Crystal Structures of Salts of Transition-metal Halide Clusters

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The ion organization in crystalline salts formed by transition-metal carbonyl cluster anions containing halide ligands has been investigated. It has been shown that the presence of the heteroligand(s) drives either towards the 'trapping' of two halogen atoms within a cage of counter ions or towards the formation of anion rows insulated by cation rows. The formation of either type of pattern appears to be due to the size and mode of bonding of the halogen atoms, the first type being preferred with small terminal halogens or with large halogens in bridging bonding mode, while the second is observed with large halogens in terminal bonding mode.

There is much current interest in the way molecules and ions are organized in the solid state to form materials with given physical and chemical properties.[1] It is surprising, in this respect, that relatively little attention has been given to the relationship between the characteristics of the ionic particle components and the way a crystalline salt is constructed and organized.[2] This is of particular importance in the field of organometallic solid-state chemistry since non-neutral species, whether constituted of mono- or poly-nuclear complexes, are extremely abundant. It is common practice in inorganic and organometallic chemistry laboratories to base the crystallization of new molecules or ions on empirical rules, 'local' recipes and tricks. We are still quite far away from the engineering of specific molecular or ion organizations which would not only result in crystalline solids with good diffracting properties but also, and more interestingly, in the design of materials of given characteristics. Although this is becoming an important goal for the inorganic chemist, our understanding of the packing choices of organometallic compounds is still very limited.

In previous papers we examined three main aspects, namely (*i*) the relationship between the crystal structures of neutral carbonyl clusters and those of the corresponding cluster anions of the same shape,[3] (*ii*) the cation control on the crystal organization of hexanuclear carbonyl cluster anions,[4] *viz.* the effect on the crystal structure of different cations with anions of similar shape and size, and (*iii*) the packing relationships amongst molecular salts formed by large cluster anions with up to 14 metal atoms.[5] These studies have been fundamental in our appreciation of the crystal-structure properties as a function of size, charge, and shape of the anions and of the type of organic counter ions. As a result of our statistical analysis of the crystal-packing modes of hexanuclear carbonyl cluster anions,[4] a correlation between the formation of preferential aggregates in the crystal lattice and the features (shape, size and charge) of the component ions was found.

In all these studies, however, we examined species in which the anionic charge is evenly distributed over the cluster anion surface, so that the particles interact essentially in van der Waals fashion. This paper focuses on a different issue. We now investigate carbonyl-halide cluster anions of low and medium nuclearity in which a supposedly uneven charge distribution accompanies an essentially spherical shape. This further investigation serves two different purposes: to verify to what extent the previously observed correlation between the relative volumes of the component ions and their crystal organization in binary cluster anions can be expected to hold in less symmetrical systems, and to establish whether the presence of a polarizing ligand on the anion can be associated with the formation of specific aggregation modes within the crystal lattice.

Methodology

The crystal structures of the carbonyl-halide metal clusters were retrieved from the Cambridge Structural Database (CSD) using the program QUEST.[6] The structures are listed in Table 1 together with some crystal and molecular qualifiers which will now be described. References to the original structural papers are also included.[7–18]

The structures examined possess the following general characteristics.

(*i*) The nuclearity of the clusters ranges between 4 and 6.

(*ii*) The number of metal-bound carbonyl ligands range between 11 and 15 with no distinction between doubly bridging, triply bridging or terminal bonding modes.

(*iii*) Only one or two halide ligands are bound to the metal core.

(*iv*) The anions have been crystallized with typical organic cations: $N(PPh_3)_2^+$, PPh_4^+, NEt_4^+ or NBu_4^+.

(*v*) All the complexes are either mono- or di-anionic.

The volumes of the component ions (V_{anion}, V_{cation}) were calculated with the integration model put forward by Gavezzotti.[19] Use was made of literature van der Waals radii for main-group elements (H 1.17, C 1.75, N 1.52, O 1.40, P 1.90, Cl 1.77, Br 1.95, I 2.1 Å) and of an arbitrary radius of 2.15 Å for the first-row and 2.35 Å for the second- and third-row transition metals.[20] The contribution of the solvent of crystallization to the total occupied volume in the crystal structure was also taken into account. The values obtained for $[N(PPh_3)_2][Ir_6(CO)_{14}I]$ and $[PPh_4][Ir_6(CO)_{14}Br]$ can be compared with those calculated previously on the basis of Kitaigorodsky's method of 'intersecting cups,'[21] (935 *vs.* 887 and 750 *vs.* 702 $Å^3$ respectively). It can be noted that the volumes obtained with the latter method tend to be slightly smaller than those calculated with the more accurate 'integration' method. These differences, however, have no great relevance in the present study because the relative ratios, on which the discussion is based, are not affected by the type of model used for the calculation of volume.

