Design, Preparation and Characterization of the Adducts of the Bis-Amido Cobalticinium Complex $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2][PF_6]$ with Fumaric and Maleic Acids

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The supramolecular hydrogen-bonded adducts obtained by treating the cationic bis-amido complex $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2]^+$ with fumaric and maleic acid are investigated and their modes of aggregation in the solid state are explored. It is shown that the bis-amido organometallic complex can be mono- and di-protonated in the reaction with the dicarboxylic acids, leading to the formation of complex, mixed-anion supramolecular salts containing either the dication $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}$, $[\mathbf{1}H]^{2+}$, or the trication $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4NH)_2]^{3+}$, $[\mathbf{1}H_2]^{3+}$. The derivatives of the reaction with fumaric acid, namely, $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}\cdot[PF_6]^-\cdot1/2[fumarate]^{2-}$, $[\mathbf{1}H]^{2+}\cdot PF_6^-\cdot1/2[fumarate]^{2-}$, and $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4NH)_2]^{3+}\cdot[PF_6]^-\cdot[H(fumarate)_2]^{3-}\cdot H_3O^+\cdot H_2O$, $[\mathbf{1}H_2]^{3+}\cdot[PF_6]^-\cdot[H(fumarate)_2]^{3-}\cdot H_3O^+\cdot H_2O$, contain either the dianion $[fumarate]^{2-}$ or the hydrogen-bridged supramolecular trianion $[H(fumarate)_2]^{3-}$, depending on the amide/acid stoichiometric ratio. In the case of maleic acid, on the other hand, the possibility of intramolecular hydrogen-bond formation generates exclusively salts of the hydrogen maleate anions, namely, $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}\cdot5/2[PF_6]^-\cdot3/2[Hmaleate]^-$, $2[\mathbf{1}H]^{2+}\cdot5/2[PF_6]^-\cdot3/2[Hmaleate]^-$, $2[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4NH)_2]^{3+}\cdot3[PF_6]^-\cdot3[Hmaleate]^-\cdot2H_2O$, $2[\mathbf{1}H_2]^{3+}\cdot3[PF_6]^-\cdot3[Hmaleate]^-\cdot2H_2O$ and $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4NH)_2]^{3+}\cdot2[PF_6]^-\cdot[Hmaleate]^-\cdot H_2O$, $[\mathbf{1}H_2]^{3+}\cdot2[PF_6]^-\cdot[Hmaleate]^-\cdot H_2O$, in which the hydrogen maleate anions act as bridges between the protonated bis-amido organometallic sandwiches.

Introduction

In the context of crystal engineering,[1] organometallic molecules and ions are beginning to attract an increasing interest since organometallic molecules and molecular ions combine the supramolecular bonding capacity of organic molecules with the presence of metal atoms. The number of possible combinations of the valence, spin and charge states of the metal atoms with the coordination geometries and supramolecular bonding capacity of functionalised organometallic complexes is virtually unlimited.[2] One of the important issues in this area of chemistry is that of being able to design, synthesize and ultimately exploit the topological properties of solid-state materials based on coordination compounds, whether linked together to form supramolecular complexes or joined in extended coordination networks through space.[3] The goal is to achieve an intelligent control of the recognition and assembly processes that lead from molecular or ionic components to superstructures,[4] hence from individual to collective chemical and physical properties.[5]

In recent years, we have directed our efforts,[6] together with others,[7] towards the exploration of the area of organometallic supramolecular solid-state chemistry and crystal engineering. While many organic compounds often utilized by the crystal engineer are commercially available and can be used directly in supramolecular assembly experiments, this is not so with organometallic species, which need, most often, to be synthesized on purpose.

With this idea in mind, we have begun to prepare, also in collaboration with others, novel organometallic building blocks with adequate supramolecular-bonding functionalities for the construction of target architectures.[8] We have focused our strategy on the possibility of adding hydrogen bonding donor/acceptor groups to robust sandwich complexes. The rationale for this choice is that the hydrogen bond is the strongest of the non-covalent interactions and the one that best combines strength and directionality.[9] Strength is synonym of cohesion and stability, while directionality implies topological control and selectivity, which are fundamental prerequisites for a successful control of the aggregation processes.[10]

It is now well demonstrated that coordination ligands functionalised with –COOH and –OH groups form essentially the same type of hydrogen-bonding interactions, whether as part of organic molecules or as part of metal

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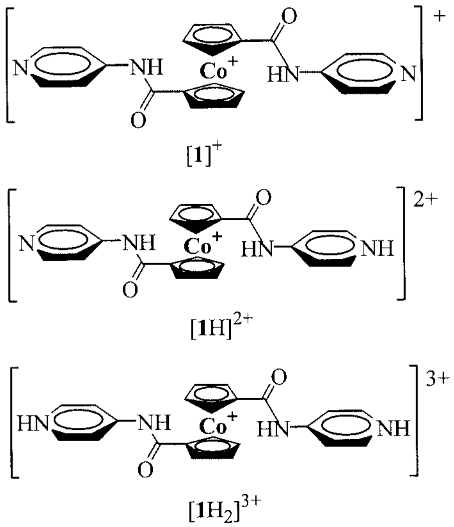
complexes.[2,7,11] This is not surprising, as hydrogen bonds formed by such strong donor and acceptor groups are at least one order of magnitude stronger than most non-covalent interactions. In terms of topology, dicarboxylic acid molecules allow construction of supramolecular networks because of the twin hydrogen-bonding function. We have extensively exploited this feature by using sandwich organometallic dicarboxylic acids such as $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$, $[Co(\eta^5\text{-}C_5H_4COOH)_2]^+$ and $[Cr(\eta^6\text{-}C_6H_5COOH)_2]$.[12] The cobalt cationic complex, in particular, has proved to be extremely versatile for applications in solid–solid and solid–gas reactions.[13]

Recently, we have expanded this chemistry towards organometallic bis-amido complexes. We have reported the solid-state investigation of the bis-amido cobalticinium complex $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2][PF_6]$, $[\mathbf{1}]^+[PF_6]^-$, together with its utilization in the formation of a hydrogen-bonded adduct with ferrocene dicarboxylic acid, namely, $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2][Fe(\eta^5\text{-}C_5H_4COOH)_2][PF_6]$.[14] It is worth stressing that $[\mathbf{1}]^+$ possesses, at least in principle, both the capacity of acting as a cationic di-base for protonation and hydrogen-bond formation, as well as that of acting as a coordination ligand. In this study we explore the first of these characteristics. The downside of this is feature is that the counterion (in all cases discussed herein the $[PF_6]^-$ anion) is also "carried through" the acid–base reaction and the subsequent crystallization, thereby decreasing the level of predictability of the supramolecular architectures resulting from acid-base aggregation. As it will be seen in the following section, our compounds can be described as hetero-anionic salts, that is, containing both $[PF_6]^-$ and the anions obtained from deprotonation of fumaric and maleic acids of the protonated bis-amide $[\mathbf{1}]^+$.

