Tunable Supramolecular Synthons and Versatile, Water-Soluble Building Blocks for Crystal Engineering: $[(\eta^5\text{-}C_5H_4COOH)_2Co^{III}]^+$ and its Zwitterionic Form $[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Co^{III}]$

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Abstract: It is shown that the water-soluble dicarboxylic cationic acid $[(\eta^5\text{-}C_5H_4COOH)_2Co^{III}]^+$ (**1**) is an extremely versatile building block for the construction of organometallic crystalline edifices. Removal of one proton from **1** leads to formation of the neutral zwitterion $[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Co^{III}]$ (**2**), while further deprotonation leads to formation of the dicarboxylate monoanion $[(\eta^5\text{-}C_5H_4COO)_2Co^{III}]^-$ (**3**). Compounds **1**, **2** and **3** possess different hydrogen-bonding capacity and participate in a variety of hydrogen-bonding networks. The cationic form **1** has been characterised as its $[PF_6]^-$ and Cl^- salts **1**-$[PF_6]$ and **1**-$Cl\cdot H_2O$, as well as in its co-crystal with urea, **1**-$Cl\cdot 3(NH_2)_2CO$, and with the zwitterionic form **2**, $[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Co^{III}][(\eta^5\text{-}C_5H_4COOH)_2Co^{III}]^+[PF_6]^-$, **2**$\cdot$**1**-$[PF_6]$. The neutral zwitterion **2** behaves as a supramolecular crown ether: it encapsulates the alkali cations K^+, Rb^+ and Cs^+ as well as the ammonium cation NH_4^+ in cages sustained by O−H⋯O and C−H⋯O hydrogen bonds to form co-crystalline salts of the type **2**$_2$-M$[PF_6]$ (M = K, Rb, Cs) and **2**$_2$-$[NH_4][PF_6]$. The deprotonated acid **3** has been characterised as its Cs^+ salt, Cs^+-**3**$\cdot 3H_2O$.

Keywords: carboxylic acids · cobalt · hydrogen bonds · organometallic compounds · zwitterions

Introduction

Polycarboxylic acids are being utilised by many scientists in the quest for a controlled assembly of molecules or ions in the solid state.[1] The COOH group is, in fact, capable of forming strong intermolecular hydrogen bonds,[2] and the presence of several COOH groups with different orientations in space allows construction of one-, two- and three-dimensional aggregates.

The crystal edifice can be made more robust if the hydrogen-bond network is embedded in the force field generated by Coulombic forces between charged species in ionic crystals.[3] This is fairly easy to achieve when using polycarboxylic acids by removal of one (or two) acidic protons. Partial deprotonation, in fact, leads to formation of hydrogen carboxylate anions, a trivial observation per se, but something valuable for crystal engineers.[4] We and others have widely exploited the possibility of reinforcing hydrogen-bond networks by using charged hydrogen-bond donor and acceptor species, for exampl, *charge-assisted* $X\text{−}H^{\delta+}\cdots Y^{\delta-}$ hydrogen bonds, in which X and Y are the usual electronegative atoms C, N, O and so forth.[5] The simultaneous presence of charged hydrogen-bonding interactions and of Coulombic forces between the ions attains the important result of combining the strength of the ionic interactions with the directionality, hence predictability and reproducibility, of the hydrogen bonds.[6] Charged O−H⋯O hydrogen-bonding interactions have their specific structural characteristics: i) they are usually shorter than neutral O−H⋯O hydrogen-bond, ii) they are linear (namely, the O−H⋯O angle approaches 180°) and iii) the H-atom is usually displaced from the "donor" towards the midpoint of the O⋯O system.

This also applies to organometallics acids, although they are much less common than polycarboxylic organic acids, most of which are also commercially available. Importantly, organometallic polycarboxylic acids are easily dissolved in water upon deprotonation. Water-soluble organometallic complexes are of great interest because of their stability and facility to handle, with fewer problems in preparation and disposal.[7]

We have directed our interest towards the preparation and study of the hydrogen-bonding behaviour of the unusual cationic cobalticinium dicarboxylic acid $[(\eta^5\text{-}C_5H_4COOH)_2Co^{III}]^+$ (see Scheme 1).[8] Removal of one proton leads to a formal charge of zero and to the formation of an

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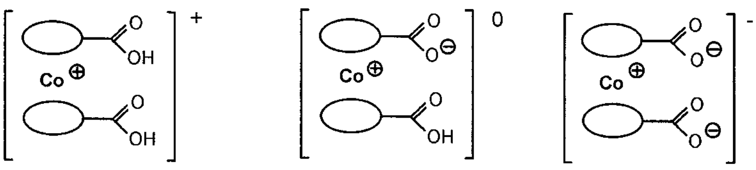


1 2 3

Scheme 1. Schematic representation of the three building blocks based on cobalticinium dicarboxylic acid complex: the cation $[(\eta^5\text{-}C_5H_4COOH)_2Co^{III}]^+$ (**1**), the zwitterionic form $[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Co^{III}]$ (**2**) and the monoanion $[(\eta^5\text{-}C_5H_4COO)_2Co^{III}]^-$ (**3**).

organometallic sandwich zwitterion $[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Co^{III}]$ (**2**), with one COOH and one COO^- group, while further deprotonation leads to the dicarboxylate monoanion $[(\eta^5C_5H_4COO)_2Co^{III}]^-$ (**3**) with two COO^- groups. Hence, the cobalticinium system can be regarded as composed of a fundamental building block, namely "$[(\eta^5\text{-}C_5H_4COO)_2Co^{III}]$", which can participate, depending on the extent of protonation, in hydrogen-bonding networks as a monocation, a neutral species and as a monoanion. These features will be discussed in the following by means of a series of examples.

