FULL PAPER

Crystal synthesis of hybrid organometallic-inorganic hydrogen bonded salts of acid oxoanions

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Partially deprotonated inorganic oxoanions derived from sulfuric and phosphoric acids have been used to assemble organometallic cations in inorganic–organometallic hybrid systems. The organometallic sandwich cations $[(\eta^5-C_5H_5)_2Co]^+$, $[(\eta^5-C_5Me_5)_2Co]^+$ and $[(\eta^5-C_5Me_5)_2Fe]^+$ have been used because they do not interfere with hydrogen bonding formation *forcing* self-assembling of the inorganic acids anions HSO₄⁻ and H₂PO₄⁻ into hydrogen bonded mono- and bi-dimensional networks.

Hydrogen bonding interactions between ions have been a subject of continuing investigations in solution¹ and in the solid state² as well as of theoretical studies by both empirical and *ab initio* methods.³ More recently hydrogen bonds (HB) between ions have begun to be systematically utilised in the crystal engineering of new materials, with remarkable achievements.^{4,5} The reason for this interest stems from the fact that HB between ions combine the strength of the Coulombic field generated by the ions with the directionality and reproducible topology of hydrogen bonding interactions.⁶

Considerable efforts have been made to correlate concepts such as acidity and basicity to HB formation and stability.⁷ Correlations between pK of the acids and HB distances are available.⁸ It has been recently argued, however, that hydrogen bonding ability can be better appreciated by examining the charge distribution in the HB system rather than its acid–base chemistry.⁹

A field of potential practical applications of HB between ions is that of protonics and superprotonic conductivity exploited in fuel cell technology. The existence of different configurations of the hydrogen atom location within O-H···O systems is at the basis of the possibility of constructing proton conducting materials. These materials, in particular those based on solid-acid salts such as CsHSO₄, Rb₃H(SeO₄)₂, etc.^{10a} have applications in a number of devices such as H₂ and H₂O sensors, fuel and steam cells and high energy density batteries. The solid-acid salts derived from polyprotic acids such as H₃PO₄ and H₂SO₄ by partial deprotonation all show the presence of strong inter-anionic hydrogen bonding association. At high temperature, these systems often undergo an order-disorder phase transition, denoted a superprotonic transition, which is associated with a dramatic increase of the conductivity.10b,c For this reason, and because they are thermally stable (up to 500-550 K), they have been recently begun to be exploited as solid fuel cell electrolytes. Hybrid anionic systems, such as Cs₂(HSeO₄)(H₂PO₄), have also begun to be investigated.¹¹ The phenomenon of superprotonic conductivity is explained with the possibility of proton jumps from one anion to the nearby one associated with the onset of the reorientational motion of the oxoacid anions

Another aspect of interest of HB between ions arises from the consideration that proton transfer processes in hydrogen bonding interactions, whether associated with a phase transition or not, may imply the transformation of a molecular crystal into a molecular salt. Wilson¹² has discussed, on the basis of an elegant neutron diffraction study, the migration of the proton along an O–H…O bond in a co-crystal, urea–phosphoric acid (1:1), whereby the proton migrates towards the mid-point of the hydrogen bonding interaction as the temperature is increased, becoming essentially centred at T = 335 K. Mootz and Wiechert,¹³ on the other hand, have isolated

two crystalline materials composed of pyridine and formic acid of different composition and different location of the H-atom in the $O \cdots H \cdots N$ bond. In a recent study, we have investigated proton location in $O-H \cdots N$ bonds by a combination of X-ray and solid-state NMR spectroscopy.¹⁴

Because of this combination of practical and academic interests, we have undertaken a systematic study of the preparation, characterization and, possibly, evaluation of hybrid systems formed by inorganic acid oxoanions and organometallic cations.

