

Molecular salts of high nuclearity cluster anions: cation control on the crystal structure

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Abstract

The crystal structures of some high nuclearity carbonyl cluster anions of rhodium and cobalt have been investigated by means of empirical packing potential energy calculations, van der Waals volume analysis and computer graphics. Data was retrieved from the Cambridge Structural Database. The relationship between shape, size and charge of the component ions and the formation of preferential aggregates in the crystalline solid has been analyzed.

Introduction

In previous studies [1] we have shown that the presence of anisotropic arrangements of the ions in the crystal structure of molecular salts formed by transition metal cluster anions (mainly carbonyl species) and large organic-type cations depends on the size and shape of the component ions while the actual ionic charge plays a very limited role in establishing the packing patterns. The term molecular salt has been used to designate materials whose component particles are ions of opposite sign but which interact essentially via van der Waals interactions. These studies originated from our interest in the packing modes of neutral mononuclear and polynuclear organometallic complexes where crystal construction is largely controlled by the size and shape of the component molecules [2].

The study of the factors controlling the structure of molecular salts was initiated by investigating the anion organization in crystals of decametallal cluster anions containing a tetracapped octahedral metal atom framework (M_{10} ; $M = Ru, Os$) [1a]. 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. Importantly, the same cluster pile was found to constitute the fundamental packing motif in the crystal of the neutral dihydride $H_2Os_{10}C(CO)_{24}$ [3]. Preferential aggregation of the anions in one-dimensional arrays was also observed in the family of prismatic carbido- and nitrido-carbonyl clusters of general formula $[M_6X(CO)_{15}]^{n-}$ ($M = Co, Rh$; $X = N, n = 1$; $X = C, n = 2$).

The $[(PhCH_2)Me_3N]^+$ salts of the $[M_6C(CO)_{15}]^{2-}$ dianions are the only clusters of this type in which direct cation–anion association is found.

More recently, we have extended our analysis to the family of octahedral carbonyl cluster anions. 28 crystal structures were retrieved from the Cambridge Structural Database allowing us to examine the size–structure–charge relationship with more statistical significance [1b].

With these studies we have been able to show that the structural features of the molecular salts formed by large anions and cations of comparable size and of roughly spherical shape resembles that of mixed molecular crystals. In these systems the components are packed in the lattice according to the same rules which govern the packing of neutral molecules in single component systems [4]. 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 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 of the anion $[Ir_4(CO)_{11}(SCN)]^-$ [5], where there is evidence for charge localization over the SCN ligand. Many chemical and physical properties [6] might arise from anion–anion, anion–cation and cation–cation interlocking within the crystal.

In this paper we report the results of an investigation on the packing modes of molecular salts formed by large cluster anions of nuclearity eleven, twelve and

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thirteen [7–12]. To this purpose we have chosen to investigate the families of Rh₁₂ and Co₁₃ dicarbido cluster anions listed in Table 1. In addition the pair of isomers [Rh₁₁(CO)₂₃]³⁻ has been examined [12].

The reasons for choosing these complexes for our analysis can be summarized as follows:

(i) The Rh₁₂ and Co₁₃ anions form two families of closely related complexes. The Rh₁₂ di-anion differs from the tri-anion and the tetra-anion only by the presence of one additional CO ligand. These two latter complexes are isostructural but possess different anionic charges. Furthermore, the di-anion and the tetra-anion are diamagnetic while the tri-anion is paramagnetic. Similarly [Co₁₃C₂(CO)₂₄]³⁻ and [Co₁₃C₂(CO)₂₄]⁴⁻ are isostructural but not isoelectronic.

(ii) The Rh₁₂ and Co₁₃ anions have been crystallized with a variety of counterions such as [(Ph₃P)₂N]⁺ (hereafter PPN⁺), tetramethylammonium NMe₄⁺, tetrapropylammonium NPr₄⁺, and benzyltrimethylammonium NMe₃(CH₂Ph)⁺ thus providing an interesting sample for studying the cation–anion packing relationship.

(iii) The Rh₁₁ case is also of some relevance. It has been shown that the [NMe₄]⁺ salt of the high nuclearity anion [Rh₁₁(CO)₂₃]³⁻ crystallizes in two different isomeric forms depending on the co-crystallization solvents (Me₂(CO), and C₆H₅Me, respectively) [12]. Although the metal framework is identical in the two species, the distribution of the 23 COs differs in the number and location of the bridging ligands.