In this paper we describe the results obtained from the reactions between $[\mathbf{1}]^+[PF_6]^-$ and the dicarboxylic fumaric and maleic acids. The idea is that of using the –COOH groups of the two acids as a probe of the hydrogen-bonding capacity of the organometallic complex $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2]^+$. Our interest stems from the observation that the cationic starting material can, at least in principle, behave both as a mono- and as a di-protonic acceptor at the two N-termini (thus leading to the formation of di- and tri-cationic complexes, see Scheme 1). These protonated forms can form hydrogen bonds with suitable acceptors. Furthermore, the presence of the two –(CO)NH amido groups confers additional hydrogen-bonding capacity to the molecule.



Scheme 1. The cationic bis-amide complex $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2]$, $[\mathbf{1}]^+$, together with the di- and tri-cationic species $[\mathbf{1}H]^{2+}$ and $[\mathbf{1}H_2]^{3+}$ obtained by mono- and di-protonation of the two N-termini.

Results and Discussion

As pointed out above, the organometallic amide $[\mathbf{1}]^+$ can exist in solution in three different forms depending on the degree of protonation, that is, $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2]^+$, $[\mathbf{1}]^+$, $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5C_5H_4CONHC_5H_4NH)]^{2+}$, $[\mathbf{1}H]^{2+}$, and $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4NH)_2]^{3+}$, $[\mathbf{1}H_2]^{3+}$. In the reaction with acids, the degree of protonation can be generally "tuned" by varying the base/acid molar ratio. Of the three cations, only the structure of $[\mathbf{1}]^+$ has been reported before and we refer the reader to the previous publication,[14] while the structures of the mono-protonated and di-protonated compounds have not yet been reported. Since the supramolecular structure of $[\mathbf{1}H]^{2+}$ is related to the following discussion, we shall first describe the packing of the dication $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}$, $[\mathbf{1}H]^{2+}$, while the tri-cation $[\mathbf{1}H_2]^{3+}$ will be seen in the structure of the adducts discussed below. Selected hydrogen bonding parameters for $[\mathbf{1}H]^{2+}$, as well as for all the other species described herein, are reported in Table 1.

The dication $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}$, $[\mathbf{1}H]^{2+}$, has been crystallized as its $[PF_6]^-$ salt in the form $2[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}\cdot 4[PF_6]^-\cdot H_2O$, $2[\mathbf{1}H]^{2+}\cdot 4[PF_6]^-\cdot H_2O$. The most interesting feature is that the dication forms hydrogen-bonded dimers in the solid state via N–H···N interactions, as shown in Figure 1. The resulting supramolecular aggregate is thus a tetracation "held together" by two N–H···N hydrogen bonds [N(4)···N(3) 2.715(4), N(8)···N(6) 2.738(4) Å, for the two crystallographically independent units shown in Figure 1].

It is worth noting that one of the tetracations is hydrogen-bridged with two water molecules [N···O 2.943(5) Å] and both cations also interact with the $[PF_6]^-$ anions, establishing N–H···F hydrogen-bonding interactions with the amidic N–H units [N···F distances in the range 3.025(4)–3.072(5) Å], as shown in Figure 2.

Reactions with Fumaric Acid

Even though it is possible to envisage several stoichiometric molar ratios between base and acid in the reaction of $[\mathbf{1}]^+$ with acids (see Table 1), our experiments show that

Table 1. Relevant hydrogen bonding parameters for all species discussed herein.

Compound	Donor···Acceptor	D···A [Å]
$2[\mathbf{1}H]^{2+}\cdot 4[PF_6]^-\cdot H_2O$	N(1)···F(19)	3.037(5)
	N(2)···F(8)	3.025(4)
	N(4)···N(3)	2.715(4)
	N(5)···F(21)	3.072(5)
	N(7)···O(5)	2.943(5)
	N(8)···N(6)	2.738(4)
$[\mathbf{1}H]^{2+}\cdot[PF_6]^-\cdot 1/2[\text{fumarate}]^{2-}$	N(2)···O(4)	2.703(6)
	N(1)···O(3)	2.809(6)
	N(3)···N(4)	2.669(7)
$[\mathbf{1}H_2]^{3+}\cdot[PF_6]^-\cdot[H(\text{fumarate})_2]^{3-}\cdot H_3O^+\cdot H_2O$	N(1)···O(3)	2.763(4)
	N(2)···O(10)	2.965(5)
	N(3)···O(100)	2.690(4)
	N(4)···O(200)	2.743(4)
	O(100)···O(8)	2.739(4)
	O(100)···O(200)	2.829(4)
	O(100)···O(6)	2.703(4)
	O(200)···O(100)	2.829(4)
	O(200)···O(5)	2.976(5)
	O(5)···O(8)	2.466(4)
$2[\mathbf{1}H]^{2+}\cdot 5/2[PF_6]^-\cdot 3/2[\text{Hmaleate}]^-$	N(4)···N(8)	2.688(6)
	N(6)···N(2)	2.686(6)
	N(1)···O(100)	2.832(6)
	N(3)···O(5)	2.923(5)
	N(5)···O(7)	2.916(6)
	N(7)···O(8)	2.836(6)
	O(6)···O(7)	2.460(5)
$2[\mathbf{1}H_2]^{3+}\cdot 3[PF_6]^-\cdot 3[\text{Hmaleate}]^-\cdot 2H_2O$	N1···O13	2.757(5)
	O100···O15	2.798(7)
	O100···O12	2.771(5)
	N2···O100	2.689(5)
	O200···O8	2.936(5)
	O200′···O8	2.838(5)
	N3···O14	3.016(5)
	N4···O8	2.789(5)
	N5···O10	2.822(5)
	N6···O12	2.791(6)
	N7···O6	2.794(4)
	N8···O200	2.702(6)
	O5···O7	2.407(4)
	O9···O11	2.416(4)
	O16···O14	2.477(5)
$[\mathbf{1}H_2]^{3+}\cdot 2[PF_6]^-\cdot[\text{Hmaleate}]^-\cdot H_2O$	O(4)···O(5)	2.411(5)
	N(1)···O(3)	2.884(7)
	N(2)···O(5)	2.923(7)
	N(2)···O(6)	2.873(8)
	N(4)···O(100)	2.787(8)
	O(100)···F(7)	3.1750(8)
	N(3)···F(12)	3.179(7)

