Cation Control on the Crystal Organization of Hexanuclear Carbonyl Cluster Anions

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Received November 5, 1992

Abstract: The crystal structures of 28 hexanuclear carbonyl cluster anions have been investigated by means of empirical packing potential energy calculations, van der Waals volume analysis, and computer graphics. Data were retrieved from the Cambridge Structural Database. The relationship between shape, size, and charge of the component ions and the formation of preferential aggregates (piles, "snakes", layers) in the crystal lattice has been analyzed. It has been shown that, with large organic cations, the packing pattern is essentially that of molecular mixed crystals, while small cations drive toward monodimensional aggregation of the anions. It has been shown that there is a (fairly precise) ratio between the relative volumes of the component ions above which one-dimensional or two-dimensional networks are preferentially established. Some representative cases are discussed in detail.

Introduction

In previous studies[1] we investigated the packing modes of neutral organometallic complexes and clusters focusing on the relationship between the structure of the individual molecules and the collective structure of the molecules within the crystal. Our approach to intermolecular interactions and crystal packing is based on the idea that the crystal should be regarded as a *giant supramolecule*, whose construction occurs through a sophisticated process of molecular self-recognition and self-assembling. For molecular crystals, such process is largely controlled by the size and shape of the component molecules.[2] Several papers have appeared on this subject, and we have begun to understand many of the factors responsible for crystal cohesion in organic[3] and organometallic solids.

On the contrary, very little is known about crystals formed of molecular ions. Crystals containing large or very large anions and cations have characteristics somewhat half-way between those of authentic molecular crystals (i.e. formed of molecular entities that can be discriminated on the basis of the interatomic separations) and that of typical ionic salts (i.e. constituted of small ions surrounded by counterions and held together by Coulombic forces). The term *molecular salt* will be used, hereafter, to designate materials in which the component particles are ions of opposite sign but which interact essentially *via* van der Waals interactions.

High nuclearity cluster anions constitute a particularly well suited class of molecular salts because of the variety of organic cations that can be (and have been) used for their crystallization. In spite of the fact that the majority of transition metal clusters are ionic species, the effect of the counterion choice on the crystallization process and on the properties of the resulting crystalline material has never been systematically investigated.

As a first step in this direction we studied the anion organization in crystals of decametallic cluster anions containing a tetracapped octahedral metal atom framework (M_{10}; M = Ru, Os).[4] We were able to show, *inter-alia*, that in the $[(Ph_3P)_2N]^+$ salt of $[Os_{10}C(CO)_{24}]^{2-}$ the cluster anions form *piles* throughout the crystal lattice and that each anionic pile is surrounded by a cation belt. The same cluster pile was found to constitute the fundamental packing motif in the crystal of the neutral dihydride $H_2Os_{10}C(CO)_{24}$.[5] Preferential aggregation of the anions in one-dimensional arrays was also observed[4] in the family of prismatic carbido- and nitridocarbonyl clusters of general formula $[M_6X(CO)_{15}]^{n-}$ [M = Co, Rh; X = N, n = 1; X = C, n = 2].[6]

These studies have provided the first indications that salts of large cluster anions show strongly anisotropic arrangements in the lattice depending on the *size* and *shape* of the component ions. Many chemical and physical properties might arise from anion–anion, anion–cation, and cation–cation interlocking within the lattice. For instance, it has been reported that high nuclearity cluster anions of Os, Pt, Pd, etc. show magnetic properties that are intermediate between those of dispersed metals and those of bulk metals.[7,8]

Molecular salts of the kind described above can be regarded essentially as *mixed molecular crystals*, whose components are packed in the lattice according to the same rules which govern the packing of neutral molecules in single-component systems.[9] The large dimension of the cluster anions, together with a homogeneous ligand distribution, leads to effective delocalization of the charge, so that repulsion between neighboring anions is seemingly not relevant to the packing. The analogy between molecular salts and mixed molecular crystals fails, however, in the presence of preferential pairing between anions and cations. Direct anion–cation association has been observed, for instance, in the case of the $[N(CH_3)_2(CH_2Ph)_2]^+$ and $[(Ph_3P)_2N]^+$ salts

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of the anion $[Ir_4(CO)_{11}(SCN)]^-$,[10] where there is evidence for charge localization over the SCN ligand.

In this paper we take these ideas a step further by investigating the relationships between size, shape, and ionic charge of the component ions in the family of crystalline 86-electron octahedral clusters. To this end we have retrieved, from the Cambridge Crystallographic Database,[11] all the cluster complexes of the general formula $[M_6(CO)_n]^{m-}$ or $[M_6X(CO)_n]^{m-}$, where n, the number of carbonyl ligands, varies from 12 to 19 (the two extremes being represented by the structures of $[Ni_6(CO)_{12}]^{2-}$ and $[Re_6C(CO)_{19}]^{2-}$, respectively), m is the charge carried by the cluster anion (in general either −1 or −2, with the notable exception of $[Co_6(CO)_{14}]^{4-}$), and X is an interstitial boron, carbon, nitrogen, or hydrogen atom. The reason for this choice is essentially that of size and variety of the sample: the *number* of anionic octahedral cluster salts characterized crystallographically is large and their crystallization attained with an ample selection of different counterions. What is more, octahedral clusters (in terms of shape) can be reasonably described as spheres with corrugated surfaces because of the protruding carbonyl oxygen atoms. The difference in *structure* between the cluster anions is mainly due to the different number of carbonyl ligands on the surface of the clusters [from 12 to 19].

The aim of this study is to address the following questions: (i) Is there a structural relationship between the *size*, *shape*, and *stoichiometric ratio* and the actual *packing motif* in this family of crystalline cluster salts? (ii) Is it possible to identify a *criterion*, based on some easily identifiable structural "qualifier" (such as shape, size, volume, etc.) of the cluster anion and of the counterion(s), to be used to predict formation of one-dimensional (piles or "snakes") or two-dimensional (layers) lattice aggregates? (iii) Is there a detectable packing effect due to the presence of the anion charges or is the charge so diffused over the cluster as to be ineffective? Is this also true when carbon monoxide is substituted by heteroligands, *i.e.* when the charge distribution over the ion surface is (supposedly) unbalanced?