In this first paper we report the investigation of hydrogen sulfate and dihydrogen phosphate salts of the organometallic sandwich cations $[(\eta^5-C_5H_5)_2Co]^+$, $[(\eta^5-C_5Me_5)_2Co]^+$ and $[(\eta^5-C_5Me_5)_2Co]^+$ $C_5Me_5)_2Fe^{+}$. In particular, we will discuss the structures and hydrogen bonding interactions in the hydrogen sulfate systems $[(\eta^{5}-C_{5}Me_{5})_{2}Co][H_{3}O]_{2}[SO_{4}HSO_{4}]\cdot 2H_{2}O, 1Co, [(\eta^{5}-C_{5}Me_{5})_{2}Fe] [H_3O]_2[SO_4HSO_4] \cdot 2H_2O$, **1Fe** and $[(\eta^5 - C_5Me_5)_2Fe]_2[H_3O][HSO_4]_3$ **2Fe**, as well as in the dihydrogen phosphate systems $[(\eta^5 C_5Me_5)_2Co][H_3PO_4][H_2PO_4],$ **3Co**, $[(\eta^{5}-C_{5}Me_{5})_{2}Fe][H_{3}PO_{4}] [H_2PO_4]$, **3Fe** and $[(\eta^5-C_5H_5)_2Co]H_3PO_4][H_2PO_4]$, **4Co**. The choice of using sandwich cations derived from cobaltocene, decamethylcobaltocene and ferrocene is dictated by the well known stability of these cations and by the structural non-rigidity of these systems and of their parent neutral molecules in the solid state.15 Furthermore, these sandwich cations do not carry functional groups able to compete in the formation of strong hydrogen bonding interactions because the periphery is covered by C-H groups that can only take part in C-H...O hydrogen bonding interactions with the oxoanions. This characteristic is required in order to force inter-anionic hydrogen bonding formation between the inorganic anions, which is a prerequisite for the desired proton mobility. The inter-anionic hydrogen bonding motifs will be compared with those observed in other organometallic salts of the same anions.

Results and discussion

In view of their structural similarity the compounds listed below will be discussed in two separate subsets, those derived from sulfuric acid and those derived from phosphoric acid. Relevant hydrogen bonding parameters are listed in Table 1.

Hydrogen bonding patterns and crystal structures of $[(\eta^5-C_5Me_5)_2C_0][H_3O]_2$ [SO₄HSO₄]·2H₂O, 1Co, $[(\eta^5-C_5Me_5)_2Fe]-[H_3O]_2$ [SO₄HSO₄]·2H₂O, 1Fe and $[(\eta^5-C_5Me_5)_2Fe]_2$ [H₃O]-[HSO₄]₃, 2Fe

Compounds **1Co** and **1Fe** possess the same stoichiometry and show the same hydrogen bonding patterns in their solids. The two crystals can be described as constituted of layers containing the