The volume ratio coefficient (v.r.), which was found to correlate with the presence of mono- and two-dimensional aggregates in crystalline binary carbonyl clusters,[4] has been calculated for all of the structures under investigation; v.r. represents the ratio between the volume of the cluster anion and that of the entire formula unit [volume of the anion plus those

Table 1 Relevant crystal and molecular qualifiers for the carbonyl-halide clusters[a]

Ref.	Refcode	Formula	Space group	p.c.	$V_{formula}$	V_{anion}	V_{cation}	v.r.	Min. X ··· X distance/Å
7	GIMHAL	$[N(PPh_3)_2][Ir_6(CO)_{14}I]$	$P2_1/c$	0.68	935[b]	431	504	0.46	5.470
7	GIMGOY	$[PPh_4][Ir_6(CO)_{14}Br]$	$P2_1/c$	0.69	750[b]	423	327	0.56	5.412
8	SIMHIF	$[PPh_4][Ir_6(CO)_{14}Cl]$	$P2_1/n$	0.68	740	418	322	0.56	5.245
9	TBAMRC	$[NBu_4][Rh_6(CO)_{15}I]$	$P2_1/n$	0.66	712	438	274	0.62	8.623
10	KUNBEA	$[N(PPh_3)_2][Rh_6(CO)_{15}Cl]$	$P2_1/n$	0.68	925	429	496	0.46	5.842
8	SIMHEB	$[PPh_4][Ir_6(CO)_{15}Cl]\cdot$thf[c]	$P\bar{1}$	0.67	815	428	316	0.53	5.797
11	PPHCIR10	$[PPh_4][Ir_4(CO)_{11}Br]$	$P2_12_12_1$	0.67	658	329	329	0.50	8.854
12	PIMOSI	$[N(PPh_3)_2][Os_5(CO)_{15}I]$	$P2_1/c$	0.66	925	427	498	0.46	3.610
13	EAMICO	$[NEt_4][Co_4(CO)_{11}I]$	$Cmca$	0.68	467	311	156	0.67	6.860
14	DEYGOD10	$[N(PPh_3)_2][Os_4(CO)_{12}H_2I]$	$P2_1/a$	0.67	853	358	495	0.42	8.647
15	BUMRAC	$[NEt_4]_2[Fe_5C(CO)_{12}Br_2]$	$P2_1/n$	0.68	673	381	146	0.57	6.245
16	DAJBIZ	$[N(PPh_3)_2][Re_4C(CO)_{15}I]$	$Cc2a$	0.66	926	430	496	0.46	7.730
17	PACIOS	$[N(PPh_3)_2][Os_5C(CO)_{15}I]$	$P2_1/n$	0.68	941	445	496	0.47	9.040
18	PHIMRU	$[N(PPh_3)_2][Ru_4(CO)_{13}Cl]$	$P\bar{1}$	0.67	850	355	495	0.42	9.800

[a] Volumes in Å^3. [b] These values differ slightly from those previously calculated with the less accurate method of the 'intersecting cups' and reported in ref. 4. [c] thf = Tetrahydrofuran.

of the cation(s) and solvent molecules which may be present, *viz.* v.r. = $V_{anion}/V_{formula}$]. The packing coefficients were estimated as p.c. = $V_{formula}\cdot(Z/V_{cell})$. For computational details of the methods the reader is referred to previous papers.[4,5] All calculations were performed with the computer program OPEC;[22a] SCHAKAL 93 was used for the graphical representation of the results.[22b]

First we report some general considerations based on the information listed in Table 1 and, secondly, describe in detail the anion–cation organization in some of the crystal structures retrieved from the CSD. It is worth recalling that the terms piles and snakes have been previously adopted to designate monodimensional aggregations of anions in straight or 'wavy' lines, respectively, layer indicates two-dimensional aggregation, and pair refers to preferential anion–anion pairing.