Our approach to these problems is basically the same as that applied to crystalline structure investigation of neutral organometallic molecules. We make use of the pairwise atom–atom potential energy method,[12] which has proven to be an extremely efficacious tool for the study of packing relationships in molecular crystals. The method can be applied (with some additional and far from trivial approximations) to the study of molecular salts of the kind described above. The structural problems related to the packing of some inorganic and organometallic salts have been similarly addressed.[13]

Methodology

Crystal structures of octahedral transition metal clusters were retrieved from the January 1992 version of the Cambridge Structural Database (94.772 entries) using the program QUEST.[11] After having manually screened all hits, our sample possessed the following general characteristics: (i) the number of carbonyl ligands on the cluster surface ranged from 12 to 19 (with no distinction between doubly bridging, triply bridging, or terminal bonding modes); (ii) some species contained interstitial carbon, boron, or nitrogen atoms; (iii) hydridic species are taken into account irrespective of the peripheral or interstitial location of the H(hydride) atom(s); (iv) heterometallic clusters are included in the analysis (with the assumption that the internal metal core contributes relatively little to the packing choice); (v) apart from the hydrated alkali salts of $[Co_6(CO)_{14}]^{4-}$ and $[Co_6(CO)_{15}]^{2-}$ (see below), all other crystalline salts contained typical organic cations—$(Ph_3P)_2N^+$ (hereafter PPN^+), PPh_4^+, NMe_4^+, NEt_4^+, $NMe_3(CH_2Ph)^+$, PPh_3Me^+, $AsPh_4^+$, and $NBu^n{}_4^+$; and (vi) with the notable exception of $[Co_6(CO)_{14}]^{4-}$, all complexes were either mono- or dianionic.

In order to decode the ion organization in the lattice we need to neglect, in a sense, the space group symmetry and concentrate on the immediate surroundings of the reference ion. This is not easily achieved with the usual crystallographic procedures (essentially based on intermolecular contact distances) and becomes particularly difficult with crystalline salts where the asymmetric unit contains two or three independent ions of large size. The pairwise atom–atom packing potential energy method[12] can be easily "adapted" to select anions and/or cations in the first coordination sphere of the reference ion. To this purpose, use is made of the Buckingham-type expression $ppe = \sum_i \sum_j [A \exp(-Br_{ij}) Cr_{ij}^{-6}]$, where r_{ij} is an interatomic distance, and index (i) and index (j) in the summation are adequately chosen in order to run over all atoms of one reference cluster and of the surrounding anions and/or cations distributed according to crystal symmetry in the lattice. A cutoff distance of 15 Å in the summation guarantees that the entire space around the reference ion is explored. The reader is directed to previous reports for a more detailed description of the computational procedures.[1,2] We ought to stress that this procedure is used *only* as a means to investigate the cluster anion environment and *is not* aimed at an (even approximate) evaluation of the crystal potential energy (ppe). No better insight into the crystal environment was obtained if a Coulombic contribution of the type $q_i q_j / r_{ij}$ was taken into account, with q_i and q_j point charges located on the centers of mass of the ions. The correctness of the approach will have to be judged heuristically.

The volumes of the ionic units (V_{anion}, V_{cation}) were calculated by Kitaigorodsky's method of "intersecting cups" by using literature van der Waals radii for main-group elements [H 1.17, C 1.75, N 1.52, O 1.40, P 1.90, As 2.15] and an arbitrary radius of 2.15 Å for first row and 2.35 Å for second and third row transition metals.[2e] As previously discussed in the case of neutral binary carbonyls,[2c,d] the choice of van der Waals radius for the metal atoms does not appear to be crucial in volume calculations since the metal framework is deeply embedded within the CO-ligand coverage. Hydrogen atom positions for the cations were calculated based on a C–H distance of 1.08 Å. The contribution of crystallization solvent to the total occupied volume in the lattice was also taken into account.

In the course of this study we have found that the presence of certain types of one-dimensional or two-dimensional lattice aggregates (see below) correlates with the ratio between the 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.* $VR = V_{anion}/V_{formula}$. Such a ratio has been calculated for all species herein discussed with the exception of the alkali salts $[Co_6(CO)_{14}]K_4 \cdot 6H_2O$ and $[Co_6(CO)_{15}]Cs_2 \cdot 3H_2O$. The packing coefficients were estimated as $pc = V_{formula}Z/V_{cell}$. Gavezzotti's OPEC suite of programs[14a] was employed for the calculation of $V_{formula}$, V_{anion}, V_{cation}, and pc, as well as that of ppe. Keller's SCHAKAL88[14b] was used for the graphical representation of the results.

Packing Motif and Cation Size

All structural parameters essential for the following discussion, together with the salt formulae and the CSD "REFCODES", are grouped in Table I. References to the original structural papers are also provided.[15–40] The following section will be devoted to

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Table I. Molecular and Crystal Qualifiers for Hexanuclear Cluster Salts

ref	reference code	formula	space group	*Z*	pc	$V_{formula}$[a] (Å^3)	V_{anion} (Å^3)	V_{cation} (Å^3)	VR	packing motif[f]
15	MANICO	$[Ni_6(CO)_{12}][NMe_4]_2$	$P\bar{3}$	1	0.62	459	275	92	0.60	MONO
16	PHPTCO	$[Pt_6(CO)_{12}][PPh_4]_2$	$C2/c$	8	~0.61[b]	~980[b]	330	~325[b]	~0.34[b]	N
17	*c*	$[Co_6(CO)_{14}]K_4{\cdot}6H_2O$	$P2_1/n$	2	*d*	*d*	230	*d*	*d*	MONO
18	FOKGUH	$[Co_6(CO)_{15}]Cs_2{\cdot}3H_2O$	$P2_1/c$	4	*d*	*d*	294	*d*	*d*	MONO
19	COYGIG20	$[Co_6C(CO)_{13}][NEt_4]_2$	$C2$	4	0.65	1240[e]	310	155	0.50	PAIRS
20	PPCHRH01	$[Rh_6C(CO)_{13}][PPh_4]_2$	$P2_1/c$	4	0.66	996	335	329	0.34	N
21	JALROD	$[Co_2Rh_4C(CO)_{13}][PPh_4]_2$	$P\bar{1}$	2	0.63	991	329	331	0.33	N
22	JESVOS	$[Ni_3Ru_3C(CO)_{13}][PPN]_2{\cdot}2CH_2Cl_2$	$P2_1/a$	4	0.68	1475	349	510	0.24	N
23	FEKPEQ	$[Co_6N(CO)_{13}][PPN]{\cdot}THF$	$P2_1nb$	4	0.64	897	311	517	0.35	MONO
24	MACONC	$[Co_4Ni_2(CO)_{14}][NMe_4]_2$	$R\bar{3}$	3	0.55	430	238	191	0.55	N
25	PIMPRH	$[PtRh_5(CO)_{15}][PPN]$	$P\bar{1}$	2	0.61	826	328	498	0.40	PAIRS
26	FISFOC	$[Fe_3Rh_3C(CO)_{15}][PPh_4]$	$P\bar{1}$	2	0.65	695	374	321	0.54	MONO
27	FOGYIJ	$[Fe_3Rh_3C(CO)_{15}][PPN]$	$P2_1/n$	4	0.66	871	376	495	0.43	N
28	MBZCIR	$[Ir_6(CO)_{15}][NMe_3Bz]_2$	$P\bar{1}$	2	0.65	704	369	336	0.52	MONO
29	PIMHCO10	$[Co_6H(CO)_{15}][PPN]$	$P2_1/n$	4	0.67	864	340	524	0.39	MONO
30	MACHFE	$[Fe_6C(CO)_{16}][NMe_4]_2$	$Pnma$	8	0.67	1170[e]	377	104	0.64	LAYER
31	MARUCB10	$[Ru_6C(CO)_{16}][NMe_4]_2$	$Pnma$	8	0.64	1162[e]	391	95	0.67	LAYER
32	CEZNAW	$[Fe_5RhC(CO)_{16}][NEt_4]$	$P4/n$	2	~0.68[b]	~552[b]	397	~155[b]	0.72[b]	N
33	FEVVAD	$[Rh_5Ru(CO)_{16}][PPN]$	$C2/c$	8	0.61	842	348	494	0.41	MONO
34	VAMPEE	$[Fe_4Rh_2B(CO)_{16}][PPN]$	$P2_1/c$	4	0.65	906	412	494	0.45	MONO
35	MPPCRU	$[Ru_6(CO)_{18}][MePh_3P]_2$	$P\bar{1}$	2	0.66	956	411	273	0.43	MONO
36	PAHCRU	$[Ru_6H(CO)_{18}][AsPh_4]$	$P2_1/n$	4	0.67	786	454	332	0.58	MONO
37	FUCPU001	$[Os_6(\mu_3\text{-}H)(CO)_{18}][NBu_4]$	$I2$	4	0.70	1516[e]	459	299	0.61	LAYER
38	*c*	$[Re_6C(CO)_{19}][PPh_4]_2$	$P\bar{1}$	4	0.67	1121[e]	479	321	0.43	N
38	*c*	$[Re_6(\mu\text{-}H)C(CO)_{19}][NEt_4]{\cdot}CH_2Cl_2$	$P\bar{1}$	2	0.69	716	483	154	0.67	MONO
39	FAVPIB	$[Fe_6C(CO)_{13}(NO)_2][PPh_4]_2$	$C2/c$	4	0.66	989	355	317	0.36	N
40	GIMHAL	$[Ir_6(CO)_{14}I][PPN]$	$P2_1/c$	4	0.64	887	384	504	0.43	PAIRS
40	GIMGOY	$[Ir_6(CO)_{14}Br][PPh_4]$	$P2_1/c$	4	0.65	702	376	326	0.53	MONO