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Compound	Interaction	O–H/Å	H····O/Å	O…O/Å	O−H···O/°	Operators for generating equivalent atoms
1Co	$\begin{array}{c} O_1 - H_{100} \cdots O_{1(1)} \\ O_5 - H_{500} \cdots O_2 \\ O_5 - H_{501} \cdots O_{3(11)} \\ O_5 - H_{502} \cdots O_6 \\ O_{6(11)} - H_{600} \cdots O_4 \\ O_6 - H_{600} \cdots O_4 \\ O_6 - H_{600} \cdots O_4 \end{array}$	$\begin{array}{c} 1.26\\ 1.16(13)\\ 0.72(5)\\ 1.12(10)\\ 0.86(5)\\ 0.73(5)\end{array}$	$\begin{array}{c} 1.26 \\ 1.40(13) \\ 1.96(5) \\ 1.33(10) \\ 1.87(5) \\ 2.00(5) \end{array}$	2.519(4) 2.546(4) 2.572(4) 2.438(4) 2.702(3) 2.718(3)	180 168(10) 143(5) 172(9) 161(5) 169(4)	-x + 1, -y + 1, -z + 1 -x + 1, y, -z + 1 -x + 1, y + 1/2, -z + 3/2 -x + 1, y - 1/2, -z + 3/2
1Fe	$\begin{array}{c} O_{6} & H_{601} & \odot_{4(1V)} \\ O_{1} - H_{100} \cdots O_{1(1)} \\ O_{5} - H_{501} \cdots O_{2} \\ O_{5} - H_{501} \cdots O_{3(1I)} \\ O_{5} - H_{502} \cdots O_{6} \\ O_{6(1II)} - H_{600} \cdots O_{4} \\ O_{6} - H_{601} \cdots O_{4(1V)} \end{array}$	1.26 0.80(8) 0.88(7) 1.12(8) 0.83(5) 0.74(5)	$\begin{array}{c} 1.26\\ 1.78(8)\\ 1.72(8)\\ 1.31(8)\\ 1.93(5)\\ 2.00(5) \end{array}$	2.515(5) 2.555(5) 2.433(6) 2.554(6) 2.705(5) 2.718(5)	180 160(9) 157(8) 173(8) 157(5) 165(5)	$-x + \frac{1}{2}, -y + \frac{3}{2}, -z$ $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$ $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$ $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$
2Fe	$\begin{array}{c} O_{1} \cdots O_{8} \\ O_{3} \cdots O_{13} \\ O_{4} \cdots O_{5} \\ O_{7} \cdots O_{13'} \end{array}$			2.52(1) 2.51(1) 2.63(1) 2.77(2)		-x + 1/2, y + 1/2, -z + 1/2
3Co	$O_1-H_{100}\cdots O_5$ $O_2-H_{200}\cdots O_6$ $O_3-H_{300}\cdots O_6$ $O_7-H_{700}\cdots O_5$ $O_8-H_{800}\cdots O_4$	$\begin{array}{c} 0.71(10) \\ 0.84(7) \\ 0.75(9) \\ 0.96(14) \\ 0.75(10) \end{array}$	1.82(9) 1.76(7) 1.80(8) 1.64(14) 1.80(9)	2.531(9) 2.559(8) 2.553(8) 2.606(8) 2.550(9)	176(9) 159(8) 173(8) 176(9) 177(10)	$x - \frac{1}{2}, y + \frac{3}{2}, z - \frac{1}{2}$ $x - \frac{1}{2}, y + \frac{3}{2}, z - \frac{1}{2}$
3Fe	$\begin{array}{c} O_1 - H_{100} \cdots O_5 \\ O_2 - H_{200} \cdots O_6 \\ O_3 - H_{300} \cdots O_6 \\ O_7 - H_{700} \cdots O_5 \\ O_8 - H_{800} \cdots O_4 \end{array}$	0.94(6) 0.92(6) 0.92(7) 0.80(7) 0.97(7)	1.59(5) 1.64(6) 1.66(7) 1.80(7) 1.59(6)	2.527(4) 2.549(4) 2.565(4) 2.590(4) 2.548(5)	174(6) 165(5) 166(6) 171(8) 172(5)	$x - \frac{1}{2}, y + \frac{3}{2}, z - \frac{1}{2}$ $x - \frac{1}{2}, y + \frac{3}{2}, z - \frac{1}{2}$
4Co	$\begin{array}{c} O_1 - H_{100} \cdots O_{3''} \\ O_2 - H_{200} \cdots O_8 \\ O_4 - H_{400} \cdots O_{5'} \\ O_6 - H_{600} \cdots O_{5'} \\ O_7 - H_{700} \cdots O_{3''} \end{array}$	1.00 0.82 0.94 1.16 0.98	1.57 1.62 1.65 1.46 1.62	2.565(4) 2.431(3) 2.562(4) 2.591(4) 2.587(4)	171 171 163 163 169	-x + 2, y + 1/2, -z + 1 -x + 1, y + 1/2, -z + 1 -x + 1, y + 1/2, -z + 1 -x + 2, y + 1/2, -z + 1
COVYUH10 ^a EDUQUP	$O_3 \cdots O_{3'}$ $O_1 - H_{21} \cdots O_{4'}$ $O_2 - H_{22} \cdots O_{3''}$	0.62(3) 0.63(3)	 1.94(3) 2.01(3)	2.679 2.559(2) 2.640(2)	175(3) 179(2)	-x + 1, -y, -z + 1 x, $-y + 1/2, z - 1/2$ x, $-y + 1/2, z + 1/2$
LELXIJ VIGVIJ ^a	$O_2 - H_{11} \cdots O_{1''}$ $O_4 \cdots O_{5'}$	1.03	1.58	2.576(4) 2.792	162	x, -y + 1, z + 1/2 -x + 1, -y, -z

organometallic cations alternated with inorganic layers (see Fig. 1). The two crystalline salts, though similar, are not isomorphous, the difference arising from the relative disposition of the inorganic layers. As shown in Fig. 1, while in compound **1Co** the layers are "anti parallel", in **1Fe** the layers are "parallel" and slightly shifted with respect to those in **1Co**.