Crystallographic information and fractional atomic coordinates were retrieved from the October 1992 version of the Cambridge Structural Database (CSD 5.04) using the program QUEST [13].

Methodology

In order to rapidly and efficiently decode how a given crystal is constructed (and to avoid the strictness of the lattice translational and point symmetry) one needs to focus on the number and distribution of the first-neighbors around the ion chosen for reference (in our case a cluster anion). Our approach to the ion organization in molecular salts is basically the same as that applied to study the crystalline structure of neutral organometallic molecules [2]. We make use of the pairwise atom–atom potential energy method [14], which has been successfully applied to the study of packing relationships in molecular crystals. The Buckingham-type expression $ppe = \sum_i \sum_j [A \exp(-Br_{ij}) - Cr_{ij}^{-6}]$ was used for the calculations. In this equation, r_{ij} is an interatomic non-bonding distance, index i and j in the summation are adequately chosen in order to run over all atoms of one reference cluster and of the surrounding anions and cations distributed according to crystal sym-

metry in the lattice. A cut-off distance of 15 Å in the summation guarantees that the entire space around the reference ion is explored. The method requires some additional (and far from trivial) approximations in order to deal with the presence of charged particles of different type in the asymmetric unit. The reader is addressed to previous papers on the subject for details of the computational procedure and of the parameter choice [1, 2]. The structural problems related to the packing of a range of molecular salts of varying size have been similarly addressed [15].

The volumes of the ionic units (V_{anion} , V_{cation}) were calculated by the ‘intersecting cups’ method [16] by using literature van der Waals radii for main-group elements and an arbitrary radius of 2.15 Å for first-row and 2.35 Å for second-row transition metals [2g]. 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 ligands 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. The so called volume ratio, $VR = V_{\text{anion}}/V_{\text{formula}}$ [1b], has also been calculated, where V_{anion} is the volume of the cluster anion and V_{formula} is the overall molecular volume, obtained as the sum of anion, cation(s) and, when present, solvent molecule volumes. In the course of our previous study we have found that the presence of certain types of one-dimensional or two-dimensional lattice aggregates (see also below) correlates with such ratio. The packing coefficients were estimated as $p.c. = V_{\text{formula}}Z/V_{\text{cell}}$. Gavazzotti’s OPEC suite of programs [17a] was employed for the calculation of V_{formula} , V_{anion} , V_{cation} and $p.c.$, as well as that of ppe . Keller’s SCHAKAL88 [17b] was used for the graphical representation of the results.

Packing motif and cation size

All structural parameters relevant for the following discussion, together with the salt formulae and the CSD ‘REFCODES’, are grouped in Table 1. References to the original structural papers are also provided. With respect to this Table the following general observations can be made.

(i) The cluster anions are comparable in size, the smallest being the Rh₁₁ species (*c.* 479 and 482) while the largest anions are the Rh₁₂ species. The intermediate size of the Co₁₃ anions reflects the smaller size of cobalt with respect to rhodium.

(ii) As expected, the NMe₄⁺ cations are the smallest while PPN⁺ possesses the largest volume (*c.* 89 versus 554 Å³). These values compare well with those previously

TABLE 1. Relevant crystal and molecular qualifiers for some high nuclearity crystalline cluster salts^a

REF-CODE	Formula	V_{anion}	V_{cation}	V_{solv}	V_{cell}	Z	$p.c.$	VR
BUDKU01	$[\text{Rh}_{11}(\text{CO})_{23}]$ $[\text{NMe}_4]_3 \cdot \text{Me}_2\text{CO}$	482	89	60	5703	4	0.57	0.60
FUNKOO	$[\text{Rh}_{11}(\text{CO})_{23}]$ $[\text{NMe}_4]_3 \cdot \text{C}_6\text{H}_5\text{Me}$	479	89	97	5939	4	0.57	0.57
BACTII10	$[\text{Rh}_{12}\text{C}_2(\text{CO})_{24}]$ $[\text{PPN}]_2$	550	554		2470	1	0.64	0.33
CAFJAU	$[\text{Rh}_{12}\text{C}_2(\text{CO})_{23}]$ $[\text{NPr}_4]_3$	603	247		16113	8	0.65	0.45
DAJHIF	$[\text{Rh}_{12}\text{C}_2(\text{CO})_{23}]$ $[\text{NPr}_4]_4$	556	218		9498	4	0.60	0.39
DABLOH	$[\text{Co}_{13}\text{C}_2(\text{CO})_{24}]$ $[\text{NMe}_3\text{Bz}]_3$	517	161		3357	2	0.60	0.52
BEGJIG	$[\text{Co}_{13}\text{C}_2(\text{CO})_{24}]$ $[\text{NMe}_3\text{Bz}]_4 \cdot \text{Me}_2\text{CO}$	512	154	60	8026	4	0.59	0.43