With the exception of crystalline $[NEt_4][Co_4(CO)_{11}I]$ (see below), the v.r. coefficient for all the structures investigated ranges from 0.42 to 0.62. In binary carbonyl cluster anions v.r.s of this order were found to correspond to a preferred monodimensional anion organization (piles or snakes) throughout the crystal lattice, while a higher degree of inter-anion aggregation (namely the formation of two-dimensional anionic layers intercalated with sheets of cations) was observed when v.r. > 0.60. The average packing coefficient was calculated to be 0.67, which, interestingly, is strictly comparable to p.c. values calculated for neutral and ionic binary carbonyls and for most organic molecular crystals.

This trend is generally followed in carbonyl-halide cluster anions as discussed below. The presence of the heteroligands, however, requires the introduction of a further descriptive element in the packing analysis, namely the relative orientation and separation of the halide ligands among neighbouring molecules. To this purpose the minimum intermolecular halogen–halogen distance within each crystal structure (X ··· X) has also been estimated and is reported in Table 1. This separation covers the range 3.6–9.8 Å, but 5.5 and 8.6 Å are the average values which most of the structures analysed seem to be associated with.

Due to the small number of structures forming our sample, our analysis has some obvious limitations in terms of statistical significance. Nevertheless, the information listed in Table 1 suggests that the complexes carrying large halides (Br and I) in bridging bonding mode, as well as Cl atoms in terminal bonding mode, are associated with short X ··· X separations (which cluster about 5.5 Å), whereas complexes carrying large halogen atoms terminally bound tend to have X ··· X separations around 8.6 Å. Deviation from this trend is observed in the case of $[N(PPh_3)_2][Ru_4(CO)_{13}Cl]$ (minimum intermolecular separation between bridging chlorides 9.8 Å), where the reduced size of the anion with respect to the other chloro-substituted compounds is thought to be the main reason for the tendency of the system toward a one-to-one halogen–cation close interaction, together with the less protrusive co-ordination mode of the halide, this spanning the hollow of a 'butterfly' rather than bridging two bonded metal atoms.

All the X ··· X separations are longer than the sum of the van der Waals radii. An exception is the crystal structure of $[N(PPh_3)_2][Os_5(CO)_{15}I]$ where the observed minimum intermolecular halogen–halogen distance (3.610 Å) resembles those observed in many organic compounds.[23]

Differences in the observed packing modes seem to arise from the different type of insulation and electrostatic neutralization of the electron density localized on the halide operated by the counter ions. The shape and degree of flexibility of the counter ions appears to be, in many cases, decisive in determining the type of ionic aggregation in the solid state. Most of the reported structures have been crystallized as salts of PPh_4^+ or $N(PPh_3)_2^+$. These cations carry phenyl groups and are less 'adaptable' to the crystalline environment than cations possessing long and flexible aliphatic arms (NEt_4^+ and NBu_4^+). It appears that with PPh_4^+ or $N(PPh_3)_2^+$ cations the compromise between the need to insulate the negative charge localized on the halide ligands and that to attain high packing efficiency can be better achieved by forming pairs ('dimers') of halide clusters and by trapping the halide ligands into a cage formed by phenyl groups.

The most representative cases will now be discussed in detail. In crystalline $[PPh_4][Ir_6(CO)_{14}Cl]$ and $[PPh_4][Ir_6(CO)_{14}Br]$ the fundamental packing motif is determined by a snake-like mono-dimensional anion aggregation (Figs. 1 and 2, respectively). In crystalline $[N(PPh_3)_2][Ir_6(CO)_{14}I]$, on the other hand, a lower degree of anion–anion interaction is observed. Accordingly, the v.r. value in the latter crystal is lower than in the other two salts (0.46 *versus* 0.56). Although the halogen–halogen distances appear to be strictly comparable for these three compounds, differences in the mutual orientations of the halides have been observed. Fig. 3 clearly shows how the anions in $[N(PPh_3)_2][Ir_6(CO)_{14}I]$ form pairs in which the iodide ligands are on opposite sides. The counter ions (omitted for clarity) occupy the interstices and 'insulate' each cluster pair from the surroundings.