 Table 1
 Relevant hydrogen bonding parameters

The sulfate and hydrogen sulfate anions are not distinguishable, since the proton lies on a crystallographic inversion centre; they form a dimer with a short interanionic hydrogen bonding interaction $[O \cdots O \ 2.519(4) \text{ and } 2.515(5) \text{ Å}$ for **1Co** and **1Fe**, respectively] so that the anionic moiety can be better described as the superanion $[SO_4HSO_4]^{3-}$.

The two solvate moieties, containing the remaining two independent oxygen atoms, are constituted by a water molecule and an oxonium ion. Although the O···O distances of 2.438(4) and 2.433(6) Å in **1Co** and **1Fe**, respectively, would be consistent with the presence of an $[H_5O_2]^+$ unit,¹⁶ the overall network of intermolecular connections and the distribution of the hydrogen atoms suggest the presence of an $[H_3O]^+$ cation and of a water molecule. The oxonium ion interacts *via* hydrogen bonding with the anions [O···O distances in the range 2.546(4)–2.572(4) and 2.554(6)–2.555(5) Å for **1Co** and **1Fe**, respectively], while the water molecule, in the addition to the short hydrogen bonding interaction with the oxonium ion mentioned above, forms significantly longer hydrogen bonding interactions with the superanions [SO₄HSO₄]³⁻ [O···O distances in the range 2.702(3)–2.718(3) and 2.705(5)–2.718(5) Å for **1Co** and **1Fe**, respectively].

The inorganic ions and solvent molecules are interconnected by means of a large number of hydrogen bonds. One of the possible ways of describing the hydrogen bonding network is by focusing the attention on the oxonium ion, which is involved in three different hydrogen bonding rings (see Fig. 2). In the following, we have adopted the graph-set notation system¹⁷ as a tool to describe the differences in the hydrogen bonding pattern.

The three ring motifs are indicated by different colours in Fig. 2. The ring evidenced in yellow and marked with "1" is, in graph set notation, of the $R_4^4(12)$ type, and is formed by the [SO₄HSO₄]³⁻ and [H₃O]⁺ ions and a water molecule. There are four different hydrogen bonds within the ring: three short ones in the [SO₄HSO₄]³⁻ unit [O···O distances 2.519(4) and 2.515(5) Å for 1Co and 1Fe, respectively], between $[H_3O]^+$ and $[H_2O][O\cdots O]$ distances 2.438(4) and 2.433(6) Å for 1Co and 1Fe, respectively], and between $[H_3O]^+$ and the anion $[O \cdots O \text{ distances } 2.572(4) \text{ and }$ 2.555(5) Å for 1Co and 1Fe, respectively], and a long one between the water molecule and the $[{\rm SO}_4{\rm HSO}_4]^{3-}$ unit $[{\rm O}{\cdots}{\rm O}$ distances 2.702(3) and 2.705(5) Å for 1Co and 1Fe, respectively]; the ring evidenced in green and marked with "2" is again of the $R_4^4(12)$ type, and is formed by two halves of [SO₄HSO₄]³⁻ (with two oxygen atoms for the sulfate moiety involved in the hydrogen bonds) and two $[H_3O]^+$; two independent O···O distances are present [O···O 2.546(4) and 2.572(4) for 1Co, 2.555(5) and 2.554(6) Å for 1Fe]. The third ring, evidenced in light blue and indicated by "3" is, in graph set notation, of the $R_5^4(12)$ type. It is constituted of one [H₃O]⁺ ion, two water molecules and two independent sulfate anions, for a total of four different hydrogen bonds. The [H₃O]⁺ forms short hydrogen bonds with the sulfate anions and the water molecule [O…O distances 2.438(4) and 2.546(4) Å for 1Co, 2.433(6) and 2.555(5) for 1Fe]; one water molecule acts as a bridge between the two sulfate anions $[O \cdots O \text{ distances } 2.702(3)]$ and 2.718(3) for 1Co, 2.705(5) and 2.718(5) for 1Fe]. The last water molecule closes the ring linking the [H₃O]⁺ ion and one sulfate ion.