[a] $V_{formula}$ obtained directly from volume calculation (OPEC) can differ slightly from the sum of the values of the individual ion components. [b] Since atomic coordinates are not available, the volume of the cation has been estimated from the average of the other crystals; this value has been used in turn to estimate $V_{formula}$ and to calculate packing coefficients (pc) and volume ratio (VR) values. [c] REFCODEs are not reported for species not present in the CSD. [d] No estimate of the volume of the alkali cations and of the water molecule is possible; only the anion volume has been calculated. [e] An average value is reported when two independent anions are present in the unit cell. [f] MONO: one-dimensional preferential aggregation (piles, "snakes"). LAYER: two-dimensional preferential aggregation (layers). PAIR: preferential anion–anion pairing. N = no preferential one- or two-dimensional aggregation.

some general observations on the content of Table I with a focus on the presence of specific anisotropic anion arrangements in the lattices. In order to facilitate the description, the terms *pile* and *snake* are used to designate one-dimensional aggregation of anions in straight or "wavy" lines, respectively, *layer* indicates two-dimensional aggregation, and *pair* indicates preferential anion–anion pairing. The code N in Table I marks the absence of preferential interanion aggregation, i.e. the anions are surrounded by cations as in "normal" ionic salts.

The volume of the anions (V_{anion}) ranges from 230 Å^3 for $[Co_6(CO)_{14}]^{4-}$ to 483 Å^3 for $[Re(\mu\text{-}H)C(CO)_{19}]^-$, and the increase in size follows more or less the increase in the number of peripheral ligands. Understandably, the volume of the cations (V_{cation}) shows a much greater variation ranging from the smallest cation in our sample (NMe_4^+, mean volume 97 Å^3) to the largest PPN$^+$ (mean volume 521 Å^3). We note here that the volumes of the cations compare well with the values reported recently within a study of the crystal packing of some inorganic salts,[13] though in this latter work the integration model put forward by Gavezzotti[14a] was used.

Packing coefficients calculated as described above appear to fall in a narrow range: the least densely packed is $[Co_4Ni_2(CO)_{14}][NMe_4]_2$ (pc = 0.55) while the most closely packed appears to be $[Os_6(\mu_3\text{-}H)(CO)_{18}][NBu_4]$ (pc = 0.70, but note the cell for this crystal was measured at 220 K, and pc values are very sensitive to variation in cell dimensions). The average packing coefficient was calculated to be 0.67 which, interestingly, is strictly comparable to pc values calculated for neutral binary carbonyls and for most organic molecular crystals.[2,3]

In terms of ion organization we can see a progression from a low degree of anion–anion organization (structures marked N) to extensive interanion aggregation leading to effectively anisotropic arrangements in the lattice (*piles*, *snakes*, and *layers*). When the anionic volume contributes little to the molecular volume the degree of anionic organization is small and we observe either complete separation of the anions or partial association such as anionic pairing. Small cations favor a higher degree of anion organization. Although the statistical significance of our sample is limited, the general trend shown in Table I is that there is no preferential anion organization when VR < 0.4, formation of

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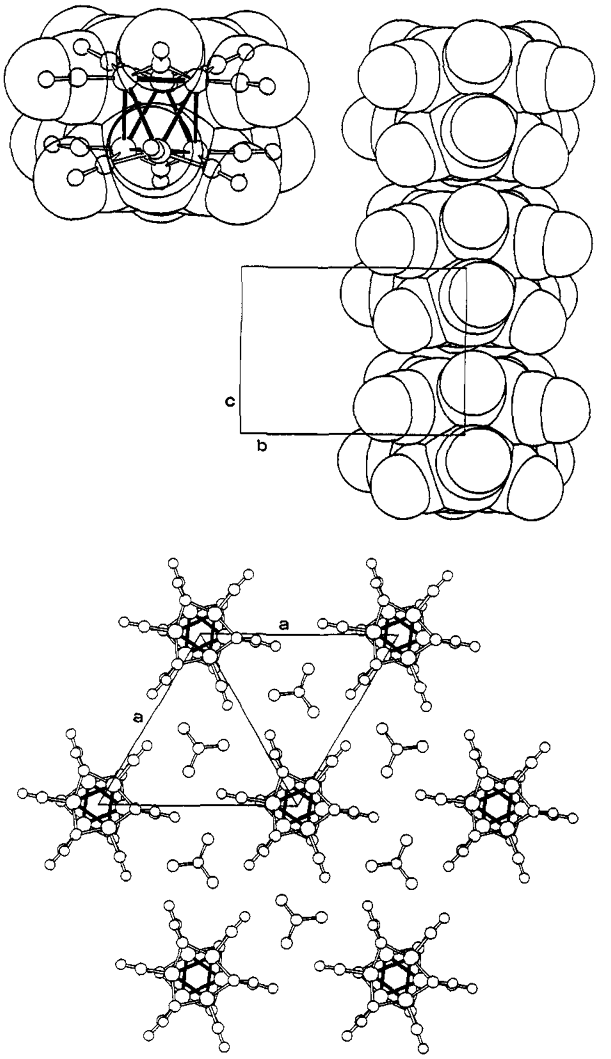