^aAll volumes in \AA^3 .

calculated [1b] and with the values reported within a study of the crystal packing of some inorganic salts [15a]. In this latter work, however, the integration model put forward by Gavezzotti [17a] was used rather than Kitaigorodsky's intersecting cups model.

(iii) Packing coefficients appear to fall in a narrow range (0.57–0.64). The least densely packed are the Rh_{11} tri-anions (0.57). In these crystals, as well as in $[\text{Co}_{13}\text{C}_2(\text{CO})_{24}]^{4-}$, the solvent of crystallization accommodates in the structure interstices contributing to crystal cohesion. The average packing coefficient for the crystals listed in Table 1 is 0.61. This value is strictly comparable to packing coefficients calculated for neutral binary carbonyls and for most organic molecular crystals.

In terms of ion organization, the crystal structures listed in Table 1 present a variety of packing motifs characterized by both high and low degree of anion–anion organization. Effectively anisotropic arrangements are observed when the contribution of the cations to the overall molecular volume is small. On the contrary, then the VR value is small (i.e. when the denominator within the VR formula is large because the cation(s) volume is large) the crystal structure does not present identifiable one-dimensional or two-dimensional packing patterns. Some representative cases will now be illustrated and compared with the results of previous studies.

The di-anion $\text{Rh}_{12}\text{C}_2(\text{CO})_{24}^{2-}$ has the lowest VR value in this sub-group (0.33). A space-filling projection of the packing in the ac plane of $[\text{Rh}_{12}\text{C}_2(\text{CO})_{24}][\text{PPN}]_2$ is shown in Fig. 1. The di-anions are in direct van der Waals contact along the c direction. Rows of cations lie on either side of the rows of anions. The structure

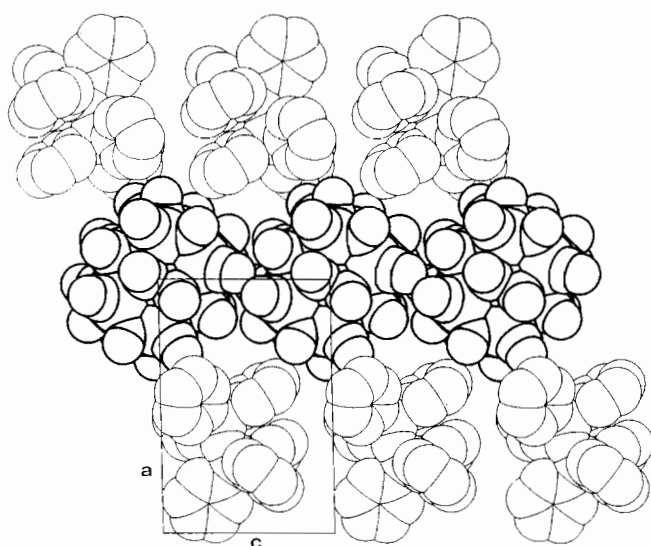


Fig. 1. Space-filling projection of the packing in the ac plane of $[\text{Rh}_{12}\text{C}_2(\text{CO})_{24}][\text{PPN}]_2$. Note how the di-anions are in direct van der Waals contact along the c direction.

of this salt can be described as formed by rows of roughly spherical ions interacting in close-packing fashion. The anion and the cation have roughly the same volume (550 versus 554 \AA^3). From Fig. 1, it can be easily appreciated how each particle is surrounded by six nearest-neighbors in the plane. This pattern is of the molecular mixed-crystal type. It is also interesting to note that the inter-anion van der Waals contact is based on $\text{CO}\dots\text{CO}$ interlocking between the ligands protruding from the cluster surface and those belonging to next neighboring anions. Similar interlocking had

been observed previously in the PPN^+ salt of the di-anion $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$.