Fig. 1 Comparison between the layered hydrogen bonded structures (view along the *b*-axis in both cases) in compounds $[(\eta^5-C_5Me_5)_2Co][H_3O]_2$ -[SO₄HSO₄]·2H₂O, **1Co** (top) and $[(\eta^5-C_5Me_5)_2Fe][H_3O]_2$ [SO₄HSO₄]·2H₂O, **1Fe** (bottom). Note how the hydrogen oxoanion chains possess different relative orientations in the two crystals (H atoms not shown for clarity).



Fig. 2 The complex hydrogen bonding pattern forming the anionic layers in crystalline 1Co and 1Fe.

The salt $[(\eta^5-C_5Me_5)_2Fe]_2[H_3O][HSO_4]_3$ **2Fe** adopts a different structure. The layered structure is lost in this salt; the hydrogen sulfate anions and the oxonium cation form parallel "wavy" chains in the crystal (see Fig. 3, top), with the organometallic cations accommodated among the chains. Fig. 3 (bottom) shows the hydrogen bonding pattern within a single chain. Two hydrogen sulfate anions (S1 and S2) form rings of the R₂²(8) type, in graph set notation [O···O 2.52(1) and 2.63(1) Å], while the third anion (S3), which is affected by rotational disorder around the S3–O9 bond



Fig. 3 Parallel "wavy" chains of inorganic moieties in crystalline [$(\eta^5 C_5 Me_5)_2 Fe]_2 [H_3 O]$ [HSO4]₃ **2Fe** (top; H atoms not shown for clarity); the hydrogen bonding pattern within a single chain (bottom). Only one of the two images of the disordered anion is shown for clarity. Blue spheres represent the oxonium cations.

(see Experimental section), takes part in the formation of an $R_3^3(10)$ ring, interacting both with the $R_2^2(8)$ ring system and the $[H_3O]^+$ cation. The oxonium cation is involved in three hydrogen bonds with the three independent hydrogen sulfate anions. Unfortunately the quality of the crystal did not allow location of the hydrogen atoms belonging to the inorganic moieties.

Hydrogen bonding and crystal structures of $[(\eta^5-C_5Me_5)_2Co]-[H_3PO_4][H_2PO_4]$, 3Co, $[(\eta^5-C_5Me_5)_2Fe][H_3PO_4][H_2PO_4]$, 3Fe and $[(\eta^5-C_5H_5)_2Co]H_3PO_4][H_2PO_4]$, 4Co

Compounds $[(\eta^5-C_5Me_5)_2Co][H_3PO_4][H_2PO_4]$, **3Co** and $[(\eta^5-C_5Me_5)_2Fe][H_3PO_4]$ [H_2PO_4], **3Fe** are isomorphous and their crystal structures will be described together. As in the case of the compounds discussed previously, the crystals can be described as constituted of alternating layers of organometallic and inorganic units. Fig. 4 shows the elegant network of hydrogen bonding: phosphoric acids and [H_2PO_4]⁻ anions are linked into rings of the R₂²(8) type, and the rings are organized in a honeycomb structure, completed by the presence of hydrogen bonded rings involving two H_3PO_4 units. The large hexagonal rings can be described as R₁₀⁶(32) in graph-set notation. O···O distances are in the range 2.527(4)–2.606(8) Å (see Table 1), with the longest values [2.606(8) and 2.590(4) Å for **3Co** and **3Fe**, respectively] observed for O–H···O interactions between the [H₂PO₄]⁻ anions.