The insulation is attained in two different ways in the three structures. In the cases of $[PPh_4][Ir_6(CO)_{14}Cl]$ and of $[N(PPh_3)_2][Ir_6(CO)_{14}I]$ (Fig. 4), the dihalide units are trapped in a phenyl cage formed by phenyl rings belonging to four surrounding cations. In $[PPh_4][Ir_6(CO)_{14}Br]$, on the other hand, two bromide ligands belonging to two anions are encapsulated by two cations (see Fig. 5).

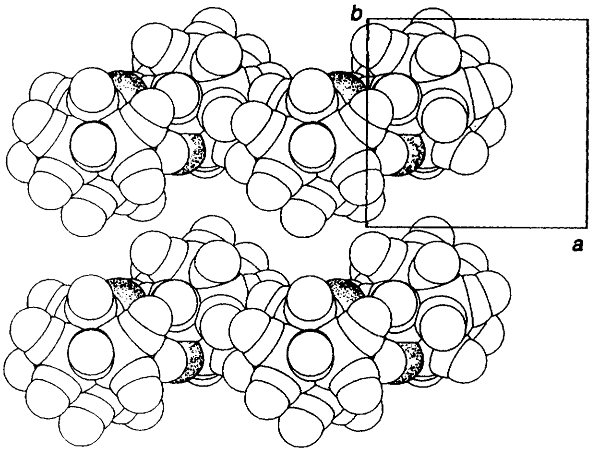

Fig. 1 Space filling projection in the 001 plane of the anionic packing arrangement in crystalline $[PPh_4][Ir_6(CO)_{14}Cl]$. The anions form 'snakes'. Shaded spheres represent the chlorine atoms

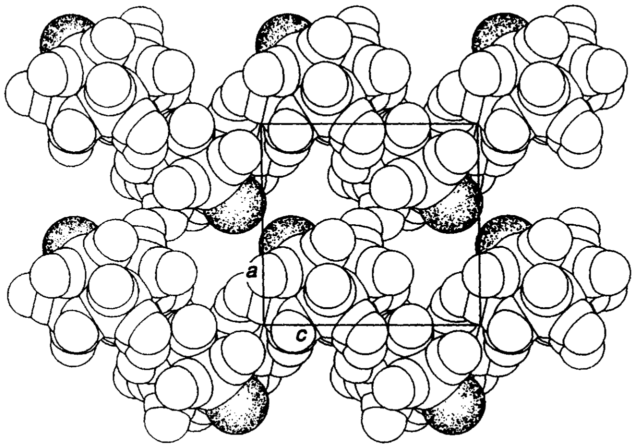

Fig. 2 View down the *b* axis of the anionic packing snake-like arrangement in crystalline $[PPh_4][Ir_6(CO)_{14}Br]$. The bromine atoms (shaded spheres) of the next neighbouring molecules point toward each other

The dianion $[Fe_5C(CO)_{12}Br_2]^{2-}$ is the only example of an anionic carbonyl cluster carrying two bromide ligands terminally bound to the same metal atom. This compound has been successfully crystallized as a salt of the flexible NEt_4^+ cation. Although the carbonyl ligands belonging to neighbouring molecules also appear to participate in the insulation of the two halide ligands, the segregation is mainly achieved by the surrounding cations. The packing arrangement is shown in Fig. 6. The minimum interhalogen distance in this structure is comparable to that observed in $[NEt_4][Co_4(CO)_{11}I]$ (6.245 and 6.860 Å respectively), where the crystallization was attained by using the same cation.

Crystalline $[N(PPh_3)_2][Os_5(CO)_{15}I]$ is the only structure with an intermolecular halogen–halogen distance shorter than the sum of the van der Waals radii. Again a small part of the enclosing cage around the diiodide unit is constituted by carbonyl ligands and a much bigger contribution to the separation of the heteroligands from the surroundings is given by two cations lending two phenyl rings each to the insulating system. This feature closely resembles that observed for longer interhalogen distances of the order of 5.5 Å. The structure is shown in Fig. 7. Although the reason for the existence of such a short halogen–halogen interaction (3.610 Å) has not been fully understood yet, interhalogen distances of this order are not unusual and can also be found in the layered crystal structure of the I_2 molecule itself (3.5 Å).[24]