The packing pattern shown by the Rh_{12} tri-anion is closely related to that of the di-anion in spite of the different anion/cation ratio and of the different counterion $[\text{NPr}_4^+]$. The cation NPr_4^+ is less than half of PPN^+ in terms of volume (218 versus 554 \AA^3) while the cluster tri-anion is slightly larger than the di-anion (603 versus 550 \AA^3). Thanks to the long aliphatic arms the NPr_4^+ cation is flexible and can easily penetrate the interstices in the packing. Figure 2 shows how the cluster tri-anions are distributed with the long molecular axes all roughly parallel to the b axis. It is interesting to mention, in passing, that this crystal contains two independent anions (and therefore six corresponding cations) in the asymmetric unit of the $P2_1/c$ space group. Figure 3 shows how the two independent anions differ

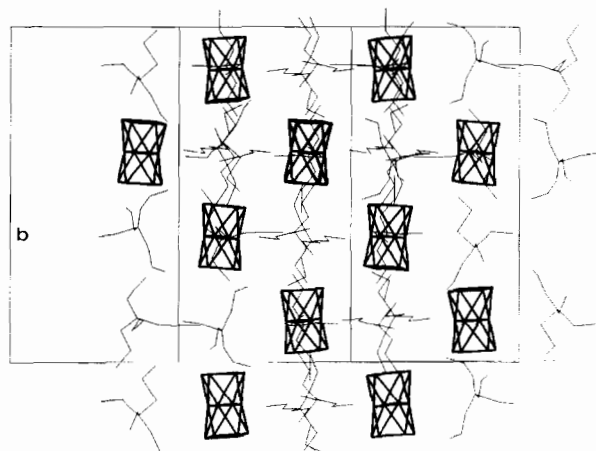


Fig. 2. Schematic representation of the distribution of Rh_{12} cluster tri-anions and of the NPr_4^+ cations in crystalline $[\text{Rh}_{12}\text{C}_2(\text{CO})_{23}][\text{NPr}_4]_3$.

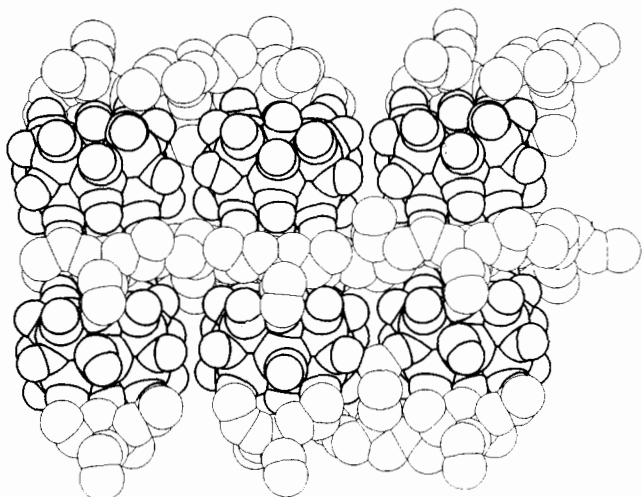


Fig. 3. Space-filling packing showing how the NPr_4^+ cations embrace the anionic pile and effectively insulate one pile from the other.

essentially for a small tilt with respect to the b cell axis; the difference is most likely caused by the interactions with the flexible NPr_4^+ , which embrace the anionic pile and effectively insulate one pile from the other. The flexibility of the NPr_4^+ cations is reflected in the variation in volume of the six independent cations (from 227 to 276 \AA^3).

The presence of anionic piles in the lattice of $[\text{Rh}_{12}\text{C}_2(\text{CO})_{23}][\text{NPr}_4]_3$ is reminiscent of the structure of some low-dimensional chalcogenides in which one-dimensional arrays are formed via stacking of square-antiprismatic tantalum polyhedra [18]. A remarkable anisotropic arrangement of cluster anions has also been found [1b] in the cluster salt $[\text{Ni}_6(\text{CO})_{12}][\text{NMe}_4]_2$ [19]. The crystal sub-lattice contains anionic columns formed via direct $\text{Ni}\dots\text{Ni}$ van der Waals contacts between the triangular bases of the octahedral Ni_6 core. The anionic columns are surrounded by a cationic 'belt' formed by six columns of $[\text{NMe}_4]^+$ cations.

