C_xC_y)^{\frac{1}{2}}$.



Scheme 1. $\Delta = a - b$

(*c*) *Packing Potential Energy* (*p.p.e.*).—This can be evaluated within the atom–atom pairwise potential-energy method[11] by means of expression (1) where r_{ij} represents the non-bonded

$$\text{p.p.e.} = \Sigma_i\Sigma_j\,[A\exp(-Br_{ij}) - Cr_{ij}^{-6}] \qquad (1)$$

atom–atom intermolecular distance. Index i in the summation encompasses all atoms of one molecule (chosen as reference, RM) and index j all the atoms of the surrounding molecules distributed according to crystal symmetry. A cut-off of 10 Å has been adopted in our calculations. The values of the coefficients A, B, and C used in this work are listed in Table 1 [note that the coefficients for C and O atoms are those for solid CO in argon matrix].[12] The metal atoms, for which such coefficients are not available, are treated as the corresponding noble gas (Kr).*

(*d*) *Pairwise Contribution* (E_{i-j}).—This is the contribution to p.p.e. of each kind of hetero- and homo-atomic intermolecular interactions in which the p.p.e. can be partitioned. A similar procedure has been successfully applied in a statistical analysis of the contributions from different kinds of atoms over a large number of hydrocarbon crystals.[14] For the binary carbonyls the partitioning is obtained by calculating separate E_{i-j} terms for the three atomic species in the crystals. The terms E_{O-C}, E_{O-O}, and E_{C-C} sum to E_{CO} which is the *total* contribution to the p.p.e. of the CO groups in the molecule. From E_{CO} the average contribution E_{CO}/n_{CO} of the single CO group to the p.p.e. can be obtained.

(*e*) *Enclosure Shell* (ES).—The results of p.p.e. calculations can also be used to investigate the molecular packing arrangement around the reference molecule (RM). First, the separate contributions to the p.p.e. of all the molecules (usually 40—60), generated around RM by space-group symmetry within a cut-off distance of 10 Å, are calculated. Then the first-neighbouring molecules (those constituting the enclosure shell, ES) are selected among the surrounding molecules on the basis of the highest number of intermolecular contacts with RM (*i.e.* those which contribute most to the p.p.e.). This procedure ensures that all relevant contributions to the p.p.e. are considered. We have found that ES is invariably constituted of 12 molecules {except for [$Ni(CO)_4$]} accounting for most (90—98%) of the total p.p.e., while the remaining molecules give very small contributions, which as expected decrease on moving away from the RM.

(*f*) *Mutual Orientation of* CO *Groups*.—Once the enclosure shell has been defined, the orientation of the CO groups belonging to ES molecules with respect to those belonging to the RM can easily be studied. Since we are interested mainly in the first-neighbour interactions, a cut-off distance of 3.3 Å for the $O_{ES}\cdots O_{RM}$ contact distances was adopted to select all relevant CO $\cdots$ CO pairs. The mutual orientation was defined by computing the angle ω between the CO vectors of each $CO_{ES}\cdots CO_{RM}$ pair, as well as the angle φ between the vectors $C_{RM}O_{RM}$ and $O_{RM}O_{ES}$ (see Scheme 1). When necessary to the understanding of the spatial relationship between CO pairs, $O_{RM}\cdots C_{ES}$ and $O_{RM}\cdots O_{ES}$ distances were also compared. If both room- and low-temperature data were available for the same species, the calculations were carried out on these latter sets.

All calculations were performed with available suite of programs: OPEC[15] was used for calculations of the crystal and molecular qualifiers listed above, XANADU[16] to investigate the relative orientations of the CO groups, and SCHAKAL[17] for graphical representation of the enclosure shells.

Results and Discussion

Table 2 collects all basic information on the crystal and molecular qualifiers (V_{mol}, S_{mol}, p.c., E_{i-j}, p.p.e, E_{CO}, E_{CO}/n_{CO} and the references to the original structural papers) for all species discussed herein. The following statements can be made.

(*a*) While the cell volumes shrink appreciably on decreasing the temperature, V_{mol} shows only small changes (if any). It is almost completely determined by the CO envelopes as shown by the ratios V_{mol}/n_{CO} which fall in the narrow range 22—26 Å^3.

(*b*) Packing coefficients (p.c.s) sum up the temperature dependence of V_{mol} and V_{cell} and as expected increase on decreasing the temperature. The species [$Cr(CO)_6$], [$Mn_2(CO)_{10}$], and [$Fe_2(CO)_9$], despite their structural diversity, have the same p.c. of 0.68, while the value is lower for [$Co_2(CO)_8$] (0.63).