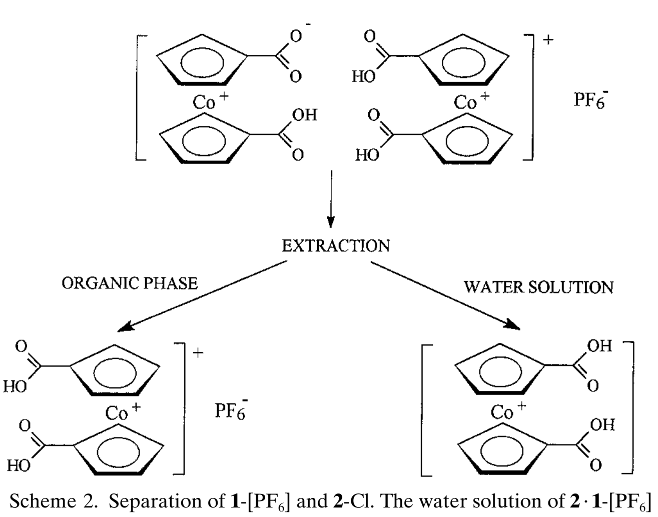
The cationic form **1** has been characterised as its $[PF_6]^-$ salt both in the binary salt, **1**-$[PF_6]$, as well as in the co-crystal with the zwitterion **2**, $[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Co^{III}][(\eta^5\text{-}C_5H_4COOH)_2Co^{III}]^+[PF_6]^-$ (**2**·**1**-$[PF_6]$). The cation has also been obtained as its Cl^- salts in co-crystals with one water molecule, **1**-Cl·H_2O and with three molecules of urea, **1**-Cl·3$(NH_2)_2CO$. The neutral zwitterion **2**, on the other hand, has been shown to be able to selectively encapsulate the alkali cations K^+, Rb^+ and Cs^+ as well as the ammonium cation NH_4^+ in cages sustained by O–H···O and C–H···O hydrogen bonds. The cage compounds have stoichiometries of the type $\mathbf{2}_2$-M$[PF_6]$ ($M^+ = K^+$, Rb^+, Cs^+) and $\mathbf{2}_2$-$[NH_4][PF_6]$. The dicarboxylate monoanion **3** has been characterised as its Cs^+ salt, Cs^+-**3**·3H_2O.

Abstract in Italian: *L'acido cationico dicarbossilico* $[(\eta^5\text{-}C_5H_4COOH)_2Co^{III}]^+$ (***1***) *solubile in acqua è un versatile mattone molecolare per la costruzione di edifici cristallini organometallici; infatti la rimozione di un protone da* ***1*** *porta alla formazione dello zwitterione neutro* $[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Co^{III}]$ (***2***)*, mentre ulteriore deprotonazione porta alla formazione del monoanione dicarbossilato* $[(\eta^5\text{-}C_5H_4COO)_2Co^{III}]^-$ (***3***)*.* ***1****,* ***2****, e* ***3*** *sono in grado di generare differenti networks di legame a idrogeno. La forma cationica* ***1*** *è stata caratterizzata sia come sale di* $[PF_6]^-$ *e di* Cl^-*,* ***1***-$[PF_6]$ ***1***-$Cl\cdot H_2O$ *che come cocristallo con l'urea,* ***1***-$Cl\cdot 3(NH_2)_2CO$*, e con lo zwitterione* ***2****,* $[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Co^{III}][(\eta^5\text{-}C_5H_4COOH)_2Co^{III}]^+[PF_6]^-$*,* ***2***·***1***-$[PF_6]$*. Lo zwitterione neutro* ***2*** *si comporta come un etere corona supramolecolare incapsulando sia i cationi alcalini* K^+*,* Rb^+*,* Cs^+ *che il catione ammonio* NH_4^+ *in gabbie tenute insieme da legami a idrogeno O-H···O e C-H···O, formando sali cocristallini del tipo* $\mathbf{2}_2$-$M[PF_6]$ *(M = K, Rb, Cs) e* $\mathbf{2}_2$-$[NH_4][PF_6]$*. L'acido deprotonato* ***3*** *è stato caratterizzato come sale di* Cs^+*,* Cs^+-***3***·$3H_2O$*.*

Results and Discussion

The dicarboxylic cationic acid $[(\eta^5\text{-}C_5H_4COOH)_2Co^{III}]^+$ (1): The diacid $[(\eta^5\text{-}C_5H_4COOH)_2Co^{III}]^+$ (**1**) was obtained from $[(\eta^5\text{-}C_5H_4CH_3)_2Co^{III}]^+$ by a modification of the synthesis available in the literature (see Experimental Section). In its crystalline form, however, the cationic acid **1** is invariably precipitated together with the zwitterionic form **2**. In fact, the species $[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Co^{III}][(\eta^5\text{-}C_5H_4COOH)_2Co^{III}]^+[PF_6]^-$ (**2**·**1**-$[PF_6]$, see below) constitutes the only product that is recovered from the solution of **1** upon crystallisation. Separation of **1** from **2** is not straightforward and has been achieved only by exploiting the different solubility in water and nitromethane of the salts **1**-$[PF_6]$ and **1**-Cl. The separation sequence proceeds as follows (see also Scheme 2):

1) Solid **2**·**1**-$[PF_6]$ was dissolved in water and treated with HCl (6 N) in order to protonate the neutral form **2** to the cationic form **1**. The resulting mixture of **1**-$[PF_6]$ and of **1**-Cl in water was extracted several times with nitromethane.
2) Since **1**-Cl is not soluble in nitromethane and **1**-$[PF_6]$ is relatively more soluble in nitromethane than in water, the nitromethane phase contains **1**-$[PF_6]$, while the water solution contains **1**-Cl.
3) If at this stage crystals are allowed to form from the solution of **1** in water, the hydrated chloride **1**-Cl·H_2O is obtained.
4) The solution of **1**-Cl in water is then subjected to several cycles of heating and evaporation to dryness, in a rotavapor apparatus, followed by dissolution in water until all HCl is removed. The hydrated form of **2**, namely **2**·3H_2O, is then crystallised as yellow swordlike crystals; anhydrous **2** can only be obtained by thermal treatment of **2**·3H_2O.[9]
5) Crystalline **1**-$[PF_6]$ is obtained as yellow-orange crystals from the nitromethane solution.



Scheme 2. Separation of **1**-$[PF_6]$ and **2**-Cl. The water solution of **2**·**1**-$[PF_6]$ is treated with HCl (6 N); **1**-$[PF_6]$ is extracted with nitromethane.