only two stoichiometries yield crystalline aggregates, namely, $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}\cdot[PF_6]^-\cdot 1/2[\text{fumarate}]^{2-}$, $[\mathbf{1}H]^{2+}\cdot PF_6^-\cdot 1/2[\text{fumarate}]^{2-}$, and $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4NH)_2]^{3+}\cdot[PF_6]^-\cdot[H(\text{fumarate})_2]^{3-}\cdot H_3O^+\cdot H_2O$, $[\mathbf{1}H_2]^{3+}\cdot[PF_6]^-\cdot[H(\text{fumarate})_2]^{3-}\cdot H_3O^+\cdot H_2O$, obtained from the 2:1 and the reverse 1:2 amide/acid ratios, respectively. Amide/acid ratios 2:1, 1:1 and 1:1.5 all yielded the fumarate derivative $[\mathbf{1}H]^{2+}\cdot[PF_6]^-\cdot 1/2[\text{fumarate}]^{2-}$, while the ratios 1:2 and 1:3 both yielded the hydrogen fumarate derivative $[\mathbf{1}H_2]^{3+}\cdot[PF_6]^-\cdot[H(\text{fumarate})_2]^{3-}\cdot H_3O^+\cdot H_2O$. Why other stoichiometries, in particular the 1:1, are not obtained, is difficult to say. One should keep in mind, however, that the acid/base protonation equilibrium in solution is not the only aspect that may influence the final solid-state product stoichiometry. Solubility equilibria, for example, may favour one species over another, while kinetic aspects may have a role in the formation of long-living crystal nuclei in solution.

In the cases yielding $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}\cdot[PF_6]^-\cdot 1/2[\text{fumarate}]^{2-}$, $[\mathbf{1}H]^{2+}\cdot PF_6^-\cdot 1/2[\text{fumarate}]^{2-}$, the diprotic acid is able to protonate two molecules of the amide, raising the charge of the organometallic moiety from +1 to +2. This product is formed with stoichiometric ratios of up to 1:1.5 (which, incidentally, implies that there is unreacted fumaric acid that precipitates together with the crystals of the adduct). Above 1:1.5 the protonation equilibrium changes: the excess of fumaric acid leads to complete protonation of the bis-amido complex, to a total cationic charge of +3 and formation of the complex $[\mathbf{1}H_2]^{3+}$. The resulting material $[\mathbf{1}H_2]^{3+}\cdot[PF_6]^-\cdot[H(\text{fumarate})_2]^{3-}\cdot H_3O^+\cdot H_2O$ is crystallized together with a protonated water molecule (see below). The expected product, $[\mathbf{1}H_2]^{3+}\cdot[PF_6]^-\cdot[\text{fumarate}]^{2-}$, corresponding to the stoichiometric ratio 1:1 was not isolated.

Thus, the two crystals $[\mathbf{1}H]^{2+}\cdot[PF_6]^-\cdot 1/2[\text{fumarate}]^{2-}$ and $[\mathbf{1}H_2]^{3+}\cdot[PF_6]^-\cdot[H(\text{fumarate})_2]^{3-}\cdot H_3O^+$ contain the diprotonated and the triprotonated organometallic complexes, respectively. In spite of this difference, the two complexes show interesting structural relationships in the solid state:

i) The organometallic complexes in both the $[\mathbf{1}H]^{2+}\cdot[PF_6]^-\cdot 1/2[\text{fumarate}]^{2-}$ and the $[\mathbf{1}H_2]^{3+}\cdot[PF_6]^-\cdot[H(\text{fumarate})_2]^{3-}\cdot H_3O^+\cdot H_2O$ crystals adopt a *cisoid* (eclipsed) conformation of the Cp-pyridyl ligands.

ii) In $[\mathbf{1}H]^{2+}\cdot[PF_6]^-\cdot 1/2[\text{fumarate}]^{2-}$ the monoprotonated amide forms a cyclic dimer with another complex through N–H···N hydrogen bonds [N(3)···N(4) 2.669(7) Å], as shown in Figure 3.

iii) The dimers are linked together in a zigzag fashion by the interaction of the deprotonated fumarate dianions and the outer amido N–H groups (see Figure 3) [N(1)···O(3) 2.809(6), N(2)···O(4) 2.703(6) Å]. Each carboxylate unit "pinches" the two N–H groups of one complex; in such a way the organometallic cation and the fumarate dianion interact via four N–H···O bonds.

iv) In the case of $[\mathbf{1}H_2]^{3+}$, on the other hand, a dimer cannot form because both N-termini are protonated, nonetheless the complex retains the eclipsed geometry of the ligands and substituents (see part a of Figure 4). The pyridyl NH groups interact through hydrogen bonding with the $[H_3O]^+$ cation and the water molecule [N(3)···O(100) 2.690(4) and N(4)···O(200) 2.743(4) Å], which in turn interact with each other [O(100)···O(200) 2.829(4) Å]. The $[H_3O]^+$ cation and the water molecule are also hydrogen bonded to the $[H(\text{fumarate})_2]^{3-}$ anions (see part b of Figure 4) [O(100)···O(6) 2.703(4), O(100)···O(8) 2.739(4), O(200)···O(5) 2.976(5) Å].

v) The trications $[\mathbf{1}H_2]^{3+}$ are linked together by a supramolecular anion formed by a hydrogen fumarate unit and a fumarate dianion. Since the proton is mid-way along the

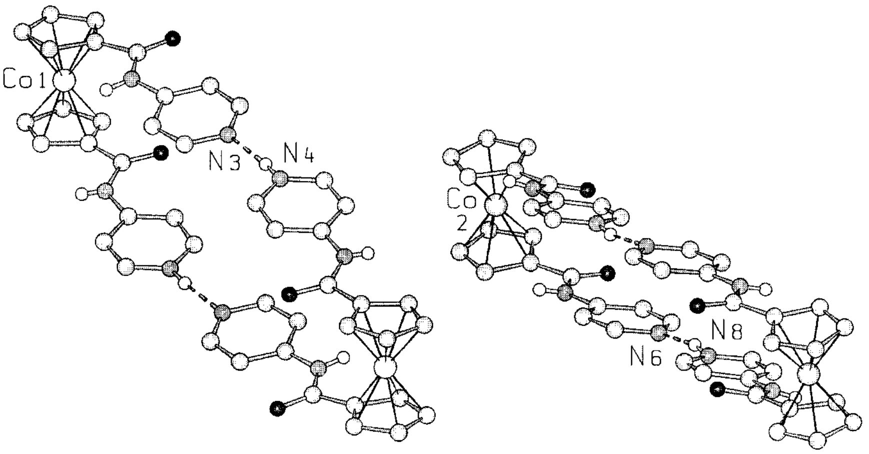


Figure 1. The supramolecular aggregates present in $2[\mathbf{1}H]^{2+}\cdot 4[PF_6]^{-}\cdot H_2O$. The tetra-cation is "held together" by two N–H···N hydrogen bonds [N(4)···N(3) 2.715(4), N(8)···N(6) 2.738(4) Å for the two crystallographically independent units]. [H_{CH}, H_{water} and $H_{[H_3O]^+}$ atoms not shown for clarity].