There is no direct relationship between molecular shape and p.c. values. Roughly cylindrical molecules such as the dimers can be very tightly {[$Mn_2(CO)_{10}$], [$Fe_2(CO)_9$]} or very loosely {[$Co_2(CO)_8$]} packed, while more 'spherical' molecules {[$Ni(CO)_4$], [$Fe(CO)_5$]} have low p.c.s. On the other hand, the packing efficiency (in the sense of volume occupation) depends both on the molecular shape *and* on the possibility of interlocking with neighbouring molecules (*i.e.* maximization of the intermolecular interactions).

(*c*) The p.p.e. is a function of essentially two factors: the number of atoms in the molecule and the number of interactions with the surrounding molecules (which depend on the packing efficiency and, ultimately, on the molecular shape). As expected, it is always cohesive (*i.e.* negative) and shows an inverse dependence on the temperature. For the species characterized at two temperatures {[$Cr(CO)_6$], [$Mn_2(CO)_{10}$], and [$Co_2(CO)_8$]}

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* At a preliminary stage of this study the inclusion of a Coulombic term of the form q_1q_2/r was considered. The values of -0.12 and $+0.09$ for the O and C atom charges {reported by Rees and Mitschler[13] for [$Cr(CO)_6$]} as well as the rather arbitrary values of ± 0.3 used previously by other authors in related work[8d] were used. In neither case did p.p.e. vary by more than ± 0.5 kcal mol^{-1} and as such (also in the light of the other approximations implied in the use of atom–atom potentials for organometallic compounds) the effect was regarded as negligible.

Table 2. Summary of crystal and molecular qualifiers[a]

Species, T/K, ref.	Space group, Z, V_{cell}	S_{mol}, V_{mol}	p.c., V_{mol}/n_{CO}	p.p.e.	$E_{O\text{–}O}$	$E_{C\text{–}C}$	$E_{O\text{–}C}$	E_{CO}, E_{CO}/n_{CO}
$[V(CO)_6]$, 245, *b*	*Pnma*, 4, 854.6	178.5, 145.5	0.68, 24.2	−30.5	−6.8	−4.8	−10.8	−22.4, −3.7
$[Cr(CO)_6]$, r.t., *c*	*Pnma*, 4, 826.6	171.7, 141.1	0.68, 23.5	−31.2	−7.0	−4.9	−11.0	−22.9, −3.8
$[Cr(CO)_6]$, 74, 19	*Pnma*, 4, 779.0	172.4, 141.6	0.73, 23.6	−33.1	−7.4	−5.4	−10.8	−23.6 −3.9
$[Fe(CO)_5]$, 193, *d*	*C*2/*c*, 4, 704.4	147.4, 119.0	0.68, 23.8	−29.2	−5.6	−4.4	−9.9	−19.9, −4.0
$[Ni(CO)_4]$, 218, 26	*Pa*3,8, 1 273.8	134.2, 104.9	0.66, 26.2	−24.4	−4.2	−3.4	−7.2	−14.8, −3.7
$[Mn_2(CO)_{10}]$ r.t., *e*	*I*2/*a*,4 1 426.6	258.4, 237.3	0.67, 23.7	−41.1	−8.8	−6.0	−14.4	−29.2, −2.9
$[Mn_2(CO)_{10}]$ 74, *f*	*I*2/*a*,4 1 327.1	258.6, 237.9	0.72, 23.8	−44.7	−9.1	−6.8	−14.8	−30.7, −3.1
$[Fe_2(CO)_9]$ r.t., *g*	*P*6$_3$/*m*,2 578.4	237.3, 195.3	0.68, 24.3	−47.5	−9.9	−7.1	−14.1	−31.1, −3.5
$[Co_2(CO)_8]$, r.t., *j*	*P*2$_1$/*m*,4, 1 167.3	226.0[h] 184.0[h,i]	0.63,[i] 23.0	−39.4	−7.8	−5.4	−11.9	−25.1, −3.1
$[Co_2(CO)_8]$ 100, *k*	*P*2$_1$/*m*,4 1 116.9	227.8 185.6	0.66 23.2	−42.0	−8.0	−6.0	−12.0	−26.0, −3.3