The cationic dicarboxylic acid **1** is isoelectronic with the neutral complex $[(\eta^5\text{-}C_5H_4COOH)_2Fe^{II}]$, which is known in two polymorphic modifications.[10] While both forms of crystalline $[(\eta^5\text{-}C_5H_4COOH)_2Fe^{II}]$ contain molecular dimers joined by twin hydrogen-bonded carboxylic rings,[11] the cation **1** forms infinite chains joined by hydrogen-bonded carboxylic rings as shown in Figure 1. The $\{[(\eta^5\text{-}C_5H_4COOH)_2Co^{III}]^+\}_n$ hydrogen-bonded chains are then organised side-by side to form a sort of two-dimensional, step-ladder cationic superstructure with the $[PF_6]^-$ anions accommodated in between the steps. Interestingly, the anions are surrounded by the cyclopentadienyl C–H groups and form a large number of charge-assisted $C{-}H^{\delta+}\cdots F^{\delta-}$ interactions, a well-established interaction when $[PF_6]^-$ is involved.[12]

While the COOH groups in **1**-$[PF_6]$ form typical dicarboxylic rings, this is not the case of the hydrated chloride salt **1**-Cl $\cdot H_2O$. The interaction between COOH groups is not direct, but mediated by water molecules ($O_{COOH}\cdots O_{water}$ 2.766(7), 2.568(7) and 2.797(7), 2.572(7) Å for the two independent molecules of cobalticinium dicarboxylic acid) as shown in Figure 2 (top). The two independent $O_{COOH}\cdots O_{water}$ distances, which are remarkably short (2.567(7) and 2.572(7) Å), indicate a substantial *electrostatic compression* with respect to similar bonds between neutral molecules.[13] The chloride anions accept hydrogen bonds from the COOH groups as well as from the water molecules ($Cl\cdots O_{COOH}$ 2.975(7), 2.951(7) Å and $Cl\cdots O_{water}$ 3.042(8), 3.044(8) Å). Although not all hydrogen atoms could be observed, the distribution of the OH groups can be easily inferred on the basis of the donor–acceptor geometry and of the length of the C–O bonds. The involvement of both OH groups and the water molecule in the interaction with the chloride ion leaves one carboxylic oxygen atom unused by $O{-}H\cdots O$ interactions. This atom participates in $C{-}H\cdots O$ interactions with the cyclopentadienyl rings, as shown in Figure 2 (bottom), forming a chain of dicarboxylic cobalticinium acids that "sneaks" between the chlorine atoms. The water molecules are also involved in short $C{-}H\cdots O_w$ interactions ($H\cdots O$ 2.217(7) and 2.188(7) Å). It is interesting to look at compound **1**-Cl $\cdot H_2O$ as the hydrogen chloride form of the zwitterion **2**, in analogy with the behaviour of many amino acids that are often obtained in the solid state as HCl derivatives, for example, $[HOOC\text{-}R\text{-}NH_3]Cl$. As mentioned above, this chloride form releases HCl upon thermal treatment yielding the zwitterion **2**.

In order to test the existence of a hierarchy in hydrogen bond formation involving ions similar to that known for neutral molecules,[14] we have crystallised **1** as its Cl^- salt in the presence of a slight excess of urea ($(NH_2)_2CO$). Whereas in **1**-Cl $\cdot H_2O$ the carboxylic groups interact directly with the Cl^-, probably due to poor competitiveness of the water molecules against the electrostatic attraction between the two ions, this is not so in crystalline **1**-Cl $\cdot 3(NH_2)_2CO$. Urea possesses four N–H hydrogen-bonding donor groups and one oxygen acceptor and can therefore compete with the carboxylic oxygens as well as with the Cl^- ion in hydrogen-bond formation. Indeed, the preference is for the urea–acid interaction, as shown in Figure 3 (top) with each COOH

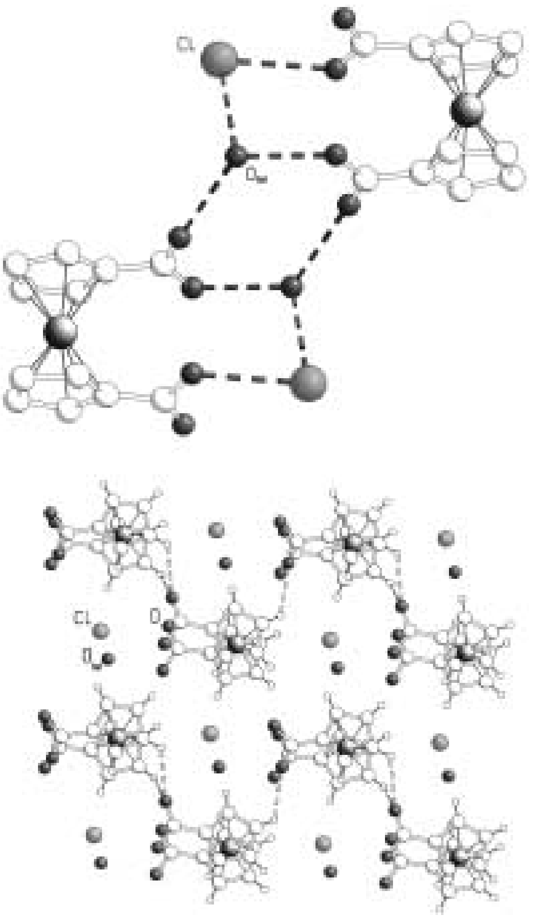


Figure 2. Top: The interaction between COOH groups in the hydrated chloride salt **1**-Cl $\cdot H_2O$. Hydrogen atoms are omitted for clarity. Bottom: Chains formed by the dicarboxylic cobalticinium acid through $C{-}H\cdots O$ interactions.

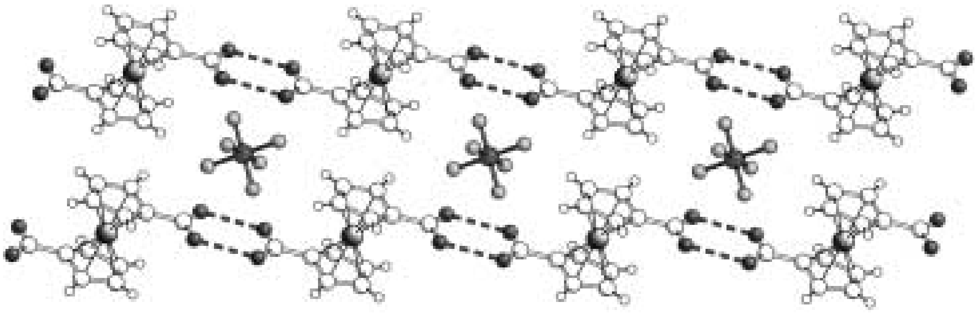


Figure 1. Parallel cationic $[\{(\eta^5\text{-}C_5H_4COOH)_2Co^{III}\}^+\}_n]$ chains form a step-ladder two-dimensional superstructure with the $[PF_6]^-$ anions accommodated in between the steps and interacting with the cyclopentadienyl ligands through charge-assisted $C{-}H^{\delta+}\cdots F^{\delta-}$ interactions.