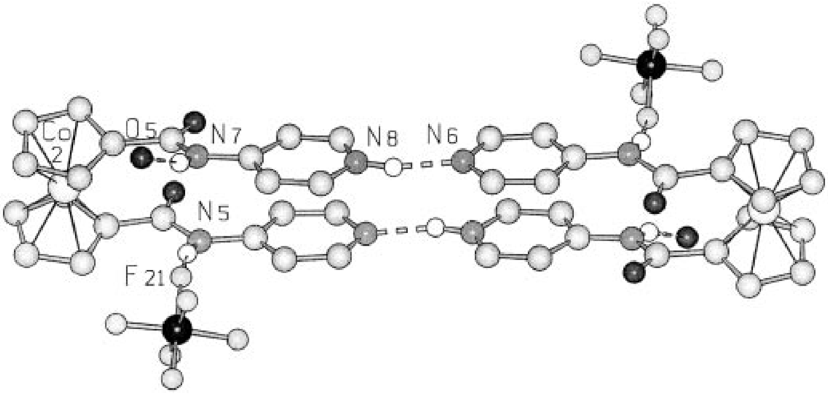


Figure 2. N–H···O and N–H···F hydrogen-bonding interactions between the bis-amide $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}$ and the hexafluorophosphate anions and the water molecules. [H_{CH}, H_{water} and $H_{[H_3O]^+}$ atoms not shown for clarity].

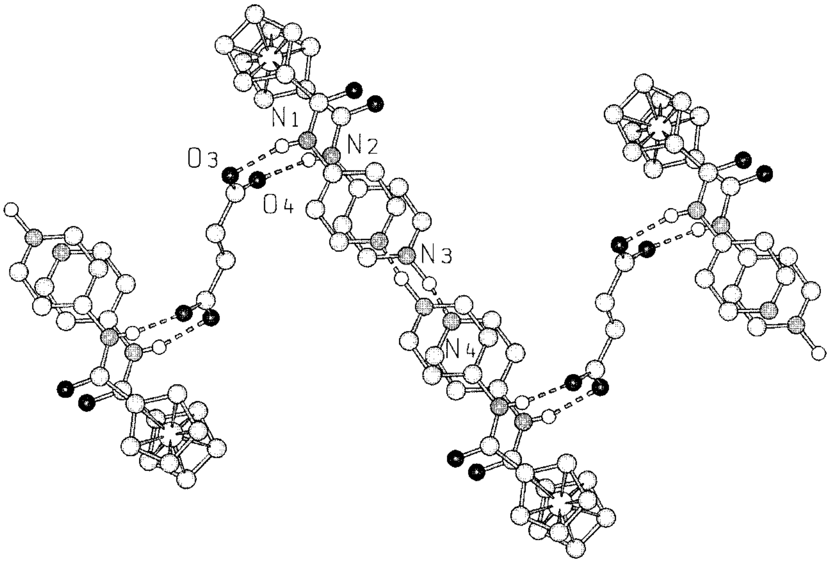


Figure 3. Crystalline $[\mathbf{1}H]^{2+}\cdot[PF_6]^{-}\cdot 1/2[\text{fumarate}]^{2-}$. The hydrogen-bridged amide dimers [N(3)···N(4) 2.669(7) Å] are linked together in a zigzag fashion through the interaction of the deprotonated fumarate dianions and the outer amido N–H groups, [N(1)···O(3) 2.809(6), N(2)···O(4) 2.703(6) Å]. Each carboxylate unit "pinches" both the amido N–H groups of one complex; in such a way each fumarate dianion interacts with the organometallic cations through four N–H···O bonds. [H_{CH}, H_{water} and $H_{[H_3O]^+}$ atoms not shown for clarity].