Compound **4Co** possesses the same stoichiometry as **3Co** and **3Fe**, and again the crystal can be seen as formed by alternating layers of organometallic cations and inorganic molecules/anions; due to the smaller size of the cations, however, the hydrogen bonding network within the inorganic layer is markedly different. Fig. 5 shows how the layer is formed by alternated chains of H_3PO_4 molecules and $[H_2PO_4]^-$ anions. The lateral oxygen atoms are involved in hydrogen bonds with adjacent chains.

In order to put the above analysis in the perspective of the hydrogen bonding motifs observed in other organometallic salts containing partially protonated oxoanions, the Cambridge Crystallographic Data Base (ConQuest version 1.6, October 2003¹⁸) has been searched for organometallic systems containing dihydrogen



Fig. 4 The honeycomb type hydrogen bonding network in compounds $[(\eta^5-C_5Me_5)_2Co][H_3PO_4][H_2PO_4]$, **3Co** and $[(\eta^5-C_5Me_5)_2Fe][H_3PO_4]-[H_2PO_4]$, **3Fe**. The elegant network of hydrogen bonding: phosphoric acids and $[H_2PO_4]$ - anions are linked into rings of the $R_2^3(8)$ type.



Fig. 5 A chain of H_3PO_4 molecules and $[H_2PO_4]^-$ anions in **4Co** (top). The lateral oxygen atoms are involved in hydrogen bonds with adjacent chains, with formation of layers (bottom).

phosphate or hydrogen sulfate anions. Four compounds (identified here by the relative CSD REFCODES: COVYUH10, EDUQUP, LELXIJ and YIGYUI) have been found that respond to the criterion that no hydrogen bonding interactions between the organometallic cationic moieties and the anionic/neutral fragments are present. Fig. 6 shows that basic packing motifs and the topology of the hydrogen bonding interactions in these four crystal structures. It can be seen that the dihydrogen phosphate anions salts EDUQUP and LELXIJ form chains of eight-membered rings (Fig. 6(b) and (c)), and that the eight-membered ring is also present in the hydrogen sulfate salt YIGYUI (Fig. 6(d)) while the dihydrogen phosphate phosphoric acid salt COVYUH10 presents a more complex system of interactions whereby a dimeric [H₃PO₄-H₂PO₄]⁻ unit is hosted in a channelled structure. The O···O distances for these compounds (see Table 1) are in the range observed for the compounds described in the present work.



Fig. 6 Hydrogen bonding patterns involving the dihydrogen phosphate and hydrogen sulfate anions in compounds (from top to bottom) CO-VYUH10, EDUQUP, LELXIJ and YIGYUI (see Table 1 for relevant distances and angles). H atoms for COVYUH10 and YIGYUI are not present in the database files.

Conclusions

In this paper we have reported the utilization of partially deprotonated inorganic oxoanions derived from sulfuric and phosphoric acids, e.g. HSO₄⁻ and H₂PO₄⁻ in the preparation of hybrid inorganic–organometallic systems. The organometallic cations $[(\eta^{\text{5}}\text{-}$ $C_5H_5)_2Co]^+$, $[(\eta^5-C_5Me_5)_2Co]^+$ and $[(\eta^5-C_5Me_5)_2Fe]^+$ have been used because they do not interfere in the formation of strong hydrogen bonding interactions. This results in preferential association of the inorganic acids anions HSO₄⁻ and H₂PO₄⁻ into chains or honeycomb type structures with or without the participation of water molecules. The formation of hydrates in the case of HSO₄⁻ salts and of anhydrous crystals in the case of H₂PO₄⁻ salts can be explained precisely on the basis of the need to increase the number of hydrogen bonding donors in the former case. The HSO4- anion possesses a total of four acceptor sites and only one hydrogen bonding donor group. On the other hand the presence of two donor groups in H₂PO₄⁻ anions brings about the possibility of hydrogen bonding ring formation within extended structures. Although the species discussed herein do not undergo a superprotonic phase transition, hence they are not suitable for proton conductivity applications, it is clear from this study that proton transfer via the mechanism associated with reorientational motion of the tetrahedral inorganic cations would be favoured by chain formation rather than by ring formation, since this latter arrangement is much more stiff. On the other hand, anhydrous species would be preferable because water may interfere with the proton transport. Work is in progress to explore the possibility of preparing mixed-cation and mixed-anion systems as well as to prepare anhydrous crystalline systems by de-hydration of the hydrated ones.