The tri-anion $\text{Co}_{13}\text{C}_2(\text{CO})_{24}^{3-}$ and the tetra-anion $\text{Co}_{13}\text{C}_2(\text{CO})_{24}^{4-}$ have been structurally characterized as their NMe_3Bz^+ salts. As shown in Table 1, the packing coefficient of these crystals, in spite of the different counterion employed, are strictly comparable with those of the NPr_4^+ salts of the Rh_{12} anions. It is also noteworthy that rather different V/R values can be associated with the packing of the same type of particles. Figure 4 shows the distribution of the Co_{13} tetra-anions in the crystal: due to the large anion/cation ratio, the anions are almost completely surrounded by the counterions. Similar packing pattern is shown by the crystal of the anions $\text{Co}_{13}\text{C}_2(\text{CO})_{24}^{3-}$ and $\text{Rh}_{12}\text{C}_2(\text{CO})_{23}^{4-}$.

As mentioned above, the crystalline salts $[\text{Rh}_{11}(\text{CO})_{23}][\text{NMe}_4]_3 \cdot \text{Me}_2\text{CO}$ and $[\text{Rh}_{11}(\text{CO})_{23}]$

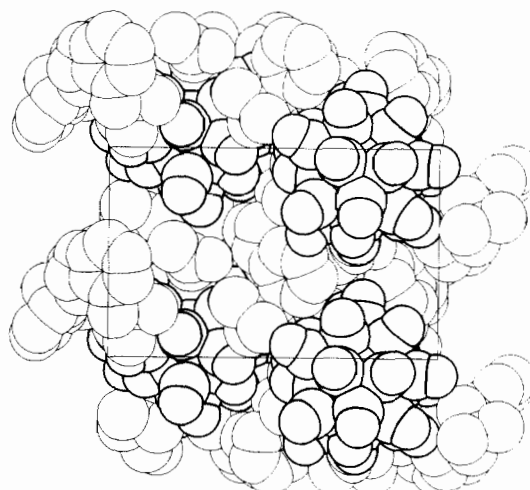


Fig. 4. Space-filling representation of a tetra-anion distribution in crystalline $[\text{Co}_{13}\text{C}_2(\text{CO})_{24}][\text{NMe}_3\text{Bz}]_4$, showing how the anions are almost completely insulated by the counterions.

$[\text{NMe}_4]_3 \cdot \text{C}_6\text{H}_5\text{Me}$ contain two different isomeric forms of the cluster tri-anion. The two anions differ in the number and distribution of the bridging CO ligands as well as in the pattern of metal–metal bond lengths. In solution both isomers have identical IR spectra and are still fluxional on the time-scale of ^{13}C NMR spectroscopy at -90°C . As pointed out in the original paper [12] the CO ligand distribution in the two species can be considered as two frozen steps of the fluxional process that occurs in solution. This is, to the authors' knowledge, the only example of isomers of a CO-scrambling fluxional process that could be separated in the crystal structure by simply varying the crystallization solvent. It could also mean, of course, that two different potential energy minima exist for this anion when thermodynamic energy terms involving the crystallization process are considered. In the crystalline salts $[\text{Ir}_4(\text{CO})_{11}(\text{SCN})][\text{N}(\text{CH}_3)_2(\text{CH}_2\text{Ph})_2]$ and $[\text{Ir}_4(\text{CO})_{11}(\text{SCN})][(\text{Ph}_3\text{P})_2\text{N}]$ the different CO ligand distribution in the two isomers is, otherwise, associated with the presence of different counterions [5].

Let us examine the relationship between the crystal and molecular structures of the Rh_{11} tri-anions in more detail. While the two *molecules* differ in geometry, the respective *crystals* are much more similar than expected on the basis of the space group symmetry. Figure 5(a) and (b) shows a comparative perspective view of the distribution of the anions and of the surrounding cations and solvent molecules in the two crystal structures. There are a few points worth noting: (i) both anions form piles throughout the crystal, the piles extend along the *a* axis in the acetone solvate and along the *b* axis in the toluene solvate (these are the shortest axes in the two cells and they are of comparable length 12.275 versus 12.590 Å); (ii) the cluster frameworks maintain more or less the same orientation along the piles, while the CO ligands are differently distributed; (iii) the anionic piles are surrounded by a 'belt' of NMe_4^+ cations while there is only one row of solvent molecules within the immediate surroundings of each anionic pile. As a matter of fact the two crystals are quasi-isomorphous, the similarity between the two crystal structures is clear to see in the schematic packing representations shown in Fig. 6(a) and (b) where the crystallographic *bc* plane of the acetone solvate crystal is compared with the *ac* plane in the crystal of the toluene solvate. Intermolecular interactions between the cations and the anions show, however, a dependence from the solvent. In both crystals the shortest contacts are between the cation hydrogen atoms and the cluster oxygens. These interactions are longer in the toluene solvate than in the acetone solvate (range 2.40–2.49 versus 2.34–2.40 Å). This difference might be caused by the different polarity of the solvent molecules. In both crystal systems, however, the solvent molecules