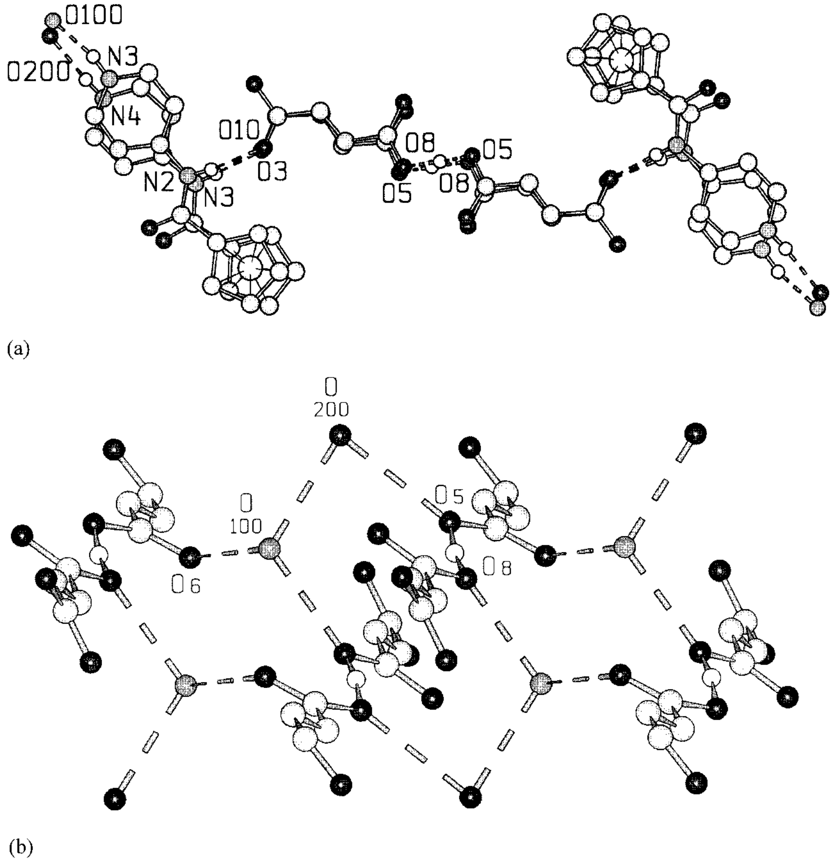


Figure 4. (a) In crystalline $[\mathbf{1}H_2]^{3+}\cdot[PF_6]^-\cdot[H(fumarate)_2]^{3-}\cdot H_3O^+\cdot H_2O$ the trications are linked together by a supramolecular anion formed by a hydrogen fumarate unit and a fumarate dianion. Since the proton is mid-way along the O···O bond in this unit, it is more appropriate to describe the systems as a superanion $[H(fumarate)_2]^{3-}$, with an O(5)···O(8) separation of 2.466(4) Å. (b) The $[H_3O]^+$ cation and the water molecule interact via hydrogen bonding with each other [O(100)···O(200) 2.829(4) Å] and with the $[H(fumarate)_2]^{3-}$ anion [O(100)···O(6) 2.703(4), O(100)···O(8) 2.739(4), O(200)···O(5) 2.976(5) Å]. [H_{CH}, H_{water} and $H_{[H_3O]^+}$ atoms not shown for clarity].

O···O bond [O(5)···O(8) 2.466(4) Å], it is more appropriate to describe the system as a superanion of formula $[H(fumarate)_2]^{3-}$.

vi) On both sides the supramolecular trianion $[H(fumarate)_2]^{3-}$ interacts with the amido N–H groups, as observed in $[\mathbf{1}H]^{2+}$ with N(1)···O(3) and N(2)···O(10) separations of 2.763(4) and 2.965(5) Å, respectively.

Reactions with Maleic Acid

In terms of supramolecular bonding capacity and hydrogen-bond formation, maleic acid differs from fumaric acid mainly in the fact that mono-deprotonation leads in general to formation of an intramolecular hydrogen bond. As a consequence of the intramolecular hydrogen-bonding formation the carboxylate groups are available only for hydrogen-bonding acceptance.

The structure of $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}\cdot 5/2[PF_6]^-\cdot 3/2[Hmaleate]^-$, $2[\mathbf{1}H]^{2+}\cdot 5/2[PF_6]^-\cdot 3/2[Hmaleate]^-$, is reminiscent of those of the mono-protonated amide salt $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}\cdot 4[PF_6]^-\cdot H_2O$ and of the hydrogen fumarate salt $[\mathbf{1}H]^{2+}\cdot[PF_6]^-\cdot 1/2[maleate]^{2-}$. These systems have in common the presence of hydrogen bond dimers in the solid state (see Figure 5). The N–H···N

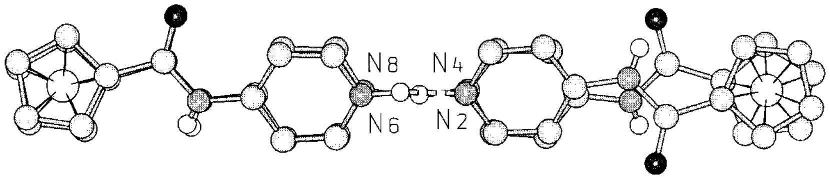


Figure 5. The hydrogen bonded dimer in crystalline $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}\cdot 5/2[PF_6]^-\cdot 3/2[Hmaleate]^-$, $2[\mathbf{1}H]^{2+}\cdot 5/2[PF_6]^-\cdot 3/2[Hmaleate]^-$. Note how the amido groups are eclipsed in one of the two dications and staggered in the other. [H_{CH}, H_{water} and $H_{[H_3O]^+}$ atoms not shown for clarity].

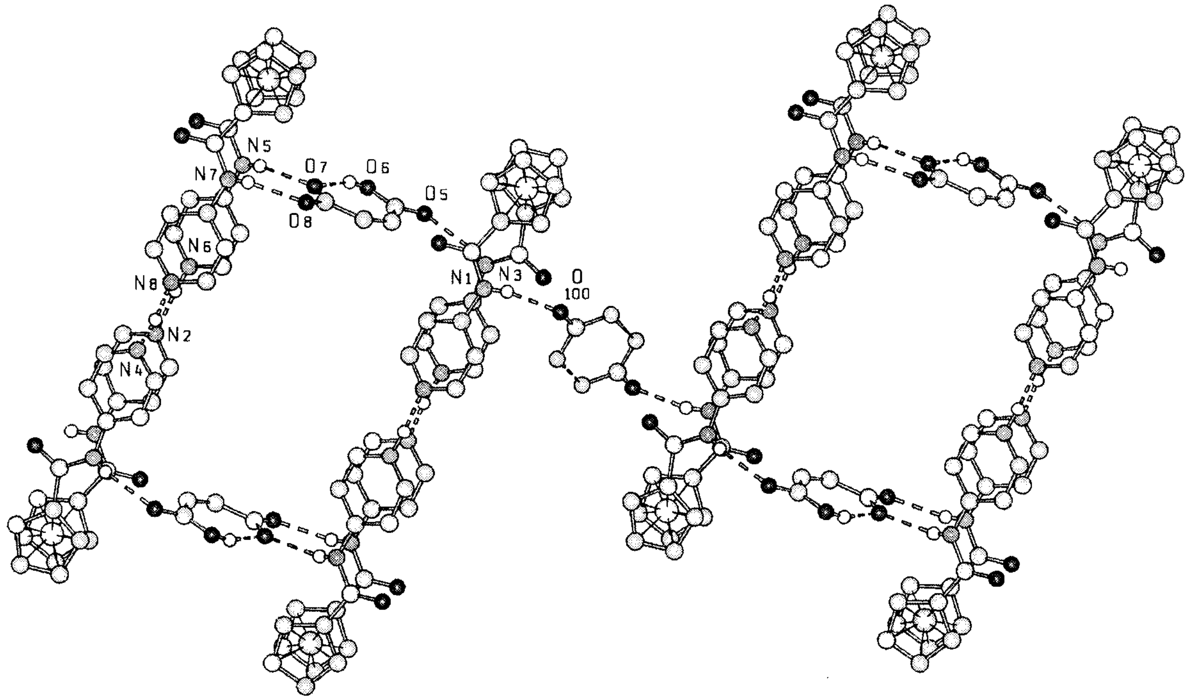


Figure 6. The structure of $2[\mathbf{1}H]^{2+}\cdot 5/2[PF_6]^-\cdot 3/2[Hmaleate]^-$ shows the presence of hydrogen-bonded dimers in the solid state of the type observed for $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)(\eta^5\text{-}C_5H_4CONHC_5H_4NH)]^{2+}\cdot[PF_6^-]_4\cdot H_2O$, as well as the hydrogen fumarate salts $[\mathbf{1}H]^{2+}\cdot[PF_6]^-\cdot 1/2[fumarate]^{2-}$. Note, however, that the amido groups are eclipsed in one of the two di-cations and staggered in the other (see Figure 5). The "dimers of dimers" are held together by a hydrogen oxalate anion, which is disordered over two orientations (only one of the two images is shown here for clarity). [H_{CH}, H_{water} and $H_{[H_3O]^+}$ atoms not shown for clarity].