Experimental

Crystal synthesis

All products were purchased from Aldrich and used without further purification.

Synthesis of 1Co. $[(\eta^5-C_5Me_5)_2Co]$ [0.235 g, 0.7 mmol] was suspended in a solution of 14 ml of 0.1 M H₂SO₄ (1.4 mmol) and 80 ml of absolute ethanol and oxidized by stirring the suspension in the presence of air for 24 h. The solution was filtered and the volume reduced to 40 ml under low pressure. The solution was

 Table 2
 Crystal data and details of measurements for all compounds

	1Co	1Fe	2Fe	3Co	3Fe	4Co
Formula	$C_{20}H_{41}CoO_{12}S_2$	$C_{20}H_{41}FeO_{12}S_2$	C ₄₀ H ₆₆ Fe ₂ O ₁₃ S ₃	C ₂₀ H ₃₅ CoO ₈ P ₂	C ₂₀ H ₃₅ FeO ₈ P ₂	C ₁₀ H ₁₅ CoO ₈ P ₂
M	596.58	593.50	962.81	524.35	521.27	384.09
System	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	Pccn	C2/c	$P2_1/n$	$P2_1/n$	$P2_{1}/c$	$P2_1$
Z	4	4	4	4	4	2
a/Å	21.213(4)	23.872(4)	9.923(1)	12.241(2)	12.27(8)	8.450(4)
b/Å	7.680(2)	7.755(7)	18.754(1)	17.457(4)	17.51(4)	9.431(2)
c/Å	16.748(3)	16.671(4)	24.377(2)	12.376(2)	12.33(2)	9.038 (2)
β/°	90	117.03(1)	91.48(1)	115.72(2)	116.06(4)	105.45(3)
V/Å ³	2729(1)	2749(3)	4534.9(6)	2382.6(8)	2380(17)	694.2(4)
F(000)	1264	1260	20040	1104	1100	392
μ (Mo-K α)/mm ⁻¹	0.838	0.757	0.838	0.897	0.810	1.502
θ Range/°	3-25	3-25	3–25	3–25	3–25	3-30
Measured reflections	2751	2490	8029	4385	4394	2244
Unique reflections	2389	2395	7841	4183	4192	2126
Refined parameters	158	159	464	254	264	174
Gof on \hat{F}^2	1.040	1.015	1.020	0.816	0.992	1.075
$R1$ [on $F, I > 2\sigma(I)$]	0.0413	0.0401	0.0782	0.0598	0.0526	0.0285
$wR2$ (on F^2 , all data)	0.1205	0.1178	0.2606	0.2322	0.1639	0.0791

allowed to slowly evaporate to obtain yellow crystals suitable for single crystal X-ray diffraction.

Synthesis of 1Fe and 2Fe. All attempts to obtain pure phases of 1Fe and 2Fe were unsuccessful since the two phases crystallize together. Fast crystallization favours formation of 1Fe. $[(\eta^5-C_5Me_5)_2Fe]$ [0.295 g, 0.9 mmol] was dissolved in 50 ml of absolute ethanol; 1 M H₂SO₄ [1.8 ml, 1.8 mmol] was added and the solution was stirred in air overnight. The green solution obtained was reduced in volume to 30 ml, slow evaporation of the solvent at room temperature yielded crystals of 1Fe and crystalline powder of 2Fe, while slow evaporation at 4 °C (15 days) resulted in crystals of 1Fe and crystalline powder of 2Fe. Unreacted $[(\eta^5-C_5Me_5)_2Fe]$ was removed by washing the solid compounds with cyclohexane.