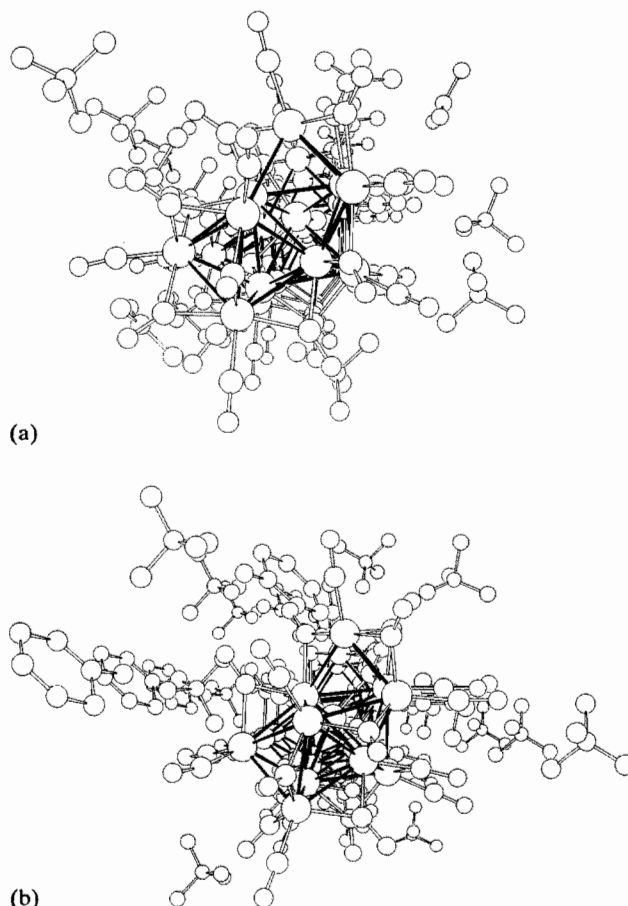


Fig. 5. (a) and (b) Comparative view of the distribution of the anions and of the surrounding cations and solvent molecules in the crystal structures of isomers of $[\text{Rh}_{11}(\text{CO})_{23}][\text{NMe}_4]_3 \cdot \text{Me}_2\text{CO}$ and $[\text{Rh}_{11}(\text{CO})_{23}][\text{NMe}_4]_3 \cdot \text{C}_6\text{H}_5\text{Me}$.

are not involved in short $\text{CH}\dots\text{O}$ interactions. $\text{CH}\dots\text{O}$ intermolecular interactions are known to be able to control the molecular or crystal structure features in subtle ways [20]. We have shown [5] that these intermolecular interactions are rather ubiquitous in crystals of cluster molecules where both CO ligands and CH donor groups are present. We have also observed, on comparing the crystal structures of the 'merry-go-round' isomers $[\text{Ir}_4(\text{CO})_9(\text{SCH}_2)_3]$ that $\text{CH}\dots\text{O}$ interactions preferentially established with the bridging CO ligands rather than with the terminally bound ones [5]. In the present case, however, it is not possible to establish a clear relationship between the type of solvent and the distribution of bridging ligands over the two cluster frameworks.

Conclusions

Crystals containing large or very large anions and cations have characteristics somewhat half-way between those of authentic molecular crystals (i.e. formed by

