Supramolecular Complexation of Alkali Cations through Mechanochemical Reactions between Crystalline Solids

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Abstract: The organometallic zwitterion $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4\text{-}COO)]$ reacts quantitatively as a solid polycrystalline phase with a number of crystalline alkali salts MX ($M = K^+$, Rb^+, Cs^+, NH_4^+; $X = Cl^-$, Br^-, I^-, PF_6^-, although not in all cation/anion permutations) to afford supramolecular complexes of the formula $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2{\cdot}M^+X^-$. In some cases, the mechanochemical complexation requires *kneading* of the two solids with a catalytic amount of water. The characterization of the solid-state products has been achieved by a combination of X-ray single-crystal and powder-diffraction experiments. The hydrogen-bonding interactions have been investigated by solid-state NMR spectroscopy. The mechanochemical reactions imply a profound solid-state rearrangement accompanied by breaking and forming of O−H···O hydrogen-bonding interactions between the organometallic molecules. All compounds could also be obtained by solution crystallization of the inorganic salts in the presence of the organometallic unit. The solid-state complexation of alkali cations by the organometallic zwitterion has been described as a special kind of solvation process taking place in the solid state.

Keywords: crystal engineering • hydrogen bonds • mechanochemistry • NMR spectroscopy • organometallic compounds • solid–solid reactions

Introduction

Mechanically induced solid-state reactions are attracting the interest of scientists engaged in the quest for sustainable chemical processes.[1]

Solvent-free reactions, such as those occurring in the solid state between molecules, between two solids, or between a solid and a gas, are important from both the environmental and topochemical viewpoints.[2] Moreover, crystal engineering strategies can be exploited for the design and construction of molecular crystals that take part in solvent-free reactions with molecules or molecular aggregates.[3]

It is useful to distinguish solvent-free reactions on the basis of the interactions that are involved in the solid-state process. When the solid-state reaction requires rupture and formation of covalent bonds,[4] the product is a new molecule, and the resulting solid is usually constituted by a unique phase. In such a case, attention is generally focused on the product molecule.

When the solid-state process proceeds by breaking and forming noncovalent interactions (such as hydrogen bonds), the crystalline product is the result of the supramolecular association of two or more units. This latter process is considered as a *supramolecular reaction* between solid supermolecules.[5] In this case, the main interest lies in the product crystal. Similar reasoning applies to the reaction between a molecular solid and a vapor to yield a new crystalline solid (Scheme 1).

Mechanochemical reactions have been known for a long time and may yield products that differ in stoichiometry or topology from those obtained in solution.[6] Such reactions have been exploited mainly with inorganic solids (alloying, milling of soft metals with ceramics, activation of minerals for catalysis, extraction, preparation of cements);[7] however, they are beginning to be appreciated for the preparation of molecular materials as well.[8] For example, condensation between *o*-phenylenediamines and 1,2-dicarbonyl compounds

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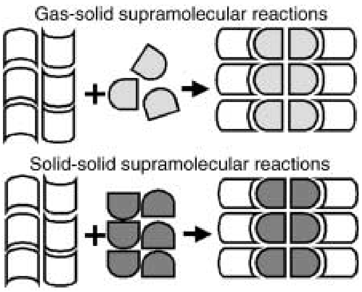


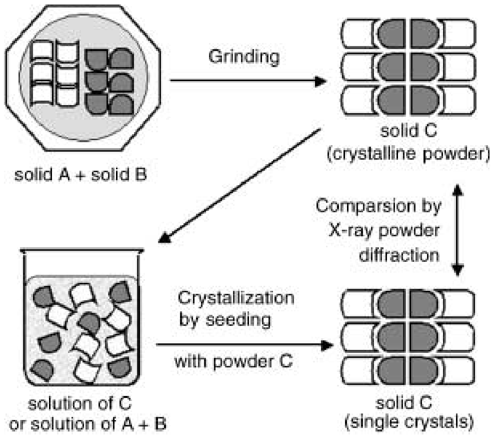
Scheme 1. Schematic representation of the relationship between a gas–solid reaction and a reaction between two molecular solids in solvent-free supramolecular processes.

can be effected by ball milling,[9] whilst phosphonium salts have been prepared by milling triphenylphosphone with solid organic bromides,[10a] and supramolecular self-assembly[10b] and coordination polymers[10c] have been obtained by grinding inorganic transition-metal salts with appropriate ligands.

It has been recently shown that solid–solid reactions are often accelerated by the addition of catalytic quantities of solvent.[11] This procedure, also known as *kneading*, is very often exploited in the preparation of inclusion compounds (e.g. cyclodextrins) for pharmaceutical applications and in many other physical processes requiring mixing and reaction of condensed phases.[12] The *kneading* procedure has also been applied in this study.

Before the results are discussed, it is worth mentioning that one of the main difficulties of solid–solid mechanochemical processes, with respect to those in solution, arises from the characterization of the reaction product, which is usually obtained as a polycrystalline powder. In the case of complex supramolecular systems, such as those discussed herein, the lack of precise structural information, usually obtained from single-crystal X-ray diffraction, is often an obstacle to the development of the research field. In some cases, the problem can be circumvented by means of *seeding*, that is, by the use of preformed microcrystals (such as those obtained by grinding) of the desired phase to grow the desired material as crystals of suitable size from the solution. One needs to be aware of the fact that, for the controlled growth by seeding to be successful, it is necessary not to dissolve the material entirely: nuclei must remain undissolved for the crystallization process to proceed towards the desired phase.[13] Seeding procedures are commonly employed in the pharmaceutical industry to ensure that the desired crystal form is always obtained from a preparative process.[14]

Once single crystals have been obtained, it is often possible to confirm a posteriori that the material obtained from solution crystallization and that yielded by solid–solid processes possess the same structure by comparing the observed X-ray powder-diffraction pattern (XRPD) with that computed on the basis of the single-crystal structure. This approach has been used previously by us and by others to determine the structure of polycrystalline products obtained by "non-solution" methods (grinding, dehydration, thermal treatment).[15] A further point to note is that crystallization from solution does not always yield the same product as that obtained by mechanical treatment.[16] This is particularly relevant in those cases in which crystallization from solution is under kinetic control and leads to crystallization of those species that nucleate first and form less soluble nuclei. The process described above is pictured in Scheme 2.