[a] S_{mol}/Å^2; V_{cell}, V_{mol}, V_{mol}/n_{CO}/Å^3; p.p.e., $E_{i\text{–}j}$, E_{CO}/n_{CO} in kcal mol^{-1}. r.t. = Room temperature. [b] S. Bellard, K. A. Rubinson, and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1979, **35**, 271. [c] A. Whitaker and J. W. Jeffery, *Acta Crystallogr.*, 1967, **23**, 977. [d] J. Donohue and A. Caron, *Acta Crystallogr.*, 1964, **17**, 663. [e] M. R. Churchill, K. N. Amoh, and H. J. Wasserman, *Inorg. Chem.*, 1981, **20**, 1609. [f] M. Martin, B. Rees, and A. Mitschler, *Acta Crystallogr., Sect. B*, 1982, **38**, 6. [g] F. A. Cotton and J. M. Troup, *J. Chem. Soc., Dalton Trans.*, 1974, 800. [h] Averaged over the two independent molecules. [i] V_{mol} and p.c. were erroneously reported as 191 Å^3 and 0.65 in ref. 10*b*. [j] G. G. Summer, H. P. Klug, and L. E. Alexander, *Acta Crystallogr.*, 1964, **17**, 732. [k] P. C. Leung and P. Coppens, *Acta Crystallogr., Sect. B*, 1983, **39**, 535.

the p.p.e. increases in absolute value on decreasing the temperature (in agreement with the p.c. values). The compounds $[Ni(CO)_4]$ and $[Fe(CO)_5]$ have the lowest p.p.e. in absolute value. Interestingly these species have also very low melting points (−25 and −20 °C, respectively[18]). The p.p.e. reaches a maximum in absolute value with $[Fe_2(CO)_9]$ which, incidentally, is known for its insolubility.[18]

(*d*) The energy gain ($\frac{1}{2}$ p.p.e.) in bringing 1 mol of isolated molecules from infinity into the crystal lattice is related to the sublimation enthalpy.[12a] Values of $\Delta H_{sub}{}^{298}$ are available only for $[Cr(CO)_6]$ (17.2 kcal mol^{-1}),[19] $[Mn_2(CO)_{10}]$ (15.0 kcal mol^{-1}),[20] and $[Co_2(CO)_8]$ (15.6[21a] and 24.8[21b] kcal mol^{-1}). Calculations of $\frac{1}{2}$ p.p.e. for the same species yields values (15.6, 20.0, and 19.7 kcal mol^{-1}) which, if not correct, have the right order of magnitude and reproduce fairly well the observed ΔH_{sub}. This is an encouraging indication, that despite the gross approximations, organometallic species can be treated within the pairwise potential-energy approach as most molecular crystals.[22]

(*e*) When p.p.e. is partitioned into separate contributions (see Table 2) the trend $E_{O\text{–}C} > E_{O\text{–}O} > E_{C\text{–}C}$ (in absolute value) is invariably observed, *i.e.* the dominant contribution comes from the heteroatomic C–O interactions (which are twice as many as the O–O and C–C ones). The energy terms involving the metal atoms have little meaning (in view of the gross approximation required in their treatment) and will not be discussed in detail. It can be pointed out only that $E_{M\text{–}M}$ is very small (about 2—3% of the total p.p.e.) while $E_{M\text{–}O}$ and $E_{M\text{–}C}$ contributions are more relevant. Altogether, the CO $\cdots$ CO interactions account for about 60—70% of the total p.p.e. The average 'packing contribution' of a CO group in a molecule can be obtained from the ratio $(E_{O\text{–}O} + E_{O\text{–}C} + E_{C\text{–}C})/n_{CO}$. For the species studied here, these values (see Table 2) fall within the narrow range $-4.0 < E_{CO}/n_{CO} < -2.9$ kcal mol^{-1}. The value of E_{CO}/n_{CO} appears to be slightly smaller for the dinuclear species than for the mononuclear ones. However, given the same number of metal atoms, the CO groups conform to the homomeric principle,[14] *i.e.* a given atomic group tends to contribute a fixed amount to p.p.e. in any crystal irrespective of the molecular structure. We pass from unbridged to triply bridged dinuclear species, and from octahedral to tetrahedral mononuclear species.

It can be predicted that on increasing the size of the metal core, for instance on going from mono- and di-nuclear species to metal-atom clusters, the CO contribution will further decrease. In the cases discussed herein no appreciable difference between terminal and bridging ligands is dectable.