Figure 1. Ion organization in crystalline $[Ni_6(CO)_{12}][NMe_4]_2$: (a, top) space-filling representation of a pile of $[Ni_6(CO)_{12}]^{2-}$ anions showing the Ni···Ni van der Waals contacts; (b, bottom) view down the *c*-axis. Note how the Ni_3 triangles form a "star of David" in projection. The anion piles are surrounded by a 6-fold cationic belt.

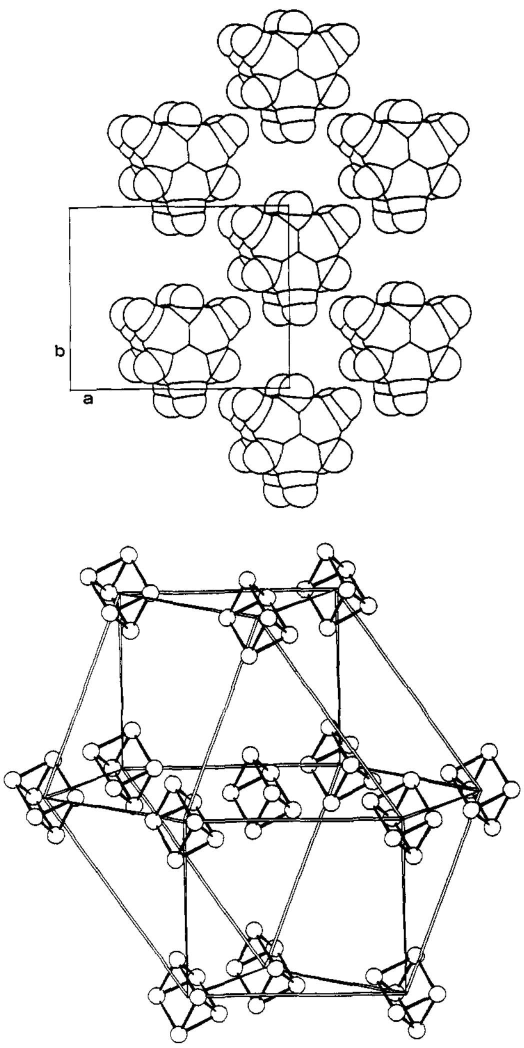

Figure 2. Ion organization in crystalline $[Pt_6(CO)_{12}][PPh_4]_2$: (a, top) space-filling projection of the anions in the *011* plane; (b, bottom) the slightly distorted cubo-octahedral distribution of the trigonal prismatic anions in the lattice (CO ligands are omitted for clarity, see also footnote to Table I).

anion piles or "snakes" requires a VR value in the range 0.40–0.60, and two-dimensional organization is identified by VR > 0.60. The most representative cases of interion lattice organization will be described in some detail in the following sections.

$[Ni_6(CO)_{12}][NMe_4]_2$ and $[Pt_6(CO)_{12}][PPh_4]_2$. The NMe_4^+ salt of $[Ni_6(CO)_{12}]^{2-}$ affords a striking example of a crystal lattice containing anionic piles surrounded by cationic belts. Contrary to what is usually observed with carbonyl clusters, the anionic piles are not formed *via* CO···CO interlocking but *via* Ni···Ni van der Waals contacts (Figure 1a). The Ni_3 triangles form a "star of David" in projection as shown in Figure 1b. The anionic piles are surrounded by six rows of NMe_4^+ cations. The separation between anions along the pile corresponds to the length of the *c*-axis (7.045 Å) in the trigonal lattice ($P\bar{3}$ space group). The stacking of the "$Ni_3(CO)_6$" units is of the (A–B)- -(A–B) type, so that the bridging CO's are eclipsed with the neighbor terminal ligands. Two contiguous sets of Ni_3 triangles are separated by 2.40 Å within the dianion and by 4.64 Å between two anions along the pile. We note, on passing, that this is one of the very few cases in which metal–metal van der Waals contact is observed between cluster molecules, since the metal atoms are usually screened by the ligands.

At this stage one may wonder if a similar anion aggregation is shown by the PPh_4^+ salt of the closely related platinum dianion $[Pt_6(CO)_{12}]^{2-}$ (whose metal polyhedron is closer to a trigonal prism than to an octahedron). The bulkier PPh_4^+ cation is expected to cause a decrease in the number of anion–anion interactions (see Figure 2a). The VR ratio, in fact, decreases from 0.60 in $[Ni_6(CO)_{12}][NMe_4]_2$ to 0.34 in the Pt dianion. Although the fractional coordinates of the PPh_4^+ cations are not available from the original structural papers or from CSD, we can still deduce how the cations will arrange within the lattice. We only need to observe that the two ions are, in this case, of similar size (330 Å^3 vs. 325 Å^3, respectively) and possess roughly spherical shape, hence we expect the packing to resemble the packing of spheres of equivalent size. The spatial arrangement of the anions is of the (distorted) cubo-octahedral type shown in Figure 2b.

$[Co_6(CO)_{14}]K_4 \cdot 6H_2O$ and $[Co_6(CO)_{15}]Cs_2 \cdot 3H_2O$. These are the only examples of octahedral binary carbonyl anions crystallized as alkali metal salts, while several other examples are known for coordination complexes.[41] In this respect they are quite unique and we shall discuss them together. Both crystals contain water of crystallization in the ratio 3:2 with respect to the alkali ion. The ion organization is, in both lattices, based on anionic piles similar to those observed in other crystal lattices of cluster anions (e.g. $[Ni_6(CO)_{12}]^{2-}$ discussed above, but also $[Os_{10}C(CO)_{24}]^{2-}$, $[Co_6N(CO)_{15}]^-$, etc.). In the present cases, however, the counterions are deeply embedded in the cluster carbonyl envelope.