Synthesis of 3Co. $[(\eta^5-C_5Me_5)_2Co]$ [0.230 g, 0.7 mmol] was suspended in a solution of 1 M H₃PO₄ [1.4 ml, 1.4 mmol] and 80 ml of absolute ethanol and oxidized by stirring the suspension in the presence of air for 24 h. The solution was filtered and the volume reduced to 40 ml under low pressure. Slow evaporation of the solution yielded yellow crystals suitable for single crystal X-ray diffraction.

Synthesis of 3Fe. $[(\eta^5-C_5Me_5)_2Fe]$ [0.300 g, 0.9 mmol] was dissolved in 80 ml of absolute ethanol; 1 M H₃PO₄ [1.8 ml, 0.18 mmol] was added, and the solution was stirred in air overnight. The green solution obtained was reduced in volume to 30 ml. Slow evaporation of the solution yielded dark green crystals suitable for single crystal X-ray diffraction. Unreacted $[(\eta^5-C_5Me_5)_2Fe]$ was removed by washing the crystals with cyclohexane.

Synthesis of 4Co. $[(\eta^5-C_5H_5)_2Co]$ [0.265 g, 1.4 mmol] was suspended in a solution of 1 M H₃PO₄ [2.8 ml, 2.8 mmol] and 80 ml of absolute ethanol and oxidized by stirring the suspension in the presence of air for 24 h. The solution was filtered and the volume reduced to 40 ml. Slow evaporation of the solution yielded yellow crystals suitable for single crystal X-ray diffraction.

DSC measurements. The thermal behaviour of compounds 1Co, 3Co, 3Fe and 4Co was characterized by DSC measurements. No solid–solid phase transition was observed, up till melting was reached. The melting points of the compounds are: 63 °C (1Co), 260 °C (3Co), 220 °C (3Fe), 146 °C (3Fe).

Crystal structure determinations. Crystal data of all compounds were collected at room temperature on a Nonius CAD4 diffractometer. Crystal data and details of measurements are summarised in Table 2. Common to all compounds: Mo-K α radiation, $\lambda = 0.71073$ Å, monochromator graphite. SHELX97^{19a} was used

for structure solution and refinement based on F^2 . Non-hydrogen atoms were refined anisotropically. H_{CH} atoms in the organometallic cations were added in calculated positions.

 H_{OH} atoms in **1Co**, **1Fe**, **3Co** and **3Fe** were located in the final difference Fourier map and refined without constraints.

The Co atom in **1Co** lies on a two-fold axis, while in **1Fe** the metal atom lies on an inversion centre. The asymmetric unit in **2Fe** contains one organometallic cation in a general position and two half independent organometallic cations on independent inversion centres. All C_5Me_5 groups were refined as rigid groups with fixed geometry. In **2Fe** one of the three hydrogen sulfate anions (S3) is disordered over two positions (occupancy ratio 50:50) around the unique S3–O9 bond. Due to the disorder, O···O distances between the hydrogen sulfate anion and the oxonium cation are poorly characterized, and they are not discussed here. H_{OH} atoms attached to O1 and O5 were added in calculated positions, while no attempt was made to model the H atom belonging to the disordered hydrogen sulfate anion and to the oxonium cation.

 H_{OH} atoms in **4Co** were located in the final difference Fourier map but not refined. The H_3PO_4 unit in **4Co** presents a short distance (1.506(2) Å) for one of the P–O single bonds; however, the shortest P–O distance in the fragment (1.490(2) Å) is, as expected, the one corresponding to the double bond. SCHAKAL99^{19b} was used for the graphical representation of the results. The program PLATON^{19c,d} was used to calculate the hydrogen bonding interactions reported in Table 1.

CCDC reference numbers 228908-228913.

See http://www.rsc.org/suppdata/dt/b4/b400667d/ for crystallographic data in CIF or other electronic format.

For all species discussed in this paper powder diffractograms were measured and compared with those calculated on the basis of the single-crystal structure.

Powder diffraction data were collected on a Philips PW-1710 automated diffractometer and on an X'Pert Philips diffractometer; both with Cu–K α radiation and graphite monochromator. The program PowderCell 2.2²⁰ was used for calculation of X-ray powder patterns.

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