Mutual orientation of CO *Groups.*—It has been reported[23] that, in transition-metal carbonyls, the lone pair of one (or more) CO groups is generally found pointing towards the π system of CO groups belonging to a neighbouring molecule. Such an interaction was considered responsible for some molecular and electronic distortions observed in experimental deformation density maps of $[Cr(C_6H_6)(CO)_3]$,[23b] and related carbyne and carbene complexes.[23c] The neutral binary carbonyls studied here are well suited for an examination of the general occurrence of this phenomenon.

The distribution of the angles between first neighbouring $CO_{RM}CO_{ES}$ pairs (ω) for all the species {except $[Ni(CO)_4]$} is shown in Figure 1. The histogram collects 144 ω values for 44 CO groups of the molecules from $[V(CO)_6]$ to $[Co_2(CO)_8]$. *In projection*, the $CO_{RM}CO_{ES}$ pairs form preferentially a 90° angle. A secondary maximum is concentrated around 130—150°, while only a very few first-neighbouring CO pairs are parallel in projection (180°). For these latter pairs, which belong exclusively to $[Mn_2(CO)_{10}]$, the angle φ (see Scheme 2) is approximately 90° ruling out a head-to-head arrangement.

All species share nearly perpendicular pairs. Figure 2 shows the histogram obtained by plotting the number of nearly

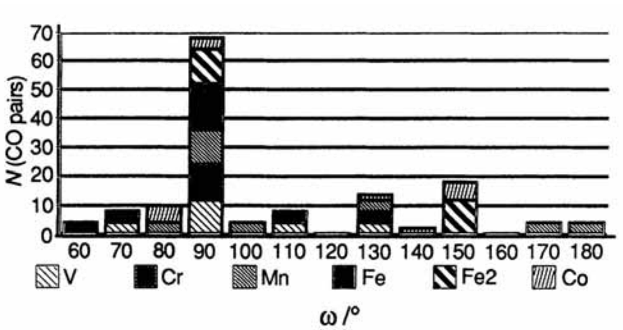
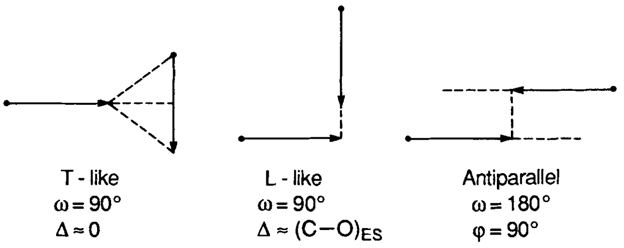


Figure 1. Histogram showing the distribution of the angles between first-neighbouring CO pairs for all the species discussed herein except $[Ni(CO)_4]$



Scheme 2.

perpendicular CO pairs against the difference (Δ) between the O_{RM}–C_{ES} and O_{RM}–O_{ES} distances. When $\Delta \approx 0$ the mutual orientation is T-like in projection, and when Δ is large (roughly the length of a C–O bond) the orientation is L-like, as sketched in Scheme 2. We have no evidence of a preferential orientation of the O atoms towards the midpoint of a neighbouring CO bond[23] (*i.e.* T-like *but* with the four atoms coplanar), nor of X-like arrangements with the CO groups crossing each other. On the other hand, the radial distribution of the CO vectors departing from the metal centres does not allow acute ω angles (< 60°) and head-to-tail arrangements. It seems that the mutual orientation of the first-neighbouring CO groups in the species under examination reflects more the balance between the molecular shape and the tendency of the molecules to stay as close as possible ('close packing principle') rather than an electronic requirement of the CO ••• CO intermolecular interactions.

Enclosure Shells.—This is a different way of looking at the crystal packing. The full translational symmetry proper of the lattice periodicity is not considered and attention is concentrated on what a molecule (the reference one, RM) 'sees' around itself. The enclosure shells of $[Cr(CO)_6]$ {and the isomorphous $[V(CO)_6]$}, $[Mn_2(CO)_{10}]$, $[Fe(CO)_5]$, $[Fe_2(CO)_9]$, and $[Co_2(CO)_8]$ are shown in Figures 3—7. Apart from $[Ni(CO)_4]$, which deserves a specific comment, in all cases 12-co-ordination is achieved. Two basic packing motives can be recognized: the cubo-octahedron (A–B–C sequence of layers), and the anticubo-octahedron (A–B–A sequence of layers). To the former belong the enclosure shells of $[Mn_2(CO)_{10}]$ (Figure 4) and $[Fe(CO)_5]$ (Figure 5), while the latter is seen for $[Cr(CO)_6]$ {and $[V(CO)_6]$}, $[Fe_2(CO)_9]$, and $[Co_2(CO)_8]$ (Figures 3, 6, and 7). In the case of $[Mn_2(CO)_{10}]$ the two staggered triangular faces of the cubo-octahedron are shifted in opposite directions with respect to the hexagonal equator, while in $[Co_2(CO)_8]$ and $[Fe_2(CO)_9]$ the enclosure polyhedron is elongated along its three-fold axis.