Scheme 2. Schematic representation of the relationship between crystallization from solution, solid-state mixing (grinding, kneading, milling), and crystallization by means of seeding in order to obtain single-crystal structures of the compounds prepared mechanochemically.

In Bologna, we have utilized organometallic building blocks to prepare novel molecular crystalline materials and to exploit the variable valence, spin, and charge states of coordination complexes.[17] Interesting results have also been obtained from solid–gas reactions.[18]

We have also exploited mechanochemical processes in the preparation of a series of novel organic and hybrid organic–organometallic hydrogen-bonded network compounds,[19] for which solid-state NMR methods have also been used to evaluate the hydrogen-bonding patterns.

Herein, we report the mechanochemical solid–solid preparation of hybrid organometallic–inorganic salts obtained by reacting the organometallic zwitterion $[Co^{III}(\eta^5\text{-}C_5H_4\text{-}COOH)(\eta^5\text{-}C_5H_4COO)]$ (**1**) with a number of alkali metal salts MX ($M = K^+, Rb^+, Cs^+, NH_4^+$; $X = Cl^-, Br^-, I^-, PF_6^-$, although not in all cation/anion permutations, see below). In all cases, exact information about the solid-state structures of the reaction products was obtained by single-crystal X-ray diffraction experiments performed on crystals obtained from the reaction powders. Information on the hydrogen-bonding nature and on the relationship between structures in solution and those obtained in the solid-state by mechanical grinding was gained by a combination of solution and solid-state NMR spectroscopy.

Our aim is to address the following questions:

1) Is the solid-state complexation observed with KBr[20] transferable to other alkali metal salts? We know from a previous study that **1** complexes with $M[PF_6]$[22] salts ($M = K^+, Rb^+, Cs^+$, and NH_4^+) to form almost isostructural "cages" in which the zwitterions encapsulate the cations.

2) What is the relationship between the products obtained by grinding and by crystallization from solution? Are there compounds that can be obtained from solution but which are impossible to prepare by grinding or vice versa?
3) What can we learn from solid-state NMR with regard to the nature of the processes and of the hydrogen-bonding interactions within the adducts?

Results and Discussion

It may be of interest to the reader to know that the beginning of this work was serendipitous. It all started with the accidental discovery of large differences in the CO stretching frequency region in the IR spectra of **1** measured in Nujol and in KBr pellets in the course of our studies of solid–gas reactions of **1**. The IR spectra are shown in Figure 1.[20] Our previous experience with solid–solid processes alerted us to the possibility that the differences we were observing could be indicative of the occurrence of a solid-state reaction. It is well-established that alkaline halogenides, such as KBr, that are used for IR pellets are highly polar compounds, and, in some cases, they are known to interact with the embedded sample[21] causing an alteration of the absorption frequencies with respect to those measured in solution or Nujol. Therefore, we decided to investigate the possibility of purposely reacting solid **1** with solid KBr, and indeed, we observed the quantitative formation of the adduct $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2{\cdot}K^+Br^-$ ($\mathbf{1}_2{\cdot}K^+Br^-$), which results from the complexation of the alkali cation by the zwitterion **1**.

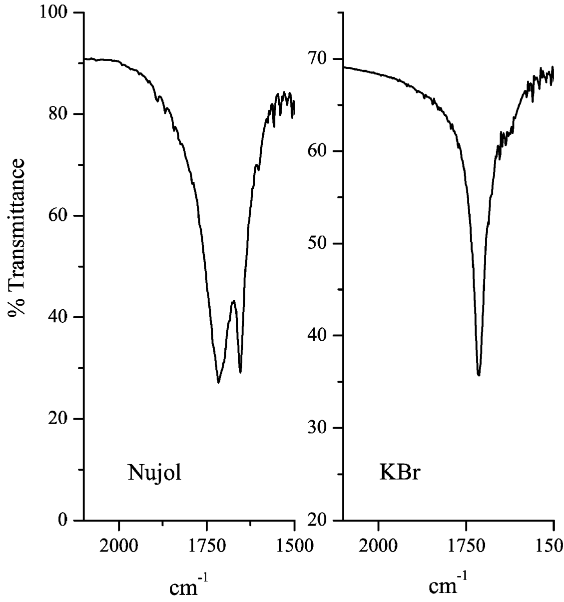


Figure 1. Comparison between the IR spectra obtained for the organometallic zwitterion $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ (**1**) in Nujol and KBr.

The preparation and characterization procedure of the solid-state adducts follows the sequence:

1) Manual grinding of the solid mixture with a mortar and pestle.
2) Measurement of the X-ray powder diffraction (XRPD) to obtain a diffractogram.
3) Crystallization from solution, by means of seeding, of the polycrystalline material obtained by grinding. In order to understand the importance of the seeding technique, complexations were also carried out in solution by dissolving **1** and the desired salt in a 2:1 stoichiometry, and by comparing the measured XRPDs with those obtained by grinding.
4) Determination of the single-crystal structure by X-ray diffraction on single crystals recovered from step 3.
5) Comparison of the observed XRPD [step 2] with that calculated on the basis of the single-crystal structure [step 4].

In view of the analogies in preparation and the likelihood of the structures obtained by solid-state complexation, the supramolecular complex $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2{\cdot}Cs^+I^-$ ($\mathbf{1}_2{\cdot}Cs^+I^-$) is used to demonstrate the characterization procedures used in this work.