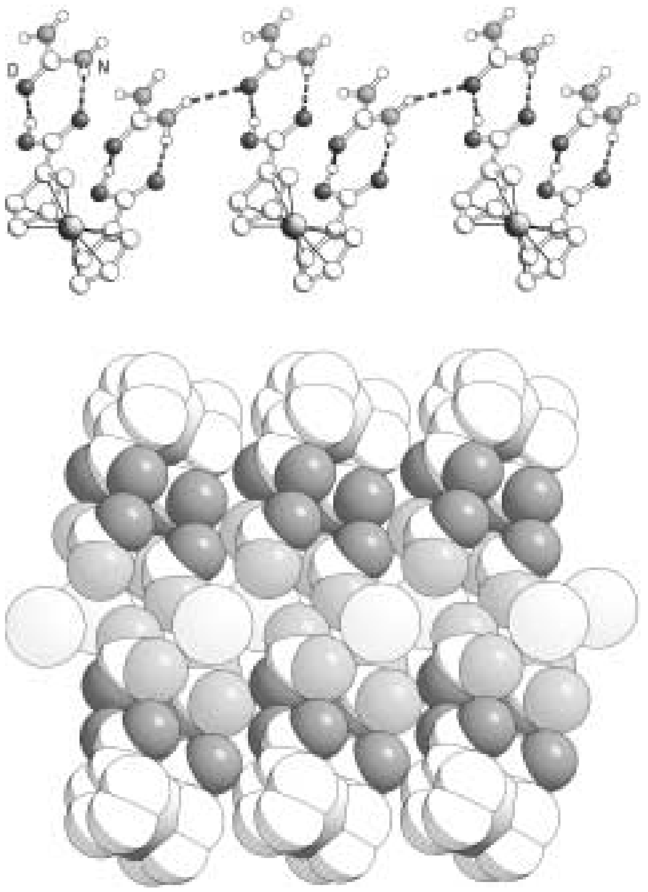


Figure 3. Top: The urea-acid interaction in **1**-Cl $\cdot$ 3[$(NH_2)_2CO$] with the COOH groups of the cation forming rings with one N–H donor and the O acceptor of the urea molecules. Bottom: Space-filling representation of the ion packing in **1**-Cl $\cdot$ 3 $(NH_2)_2CO$. Large light grey spheres represent the Cl^- ions, dark grey spheres the oxygen atoms. Hydrogen atoms are omitted for clarity.

group of the cation forming rings with one N–H donor and the O acceptor of the urea molecules. Interestingly, the $O(H)_{cation} \cdots O_{urea}$ distances are very short (2.431(7), and 2.477(7) Å), while the $N(H)_{urea} \cdots O_{cation}$ distances (2.945(7), 2.907(7), 2.980(8) Å) are longer and compare with values normally found in neutral N–H $\cdots$ O bonds.[15] Figure 3 also shows how the urea molecules are connected through another N–H $\cdots$ O bond that involves the NH_2 group interacting with the complex, while the second NH_2 group interacts with the Cl^- ion (not shown). In such a way {**1** $\cdot$ 2 $(NH_2)_2CO$} units are joined in a step-ladder assembly as shown in Figure 3 (bottom). The coordination sphere of the Cl^- ion is formed by five molecules of urea and one cation through N–H $\cdots$ Cl and C–H $\cdots$ Cl interactions. The presence of an additional partially disordered molecule of urea in the crystal structure suggests that the Cl anions and the cationic chains are not sufficient to fill all the voids generated by the hydrogen-bond scaffolding.

As mentioned above the cationic diacid **1** precipitates from the reaction solution as $[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Co^{III}][(\eta^5\text{-}C_5H_4COOH)_2Co^{III}]^+[PF_6]^-$ (**2** $\cdot$ **1**-[PF_6]).[8] Although the compound can be ideally regarded as a co-crystal of **2** and **1**, that is **2** $\cdot$ **1**-[PF_6], an analysis of the hydrogen-bond interaction pattern suggests that the crystalline material is more appropriately described as a *supramolecular salt* in which a supra-cationic unit $[\{(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Co^{III}\}\{(\eta^5\text{-}C_5H_4COOH)_2Co^{III}\}]^+$ results from the formal aggregation of the cationic dicarboxylic acid $[(\eta^5\text{-}C_5H_4COOH)_2Co^{III}]^+$ (present in **1**) with the zwitterionic species $[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Co^{III}]$ (**2**). Although we retain the **2** $\cdot$ **1** description of the system, one should be aware of the fact that the properties of this aggregate are very different from those of the two components. In one respect, for example, the difference is dramatic; in contrast to **1**-[PF_6], **2** $\cdot$ **1** is extremely stable and requires tough pH and thermal treatment to be broken and separated in its two components. Whenever the $[PF_6]^-$ counterion is present **2** $\cdot$ **1**-[PF_6] is always precipitated first from water solutions forming very stable, dark yellow crystals. The **2** $\cdot$ **1** aggregate is probably present in solution although an assessment requires additional information of spectroscopic nature. Figure 4 (top) shows the dimeric arrangement of the **2** $\cdot$ **1** system. Of the three hydrogen-bonding interactions the two outer O $\cdots$ O ones are significantly longer than the inner one (2.594(5), and 2.609(5) versus 2.488(5) Å); this sequence of hydrogen bonding results in a kind of "S" connection the four COO groups, which are tilted with respect to the C_5 plane in order to accommodate the three hydrogen bonds. The tilting of the COOH groups, combined with the rotational freedom of the C_5 rings around the coordination axes, yields a very flexible building block. Conformational freedom is often responsible for low-energy dynamical processes both in solution and in the solid state.[16] In a crystal engineering context these degrees of conformational and torsional freedom render the building blocks more *adaptable* than stiff units to the process of self-assembly, but also open up the possibility of polymorph formation.[17]

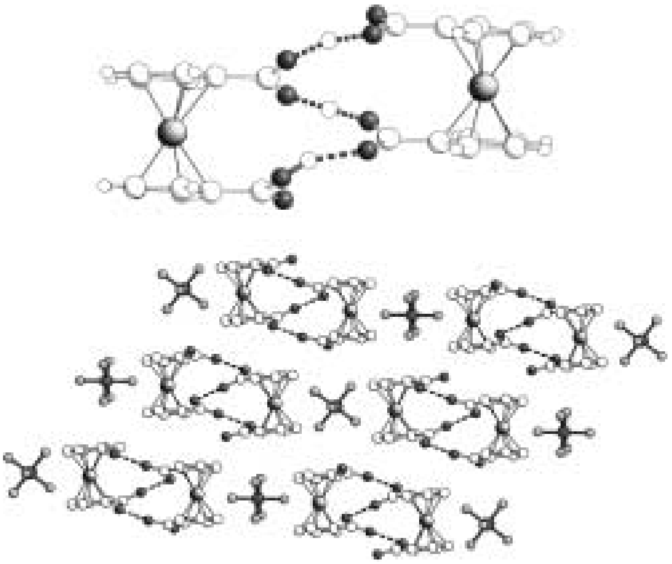


Figure 4. Top: The dimeric arrangement of the **2** $\cdot$ **1** system in crystalline **2** $\cdot$ **1**-[PF_6]. The two external O $\cdots$ O bonds are significantly longer than the inner one (2.594(5), and 2.609(5) versus 2.488(5) Å). Two out of the three hydrogen atoms involved in the bonding were observed. Bottom: The $[PF_6]^-$ anions interact exclusively with the H atoms of the C_5H_4 systems acting as ion-paring bridges between the units (but note that cyclopentadienyl hydrogen atoms have been omitted for clarity).