separations are comparable in length [N(4)···N(8) 2.688(6); N(6)···N(2) 2.686(6) Å]. Note, however, that the amido groups are eclipsed in one of the two dications and staggered in the other. This difference seems to suggest that in solution the complex is present with both, possibly dynamically interconverting conformations, which are frozen out at the stage of crystallization. It is also noteworthy that compound $2[\mathbf{1}H]^{2+}\cdot 5/2[PF_6]^-\cdot 3/2[Hmaleate]^-$ is the only case, in this study, where the Cp-amido ligands show both the staggered and eclipsed relative orientations of the C(=O)NH units. The arrangement of the hydrogen maleate anions provides a possible rationale for the difference. As shown in Figure 6, the hydrogen maleate anions provide two types of bridges between neighbouring dimers.

Because of the mentioned scarcity of hydrogen-bonding donor sites, the interaction links have to utilize the amido N–H groups. The structure can be described as formed of "dimers of dimers" held together by two ordered hydrogen maleate anions, for a total of six N–H···O interactions [N(3)···O(5) 2.923(5), N(5)···O(7) 2.916(6), N(7)···O(8) 2.836(6) Å]. The N(1)–H(100) donor group, which is not involved in the "dimer of dimer" formation, can thus be used to link together the "dimers of dimers" through the disordered hydrogen maleate [N(1)···O(100) 2.832(6) Å] (see Figure 6). This picture also provides a rationale for the disorder observed in the latter hydrogen maleate anion, which is oriented randomly in two positions around the crystallographic inversion centre.

Let us now consider the cases of compounds $2[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4NH)_2]^{3+}\cdot 3[PF_6]^-\cdot 3[Hmaleate]^-\cdot 2H_2O$, $2[\mathbf{1}H_2]^{3+}\cdot 3[PF_6]^-\cdot 3[Hmaleate]^-\cdot 2H_2O$, and $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4NH)_2]^{3+}\cdot 2[PF_6]^-\cdot[Hmaleate]^-\cdot H_2O$, $[\mathbf{1}H_2]^{3+}\cdot 2[PF_6]^-\cdot[Hmaleate]^-\cdot H_2O$. These two crystalline materials, in spite of the different stoichiometry, bear some close structural relationships. In both systems the intramolecular hydrogen maleate anion acts as a bridge between two trications (compare Figure 7 and Figure 8) by accepting hydrogen-bond donation from the protonated pyridine N-terminus and from the amido N–H system of two distinct cations [N···O distances in the range 2.789(5)–2.923(7) Å]. The hydrogen maleate bridges thus generate an extended network of alternating cations and anions, thanks also to the rotational freedom about the Cp–Co–Cp axis. In addition to this, in compound $2[\mathbf{1}H_2]^{3+}\cdot 3[PF_6]^-\cdot 3[Hmaleate]^-\cdot 2H_2O$ the two hydrogen maleates that do not act as bridges still interact each with an organometallic cation via NH···O hydrogen bonds [N(5)···O(10), N(8)···O(9), N(1)···O(13) Å] (Figure 7) and establish hydrogen-bonding interactions with the water molecules [O···O distances in the range 2.771(5)–2.936(5) Å].

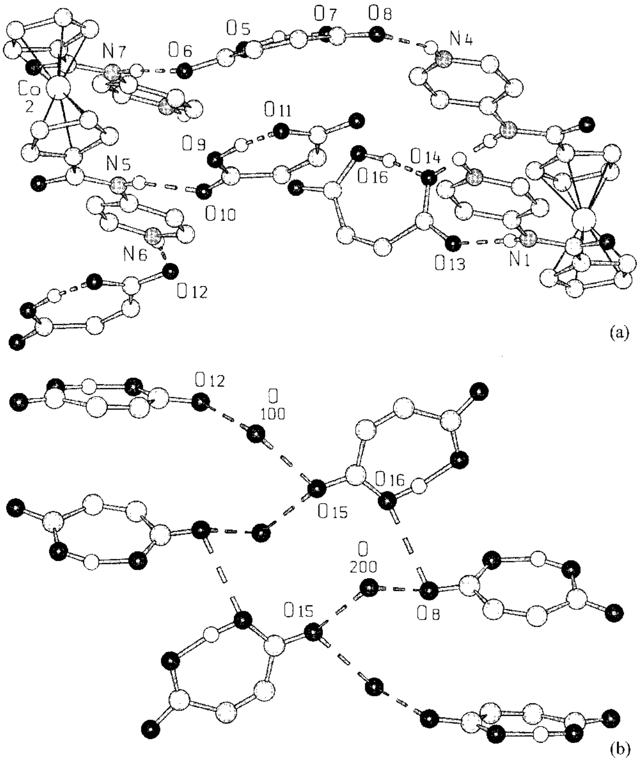


Figure 7. (a) The extended hydrogen-bonded network in crystalline $2[\mathbf{1}H_2]^{3+}\cdot 3[PF_6]^-\cdot 3[Hmaleate]^-\cdot 2H_2O$. Note how one hydrogen maleate anion acts as a bridge between trications while another one establishes hydrogen at the intracation level. (b) The hydrogen bonding interactions between the water molecules and the hydrogen maleates that are not involved in the cation bridging (water hydrogen atoms not shown for clarity). [H_{CH}, H_{water} and $H_{[H_3O]^+}$ atoms not shown for clarity].