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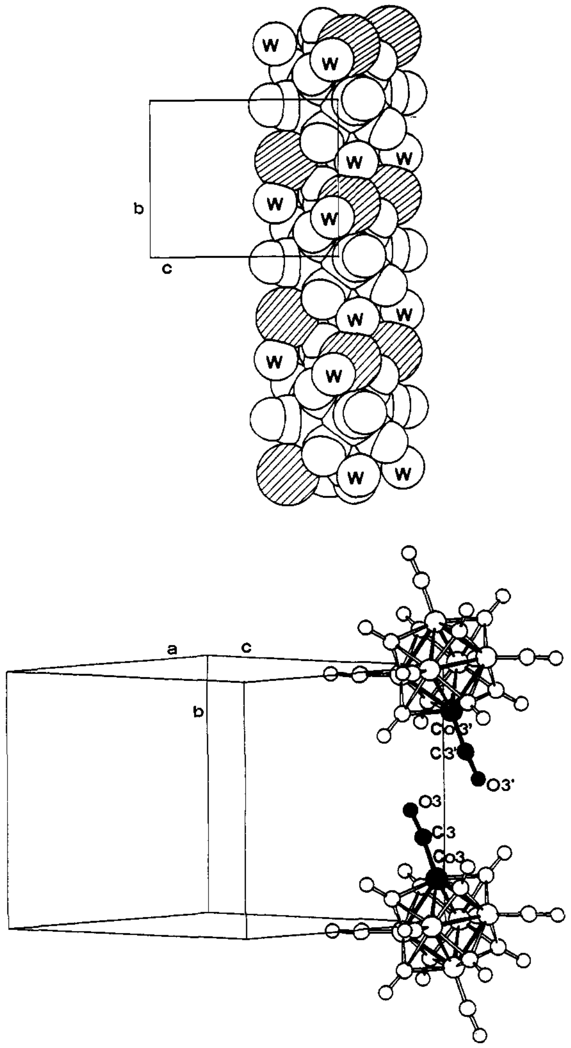

Figure 3. Ion organization in crystalline $[Co_6(CO)_{14}]K_4{\cdot}6H_2O$: (a, top) an anionic pile along the *b*-axis showing how the K^+ ions (shaded atoms) are surrounded by O(CO) and $O(H_2O)$ atoms (these latter oxygens are marked W); (b, bottom) effect of the interanion interactions on the geometry of the $[Co_6(CO)_{14}]^{4-}$ cluster anion—the progressive bending of the Co–C–O system [Co(3)C(3)O(3)] pointing toward the next neighboring molecule can be appreciated.

The oxophilic alkali metals attain a coordination sphere of oxygen atoms. This is also achieved via $H_2O{\cdots}M^+$ (M = K, Cs) solvate interactions with the water molecules. These water molecules seem to play a vital role in the stabilization of the crystal lattice, as they establish $C{=}O{\cdots}HOH$ hydrogen bonding interactions and thus effectively link the anions throughout the lattice. It should be stressed that, in the presence of such specific interactions of the anions with the cations and the solvent molecules, generalized packing parameters fail to be meaningful for prediction. For this reason VR values were not estimated and only the anion van der Waals volumes are reported in Table I.

Figure 3a shows how the K^+ cations surround the anionic piles in crystalline $[Co_6(CO)_{14}]K_4{\cdot}6H_2O$. The anionic piles are connected together through $O{-}K^+{\cdots}O$ bridges. As noted in the original structural paper[18a] there is no appreciable difference between carbonyl and water oxygen atoms in their O···O interactions: $O(CO){\cdots}O(H_2O)$ distances range from 2.86(2) to 2.94(1) Å, while $O(H_2O){\cdots}O(H_2O)$ separations range from 2.85(2) to 2.98(1) Å. $K^+{\cdots}O(CO)$ and $K^+{\cdots}O(H_2O)$ interactions are also strictly comparable: $K^+{\cdots}O(CO)$ from 2.70(1) to 2.91(1) Å, and $K^+{\cdots}O(H_2O)$ from 2.70(1) to 2.77(1) Å. Both O(CO) and $O(H_2O)$ establish a network of K···O···K interactions by asymmetrically bridging pairs of neighboring cations.

The interanion interaction along the column has a clearly recognizable effect on the geometry of the cluster. Figure 3b shows how the terminal carbonyls of consecutive anions along the *b*-axis are tilted away from the axis. Following the "route" from the center of the metal octahedron to the terminal carbonyl along the pile axis, each atom appears to be shifted further from the *b*-axis as shown by the gradual increase of the following angular values: axis–center–Co(3) 11.6°, axis–center–C(3) 15.4°, and axis–center–O(3) 18.3°. The progressive bending of the Co–C–O system is presumably needed to accommodate the terminal carbonyl C(3′)O(3′) belonging to the next neighboring molecule in the row without much loss of interanion cohesion.

Equally interesting is the packing in the Cs^+ salt of $[Co_6(CO)_{15}]^{2-}$ shown in Figure 4a. As in the case of the tetraanion, the anions form piles down the shortest cell axis (the *a*-axis, 9.26 Å). The Cs^+ ions form a string on one side of the anionic pile. Each ion is embedded in a coordination polyhedron formed by nine oxygen atoms (Cs···O separations in the range 3.02–3.85 Å). As in the case of the K^+ salt, neighboring cations are bridged by carbonyl and water oxygen atoms as shown in Figure 4b. However, only two of the three crystallographically independent water molecules participate in the bridging interactions, while the third one interacts only *via* hydrogen bonding with $O(H_2O)$ and O(CO) atoms [$O(H_2O){\cdots}O(CO)$ interactions range from 2.82(2) to 3.70(2) Å, the shortest ones involving triply bridging CO's, while $O(H_2O){\cdots}O(H_2O)$ separations are 2.88(2) and 2.94(2) Å]. An overall view of the packing organization is shown in Figure 4c.

$[Ru_6C(CO)_{16}][NMe_4]_2$ and $[Fe_6C(CO)_{16}][NMe_4]_2$. The NMe_4^+ salts of $[Ru_6C(CO)_{16}]^{2-}$ and of $[Fe_6C(CO)_{16}]^{2-}$ are isomorphous, and the two cluster complexes are isostructural. Because of the presence of the small NMe_4^+ cation, the packing VR values for both crystals are very high (0.67 and 0.66), larger values being observed only for crystalline $[Re_6(\mu\text{-}H)C(CO)_{19}][NEt_4]$ (VR = 0.67) and for $[Fe_5RhC(CO)_{16}][NEt_4]$ (VR = 0.72). The high VR values correspond to a high degree of anion organization: the anions form hexagonally close packed layers parallel to the *ac*-plane (Figure 5a) and piles along the *b*-axis (Figure 5b). The hexagonally packed layers of $[Ru_6C(CO)_{16}]^{2-}$ anions are separated by 9.708 Å (half the *b*-axis length) while the small cations occupy the interstices between the planes of anions (see Figure 5c). In crystalline $[Fe_6C(CO)_{16}][NMe_4]_2$ the slightly smaller size of the anion (377 Å^3 vs. 391 Å^3 in the Ru analogue) causes an increase in packing efficiency (pc values 0.67 and 0.64 for the iron and ruthenium clusters, respectively). It appears that the slightly looser interlocking of the anions in the hexagonal plane (compare Figure 6 with Figure 5a) is more than compensated perpendicularly to this plane.