The $[PF_6]^-$ anions are not at contact distance with the COO/COOH groups and interact exclusively with the H atoms of the C_5H_4 systems, in agreement with the favourable formation of charge-assisted $C{-}H^{\delta+}\cdots F^{\delta-}$ interactions. Hence, the anions act as ion-paring bridges between the cationic units (see Figure 4 bottom).

The deprotonated anionic species $[(\eta^5\text{-}C_5H_4COO)_2Co^{III}]^-$ (3): In its fully deprotonated form **3** the dicarboxylate derivative is a monoanion (see Scheme 1). The only successful attempt to isolate suitable crystals of a salt of **3** has been upon treatment of the **2**·**1**-$[PF_6]$ with an excess of CsOH, to yield the trihydrated species Cs-**3**·$3H_2O$. In view of the large number of hydrogen-bond acceptor sites in the structure of Cs-**3**·$3H_2O$ it is not surprising that crystallisation from water leads to formation of a hydrated species. The water molecules, as in most hydrated acidates of alkali metal cations, interact on the one hand with the electropositive Cs^+ ion through the lone pairs on the oxygen atom and, on the other hand, with the COO groups on the anions through the O–H systems. Direct $COO\cdots Cs^+$ interactions are also formed as shown in Figure 5 (top). Each Cs^+ cation is surrounded by eight oxygen atoms. One water molecule (O6) interacts only with other water molecules (O⋯O 2.789(10) Å), while O5 and O7 interact also with the carboxylic oxygens (O1⋯O7 2.719(9), O3⋯O7 2.775(9), O5⋯O4 2.688(9) Å). The Cs^+ cations form rows in the crystal and are alternatively bridged by water and COO oxygens as shown in Figure 5 (bottom).

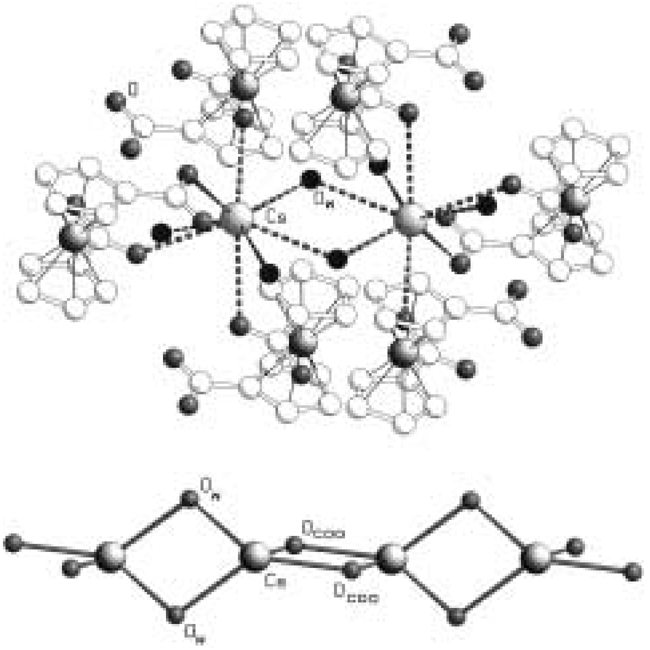


Figure 5. Top: Water-mediated interactions (water oxygen is black) in crystalline Cs^+-**3**·$3H_2O$. Bottom: The water molecules O1 and O7 bridge the Cs^+ ions to form a cationic row that interacts with the fully deprotonated anions **3**.

The zwitterionic cages: The most striking results of this study are obtained when the zwitterion **2** is employed. If water solutions of **2**·**1**-$[PF_6]$ are treated with alkali metal hydroxides MOH (M = K, Rb, Cs) in 1:1 stoichiometric ratio the acid cation **1** is partially deprotonated. A similar acid–base reaction occurs upon treatment of the solution of **2**·**1**-$[PF_6]$ with concentrated ammonia. The resulting solution contains, beside the zwitterion **2**, the alkali cations or the ammonium cation and the $[PF_6]^-$ anions. Upon crystallization **2** forms nearly isomorphous supramolecular aggregates with the inorganic salts $M[PF_6]$ ($M^+ = K^+$, Rb^+, Cs^+) and with $[NH_4][PF_6]$. Alternatively, the same compounds can be prepared by treating solutions of **2** in water with the stoichiometric amount of the appropriate $[PF_6]^-$ salts, that is, $M^+[PF_6]^-$ ($M^+ = K^+$, Rb^+, Cs^+) and $[NH_4]^+[PF_6]^-$. Reactions with LiOH and NaOH did not yield crystals suitable for single-crystal diffraction experiments.

The structural features of the four crystalline materials can be summarised as follows (see also Table 1):

1) The cations are encapsulated within a cage formed by four molecules of **2**. The tetrameric cages share a face so that the stoichiometry of the systems is $\mathbf{2}_2$-$[NH_4][PF_6]$ and $\mathbf{2}_2$-$M[PF_6]$. The K^+, Rb^+ and Cs^+ species are quasi isostructural and isomorphous with the ammonium salt aggregate $\mathbf{2}_2$-$[NH_4][PF_6]$ (see Figure 6, top). No adduct has been (so far) obtained with Li^+ and Na^+. The walls of the cage consist of two *dimeric units* of **2** held together by two O-H⋯O hydrogen bonds and by two C-H⋯O bonds; these latter involve the H atoms of the C_5H_4-systems and the "free" lone pairs on the carboxylic oxygens.
2) This hydrogen-bond framework results in eight oxygen atoms from the carboxylic/carboxylate groups pointing inwards thus forming a strongly nucleophilic cage (see Figure 6, bottom) in which the cations are encapsulated through either $M^+\cdots O$ interactions (in the cases of K^+, Rb^+, Cs^+) or N–H⋯O hydrogen bonds in the case of the $[NH_4]^+$ cation.
3) The basic packing motif can be described as a sequence of C–H⋯O hydrogen-bonded **2**+**2** dimers encapsulating the cations, while the fluorine atoms belonging to the $[PF_6]^-$ anions form charge-assisted $C{-}H^{\delta+}\cdots F^{\delta-}$ interactions with the cyclopentadienyl ligands (see Figure 7).

