The hydrogen oxalate anion allows one-dimensional columnar aggregation of organometallic sandwich cations

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Oxalic acid reacts with sandwich compounds such as decamethyl ferrocene, decamethyl cobaltocene, bis-benzene chromium and cobaltocene, in the presence of oxygen, *via* a multi-step process involving oxidation, deprotonation and precipitation, to form crystalline superstructures containing columns of organometallic sandwich cations and hydrogen oxalate anions. Five novel crystalline compounds are reported, namely $[Fe(\eta^5\text{-}C_5Me_5)_2][HC_2O_4]\cdot[H_2C_2O_4]_{0.5}$, **1a**, $[Co(\eta^5\text{-}C_5Me_5)_2][HC_2O_4]\cdot[H_2C_2O_4]_{0.5}$, **1b**, $[Fe(\eta^5\text{-}C_5Me_5)_2][HC_2O_4]\cdot[H_2C_2O_4]$, **2**, $[Cr(\eta^6\text{-}C_6H_6)_2][HC_2O_4]\cdot[H_2O]$, **3**, and $[Co(\eta^5\text{-}C_5H_5)_2][HC_2O_4]\cdot[H_2C_2O_4]_{0.5}[H_2O]$ **4**. The anionic network in $[M(\eta^5\text{-}C_5Me_5)_2][HC_2O_4]\cdot[H_2C_2O_4]_{0.5}$ (M = Fe, Co) is based on an unusual deca-atomic ring formed by hydrogen oxalate anions linked side-to-side *via* $^{(-)}O\text{–}H\cdots O^{(-)}$ hydrogen bonding interactions. The magnetic behaviour of compounds **1a**, **2**, and **3** has been investigated by SQUID magnetometry. Both compounds **1a** and **2** present weak antiferromagnetic interactions, which are significantly stronger in **1a**. The structure of the chloride salt $[(\eta^5\text{-}C_5H_5)_2Co][Cl]\cdot[H_2C_2O_4][H_2O]$, **5**, is also described.

Introduction

The bottom-up construction of functional materials from molecules or ions is at the core of modern crystal engineering.[1] The idea is that of attaining collective crystal properties *via* an adequate choice of the building blocks.[2] We have shown previously that the utilisation of *ions* able to form hydrogen bonding interactions allows the simultaneous exploitation of the directionality and reproducibility of these interactions and the strength of the Coulombic field generated by the ionic charges.[3] With this strategy we have been able to construct honeycomb type organic frameworks,[4a] intercalated structures,[4b] mixed metal[4c] and chiral organic–organometallic[4d] crystals, where organometallic cations could be accommodated. Analogous strategies have been used by others to construct a variety of novel architectures based on coordination complexes.[5] When dealing with metal complexes, magnetic interactions also become amenable.[6]

In this context we have recently shown that[7] squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione, H_2SQA) reacts with $[Co(\eta^5\text{-}C_5H_5)_2]$ and $[Cr(\eta^6\text{-}C_6H_6)_2]$ in water or THF to yield *quasi*-isomorphous crystalline materials of formula $[Co(\eta^5\text{-}C_5H_5)_2][HSQA]$ and $[Cr(\eta^6\text{-}C_6H_6)_2][HSQA]$. In the case of this latter paramagnetic salt, a weak antiferromagnetic interaction between the $S = 1/2$ of the $[Cr(\eta^6\text{-}C_6H_6)_2]^+$ cations has been measured by SQUID magnetometry. The interaction has been ascribed to the intercalation of hydrogen squarate anions in between the paramagnetic cations.

After these studies we were intrigued by the possibility of *forcing* paramagnetic sandwich cations to closer contact without anion intercalation. This could be of some interest because earlier studies[8] of crystals containing flat radical anions such as tetracyanoethylene ($TCNE^{\bullet -}$), tetracyano-*p*-quinodimethane ($TCNQ^{\bullet -}$) or other similar anions, and radical cations such as $[Fe(\eta^5\text{-}C_5Me_5)_2]^+$ as well as other sandwich cations (*e.g.* $[Cr(\eta^6\text{-}C_6Me_xH_{6-x})_2]^+$) have led to the formulation of the *linear-chain paradigm*,[8] which postulates the formation of sequences of the type $A^{(-)}\text{–}C^{(+)}\text{–}A^{(-)}\text{–}C^{(+)}$ between radical anions and cations in crystals. This one-dimensional arrangement has been shown to lead to unusual cooperative magnetic properties.[8] Linear arrangements of the type $C^{(+)}\text{–}C^{(+)}\text{–}C^{(+)}\text{–}C^{(+)}$ surrounded by chains of $A^{(-)}\text{–}A^{(-)}\text{–}A^{(-)}\text{–}A^{(-)}$ anions or intercalated between layers of anions are not easily obtained because of the tendency of the ions of a given sign to be surrounded by ions of opposite sign. It was thought that the use of systems smaller than squaric acid, and yet capable of self-assembling by means of directional hydrogen bonding interactions, may attain the desired stack of cations (see Scheme 1).