We will first discuss the structural features obtained from single-crystal X-ray diffraction. Compound $\mathbf{1}_2{\cdot}Cs^+I^-$ is isostructural with the members of the family of hexafluorophosphate salts $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2{\cdot}M^+[PF_6]^-$ ($\mathbf{1}_2{\cdot}M^+[PF_6]^-$, M = K^+, Rb^+, Cs^+, $[NH_4]^+$) previously obtained from the cationic acid $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2][Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]^+[PF_6]^-$ by treatment with MOH or ammonia.[22] Compound $\mathbf{1}_2{\cdot}Cs^+I^-$ is thus characterized by the presence of a supramolecular cage formed by four zwitterionic molecules encapsulating the Cs^+ cations. The cage is sustained by O–H···O hydrogen bonds between carboxylic (COOH) and carboxylate (COO^-) groups, and by C–H···O bonds between $\text{-}CH_{Cp}$ and -CO groups, while the I^- ions form layers in between the cationic complexes (Figure 2).

The structure determination was instrumental to the identification and characterization of the product obtained by solid-state grinding. Figure 3 shows a comparison of the XRPD patterns of polycrystalline $\mathbf{1}_2{\cdot}Cs^+I^-$, obtained by grinding the reagents together, and that calculated on the basis of the single-crystal structure described above.

It is worth stressing that the solid-state reaction implies that the O–H···O hydrogen-bonded chains present in crystalline **1** are disrupted with formation of O–H···O hydrogen-bonded dimeric units. The whole process (Figure 4) also requires a change from *trans* to *cis* in the conformation of the C_5H_4-COO/COOH units, with formation of cages able to encapsulate the alkali cations by means of O···Cs^+ interactions. The overall arrangement of the eight COO^-/COOH groups around the cation is reminiscent of crown-ether complexation, even though the cage components are held together by hydrogen bonds rather than by covalent bonds; hence the

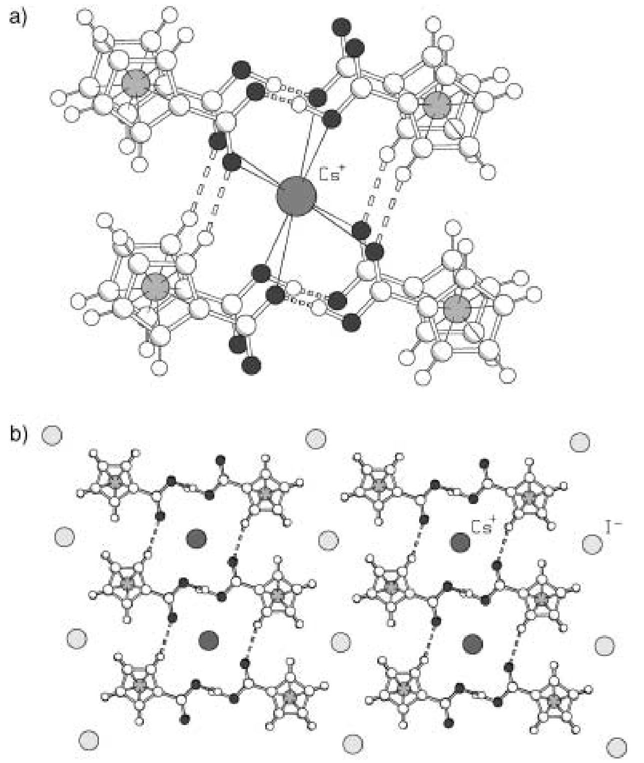


Figure 2. The structure of $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2{\cdot}Cs^+I^-$ ($\mathbf{1}_2{\cdot}Cs^+I^-$) obtained by crystallization from water. a) The supramolecular cage formed by encapsulation of the Cs^+ ion within a cage formed by four zwitterionic molecules, dimerized through O–H···O hydrogen bonds between carboxylic -COOH and carboxylate -COO⁻ groups. b) The I^- ions form aggregates in layers between the organometallic layers.

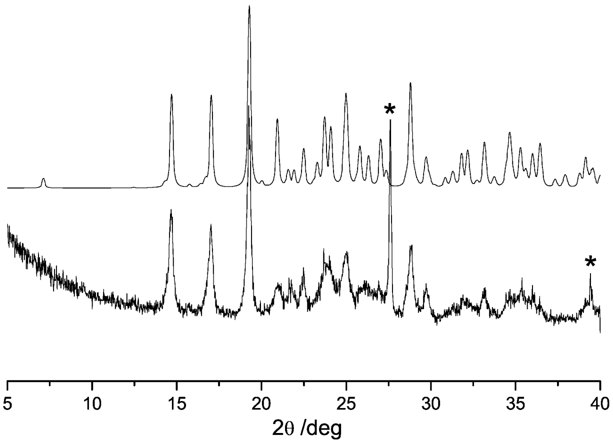


Figure 3. Comparison between the experimental XRPD obtained from (bottom) polycrystalline $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2{\cdot}Cs^+I^-$, and that calculated (top) on the basis of the crystal structures shown in Figure 2 for $\mathbf{1}_2{\cdot}Cs^+I^-$. Note the extra peaks assigned to the presence of a small amount of unreacted CsI.

epithet of "supramolecular crown ethers" for compounds of this type.

A similar procedure was applied to all compounds listed in Table 1. It can be seen that, while all bromide salts directly form the cage compound by simple grinding, and this applies also to the case of CsI discussed above, the preparation of the rubidium and cesium chlorides, as well as of the potassium and rubidium iodide derivatives, required the *kneading* procedure, in our case, the addition of 1 μL of water per 20 mg of reactants. Although a paste is not formed and the reactants are still powdery, the reactions proceed in quantitative yields. It is important to appreciate that water, even in tiny amounts, may act as a microsolution environment that helps to overcome lattice energies and to activate the dissolution, diffusion, and crystallization sequence that will eventually lead to the formation of the polycrystalline product.

Table 1. Summary of solid-solid reactions of **1** with MX salts.