Table 1. Comparison of relevant hydrogen bond parameters [Å] and angles [°] for $\mathbf{2}_2$-$M[PF_6]$ (M = K, Rb, Cs) and $\mathbf{2}_2$-$[NH_4][PF_6]$.

	$\mathbf{2}_2$-K$[PF_6]$	$\mathbf{2}_2$-Rb$[PF_6]$	$\mathbf{2}_2$-Cs$[PF_6]$	$\mathbf{2}_2$-$NH_4[PF_6]$
O⋯O	2.454(5)	2.455(2)	2.465(3)	2.470(5)
O–H, (O)H⋯O	–[a]	–[a]	1.21,	1.18,
O–H⋯O			1.25	1.31
			179.4	167.6
C(H)⋯O	3.334	3.390	3.410	3.381
	3.423	3.420	3.455	3.417
(C)H⋯O	2.311	2.327	2.374	2.319
	2.367	2.355	2.412	2.355
C-H⋯O	157.42	167.64	160.23	167.52
	165.42	168.13	162.06	167.56
$M^+\cdots O > 3.5$ Å	2.792(5)	2.871(2)	3.005(3)	2.858(3)
	2.824(6)	3.014(2)	3.175(3)	2.999(3)
	2.857(6)	3.143(2)	3.225(2)	3.155(3)
	3.463(6)	3.227(2)	3.291(3)	3.219(4)
r_{M^+} (CN 8)[18a]	1.65	1.75	1.88	1.66–1.75[18b]

[a] H atoms not observed

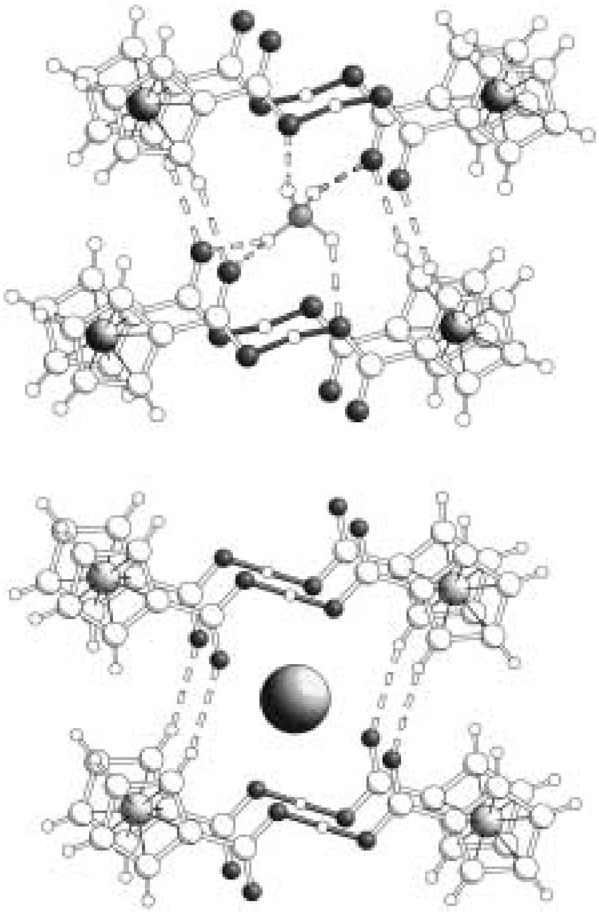


Figure 6. The zwitterionic cages $\mathbf{2}_2$-[NH_4][PF_6] and $\mathbf{2}_2$-Cs[PF_6]. Top: The N–H···O hydrogen bonds between the guest [NH_4]$^+$ cation and the surrounding O atoms in $\mathbf{2}_2$-[NH_4][PF_6] (only one of the two disordered images is shown for the cation within the cage); Bottom: the hydrogen-bonded cage formed by four molecules of **2** with $\mathbf{2}_2$-Cs[PF_6].

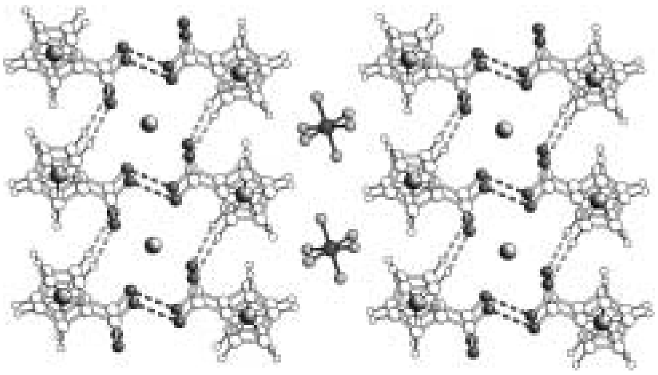


Figure 7. Ball and stick representation of the cage arrangement in crystalline $\mathbf{2}_2$-K[PF_6]. Note how the [PF_6]$^-$ anions pile up on both sides of the supramolecular cages and ideally join the zwitterion molecules (compare with Figure 4, bottom).

The hydrogen-bond framework is not stiff; it permits some limited degree of flexibility as demonstrated by an analysis of the data in Table 1:

1) While O–H···O and C–H···O interactions appear to vary only little on changing the nature of the guest, a comparison of the O···M$^+$ distances shows that the *shape* of the cage changes on changing the guest species.
2) The cation coordination number is close to six in the case of K$^+$ (i.e., six bonds of comparable length in the range 2.792(5) – 2.857(6) and two elongated ones, 3.463(6) Å), while it is eight in the case of Cs$^+$ (range 3.005(3) – 3.291(3) Å). The Rb$^+$ and NH_4^+ cages are roughly intermediate (bond length ranges 2.871(2)-3.227(2), and 2.858(3)-3.219(4) Å for Rb$^+$ and NH_4^+, respectively). The progressive cage symmetrisation on passing from K$^+$ to Cs$^+$ is visualised in Figure 8.