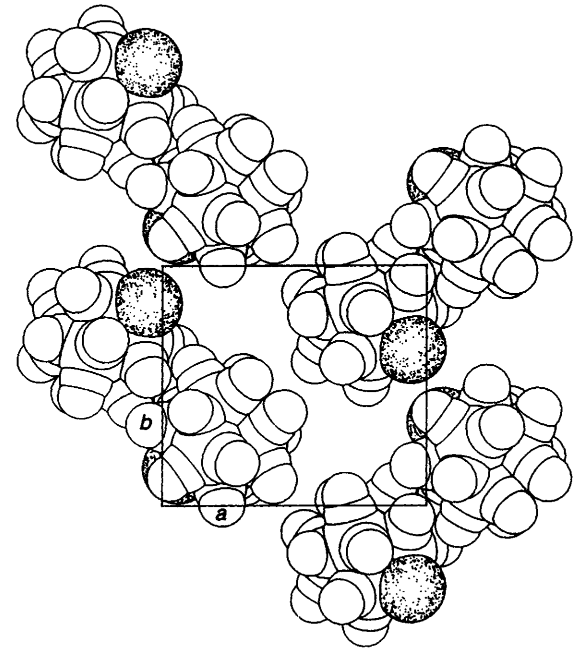

Fig. 3 Anionic packing arrangement in crystalline $[N(PPh_3)_2]$-$[Ir_6(CO)_{14}I]$: view down the *c* axis of the monoclinic cell showing anion–anion pairing. Iodine atoms (shaded spheres) belonging to the next neighbouring molecules face each other in the lattice

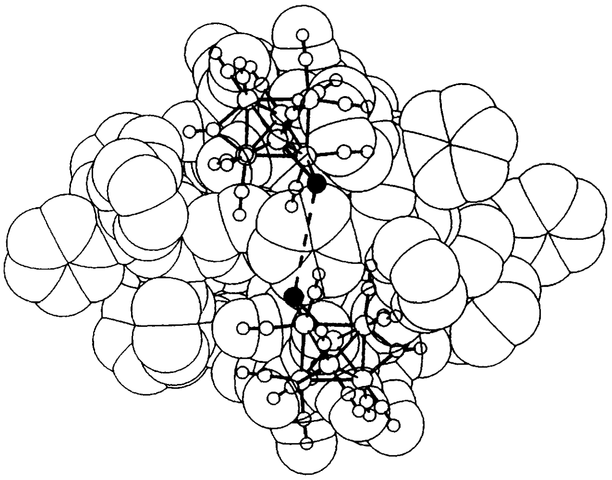

Fig. 4 Space filling diagram of the packing arrangement around the shortest halogen–halogen distance in $[N(PPh_3)_2][Ir_6(CO)_{14}I]$. The insulation of the dihalide system from the surroundings is achieved by means of a phenyl cage. Filled atoms represent the halogen atoms

In crystalline $[N(PPh_3)_2][Rh_6(CO)_{15}Cl]$, in spite of a low v.r. coefficient (0.46), a high degree of interanion aggregation is observed. Layers of loosely packed anions are intercalated with layers of cations. As shown in Fig. 8, the halide ligands are alternated on the two sides of the layers so that rows of iodine atoms face each other. The iodine–iodine separation is 5.842 Å. The insulation from the surroundings is achieved by means of the same type of interaction described above for $[PPh_4]$-$[Ir_6(CO)_{14}Br]$, $[PPh_4][Ir_6(CO)_{14}Cl]$ and others, *viz.* with four phenyl groups of the cations forming the cage.