1	Cl^-	Br^-	I^-
K^+	no reaction	$\mathbf{1}_2{\cdot}K^+Br^-$	$\mathbf{1}_2{\cdot}K^+I^-$
Rb^+	$\mathbf{1}_2{\cdot}Rb^+Cl^-$	$\mathbf{1}_2{\cdot}Rb^+Br^-$	$\mathbf{1}_2{\cdot}Rb^+I^-$
Cs^+	$\mathbf{1}_2{\cdot}Cs^+Cl^-$	$\mathbf{1}_2{\cdot}Cs^+Br^-$	$\mathbf{1}_2{\cdot}Cs^+I^-$

As mentioned in the introduction, it has already been established that solid–solid reactions are sometimes accelerated by the addition of catalytic quantities of solvent.[11]

With respect to the information collected in Table 1, it can be added that the role of water is fundamental to the reaction. The water absorbed from the air during the grinding of bromides and CsI[23] is sufficient to enable the reaction, while in the other cases a slightly larger amount of water is required (kneading technique). Grinding dry KBr and dry **1** in an anhydrous atmosphere gave no reaction. It is also interesting to observe that **1** does not react with KCl either with or without *kneading* or in solution so that the resulting mixture consists of solid KCl and **1**.

Although it was possible to collect single-crystal X-ray data (see the Experimental Section) from all products, this was not strictly necessary because the "cage" compounds are nearly isomorphous and the respective observed XRPD patterns show similar features. The grinding experiment of **1** was also carried out with hexafluorophosphate salts, such as $K[PF_6]$ and $[NH_4][PF_6]$, which are known to yield adducts of the type $\mathbf{1}_2{\cdot}[NH_4/K]^+[PF_6]^-$ from solution. These two inorganic salts were selected because crystalline $\mathbf{1}_2{\cdot}[NH_4/K]^+[PF_6^-]$ possess similar structural features to $\mathbf{1}_2{\cdot}K^+Br^-$, and the cages are almost isostructural. A comparison of the calculated and observed powder diffraction patterns confirmed that the mechanochemical reaction had led to encapsulation, as expected.

Solid-state structures determined from single-crystal X-ray experiments: Although the main focus of this paper is on solid-state complexation of alkali metal cations with the organometallic unit **1**, the availability of a small database of nearly isomorphous compounds allows useful comparisons to be made between noncovalent interactions, in particular the inter-zwitterion O···O bonds, and the interactions of the organometallic moiety with different alkali metal cations. The structural features of the crystalline materials, whose structures have been determined by single-crystal X-ray diffraction, can be summarized as follows (see also Table 2). The following features are shared:

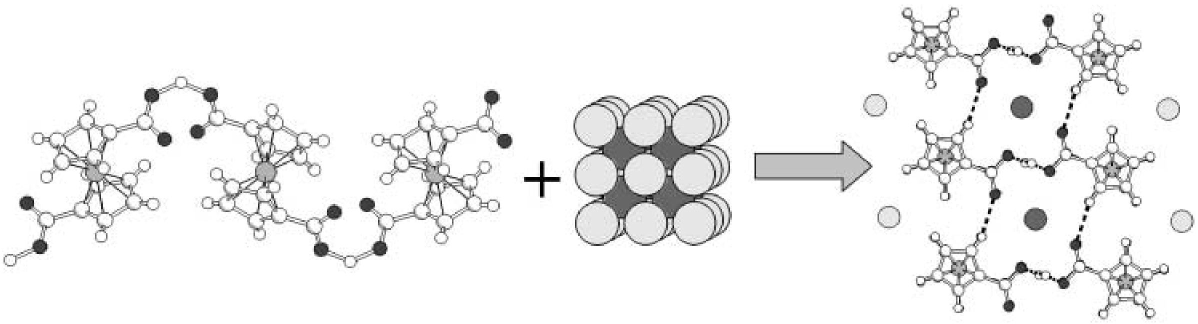


Figure 4. The supramolecular rearrangement leading from solid **1** and solid CsI to solid $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]_2\cdot Cs^+I^-$. Note how the O–H···O hydrogen-bonded chains need to be broken to allow formation of the "crown ether-like" supramolecular cages.

Table 2. Relevant structural parameters for compounds characterized by single-crystal X-ray diffraction.

Compound	O···O [Å]	(C)H···O [Å][a]	$M^+\cdots O < 3.5$ Å
$\mathbf{1}_2\cdot Rb^+Cl^-$	2.463(4)	2.365 2.306	2.833(3) 3.148(3) 3.039(3) 3.180(3)
$\mathbf{1}_2\cdot Cs^+Cl^-$	2.465(10)	2.362 2.416	2.968(7) 3.205(7) 3.221(7) 3.246(7)
$\mathbf{1}_2\cdot K^+Br^-$	2.456(4)	2.387 2.318	2.968(7) 3.205(7) 3.221(7) 3.246(7)
$\mathbf{1}_2\cdot Rb^+Br^-$	2.475(7)	2.366 2.410	2.867(5) 3.019(6) 3.199(5) 3.222(5)
$\mathbf{1}_2\cdot Cs^+Br^-$	2.440(5)	2.414 2.369	2.969(7) 3.211(7) 3.229(6) 3.273(6)
$\mathbf{1}_2\cdot K^+I^-$	2.448(4)	2.310 2.368	2.751(4) 2.944(4) 3.114(4) 3.204(4)
$\mathbf{1}_2\cdot Rb^+I^-$	2.463(4)	2.369 2.311	2.849(3) 3.050(3) 3.156(3) 3.207(3)
$\mathbf{1}_2\cdot Cs^+I^-$	2.482(7)	2.427 2.366	2.996(5) 3.216(6) 3.227(5) 3.282(5)
$\mathbf{1}_2\cdot K^+[PF_6]^-$	2.454(4)	2.311 2.368	2.792(5) 2.824(6) 2.857(6) 3.463(6)
$\mathbf{1}_2\cdot Rb^+[PF_6]^-$	2.455(2)	2.327 2.355	2.871(5) 3.014(5) 3.143(6) 3.227(6)
$\mathbf{1}_2\cdot Cs^+[PF_6]^-$	2.465(3)	2.374 2.412	3.005(2) 3.175(2) 3.226(2) 3.290(2)

[a] The esd values for C–H···O are on average the same as those of the corresponding $M^+\cdots O$.