In this paper we report that hydrogen oxalate anions obtained by partial deprotonation of oxalic acid can indeed be used as simple building blocks in the engineering of crystals containing columns of cationic sandwich compounds. In the case of radical cations, such as $[Fe(\eta^5\text{-}C_5Me_5)_2]^+$ and $[Cr(\eta^6\text{-}C_6H_6)_2]^+$, this could lead to an increased magnetic interaction with respect to intercalated systems. Although the oxalate unit has been extensively exploited in studies of molecular magnetism in coordination chemistry,[9] it will be used here only as a structural unit since no coordination to metal centres will take place.

The synthetic procedure requires that the neutral organometallic sandwich compounds are oxidised by the air in the presence of the acidic species. The presence of the acid is essential in the case of $[Fe(\eta^5\text{-}C_5Me_5)_2]$ because of the only

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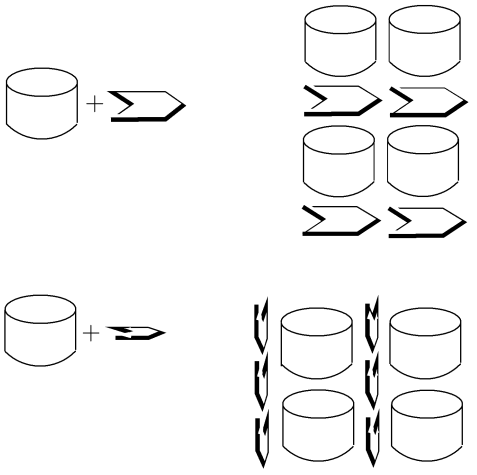


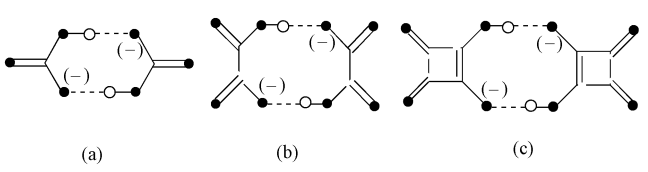
Scheme 1

slightly favourable redox potential, while oxidation of cobaltocene or bis-benzene chromium takes place in water.[10] A sequence of redox and acid–base processes[11] ultimately leads to formation of the mono-deprotonated hydrogen oxalate $[HC_2O_4]^-$ anion and of the organometallic sandwich cation $[Fe(\eta^5\text{-}C_5Me_5)_2]^+$. It is worth noting that $[Fe(\eta^5\text{-}C_5Me_5)_2]^+$ and $[Cr(\eta^6\text{-}C_6H_6)_2]^+$ are paramagnetic, while $[Co(\eta^5\text{-}C_5Me_5)_2]^+$ and $[Co(\eta^5\text{-}C_5H_5)_2]^+$ are diamagnetic. The organometallic complexes were reacted with oxalic acid both in various stoichiometric ratios (see Experimental). By using this strategy we have obtained five novel crystalline compounds, namely $[Fe(\eta^5\text{-}C_5Me_5)_2][HC_2O_4]\cdot[H_2C_2O_4]_{0.5}$, **1a**, $[Co(\eta^5\text{-}C_5Me_5)_2][HC_2O_4]\cdot[H_2C_2O_4]_{0.5}$, **1b**, $[Fe(\eta^5\text{-}C_5Me_5)_2]\text{-}[HC_2O_4)]\cdot[H_2C_2O_4]$, **2**, $[Cr(\eta^6\text{-}C_6H_6)_2][HC_2O_4]\cdot[H_2O]$, **3**, and $[Co(\eta^5\text{-}C_5H_5)_2][HC_2O_4]\cdot[H_2C_2O_4]_{0.5}[H_2O]$, **4**. All of these systems have been shown to possess a one-dimensional columnar aggregation of the cations. The magnetic behaviour of the crystalline materials containing the paramagnetic cations decamethylferricinium $[Fe(\eta^5\text{-}C_5Me_5)_2]^+$ and $[Cr(\eta^6\text{-}C_6H_6)_2]^+$ has been investigated. The structure of the chloride salt $[Co(\eta^5\text{-}C_5H_5)_2][Cl]\cdot[H_2C_2O_4][H_2O]$, **5**, is also reported.