Conclusion

In previous studies we have been able to show that the main factor controlling the degree of anionic association in molecular salts of binary carbonyl clusters is essentially the relative size of the component ions.[3,4] Large anions crystallizing with small cations are usually associated with mono- or two-dimensional

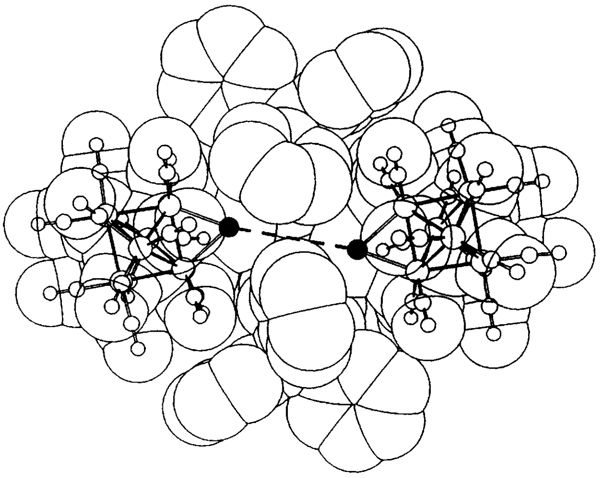

Fig. 5 Space filling diagram of the packing arrangement around the shortest halogen–halogen distance in $[PPh_4][Ir_6(CO)_{14}Br]$. The phenyl cage encapsulates the dihalide system, thus insulating it from the surroundings. Filled atoms represent the halogen atoms

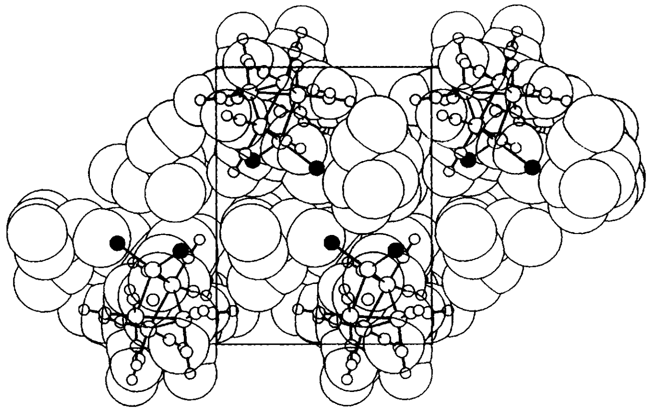

Fig. 6 Space filling diagram of the packing arrangement perpendicular to the *ab* plane in crystalline $[NEt_4]_2[Fe_5C(CO)_{12}Br_2]$. Filled atoms represent the halogen atoms

networks throughout the crystal. The size of the anion becomes a critical factor as the dimension of the cluster increases. This is one of the reasons, for instance, why high nuclearity clusters can be more easily isolated in stable and ordered crystalline materials when the anion charge is high,[5] *viz.* when a large number of cations are 'brought' into the crystal by a single anion. In this way space is used more efficiently and crystal cohesion is guaranteed.[5] In some cases, solvent of crystallization is also required in order to fill in interstices in the crystals.

In this paper we have shown that, as the complexity of the molecular salts increases by placing one or two heteroligands on the anion, additional factors have to be taken into account in order to appreciate the modes of packing and the inter-ion assembly. The rationalization of the crystal structures needs the consideration of two factors: (*i*) the ratio between the relative volumes of the component ions, and (*ii*) the effect that a non-homogeneous charge distribution on the anion surface can have on the formation of ionic aggregates in the lattice. It has been shown that the tendency toward the insulation of the negatively charged halide can be achieved in several ways, depending on the nature and co-ordination mode of the halide ligand itself, as well as on the flexibility of the counter ion. Most of the enclosing systems are made up of cationic phenyl rings or aliphatic chains. The carbonyl ligands belonging to surrounding anions also contribute to the insulation of the halide ligands.

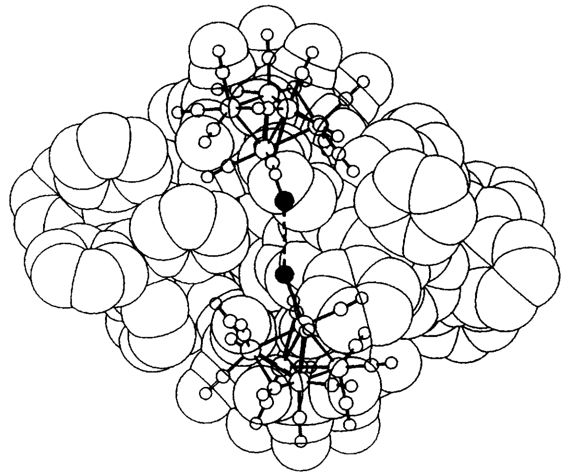

Fig. 7 Space filling diagram of the packing arrangement around the shortest halogen–halogen distance in $[N(PPh_3)_2][Os_5(CO)_{15}I]$. The intermolecular dihalide unit is insulated from the surroundings by two cations lending two phenyl rings each to the enclosing cage. Filled atoms represent the halogen atoms