1) As mentioned above, all cations are encapsulated within cages formed by four molecules of **1**. The cages share a face (viz. two units of **1**) so that the stoichiometry of the systems is $\mathbf{1}_2\cdot M^+X^-$. The walls of the cage consist of two *dimeric units* of **1** held together by a twin O–H···O hydrogen bond and by two C–H···O bonds, the latter involve the H atoms of the C_5H_4 systems and the lone pairs on the carboxylic oxygen atoms.
2) The hydrogen bond framework results in eight oxygen atoms from the carboxylic/carboxylate groups pointing inwards to form a strongly nucleophilic cage in which the cations are encapsulated by $M^+\cdots O$ interactions.
3) The basic packing motif can be described as a sequence of C–H···O hydrogen-bonded **1**+**1** dimers encapsulating the cations, while the anions occupy cavities between the cages. The anions are not involved in strong $C\text{–}H^{\delta+}\cdots X^{\delta-}$ interactions with the cyclopentadienyl ligands, while $[PF_6]^-$ stabilizes the structure via $C\text{-}H^{\delta+}\cdots F^{\delta-}$ interactions.
4) The hydrogen-bond framework permits a limited degree of flexibility, as demonstrated by an analysis of the data in Table 2. While O–H···O and C–H···O interactions appear to vary only slightly as the nature of the guest changes [O···O distances range from 2.440(5) Å in to $\mathbf{1}_2\cdot Cs^+Br^-$ to 2.482(7) Å in $\mathbf{1}_2\cdot Cs^+I^-$, C–H···O distances are in the range 2.310(3)–2.427(3) Å], a comparison of $O\cdots M^+$ distances shows that the *shape* of the cage changes slightly when the guest species is changed.
5) As previously noted, O···O distances within the zwitterionic **1** dimers are shorter than those usually observed for neutral O–H···O carboxylic groups, while they compare well with *charged* hydrogen bonds, for example, $\text{-COO}^-\cdots\text{HOOC-}$ between partially deprotonated polycarboxylic acids. The structural evidence accumulated in this work indicates that the negative charge is localized on the deprotonated -COO group rather than over the whole molecular unit. Therefore, the two bonds are better described as charge-assisted $O\text{–}H\cdots O^-$ bonds than as neutral O-H···O bonds.

The data in Table 2 allows a comparison between the various cages. If one takes the difference between shortest and longest $M^+\cdots O$ distances as a "distortion" parameter, it is clear that the more "cubic" cages are obtained with Cs^+, while the extent of deformation increases as the cation size decreases in the order Cs^+, Rb^+, K^+, irrespective of the nature of the halide anion. However, in the previously determined structure of $\mathbf{1}_2{\cdot}K^+[PF_6]^-$, the distortion is much larger than in $\mathbf{1}_2{\cdot}K^+Br^-$ and $\mathbf{1}_2{\cdot}K^+I^-$, possibly as a consequence of the octahedral vs. spherical shape of the anions. The need to optimize directional interactions of the C–H···F type should also be taken into account.

The zwitterion **1** self-assembles around a great variety of monovalent cations. Beside the conceptual analogy, albeit in the solid state, with crown-ether complexation[24] the hydrogen bond aggregation is reminiscent of the so-called "G quartets" formed around alkali cations by guanosine.[25a] Very recently, analogous pentamers formed by isoguanosine around Cs^+ have also been described.[25b] Guanosine and isoguanosine supramolecular aggregates are sustained by N–H···N and N–H···O hydrogen bonds, while C–H···O bonds play a fundamental role in the aggregation of the cage-salts $\mathbf{1}_2{\cdot}M^+X^-$ and $\mathbf{1}_2{\cdot}[M/NH_4]^+[PF_6]^-$.

Solid-state NMR experiments: ^{13}C CPMAS NMR spectroscopy has been widely used to obtain information about solid structures and supramolecular interactions in the solid state as well as to identify interactions in crystalline and amorphous material. In fact, ^{13}C CPMAS NMR spectroscopy is a useful tool particularly when solids do not exhibit the long-range order essential for a diffraction study, precluding obtaining detailed structural information from these techniques, and when the interaction involve hydrogen atoms because of the intrinsic limitations of X-ray diffraction when dealing with hydrogen atom positions. This technique has the advantage over other solid-state techniques (i.e. IR spectroscopy) of giving rise to a better resolution, and of being inherently quantitative. These features are particularly useful in the structural analysis of disordered and amorphous systems, and the information gained is often complementary to that obtained by X-ray structure analysis.

The ^{13}C CPMAS NMR spectrum of $\mathbf{1}_2{\cdot}Cs^+I^-$ is shown in Figure 5. The spectrum reveals the presence of a sharp peak at $\delta = 166.3$ ppm and of a broader resonance centered at $\delta \approx 91.3$ ppm: the former is assigned to the carboxylic groups and the latter is assigned to the partial overlapping of the different cyclopentadienyl carbon atoms of the cobaltocenium moiety. As observed previously,[26] the presence of only one resonance signal for the carboxylic groups of $\mathbf{1}_2{\cdot}Cs^+I^-$ is attributed to the fast proton exchange rate on the NMR timescale between the carboxylic and the carboxylate groups.

The expanded carboxylic regions in ^{13}C CPMAS NMR spectra for the compounds $\mathbf{1}_2{\cdot}M^+I^-$ ($M^+ = K^+, Rb^+, Cs^+$) are compared in Figure 6, and the ^{13}C data are reported in Table 3.

The first evidence is that the K^+, Rb^+, and Cs^+ adducts with the zwitterions **1** do not show significant differences in the carboxylic chemical shift (except a limited downfield shift on descending the alkaline series) and in the linewidth, in agreement with a substantial similarity of the three X-ray structures obtained from the single-crystal X-ray analysis.