It is interesting to observe that the packing arrangement in these two salts envisages the progression toward a *purely molecular crystal* of the type observed for neutral species, as the anionic volume occupies more of the overall molecular volume. This observation strengthens the idea that the anion charge is so delocalized in these systems that anion–anion repulsions have a negligible effect on the packing choice.

$[Ir_6(CO)_{15}][NMe_3(CH_2Ph)]_2$, $[Ir_6(CO)_{14}Br][PPh_4]$, and $[Ir_6(CO)_{14}I][PPN]$. In agreement with a VR value of 0.52, the crystal of $[Ir_6(CO)_{15}][NMe_3(CH_2Ph)]_2$ contains anionic piles. The anions are related by pure translation along the *b*-axis (9.806 Å). The $NMe_3(CH_2Ph)^+$ cations form pairs with the nitrogen centers mutually *trans* (see Figure 7a). The distance between the aromatic ring planes is 3.534 and 3.615 Å for the two pairs of crystallographically independent cations in the lattice. The cations are associated in such a way in the lattice that they also form piles in between the anionic piles, as illustrated in Figure 7b.

When the cations possess long and flexible aliphatic arms and deviate significantly from a spherical shape (as in the case of NEt_4^+ and $NBu^n{}_4^+$) the ratio in volume cannot be the only factor

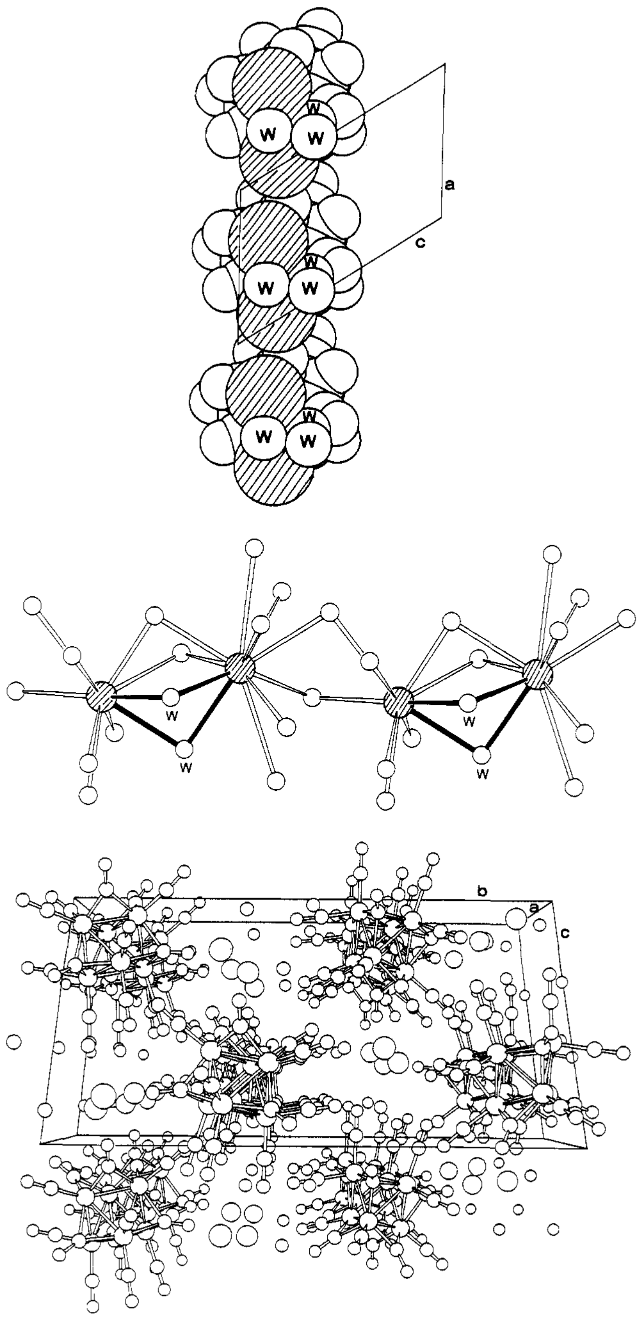

Figure 4. Ion organization in crystalline $[Co_6(CO)_{15}]Cs_2{\cdot}3H_2O$: (a, top) an anionic pile along the *a*-axis showing how the Cs^+ ions (shaded spheres) form a string parallel to the anion pile [$O(H_2O)$ atoms are marked W]; (b, middle) schematic representation of the Cs^+–O interactions showing how both O(CO) and $O(H_2O)$ atoms "bridge" the cesium atoms along the row (filled "bonds" mark the water oxygens); and (c, bottom) perspective projection down the *a*-axis showing the overall ion distribution in the lattice.

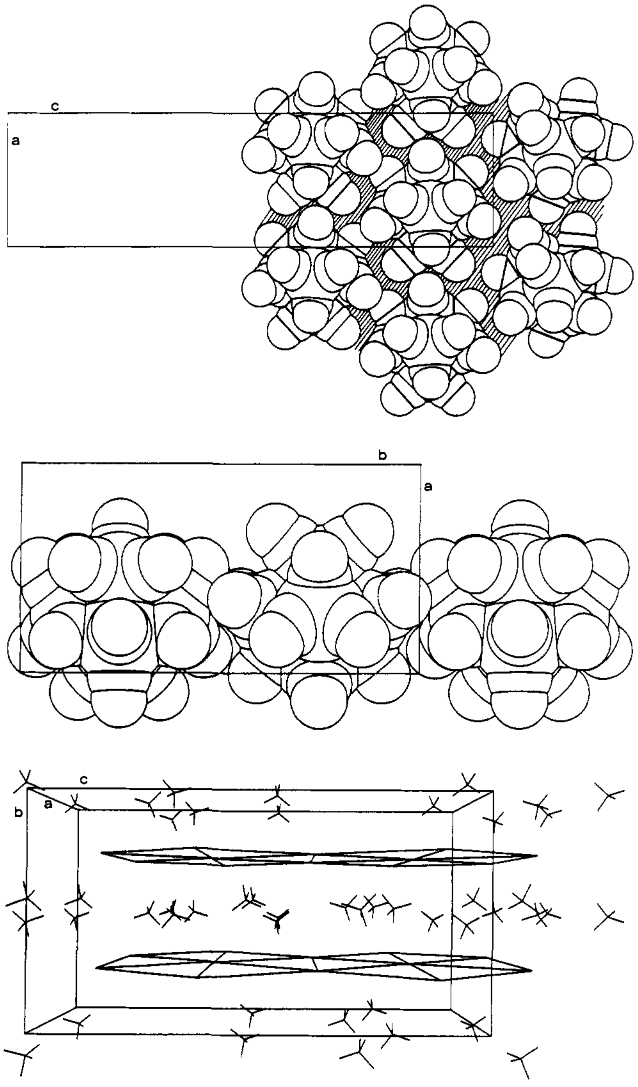

Figure 5. Ion organization in crystalline $[Ru_6(CO)_{16}][NMe_4]_2$: (a, top) space-filling projection perpendicular to the *010* plane of the orthorhombic lattice showing the hexagonal close packing of the anions; (b, middle) anion interlocking along the *b*-axis; and (c, bottom) stacking of the anion and cation layers. The hexagonally packed cluster anions (see Figure 5b) are represented by solid lines joining the cluster mass centers.