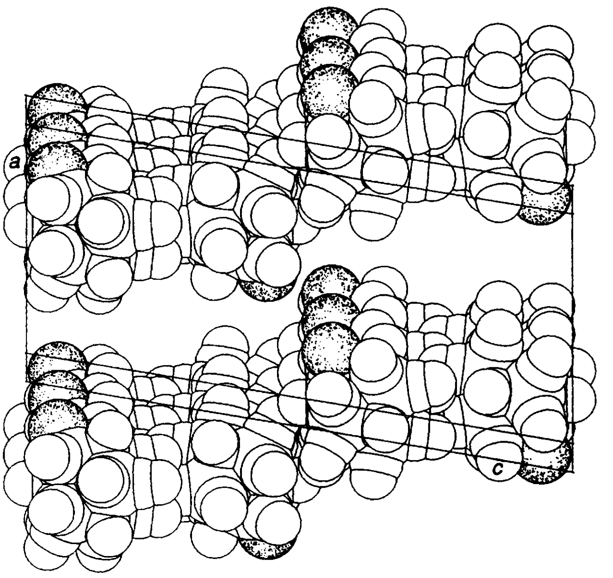

Fig. 8 Anionic packing arrangement in crystalline $[N(PPh_3)_2][Rh_6(CO)_{15}Cl]$. Shaded atoms represent the chlorine atoms. 'Undulated planes' of loosely packed anions are intercalated in the crystal with layers of cations

Two basic patterns have been observed in the $N(PPh_3)_2^+$ and PPh_4^+ salts: a one-to-one close halogen–cation interaction has been found for the structures where the halogen–halogen distance is the longest (*ca.* 8.6 Å), while the trapping of halogen pairs into phenyl cages formed by rings belonging to two (or more) cations has been observed in the case of interhalogen distances of *ca.* 5.5 Å. It is worth recalling here that these two types of cation–anion interactions have been found to constitute the basic packing motifs in the crystal structures of the 'merry-go-round' isomers $[NMe_2(CH_2Ph)_2][Ir_4(CO)_{11}(SCN)]$, and $[N(PPh_3)_2][Ir_4(CO)_8(\mu\text{-}CO)_3(SCN)]$ where there is clear evidence that the negative charge is carried by the SCN group and not delocalized over the whole cluster molecule. In the former crystal the ligands are segregated within a 'cage' generated by four surrounding $[NMe_2(CH_2Ph)_2]^+$ cations, while in the bridged form the crystal contains anionic piles embraced by the $N(PPh_3)_2^+$ cations.[25]

In summary, this study indicates the following.

(*i*) While there is no apparent relationship between the nature of the halide ligand and structure adopted in the crystal, most certainly the formation of either type of pattern described above appears to depend on the size and mode of bonding of the halogen atoms.

(*ii*) Small terminal halogens or large halogens in bridging bonding mode drive towards 'trapping' of the halogen atoms within a cage of counter ions.

(*iii*) Large halogens in terminal bonding mode drive towards the formation of anion rows insulated by cation rows.

(*iv*) With ions of comparable size the packing modes adopted in the solid state are essentially of the type observed for molecular co-crystals, where the main control on the packing choice is exerted by the size and shape of the component particles, *viz*. by the optimization of the van der Waals interactions.

(*v*) Although the presence of a halide might result in an enhanced charge polarization this does not appear to be decisive in driving the crystallization process towards the formation of specific ionic aggregates.

In conclusion, we have evidence that the construction of crystals containing carbonyl-halide anions is essentially based on the packing of large aggregates of the van der Waals type. These aggregates are generated from the component ionic particles by segregating and insulating the most polar parts *via* direct interaction with the cations. The final aggregate is a dimer of anions plus counter ions or a more complex globular object that can then be packed in a molecular-crystal manner.

Acknowledgements

Financial support by the Ministero della Universita' e della Ricerca Scientifica e Tecnologica is acknowledged.

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Received 28th June 1994; *Paper* 4/03904A