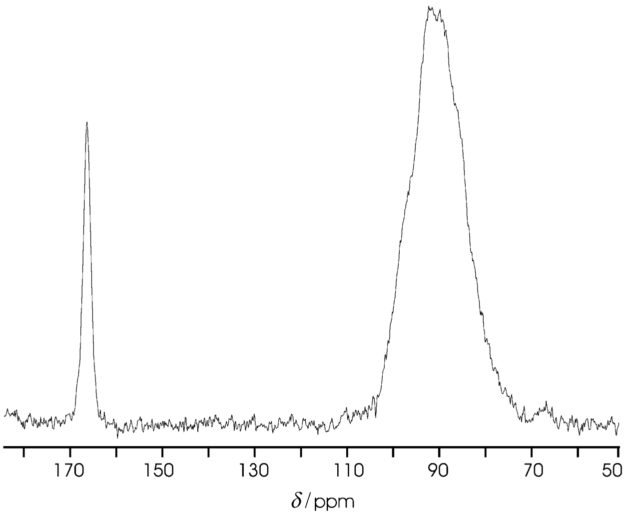


Figure 5. The ^{13}C CPMAS NMR spectrum of $\mathbf{1}_2{\cdot}Cs^+I^-$ obtained at a spinning speed of 6000 Hz.

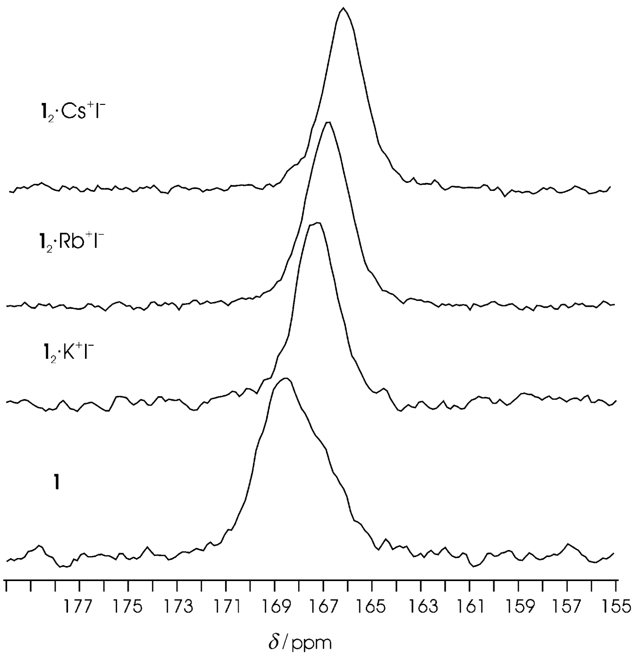


Figure 6. Comparison of the expanded carboxylic regions in ^{13}C CPMAS NMR spectra for the compounds $\mathbf{1}_2{\cdot}X^+I^-$ ($X^+ = K^+, Rb^+, Cs^+$).

Table 3. Comparison between the ^{13}C CPMAS NMR data.

	Cl^-	Br^-	I^-
$\mathbf{1}_2{\cdot}K^+$	no reaction	167.2 COOH 91.0 Cp	167.2 COOH 90.1 Cp
$\mathbf{1}_2{\cdot}Rb^+$	167.2 COOH 91.1 Cp	167.0 COOH 92.3 Cp	166.8 COOH 90.6 Cp
$\mathbf{1}_2{\cdot}Cs^+$	166.8 COOH 91.3 Cp	166.6 COOH 92.0 Cp	166.3 COOH 91.3 Cp
1	168.3 COOH 91.1 Cp		
2	168.5 163.2 88.4 Cp 96.5 shoulder		

There are three major factors that influence the chemical shift of the carboxylic group in the solid state: 1) the chemical structure of the anion including factors, such as conformations and the bonding involving carboxylate oxygen atoms, 2) the chemical structure of the cation, and 3) the crystallographic symmetry and solid-state packing.

Unfortunately, there is currently insufficient data available to separate the contribution of all these factors. Based on the specific pattern of the carboxyl chemical shifts, compounds with known crystal structure can be used as model compounds to study the relationship between structural types and ^{13}C CPMAS NMR spectroscopic data. For this reason, we also investigated the salt $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)][Co^{III}(\eta^5\text{-}C_5H_4COOH)_2][PF_6]$ (**2**), which contains a dimer formed between the zwitterion molecule **1** and the fully protonated, cationic, dicarboxylic acid complex $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]^+$. This compound was previously synthesized and structurally characterized.[22]

The structures of the crystallographically characterized products can be rationalized in terms of a strong anion–cation interaction that appears to be influenced by the size of the cations and the tendency to maximize hydrogen bonding in the lattice.

Conclusion

Mechanochemistry involves solid-state reactions caused by mechanical energy. Mechanochemical methods (grinding, kneading) are often regarded as fundamentally "*nonchemical*" by more traditional solution chemists who consider the solvent to be the typical environment for a chemical reaction. This attitude, however, is rapidly changing and alternative solid-state preparation routes, to old and new chemicals, are becoming increasingly important.[1–3] Even in the burgeoning field of supramolecular chemistry, solvent-free synthetic procedures are being considered as viable alternative routes for the preparation of molecular aggregates. These processes are of obvious interest in crystal engineering studies where ways for the bottom-up construction of molecular materials from molecular or ionic building blocks are being sought.

The discovery that supramolecular aggregation of the organometallic complex **1** around a variety of alkali metal cations and in various salts can be achieved by means of solvent-free solid–solid reactions opens new avenues to our crystal engineering endeavor (which is focused on the possibility of controlling breaking and formation of supramolecular bonding interactions between ions). We commented earlier on the topological analogy between the complexation of cations of appropriate size by $[Co^{III}(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$ and the formation of supramolecular crown ethers.

In this study, we have shown that the organometallic species **1** is able to react in the solid state with a variety of alkali metal salts. However, there appears to be a rather precise limit with regard to the size of anions and cations that is required to obtain the kind of complexation discussed herein, for example, encapsulation of the alkali metal cations by four molecules of **1**. We have evidence that chlorides only reacted with the larger cations, Rb^+ and Cs^+, while iodides can also form cages with K^+. In this respect, we need to mention that, thus far, we have been unable to obtain a reaction with KCl. We are still at a preliminary stage of investigation for compounds obtained with LiX and NaX ($X = Cl^-, Br^-, I^-$). We have evidence for the formation of a mixture of phases; however, we have been unable to characterize these fully. It is possible that the smaller size of the two cations might require that water molecules are brought into the crystal as "space fillers" thus generating different stoichiometries. We hope to be able to report on these adducts in the near future.