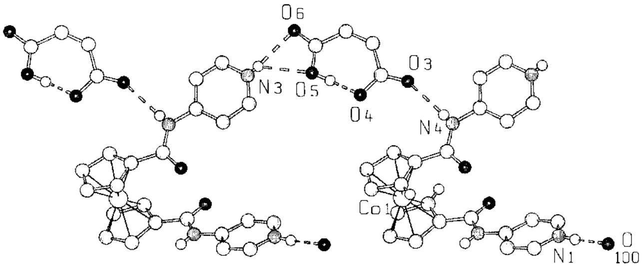


Figure 8. (a) The extended hydrogen-bonded network in crystalline $[\mathbf{1}H_2]^{3+}\cdot 2[PF_6]^-\cdot [Hmaleate]^-\cdot H_2O$. Note how the hydrogen maleate anion acts as a bridge between trications forming an extended network. [H_{CH}, H_{water} and $H_{[H_3O]^+}$ atoms not shown for clarity]

Conclusions

The aim of this study was to explore the supramolecular bonding capacity of the cationic bis-amide complex $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2][PF_6]$, $[\mathbf{1}]^+[PF_6]^-$, towards the dicarboxylic fumaric and maleic acids. The idea was to use the –COOH groups as a probe of the hydrogen-bonding capacity of the organometallic complex.

In previous studies we have extensively investigated the behaviour of organometallic dicarboxylic acids, such as, $[Fe(\eta^5\text{-}C_5H_4COOH)_2]$, $[Co(\eta^5\text{-}C_5H_4COOH)_2]^+$ and $[Cr(\eta^6\text{-}C_6H_5COOH)_2]$[12] towards a variety of organic and inorganic acids or bases. The results of these studies have led us to the successful exploitation of the acid/base behaviour of one such species, namely the zwitterionic form $[Co(\eta^5\text{-}C_5H_4COOH)(\eta^5\text{-}C_5H_4COO)]$, obtained by deprotonation of the cobalticinium cationic acid, in heterogeneous reactions with vapours of acids and bases.[13,15] In a parallel investigation we have studied the reactivity of neutral disubstituted pyridyl and pyrimidyl ferrocenyl species towards acids and metal complexes.[16] With the present work we intended to extend these findings to a new class of supramolecular synthons, namely that of cationic bis-amido complexes, of which $[Co^{III}(\eta^5\text{-}C_5H_4CONHC_5H_4N)_2]^+$ is the prototype.[17]

In the course of this investigation we have shown that both fumaric and maleic acids are sufficiently strong as to protonate the pyridine moiety. However, in the case of maleic acid, formation of the intramolecular hydrogen bond yields compounds that contain only the hydrogen maleate monoanion, while in the case of fumaric acid, both the completely deprotonated fumarate dianion and the supramolecular trianion formed by one hydrogen fumarate mono-anion and one fumarate dianion were obtained.

In terms of organometallic moieties, most adducts, but not all, contain the dimer formed by the monoprotonated dication $[\mathbf{1}H]^{2+}$ and are held together by intercation N–H···N hydrogen bonds between a protonated and a free pyridyl N atom, while the O-atom acceptors on the fumarate and hydrogen maleate anions appear to be involvedexclusively in interactions with the amido –(CO)N–H hydrogen-bond donors. Only in the case of $[\mathbf{1}H_2]^{3+}\cdot 2[PF_6]^-\cdot [Hmaleate]^-\cdot H_2O$ an interaction between the N-atom and the acid is observed.

Further studies are in progress to utilize the bis-amido complexes in the formation of complexes of complexes, for applications in coordination chemistry and crystal engineering.

Experimental Section

All reactants were purchased from Aldrich and used without further purification. Reagent grade solvents and bidistilled water were used.

Synthesis of $[\mathbf{1}H]^{2+}\cdot 2[PF_6]^-$: $[\mathbf{1}H]^{2+}$ was synthesized following a procedure, slightly modified, reported by Beer and Stokes.[18]

Synthesis of $[\mathbf{1}]^+\cdot [PF_6]^-$: $[\mathbf{1}H]^{2+}$ was treated with a 0.1 M solution of NH_3, in order to obtain deprotonation of the two pyridine moieties. Elementary analysis: calcd. C 46.01, N 9.55, H 3.16; found C 46.04, N 9.53, H 3.12.

Synthesis of $[\mathbf{1}H]^{2+}\cdot [PF_6]^-\cdot 1/2[fumarate]^{2-}$: $[\mathbf{1}]^+\cdot [PF_6]^-$ (0.11 mmol) and fumaric acid, $C_4H_2O_4$ (0.11 mmol) were dissolved in 5 mL of water. Crystals suitable for single-crystal X-ray diffraction were obtained by slow evaporation of water. The same compound was obtained after reaction of $[\mathbf{1}]^+\cdot [PF_6]^-$ (0.11 mmol) with $C_4H_2O_4$ (0.5 and 1.5 mmol; 2:1 and 1:1.5 reagents ratio, respectively). Elementary analysis: calcd. C 45.59, N 8.86, H 3.19; found C 45.57, N 8.85, H 3.20.

Synthesis of [1H$_2$]$^{3+}$·[PF$_6$]$^-$·[H(fumarate)$_2$]$^{3-}$·H$_3$O$^+$·H$_2$O: [**1**]$^+$·[PF$_6$]$^-$ (0.11 mmol) and fumaric acid, $C_4H_2O_4$, (0.22 mmol) were dissolved in 5 mL of water. Crystals suitable for single-crystal X-ray diffraction were obtained by slow evaporation of water. The same compound was obtained after reaction of [**1**]$^+$·[PF$_6$]$^-$ (0.11 mmol) with $C_4O_4H_2$ (0.33 mmol; 1:3 reagents ratio). Elementary analysis: calcd. C 42.77, N 6.65, H 3.59; found C 42.78, N 6.63, H 3.60.

Synthesis of 2[1H]$^{2+}$·5/2[PF$_6$]$^-$·3/2[maleate]$^{2-}$: [**1**]$^+$·[PF$_6$]$^-$ (0.22 mmol) and maleic acid, $C_4H_2O_4$, (0.11 mmol) were dissolved in 5 mL of water. Crystals suitable for single-crystal X-ray diffraction were obtained by slow evaporation of water. Elementary analysis: calcd. C 43.12, N 8.04, H 2.86; found C 42.14, N 80.02, H 2.86.

Synthesis of 2[1H$_2$]$^{3+}$·3[PF$_6$]$^-$·3[Hmaleate]$^-$·2H$_2$O: [**1**]$^+$·[PF$_6$]$^-$ (0.11 mmol) and maleic acid, $C_4H_2O_4$, (0.22 mmol) were dissolved in 5 mL of water. Crystals suitable for single-crystal X-ray diffraction were obtained by slow evaporation of water. Elementary analysis: calcd. C 40.21, N 6.69, H 2.83; found C 40.22, N 6.70, H 2.83.