It is worth spending a few more words on the relationship between these two latter species, also in the light of the extremely different behaviour shown under ^{13}C m.a.s. n.m.r. experimental conditions {$[Fe_2(CO)_9]$ is 'static',[24] while $[Co_2(CO)_8]$ shows the typical features of a highly fluxional molecule[25]}. We have previously shown[10b] that there is a precise relationship between the unit cells of the two species, though they crystallize in two substantially different space groups ($P6_3/m$ and $P2_1/m$, respectively). We can now see that the two molecules pack in exactly the same way with the metal–metal axes parallel to each other and parallel to the anti-cubo-octahedron axis. In $[Fe_2(CO)_9]$ this axis is coincident with the molecular three-fold axis. From Figures 6 and 7, the relationship between $[Fe_2(CO)_9]$ and $[Co_2(CO)_8]$ is clear: on passing from $[Fe_2(CO)_9]$ to $[Co_2(CO)_8]$ the parallel arrangement of the M–M axis along the ES axis is retained, while two *differently oriented* bridging CO groups from each pair of next-neighbouring $[Fe_2(CO)_9]$ molecules are ideally 'removed'. As a consequence, the *m* symmetry (the plane bisecting the M–M bonds and comprising the bridging CO groups) is preserved, while the symmetry relationship between two neighbouring molecules is lost, resulting in the two 'half' molecules in the asymmetric unit of $[Co_2(CO)_8]$. This causes a loss of packing efficiency, decrease in p.p.e. (in absolute value), and more freedom for motion (*i.e.* the appearance of dynamic behaviour in the solid state). In other words the effective molecular shape of $[Co_2(CO)_8]$ and $[Fe_2(CO)_9]$ is essentially

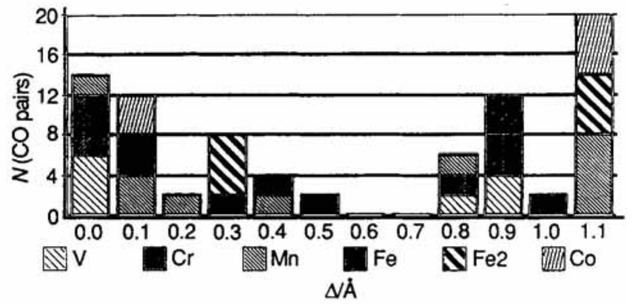


Figure 2. Histogram showing the distribution of the nearly perpendicular CO pairs (from Figure 1) as a function of the difference (Δ) between $O_{RM} \cdots C_{ES}$, and $O_{RM} \cdots O_{ES}$ distances. In projection $\Delta \approx 0$, T-like CO pairs, and $\Delta \approx 1$ Å, L-like CO pairs

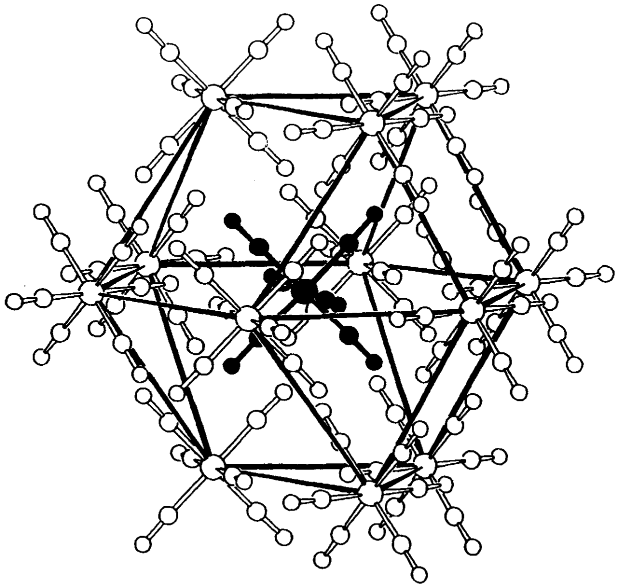


Figure 3. Anti-cubo-octahedral enclosure shell of $[Cr(CO)_6]$ {and $[V(CO)_6]$}. The twelve molecules of the ES account for 91% of the total p.p.e.