As on previous occasions, solid-state NMR spectroscopy has proved to be an invaluable tool for the understanding of the nature of the intermolecular interactions that keep the "cages" together and also for appreciating the relationship between solution and solid-state measurements. We plan to extend our studies to a number of inorganic salts to test the selectivity of the solid–solid complexation with respect to a mixture of different salts.

Experimental Section

Complex **1** was obtained as previously reported.[22] All starting materials were purchased from Aldrich. Reagent-grade solvents and doubly distilled water were used. In all cases, correspondence between the structure of the solid residue and that obtained by single-crystal X-ray diffraction was ascertained by comparing measured X-ray powder diffractograms with those calculated on the basis of the single-crystal experiments.

Solid-state syntheses

1_2·Rb$^+$Cl$^-$: Complex **1** (0.22 mmol, 30 mg) and RbCl (0.11 mmol, 26 mg) were manually ground in an agate mortar for 10 min after the addition of water (1 μL) to give a quantitative reaction.

1_2·Cs$^+$Cl$^-$: Complex **1** (0.22 mmol, 30 mg) and CsCl (0.11 mmol, 37 mg) were manually ground in an agate mortar for 10 min after the addition of water (1 μL) to give a quantitative reaction.

1_2·Rb$^+$Br$^-$: Complex **1** (0.22 mmol, 30 mg) and RbBr (0.11 mmol, 36 mg) were manually ground in an agate mortar for 10 min.

1_2·Cs$^+$Br$^-$: Complex **1** (0.22 mmol, 30 mg) and CsBr (0.11 mmol, 47 mg) were manually ground in an agate mortar for 10 min.

1_2·K$^+$I$^-$: Complex **1** (0.22 mmol, 30 mg) and KI (0.11 mmol, 37 mg) were manually ground in an agate mortar for 10 min after the addition of water (1 μL) to give a quantitative reaction.

1_2·Rb$^+$I$^-$: Complex **1** (0.22 mmol, 30 mg) and RbI (0.11 mmol, 47 mg) were manually ground in an agate mortar for 10 min after the addition of water (1 μL) to give a quantitative reaction.

1_2·Cs$^+$I$^-$: Complex **1** (0.22 mmol, 30 mg) and CsI (0.11 mmol, 57 mg) were manually ground in an agate mortar for 10 min.

Solution syntheses

1_2·Rb$^+$Cl$^-$: Complex **1** (0.22 mmol, 30 mg) and RbCl (0.11 mmol, 26 mg) were dissolved in water (5 mL). Crystals suitable for X-ray single-crystal diffraction were obtained by slow evaporation of the water. The same kind of crystals were obtained by crystallization from water of the ground powder of **1** with the alkali metal salt.

1_2·Cs$^+$Cl$^-$: Complex **1** (0.22 mmol, 30 mg) and CsCl (0.11 mmol, 37 mg) were dissolved in water (5 mL). Crystals suitable for X-ray single-crystal diffraction were obtained by slow evaporation of the water. The same kind of crystals were obtained by crystallization from water of the ground powder of **1** with the alkali metal salt.

1_2·Rb$^+$Br$^-$: Complex **1** (0.22 mmol, 30 mg) and RbBr (0.11 mmol, 36 mg) were dissolved in water (5 mL). Crystals suitable for X-ray single-crystal diffraction were obtained by slow evaporation of the water. The same kind of crystals were obtained by crystallization from water of the ground powder of **1** with the alkali metal salt.

$\mathbf{1}_2\cdot\mathrm{Cs}^+\mathrm{Br}^-$: Complex **1** (0.22 mmol, 30 mg) and CsBr (0.11 mmol, 47 mg) were dissolved in water (5 mL). Crystals suitable for X-ray single-crystal diffraction were obtained by slow evaporation of the water. The same kind of crystals were obtained by crystallization from water of the ground powder of **1** with the alkali metal salt.

$\mathbf{1}_2\cdot\mathrm{K}^+\mathrm{I}^-$: Complex **1** (0.22 mmol, 30 mg) and KI (0.11 mmol, 37 mg) were dissolved in water (5 mL). Crystals suitable for X-ray single-crystal diffraction were obtained by slow evaporation of the water. The same kind of crystals were obtained by crystallization from water of the ground powder of **1** with the alkali metal salt.

$\mathbf{1}_2\cdot\mathrm{Rb}^+\mathrm{I}^-$: Complex **1** (0.22 mmol, 30 mg) and RbI (0.11 mmol, 47 mg) were dissolved in water (5 mL). Crystals suitable for X-ray single-crystal diffraction were obtained by slow evaporation of the water. The same kind of crystals were obtained by crystallization from water of the ground powder of **1** with the alkali metal salt.

$\mathbf{1}_2\cdot\mathrm{Cs}^+\mathrm{I}^-$: Complex **1** (0.22 mmol, 30 mg) and CsI (0.11 mmol, 57 mg) were dissolved in water (5 mL). Crystals suitable for X-ray single-crystal diffraction were obtained by slow evaporation of the water. The same kind of crystals were obtained by crystallization from water of the ground powder of **1** with the alkali metal salt.