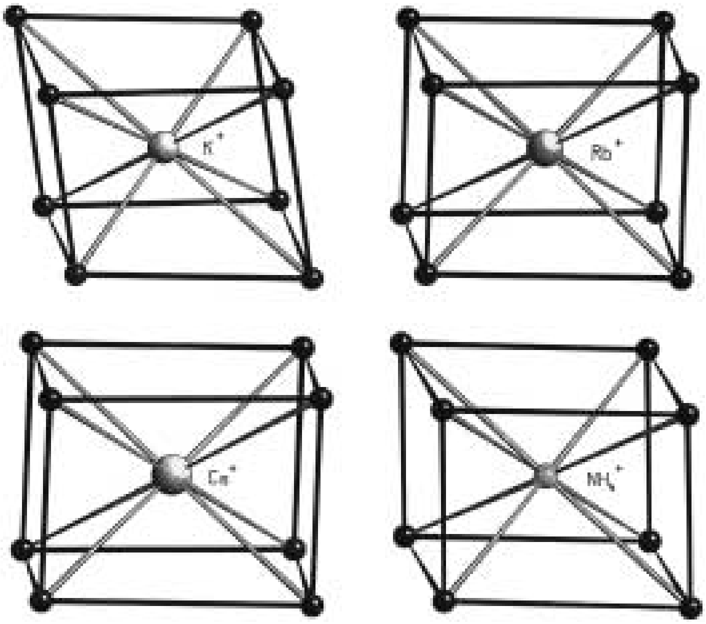


Figure 8. The progressive cage symmetrisation on passing from K$^+$ to [NH_4]$^+$ in $\mathbf{2}_2$-M[PF_6].

3) In the case of the aggregate involving NH_4^+ the M···O interactions are, of course, replaced by N–H···O hydrogen bonds (see Figure 6, top). The apparent size of the cation is, however, comparable with those of the larger alkali cations (K$^+$ 1.65, Rb$^+$ 1.75, Cs$^+$ 1.88 Å).[18]
4) It is noteworthy that the O···O distances (ca. 2.46 Å) between the formally neutral **2**+**2** dimers are shorter than usually observed for neutral O–H···O carboxylic groups, while they compare well with *charged* hydrogen bonds, for example, –COO$^-$···HOOC–.[19] The structural evidence is, therefore, for a localisation of the negative charge onto the deprotonated COO group rather than its delocalisation over the whole molecular unit. In such a way the two bonds are better described as charge-assisted O–H···O$^-$ bonds. At least in the cases of the Cs$^+$ and NH_4^+ cages, in which H atoms could be observed, the bond is almost symmetric with the H atom roughly midway between the two O atoms.

The organisation in the cage salts $\mathbf{2}_2$-M[PF_6] and $\mathbf{2}_2$-[NH_4][PF_6] demonstrates a remarkable capacity for the zwitterion **2** to self-assemble around monovalent cations. Beside the conceptual analogy with crown ether complexation[20] (albeit in the solid state) the hydrogen-bond aggregation recalls the so called "G-quartets" formed around alkali cations by guanosine.[21a] Very recently, analogous pentamers formed by isoguanosine around Cs^+ have also been described.[21b] 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 on the aggregation of the cage-salts $\mathbf{2}_2$-M[PF_6] and $\mathbf{2}_2$-[NH_4][PF_6]. In a way, the cage formed by **2** can be seen as a sort of *noncovalent* crown ether. It is very likely that crystallisation of the four species is preceded by self-assembly of **2** around cations of appropriate size in solution (radii 1.60–1.90 Å). The interaction with the smaller cations, for example, Li^+ and Na^+, might require a deformation of the cage that is not compatible with preservation of the hydrogen-bond networks and this could be one of the reasons why similar cages have not been obtained with these cations.

Conclusion

Water-soluble organometallic synthons are extremely valuable in crystal engineering and in materials chemistry because of their stability and ease of preparation and disposal. Besides, the presence of metal centres permits the achievement of magnetic and electronic properties that are not otherwise amenable with organic molecules.[22] The presence of multiple oxidation states permits the exploitation of the formation of charged species, hence to reinforce the crystal structures by means of Coulombic forces. The organometallic dicarboxylic acid $[(\eta^5\text{-}C_5H_4COOH)_2Co^{III}]^+$ possesses all these features. Besides, it provides a bench-mark system for further developments of the strategy. For instance, substitution of the bisbenzene chromium cation, for example, $[(\eta^6\text{-}C_6H_5COOH)_2Cr^I]^+$, for the bis-cyclopentadienyl cobalticinium moiety will "bring in the solid" paramagnetic centres with prospective magnetic properties.[23] Previous attempts in this direction by using paramagnetic $[(\eta^6\text{-}C_6H_6)_2Cr^I]^+$ in the self-assembly with monohydrogen squarate anions, $[HC_4O_4]^-$ have been successful.[24]

Another promising application of metallocene and metalloarene polycarboxylic acids is their use as sophisticated ligands in the construction of supramolecular coordination compounds. The presence of the COO functions and the ionic charge carried by the central metal atoms allows us to envisage the preparation of coordination networks in which the spacer is the organometallic moiety that may form one-, two- and three-dimensional arrays depending on the coordination geometry of the metal. This line of research has also begun to yield interesting results.

Besides these applications in supramolecular organometallic chemistry[25] and in inorganic crystal engineering, the availability of stable, water-soluble, polycarboxylic acids that carry a positive charge in their fully protonated forms offers the opportunity to study the chemistry and structure of organometallic zwitterions, such as $[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Co^{III}]$. Since compound **2** behaves as a sort of supramolecular organometallic crown ether, we are now exploring both the possibility of encapsulating alkali earth and late transition metal cations (Ba^{2+}, Ag^+, Au^+) and the selectivity towards separation of mixtures of cations of different size in solution.

Experimental Section

All the starting materials were purchased from Aldrich and used without further purification. 1,1′-Dicarboxylic cobalticinium acid, $[Co^{III}(\eta^5\text{-}C_5H_4COOH)_2]^+$ was obtained as $[\{(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)\}\{Co^{III}(\eta^5\text{-}C_5H_4COOH)_2\}Co^{III}]^+[PF_6]^-$ by oxidising 1,1′-dimethylcobalticinium[26a] with $KMnO_4$ in a basic solution as described by Sheats et al.[26b]

Synthesis of $[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Co^{III}]\cdot 3H_2O$, ($\mathbf{2}\cdot 3H_2O$) and $[(\eta^5\text{-}C_5H_4COOH)_2Co^{III}][PF_6]$ (1-[PF_6]): $[\{(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Co^{III}\}\{(\eta^5\text{-}C_5H_4COOH)_2Co^{III}\}]^+[PF_6]^-$ (0.209 g, 0.3 mmol) was dissolved in HCl (6 N, 20 mL). The solution was extracted three times with a total of 70 mL of nitromethane. Evaporation of the nitromethane solution gave yellow crystals of **1**-[PF_6]. Evaporation of the water solution yielded yellow, swordlike crystals of $\mathbf{2}\cdot 3H_2O$ (0.099 g).