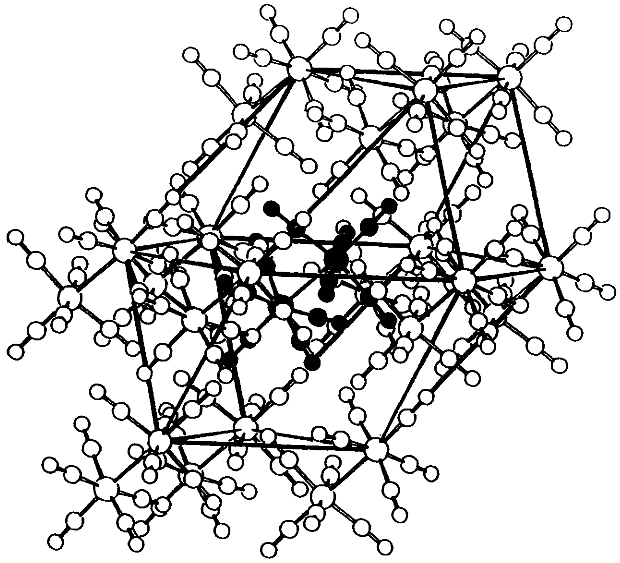


Figure 4. Cubo-octahedral enclosure shell (94% total p.p.e.) of $[Mn_2(CO)_{10}]$

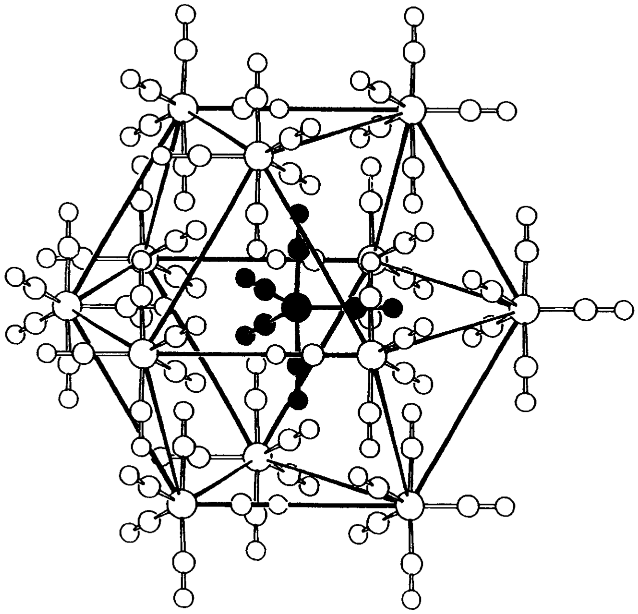


Figure 5. Cubo-octahedral enclosure shell (92% total p.p.e.) of $[Fe(CO)_5]$

the same (*i.e.* removal of a bridging CO leaves a 'hole' which can not be used by neighbouring molecules) so that the two objects have to pack in the same way.

The compound $[Ni(CO)_4]$ is peculiar in many aspects. There is a dominant interaction between the reference molecule and its first neighbour related by centrosymmetry ($Ni \cdots Ni$ 4.61 Å).[26] A regular enclosure shell can be obtained by treating the crystal of $[Ni(CO)_4]$ as formed by 'dimeric' $[\{Ni(CO)_4\}_2]$ units. The ES is made up of 18 molecules and can be described as an hexacapped icosahedron, thus differing substantially from all related compounds. However it is worth recalling that $[Ni(CO)_4]$ has the lowest melting and boiling points in this series of compounds, which, together with the low p.p.e. (in absolute value), is indicative of a poorly efficient crystal packing. As an aside it seems that the crystal structure of this fundamental molecule deserves redetermination by current *X*-ray techniques.*