Crystal structure determination: Crystal data of compounds $\mathbf{1}_2\cdot\mathrm{Rb}^+\mathrm{Cl}^-$, $\mathbf{1}_2\cdot\mathrm{Cs}^+\mathrm{Br}^-$, $\mathbf{1}_2\cdot\mathrm{K}^+\mathrm{I}^-$, $\mathbf{1}_2\cdot\mathrm{Rb}^+\mathrm{I}^-$, $\mathbf{1}_2\cdot\mathrm{Cs}^+\mathrm{I}^-$ were collected on a Nonius CAD4 diffractometer. Crystal data of compounds $\mathbf{1}_2\cdot\mathrm{Cs}^+\mathrm{Cl}^-$, $\mathbf{1}_2\cdot\mathrm{Rb}^+\mathrm{Br}^-$ were collected on a Bruker Smart CCD diffractometer. Crystal data and details of measurements are summarized in Table 4. Common to all compounds: $\mathrm{Mo}_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, monochromator graphite. SHELX97[27a] was used for structure solution and refinement based on F^2. Non-hydrogen atoms were refined anisotropically. All datasets were collected at room temperature. Hydrogen atoms bound to carbon atoms were added in calculated positions. In $\mathbf{1}_2\cdot\mathrm{Rb}^+\mathrm{Br}^-$, $\mathbf{1}_2\cdot\mathrm{Cs}^+\mathrm{Br}^-$, and $\mathbf{1}_2\cdot\mathrm{Cs}^+\mathrm{I}^-$, the $\mathrm{H}_{\mathrm{COOH}}$ atoms were found but not refined, while in $\mathbf{1}_2\cdot\mathrm{Rb}^+\mathrm{Cl}^-$ and $\mathbf{1}_2\cdot\mathrm{Rb}^+\mathrm{I}^-$ $\mathrm{H}_{\mathrm{COOH}}$ atoms were found and refined. In order to evaluate (C)–H···O bonds, the C–H bond lengths were normalized to the neutron-derived value of 1.08 Å. SCHAKAL99[27b] was used for the graphical representation of the results. The program PLATON[27c] was used to calculate the hydrogen-bonding interactions reported in Table 2.

For all species discussed in this paper, powder diffractograms were measured for all compounds obtained by grinding. These diffractograms were compared with those calculated[28] on the basis of the structures determined by means of single-crystal X-ray diffraction, as described above.

CCDC-225035–225041 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

Powder diffraction experiments: Powder data were collected on a Philips PW-1710 automated diffractometer and on a X'Pert Philips diffractometer, both with $\mathrm{Cu}_{K\alpha}$ radiation and a graphite monochromator. All measurements were carried out at room temperature.

Solid-state NMR measurements: High-resolution solid-state ^{13}C NMR spectra were recorded on a JEOL GSE 270 spectrometer equipped with a Doty probe operating at 67.8 MHz for ^{13}C. A single-contact cross-polarization (CP) pulse sequence[29] was employed with a pulse to flip back the remaining ^{1}H magnetization after the acquisition time. The Hartmann–Hahn conditions[30] were set with glycine. Sample were placed in a cylindrical zirconia rotor with sample volume of 120 µL and spun as fast as 6–7 kHz. Generally, an acquisition time of 0.051 s was used with a contact time of 3.5 ms, a recycle delay of 10 s, and the spectral width was 40 kHz. The chemical shift scale was referenced by setting the CH_3 peak in a sample of solid hexamethylbenzene run separately under the same conditions to $\delta = 17.4$ ppm.

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Table 4. Crystal data and details of measurements.

	$\mathbf{1}_2\cdot\mathrm{Rb}^+\mathrm{Cl}^-$	$\mathbf{1}_2\cdot\mathrm{Cs}^+\mathrm{Cl}^-$	$\mathbf{1}_2\cdot\mathrm{Rb}^+\mathrm{Br}^-$	$\mathbf{1}_2\cdot\mathrm{Cs}^+\mathrm{Br}^-$	$\mathbf{1}_2\cdot\mathrm{K}^+\mathrm{I}^-$	$\mathbf{1}_2\cdot\mathrm{Rb}^+\mathrm{I}^-$	$\mathbf{1}_2\cdot\mathrm{Cs}^+\mathrm{I}^-$
formula	$C_{24}H_{18}Co_2O_8RbCl$	$C_{24}H_{18}Co_2O_8CsCl$	$C_{24}H_{18}Co_2O_8RbBr$	$C_{24}H_{18}Co_2O_8CsBr$	$C_{24}H_{18}Co_2O_8KI$	$C_{24}H_{18}Co_2O_8RbI$	$C_{24}H_{18}Co_2O_8CsI$
M_W	673.16	720.60	717.62	765.06	718.24	764.61	812.05
system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	6.037(3)	6.1960(5)	6.1200(12)	6.2240(12)	6.007(4)	6.079(2)	6.2593(6)
b [Å]	8.078(3)	8.1078(7)	8.1500(16)	8.0800(16)	8.058(4)	8.063(6)	8.0630(8)
c [Å]	12.182(4)	12.0849(10)	12.560(3)	12.300(3)	13.093(9)	12.962(2)	12.7570(13)
α [°]	79.64(3)	80.021(3)	78.68(3)	79.00(3)	76.62(5)	76.82(4)	77.562(2)
β [°]	80.87(3)	81.475(3)	80.72(3)	81.30(3)	80.27(6)	80.68(2)	81.318(2)
γ [°]	74.42(4)	74.930(3)	74.23(3)	74.70(3)	73.36(5)	73.91(4)	74.432(2)
V [Å°]	559.1(4)	573.94(8)	587.3(2)	582.3(2)	587.1(6)	591.0(5)	602.68(10)
Z	1	1	1	1	1	1	1
$F(000)$	334	352	352	370	352	370	388
$\mu(\mathrm{Mo}_{K\alpha})$ [mm^{-1}]	3.818	3.175	5.222	4.730	2.955	4.805	4.194
measured reflns	2064	4008	5501	3446	3553	2951	6920
unique reflns	1963	1637	2557	3300	3415	2828	3477
parameters	152	149	149	149	149	148	148
GOF on $\dot{F}$	1.093	0.936	1.078	1.069	0.657	1.078	1.070
$R1$ (on $F[I>2\sigma(I)]$)	0.0398	0.0524	0.0957	0.0674	0.0397	0.0318	0.0809
$wR2$ (on $\dot{F}$, all data)	0.1093	0.1209	0.2619	0.1789	0.1191	0.0904	0.2480

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