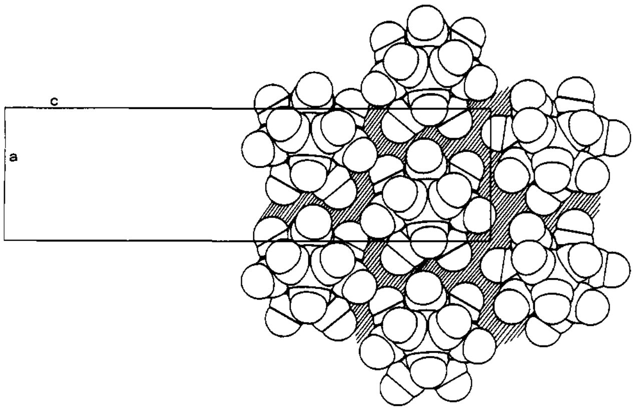

Figure 6. Ion organization in crystalline $[Fe_6(CO)_{16}][NMe_4]_2$: space-filling projection in the *010* plane (compare with Figure 5a).

controlling the packing motif. In these cases relevant deviations from the general trends are observed. For instance, the $NBu^n_4{}^+$ salt of $[Os_6(\mu_3\text{-}H)C(CO)_{18}]^-$ has a VR value of 0.61 and presents a layered structure. This is due to the flexibility of the $NBu^n_4{}^+$ cation, which can adopt an almost flat and discoidal shape and is easily intercalated between sheets of anions. In the $NEt_4{}^+$ salts of $[Re_6(\mu\text{-}H)C(CO)_{19}]^-$ and of $[Fe_5RhC(CO)_{16}]^-$, on the other hand, no anion aggregation is observed in spite of the very high VR values (0.67 and 0.72). In the $NEt_4{}^+$ salt of $[Co_6C(CO)_{13}]^{2-}$ (VR = 0.50) only anionic pairs are observed. In general, it would appear that $NEt_4{}^+$ prevents formation of one- or two-dimensional anion aggregates. It can also be predicted that the packing would be greatly changed if anions and cations bear fragments of similar shape, for example phenyl groups, which can afford additional interion van der Waals linkages.

Finally, we have investigated the carbonyl halide cluster salts $[Ir_6(CO)_{14}Br][PPh_4]$ and $[Ir_6(CO)_{14}I][PPN]$ with the aim of understanding whether the presence of ligands other than CO (or

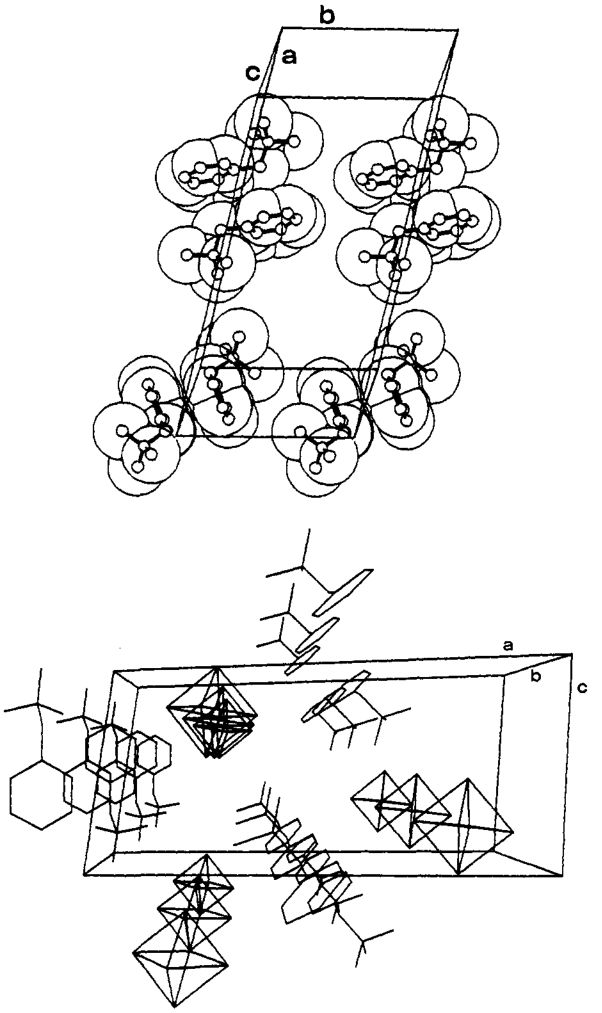

Figure 7. Ion organization in crystalline $[Ir_6(CO)_{15}][NMe_3(CH_2Ph)]_2$: (a, top) pairing of the $NMe_3(CH_2Ph)+$ cations; (b, bottom) perspective view down the *b*-axis of the triclinic cell showing cation columns in between the anionic piles (only the cluster skeletons are shown for sake of clarity).

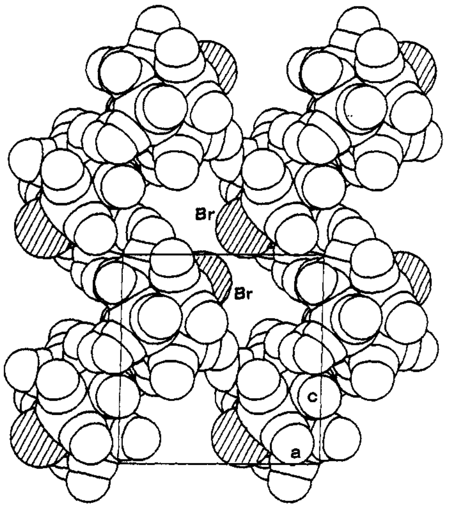

Figure 8. Anionic packing arrangement in crystalline $[Ir_6(CO)_{14}Br][PPh_4]$: the anions forms "snakes" (note how the bromine atoms (shaded spheres) of next neighboring molecules point toward each other).