Synthesis of $[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Co^{III}]\cdot M^+[PF_6]^-$, ($\mathbf{2}_2$-M[$PF_6$]) and $[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Co^{III}][NH_4]^+[PF_6]^-$ ($\mathbf{2}_2$-[NH_4][PF_6]). Crystals of $\mathbf{2}_2$-M[PF_6] were obtained by treating $\mathbf{2}\cdot\mathbf{1}$-[$PF_6$] with a stoichiometric amount of MOH in boiling water. Crystals suitable for X-ray diffraction were obtained from slow evaporation at room temperature. The same procedure was used for the crystallisation of $[(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)Co^{III}][NH_4]^+[PF_6]^-$.

Crystallography: The structures of **1**-[PF_6], $\mathbf{2}\cdot\mathbf{1}$-[$PF_6$], and $\mathbf{2}_2$-[PF_6] have been the subject of a preliminary report.[8] Crystal data and details of measurements for these species as well as for the new compounds $\mathbf{1}\text{-Cl}\cdot H_2O$, $\mathbf{1}\text{-Cl}\cdot 3(NH_2)_2CO$, $Cs^+\text{-}\mathbf{3}\cdot 3H_2O$, $\mathbf{2}_2$-Rb[PF_6], $\mathbf{2}_2$-Cs[PF_6], $\mathbf{2}_2$-[NH_4][PF_6] are reported in Table 2. Common to all compounds: $Mo_{K\alpha}$ radiation, $\lambda = 0.71069$ Å, monochromator graphite, ψ-scan absorption correction. All non-H atoms were refined anisotropically. (O)H atoms were directly located from Fourier maps and not refined. The $[PF_6]^-$ ions were found to be affected by orientational disordered, which was dealt with by refining combined site occupancy factors for the different orientations with occupancies ratios 1:3 in $\mathbf{2}_2$-Rb[PF_6], 1:1 in $\mathbf{2}_2$-[Cs][PF_6] and 2:3 in $\mathbf{2}_2$-[NH_4][PF_6]. H atoms bound to C atoms were added in calculated positions. The computer program SHELX-97[27a] was used for structure solution and refinement. The computer program SCHAKAL-97[27b] was used for all graphical representations. In order to evaluate the C–H···O bonds the C–H bond lengths were normalised to the neutron derived value of 1.08 Å and the program PLATON was used.[27c] In all cases, correspondence between the structures determined by single-crystal X-ray diffraction and that of the bulk materials precipitated from solution was confirmed by comparing the experimental powder diffractograms obtained from the bulk material with those calculated on the basis of the single-crystal structures. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-143655, CCDC-143656, CCDC-143657, CCDC-143658, CCDC-143659, CCDC-143660. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Table 2a. Crystal data and details of measurements.

	1-[PF$_6$]	**1**-Cl · H$_2$O	**1**-Cl · 3(NH$_2$)$_2$CO	**2** · **1**-[PF$_6$]	Cs$^+$ · **3** · 3H$_2$O
formula	$C_{12}H_{10}CoF_6O_4P$	$C_{12}H_{12}ClCoO_5$	$C_{15}H_{22}ClCoN_6O_7$	$C_{24}H_{19}Co_2\ F_6O_8P$	$C_{12}H_{14}CoCsO_7$
M_w	422.10	330.60	492.77	698.22	462.07
T [K]	223(2)	203(2)	223(2)	223(2)	293(2)
system	monoclinic	triclinic	triclinic	triclinic	triclinic
space group	$C2/m$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	10.99(2)	9.477(3)	7.515(5)	6.953(2)	7.522(2)
b [Å]	9.930(10)	10.662(6)	9.579(3)	11.856(9)	8.694(3)
c [Å]	7.462(8)	13.045(9)	14.987(5)	14.862(5)	11.569(3)
α [°]	90	105.38(5)	104.00(3)	86.98(5)	98.010(10)
β [°]	120.480(10)	98.43(4)	98.07(4)	80.55(2)	91.52(2)
γ [°]	90	91.35(4)	106.12(4)	82.69(4)	104.900(10)
V [Å^3]	701.8(16)	1254.5(12)	980.4(8)	1198.1(11)	722.5(4)
Z	2	4	2	2	2
$F(000)$	420	672	508	700	448
μ (Mo$_{K\alpha}$) [mm^{-1}]	1.426	1.593	1.065	1.550	3.700
measured reflns	495	4263	3512	4172	2277
unique reflns	495	4263	3375	3997	2277
parameters	61	308	234	349	173
GOF on F^2	0.832	0.967	1.109	0.983	1.205
$R1$ (on F [I > 2σ(I)])	0.0782	0.0727	0.0764	0.0472	0.0987
$wR2$ (on F^2,all data)	0.2535	0.2423	0.2124	0.1607	0.2425

Table 2b. Crystal data and details of measurements.

	2$_2$-K[PF$_6$]	**2**$_2$-Rb[PF$_6$]	**2**$_2$-Cs[PF$_6$]	**2**$_2$-[NH$_4$][PF$_6$]
formula	$C_{24}H_{18}F_6KO_8P$	$C_{24}H_{18}Co_2F_6O_8PRb$	$C_{24}H_{18}Co_2F_6O_8PCs$	$C_{24}H_{22}Co_2F_6NO_8P$
M$_w$	736.31	782.68	830.12	715.26
T [K]	223(2)	223(2)	223(2)	273(2)
system	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	5.951(2)	6.087(2)	6.264(2)	6.084(7)
b [Å]	7.8640(10)	8.026(2)	8.027(3)	8.045(3)
c [Å]	14.298(8)	13.756(1)	13.598(3)	13.779(8)
α [°]	74.40(3)	75.150(10)	75.74(2)	74.85(4)
β [°]	78.22(3)	80.01(2)	80.53(2)	80.18(7)
γ [°]	74.45(2)	74.08(2)	74.69(2)	73.84(8)
V [Å^3]	614.6(4)	620.8(3)	635.5(3)	621.8(8)
Z	1	1	1	1
$F(000)$	368	386	404	360
μ(Mo$_{K\alpha}$) [mm^{-1}]	1.682	2.093	2.874	1.497
measuredd reflns	3242	1869	2338	2262
unique reflns	2931	1869	2234	2166
parameters	188	187	202	188
GOF on F^2	0.891	1.038	1.042	1.050
$R1$ (on F [I > 2σ(I)])	0.0688	0.0663	0.0196	0.0675
$wR2$ (on F^2,all data)	0.1999	0.1878	0.0560	0.1472

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