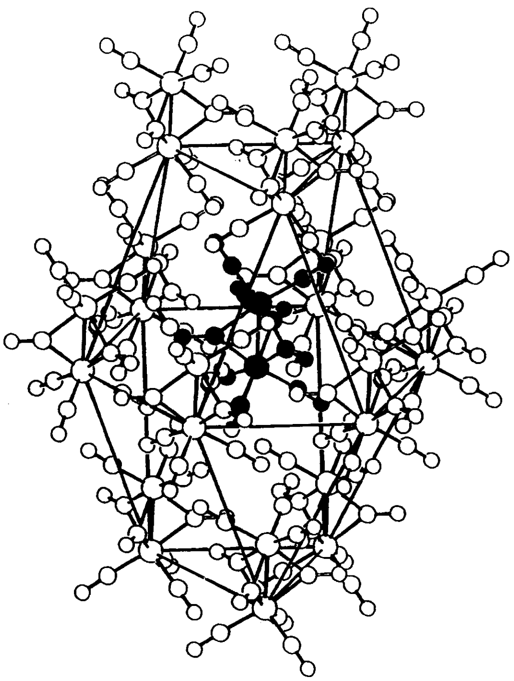


Figure 6. Anti-cubo-octahedral enclosure shell (95% total p.p.e.) of $[Fe_2(CO)_9]$

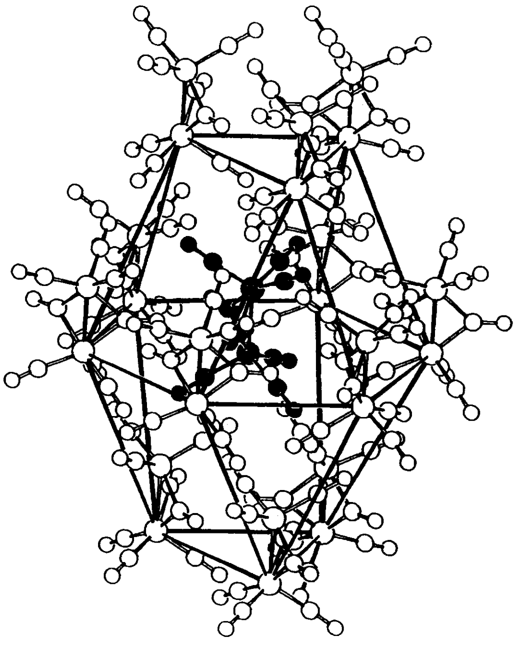


Figure 7. Anti-cubo-octahedral enclosure shell (98% total p.p.e) of $[Co_2(CO)_8]$. The ES is centred around one of the two independent 'half' molecules

Conclusion

In this paper we have undertaken an analysis of the geometric and energetic factors at the origin of the crystal packing of neutral mono- and di-nuclear metal carbonyls. Methods

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* It is remarkable, in this respect, that the only structural information available on this fundamental complex is based on visual data, collected in 1952, with an *R* factor of 0.28.[26]

diffusely applied and tested in other areas of research were used for this purpose. We have shown that much interesting information on intermolecular interactions and packing of these substances is afforded by diffraction studies of reasonable quality. The main outcomes of this study can be summarized as follows.

(*i*) Neutral binary carbonyls constitute true molecular crystals and pack essentially in accord with the close-packing principle.

(*ii*) Two basic packing arrangements, the cubo-octahedron (A–B–C sequence of layers) and the anti-cubo-octahedron (A–B–A sequence of layers), survive changes in space-group symmetry in spite of the great structural diversity of these species. Differences in molecular shape and analogies in crystal packing can be used to interpret differences in solid-state dynamic behaviours.

(*iii*) Packing potential-energy calculations, in conjunction with molecular volumes and packing coefficient estimates, though based on some rather crude assumptions, recognize correctly the packing differences between the various species.

(*iv*) The CO ligands are found to conform reasonably to the homomeric principle.

(*v*) An exact knowledge of the molecular environment can be obtained from the partitioning of the p.p.e. between the molecules neighbouring the reference one. This allows a direct study of the geometric features of the CO $\cdots$ CO intermolecular interactions. We have found that in neutral binary carbonyls orthogonal interactions (in projection) are largely preferred. T-Like interactions and antiparallel interactions are also important. In this context it is worth stressing that the interpretation of solid-state n.m.r. results requires a knowledge of the environment around each nucleus which is probed by the spectroscopic experiment.

Altogether the results obtained are considered qualitatively (if not quantitatively) encouraging in view of future applications to more complex systems.

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References

1 M. C. Etter, R. C. Hoye, and G. M. Vojta, *Crystal Rev.*, 1988, **1**, 281; C. A. Fyfe and R. E. Wasylishen, 'Solid State Chemistry Techniques,' eds. A. K. Cheetham and P. Day, 1987, ch. 6, p. 190.

2 D. Braga, C. Gradella, and F. Grepioni, *J. Chem. Soc., Dalton Trans.*, 1989, 1721; D. Braga and F. Grepioni, *Polyhedron*, 1989, **8**, 2237.