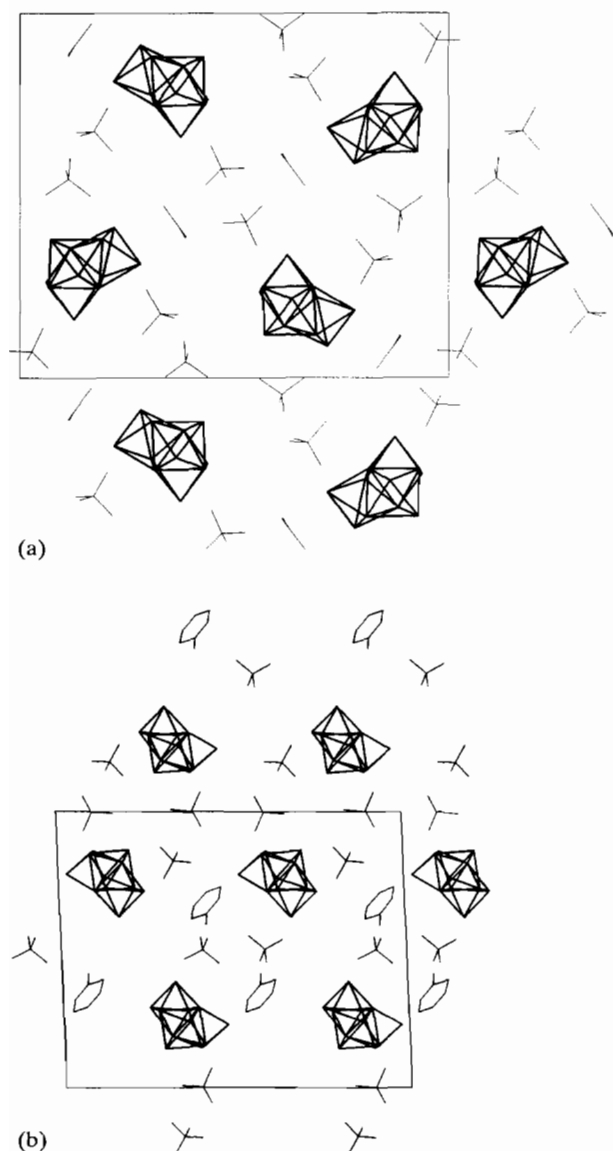


Fig. 6. (a) and (b) Schematic packing representations comparing the crystallographic bc plane of the acetone solvate crystal with the ac plane in the crystal of the toluene solvate of the anion $\text{Rh}_{11}(\text{CO})_{23}^{3-}$.

particles 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). 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 structure of the resulting crystalline material has never been systematically investigated. It appears that 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), anisotropic arrangements in the crystal are generated. 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 has to compromise with the need for electroneutrality.

Our analysis also demonstrates that the actual ionic charge is diffused over the whole cation and anion bodies so as to have no recognizable effect on the organization of the molecular ions in the crystal structure. 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, in this respect, that high nuclearity clusters anion tend to undergo a different type of reaction chemistry compared to lower nuclearity systems. Mono- and di-anions with nuclearity greater than ten behave very much like neutral species and do not easily react with cations because the charge is not localized sufficiently.

Preferential anion-cation association has been so far detected only in the salts of the anion $[\text{Ir}_4(\text{CO})_9(\text{SCN})]^-$, where a strongly polar SCN^- group is present, and in the $\text{NMe}_3(\text{CH}_2\text{Ph})^+$ salt of $[\text{M}_6\text{C}(\text{CO})_{15}]^{2-}$ ($\text{M} = \text{Co}, \text{Rh}$). In the SCN derivatives there is clear evidence that the negative charge is carried by the hetero-ligand and not delocalized over the whole cluster molecule. The SCN ligands establish a contact pair with the respective counterions. In the unbridged form the ligands are segregated within a 'cage' generated by four surrounding $[\text{NMe}_2(\text{CH}_2\text{Ph})_2]^+$ cations, while in the bridged form the anionic piles are embraced by the $[\text{PPN}]^+$ cations. The rhodium and cobalt prismatic carbides, on the other hand, form contact-ion pairs with the $\text{NMe}_3(\text{CH}_2\text{Ph})^+$ cations.

The degree of flexibility of the counterion is another factor that plays a relevant role in the packing choice. Organic-type cations containing long aliphatic arms (such as NEt_4^+ , NPr_4^+ and NBu_4^+) are highly adaptable and can vary volume and shape by folding or unfolding around the anions.

In summary, we believe that much can be learned by investigating (or reinvestigating) the crystal structure of neutral or ionic transition metal clusters. The very concept of molecular structure for highly flexible systems such as most transition metal clusters has to be approached with great care. When intermolecular interactions are in competition with finely balanced bonding and non-bonding intramolecular interactions, the resulting solid state molecular structure can be difficult to predict. Different molecular structures, for instance, might be obtained by varying the counterion and/or the crystallization solvent or by controlling the extent of intermolecular hydrogen bonding in solution and in the solid state. These aspects of cluster chemistry represent an extremely promising field of research.

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