Synthesis of [1H$_2$]$^{3+}$·2[PF$_6$]$^-$·[Hmaleate]$^-$·H$_2$O: [**1**]$^+$·[PF$_6$]$^-$ (0.11 mmol)and an excess of maleic acid, $C_4H_2O_4$, were dissolved in 5 mL of water. Crystals suitable for single-crystal X-ray diffraction were obtained by slow evaporation of water. Elementary analysis: calcd. C 36.64, N 6.57, H 2.72; found C 36.62, N 6.55, H 2.72.

Crystal Structure Determination: Crystal data for all compounds were collected on a Bruker ApexII CCD diffractometer. Crystal data and details of measurements are summarised in Table 2. Common to all compounds: Mo-*K*α radiation, λ = 0.71073 Å, monochromator: graphite. Data for 2[**1**H]$^{2+}$·5/2[PF$_6$]$^-$·3/2[Hmaleate]$^-$ were collected at 293 K, all other data were collected at 273 K. SHELX97[19a] was used for structure solution and refinement based on F^2. Non-hydrogen atoms were refined anisotropically. The [PF$_6$]$^-$ anion in [**1**H]$^{2+}$·[PF$_6$]$^-$·1/2[fumarate]$^{2-}$ is disordered over two positions (refined with an occupancy ratio of 80:20) around the F1–F5 axis. One of the two [Hmaleate]$^-$ ions in [**1**H]$^{2+}$·5/2[PF$_6$]$^-$·3/2[Hmaleate]$^-$ is disordered over two equivalent positions around an inver-

Table 2. Crystal data and details of measurements for 2[1H]$^{2+}$·4[PF$_6$]$^-$·H$_2$O, [1H]$^{2+}$·[PF$_6$]$^-$·1/2[fumarate]$^{2-}$, [1H$_2$]$^{3+}$·[PF$_6$]$^-$·[H(fumarate)$_2$]$^{3-}$·H$_3$O$^+$·H$_2$O, 2[1H]$^{2+}$·5/2[PF$_6$]$^-$·3/2[Hmaleate]$^-$, 2[1H$_2$]$^{3+}$·3[PF$_6$]$^-$·3[Hmaleate]$^-$·2H$_2$O and [1H$_2$]$^{3+}$·2[PF$_6$]$^-$·[Hmaleate]$^-$·H$_2$O.

Compound	2[1H]$^{2+}$·4[PF$_6$]$^-$·H$_2$O	[1H]$^{2+}$·[PF$_6$]$^-$·1/2[fumarate]$^{2-}$	[1H$_2$]$^{3+}$·[PF$_6$]$^-$·[H(fumarate)$_2$]$^{3-}$·H$_3$O$^+$·H$_2$O
Formula	$C_{44}H_{40}Co_2F_{24}N_8O_5P_4$	$C_{24}H_{20}CoF_6N_4O_4P$	$C_{30}H_{30}CoF_6N_4O_{12}P$
M_r	1458.58	632.34	482.48
System	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a [Å]	23.468(2)	7.9833(3)	7.583(7)
b [Å]	15.373(1)	29.284(1)	13.552(5)
c [Å]	15.304(1)	10.5411(4)	16.526(4)
α [°]	90	90	89.38(2)
β [°]	92.714(3)	90.836(1)	84.90(4)
γ [°]	90	90	80.66(5)
V [Å³]	5515.1(7)	2464.1(2)	1669(2)
Z	4	4	2
T [K]	293	293	293
μ(Mo-K_α) [mm^{-1}]	0.852	0.848	1.676
Measured reflns.	63612	23263	13537
Unique reflns.	16083	5369	5844
Refined parameters	823	372	471
GOF on F^2	1.018	0.885	1.010
R_1 [on F, $I > 2\sigma(I)$]	0.0641	0.0611	0.0648
wR_2 (on F^2,all data)	0.2342	0.1832	0.1392
Compound	2[1H]$^{2+}$·5/2[PF$_6$]$^-$·3/2[Hmaleate]$^-$	2[1H$_2$]$^{3+}$·3[PF$_6$]$^-$·3[Hmaleate]$^-$·2H$_2$O	[1H$_2$]$^{3+}$·2[PF$_6$]$^-$·[Hmaleate]$^-$·H$_2$O
Formula	$C_{50}H_{41.50}Co_2F_{15}N_8O_{10}P_{2.5}$	$C_{56}H_{53}Co_2F_{18}N_8O_{18}P_3$	$C_{26}H_{25}CoF_{12}N_4O_7P_2$
M_r	1394.70	1678.83	854.37
System	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/a$
a [Å]	10.6826(5)	12.7015(8)	13.1655(4)
b [Å]	14.2849(7)	14.6608(9)	12.7040(4)
c [Å]	19.6711(9)	19.758(1)	19.7122(6)
α [°]	95.080(1)	70.667(1)	90
β [°]	104.807(1)	86.814(1)	97.7600(10)
γ [°]	107.763(1)	70.147(1)	90
V [Å³]	2718.2(2)	3258.7(3)	3266.8(2)
Z	2	2	4
T [K]	273	293	293
μ(Mo-K_α) [mm^{-1}]	0.802	0.712	1.737
Measured reflns	26312	38487	25629
Unique reflns.	9654	15238	5745
Refined parameters	782	970	463
GOF on F^2	1.074	0.823	1.024
R_1 [on F, $I > 2\sigma(I)$]	0.0550	0.0543	0.0656
wR_2 (on F^2,all data)	0.1758	0.1576	0.2010

sion centre, and was difficult to model; the position of the independent carbon atom and of the oxygen atom involved in the intramolecular hydrogen bond could not be separated well from those of the second, inverted image; the refinement was then done by attributing an average C/O scattering factor to the two atoms. All hydrogen atoms bound to nitrogen and oxygen atoms were located by difference Fourier syntheses. Only the hydrogen atoms bound to the water molecule in $2[\mathbf{1}H]^{2+}\cdot 4[PF_6]^{-}\cdot H_2O$ and $[\mathbf{1}H_2]^{3+}\cdot 2[PF_6]^{-}\cdot[Hmaleate]^{-}\cdot H_2O$, and the H_{COOH} hydrogen in the disordered maleate monoanion in $2[\mathbf{1}H]^{2+}\cdot 5/2[PF_6]^{-}\cdot 3/2[Hmaleate]^{-}$ could not be located. Hydrogen atoms bound to carbon atoms were added in calculated positions. SCHAKAL99[19b] was used for the graphical representation of the results. The program PLATON[19c] was used to calculate the hydrogen-bonding interactions reported in Table 1.

CCDC-260092 to -260097 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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