3 H. Dorn, B. E. Hanson, and E. Motell, *Inorg. Chim. Acta*, 1981, **54**, L71; B. E. Hanson, C. E. Lisic, J. T. Petty, and G. Iannacone, *Inorg. Chem.*, 1984, **25**, 4062.

4 S. Aime, M. Botta, R. Gobetto, D. Osella, and L. Milone, *Inorg. Chim. Acta*, 1988, **146**, 151.

5 E. Maverick and J. D. Dunitz, *Mol. Phys.*, 1987, **2**, 451.

6 'Organic Solid State Chemistry,' ed. G. R. Desiraju, Elsevier, Amsterdam, 1987.

7 A. I. Kitaigorodsky, 'Molecular Crystals and Molecules,' Academic Press, New York, 1973.

8 (*a*) I. H. Hillier and V. R. Sanders, *Mol. Phys.*, 1971, **22**, 1025; (*b*) E. J. Baerends and P. Ros, *ibid.*, 1975, **30**, 1735; (*c*) A. Serafini, M. Pelissier, J. M. Savariault, P. Cassoux, and J. F. Labarre, *Theor. Chim. Acta*, 1975, **39**, 229; see also ref. 13; (*d*) A. Gavezzotti, G. F. Tantardini, and M. Simonetta, *Chem. Phys.*, 1986, **105**, 333.

9 A. Gavezzotti, *J. Am. Chem. Soc.*, 1983, **105**, 5220; 1985, **107**, 962.

10 (*a*) A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441; (*b*) D. Braga and F. Grepioni, *Acta Crystallogr., Sect. B*, 1989, **45**, 378.

11 A. J. Pertsin and A. I. Kitaigorodsky, 'The Atom–Atom Potential Method,' Springer, Berlin, 1987.

12 (*a*) A. Gavezzotti, *Nouv. J. Chim.*, 1982, **6**, 433; (*b*) K. Mirsky, 'Computing in Crystallography, Proceedings of the International School on Crystallographic Computing,' Delft University Press, Twente, 1978, vol. 169; (*c*) K. Mirsky, *Chem. Phys.*, 1980, **40**, 445.

13 B. Rees and A. Mitschler, *J. Am. Chem. Soc.*, 1976, **98**, 7918.

14 A. Gavezzotti, *J. Am. Chem. Soc.*, 1989, **111**, 1835.

15 A. Gavezzotti, OPEC, Organic Packing Potential Energy Calculations,' University of Milano, 1975.

16 P. J. Roberts and G. M. Sheldrick, XANADU, University of Cambridge, 1976.

17 E. Keller, SCHAKAL 88, Program for the Graphical Representation of Molecular Models, University of Freiburg, 1988.

18 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Wiley, New York, 1980.

19 L. Fabbrizzi, R. Mascherini, and P. Paoletti, *J. Chem. Soc., Faraday 1*, 1976, 896.

20 J. A. Connor, H. A. Skinner, and Y. Virmani, *J. Chem. Soc., Faraday 1*, 1972, 1754.

21 (*a*) P. J. Gardner, A. Cartner, R. G. Cunninghame, and B. H. Robinson, *J. Chem. Soc., Dalton Trans.*, 1975, 2582; (*b*) A. K. Baev, *Vestsi Akad. Navuk B. SSR, Ser. Khim. Navuk*, 1968, **4**, 76.

22 A. Gavezzotti and M. Simonetta, *Acta Crystallogr., Sect. A*, 1975, **31**, 645; A. Gavezzotti and G. R. Desiraju, *Acta Crystallogr., Sect. B*, 1988, **44**, 427.

23 C. Kruger in 'Advances in Metal Carbene Chemistry,' ed. U. Schubert, Kluver Academic Publishers, Dordrecht, 1988, p. 385; Y. Wang, K. Angermund, R. Goddard, and C. Kruger, *J. Am. Chem. Soc.*, 1987, **109**, 587; C. Kruger, R. Goddard, and K. H. Claus, *Z. Naturforsch., Teil B*, 1983, **38**, 1431.

24 H. C. Dorn, B. E. Hanson, and E. Motell, *J. Organomet. Chem.*, 1982, **224**, 181.

25 B. E. Hanson, M. J. Sullivan, and R. J. Davis, *J. Am. Chem. Soc.*, 1984, **106**, 251.

26 J. Ladell, B. Post, and I. Fankuchen, *Acta Crystallogr.*, 1952, **5**, 795.

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