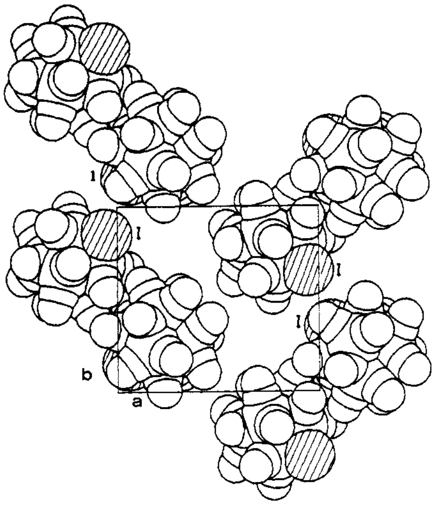

Figure 9. Anionic packing arrangement in crystalline $[Ir_6(CO)_{14}I][PPN]$: view down the *c*-axis of the monoclinic cell showing anion–anion pairing (iodine atoms (shaded spheres) belonging to next neighboring molecules face each other in the lattice (compare with Figure 8)).

H) has recognizable effects on the packing pattern. The PPh_4^+ salt of the bromide derivative contains anionic snakes (Figure 8), while in the PPN^+ salt (Figure 9) the anions show a lower degree of aggregation (in agreement with the lower VR value). In both crystals, however, the halogen atoms appear to play an important part in the packing cohesion affording loose "bridges" to the next snake (intermolecular Br···Br distance 5.412 Å, I···I distance 5.470 Å). The cations occupy the "voids" shown in the space filling diagrams of Figures 8 and 9 and effectively insulate the halogen pairs from the surroundings. A similar trapping of the heteroligands (with respect to CO) has been observed in crystalline $[N(CH_3)_2(CH_2Ph)_2][Ir_4(CO)_{11}(SCN)]$ and $[PPN][Ir_4(CO)_{11}(SCN)]$.[10]

Conclusions and Outlook

We have been able to show that the association of anions and cations in molecular salts of transition metal clusters is essentially governed by the *relative* size of the component ions. When the anion is large with respect to the cation (or cations), one- and two-dimensional aggregation is produced under the control of several (not necessarily converging) factors:

(i) First is the translational symmetry, i.e. *lattice periodicity*. We note that pure translation is the most common symmetry element relating cluster anions in lattice piles. Incidentally, it should be stressed that our sample cannot include systems characterized by low-range order or low-dimensionality phases (such as incommensurate phases etc.) simply because exact translational symmetry is a necessary requisite in diffraction studies. Crystalline materials not possessing this feature would not be suitable for single-crystal studies.

(ii) Second is the optimization (*close-packing*) of components with different shapes, *viz.* metal clusters covered by (cylindrical) CO-molecules *and* organic type cations containing essentially (conical) methyl and (flat) phenyl groups.

(iii) Next is the electroneutrality. Our analysis demonstrates that the actual ionic charge is diffused over the whole cation and anion bodies so as to have no recognizable effect on the lattice organization. As a consequence, anions (and cations) can approach each other as if basically neutral, i.e. without any appreciable Coulombic effect. It is worth recalling that preferential anion–cation association has been so far detected only in the salts of the anion $[Ir_4(CO)_9(SCN)]^-$, where a strongly polar SCN^- group is present,[10] and in the $NMe_3(CH_2Ph)^+$ salt of $[M_6C(CO)_{15}]^{2-}$ (M = Co, Rh).[4]

(iv) When the anion size is comparable to that of the cation(s), intermixing of the two kinds of charged particles is attained. Although each ion tends to surround itself with a first coordination enclosure shell of ions of the opposite sign, these crystals are more appropriately described as molecular mixed crystals rather than ionic salts (see Introduction).

(v) Halogen atoms appear to contribute to crystal cohesion by affording additional intermolecular linkages. Although the effect of heteroatoms on the packing arrangements in neutral or ionic organometallic crystals needs a more detailed analysis, it is interesting to note that analogous preferential interhalide association has been observed in crystals of halogenated organic compounds as well as in crystalline Cl_2, Br_2, and I_2.[42] Although the exact nature of these interactions is still a matter of debate, there is agreement on the fact that short halogen–halogen interactions are attractive and exert a significant control on the packing choice.

In summary, what we have attempted is a first (and, perhaps, uncertain) step toward crystal engineering in the cluster chemistry area. We have shown that (rather unawarely) many chemists have, on many occasions, produced materials with strongly anisotropic arrangements and distributions of the component particles. These materials include columnar lattices, layered stacks of anions and cations, and packings showing anion–anion and cation–cation direct association. The remarkable anisotropic arrangement shown by $[Ni_6(CO)_{12}]^{2-}$ and by several other salts may participate in some interesting solid state properties. For instance, one can speculate that upon cooling (or even by applying pressure along the *c*-axis) the nickel atoms can be brought in closer contact (*i.e.* compressed into a $[Ni_6(CO)_{12}]_n$ polymeric rod with a charge of $2n-$).[43] We plan to investigate the band structure and conducting properties of this and related materials. Similar considerations apply to the preferential one-dimensional aggregation of the anions present in the alkali salts of the cobalt anions. Furthermore, the stacking of anions and cations observed, for instance, in the NMe_4^+ salts of $[Ru_6C(CO)_{16}]^{2-}$ and of $[Fe_6C(CO)_{16}]^{2-}$ is the prerequisite for the formation of charge transfer and conducting materials.[3b]

We wish to conclude by paraphrasing Basolo's well-known empirical rule "*solid metal complexes are stabilized by large counter ions*".[44] It seems possible to state that small counterions can stabilize one-dimensional and two-dimensional lattices of anions thus providing access to anisotropic arrangements in the crystal, while large cations tend to form typical molecular-like crystals. This approach establishes a common ground between solid-state and coordination chemistry. For instance, low-dimensional solids, such as some chainlike niobium and tantalum chalcogenides,[45] show structural arrangements that closely recall the anion piles and layers observed in this study.

We have also shown that the *structure of the crystal* contains a large body of information. In spite of that, the attention of cluster chemists and crystallographers has always been mainly (if not only) concentrated on the structure of the individual molecule or ion "denuded" of its crystalline environment. It seems worth stressing that the investigation of solid-state properties of cluster materials (which are receiving increasing attention in the organometallic chemistry field) must rely on a detailed knowledge of the structure of the molecular ensemble constituting the crystalline material.[46] It will be difficult otherwise to fully appreciate the relationship between the properties of an *individual* molecule or ion and the *collective* properties of the molecules or ions in the solid. We believe that the investigation (or reinvestigation) of the crystal structure of transition metal clusters will put solid-state organometallic cluster chemistry in a different perspective.

Acknowledgment. We thank A. G. Orpen (Bristol) for many useful discussions during his sabbatical leave at the University of Bologna. P.M. acknowledges the ERASMUS project "Crystallography" for financing his stay. MURST is acknowledged for financial support.

Supplementary Material Available: Table of coefficients for the atom–atom pairwise packing potential energy calculations (1 page). Ordering information is given on any current masthead page.

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