In the course of this study we have also discovered that compounds **1a** and **1b** contain oxalate–oxalic acid intermolecular chains never observed before. These chains are formed by deca-atomic $\mathbf{R_2^2(10)}$ ring[12] linked by neutral oxalic acid molecules. A similar deca-atomic ring has been previously observed only in the case of the salt $[HN(CH_2CH_2)_3NH][HC_2O_4]_2$, $[DABCO][HC_2O_4]_2$.[13] It is interesting to note that this ring motif is analogous to the one commonly found in larger oxocarbon anions, $[HC_4O_4]^-$, $[HC_5O_5]^-$, while the kind of ring shown by the smaller hydrogen carbonate anion[14] is not known for the oxalate anion (see Scheme 2).

Experimental

All reactants were purchased from Aldrich and used without further purification. Reagent grade solvents and bidistilled water were used. In all cases correspondence between the structure of the solid residue and that obtained by single crystal X-ray diffraction was ascertained by comparing measured X-ray powder diffractograms with those calculated on the basis of the single crystal experiments. All organometallic complexes were reacted with oxalic acid in 1:1, 1:1.5 and 1:2 stoichiometric ratios respectively. In the following only the stoichiometric ratios leading to a single crystalline phase are described. The synthesis of all crystalline compounds was quantitative, with yields in the range 0.85–0.90%.



(a): the $[HCO_3]$– ring dimer
(b): the $[HC_2O_4]$– ring dimer
(c): the $[HC_4O_4]$– ring dimer

Scheme 2

Synthesis of $[Fe(\eta^5\text{-}C_5Me_5)_2][HC_2O_4]\cdot[H_2C_2O_4]_{0.5}$, 1a

32.6 mg (0.10 mmol) of $[Fe(\eta^5\text{-}C_5Me_5)_2]$ were dissolved in 20 ml of nitromethane. 13.5 mg (0.15 mmol) of anhydrous oxalic acid were added to the solution and, after two hours, the solvent was removed under reduced pressure. The green precipitate was washed with hexane and recrystallised in nitromethane. Green crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent. A 1:1 ratio gave a mixture of **1a** and $[Fe(\eta^5\text{-}C_5Me_5)_2]$.

Synthesis of $[Co(\eta^5\text{-}C_5Me_5)_2][HC_2O_4]\cdot[H_2C_2O_4]_{0.5}$, 1b

32.9 mg (0.10 mmol) of $[Co(\eta^5\text{-}C_5Me_5)_2]$ were suspended in 15 ml of H_2O. The suspension was stirred in the presence of air to ensure complete oxidation of the complex. 13.5 mg (0.15 mmol) of anhydrous oxalic acid were added and the solution was stirred for two hours. Yellow crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent. With the 1:1 and 1:2 ratios mixtures of **1b** and of the excess reagent were obtained.

Synthesis of $[Fe(\eta^5\text{-}C_5Me_5)_2][HC_2O_4]\cdot[H_2C_2O_4]$, 2

32.5 mg (0.10 mmol) of $[Fe(\eta^5\text{-}C_5Me_5)_2]$ were dissolved in 20 ml of nitromethane; 18.0 mg (0.20 mmol) of anhydrous oxalic acid were then added to the solution. After two hours of stirring, the green solution was allowed to evaporate at room temperature and large green crystals were obtained.

Synthesis of $[(\eta^6\text{-}C_6H_6)_2Cr][HC_2O_4]\cdot[H_2O]$, 3

30.0 mg (0.14 mmol) of $[Cr(\eta^6\text{-}C_6H_6)_2]$ were dissolved in 15 ml of THF under inert atmosphere, then anhydrous oxalic acid (12.6 mg, 0.14 mmol) was added and the solution stirred for 30 minutes in the presence of air. The yellow precipitate thus obtained was filtered and recrystallised from nitromethane. Yellow crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent. With the 1:1.5 and 1:2 ratios decomposition of $[Cr(\eta^6\text{-}C_6H_6)_2]$ was observed.

Synthesis of $[Co(\eta^5\text{-}C_5H_5)_2][HC_2O_4]\cdot[H_2C_2O_4]_{0.5}[H_2O]$, 4

$[Co(\eta^5\text{-}C_5H_5)_2]$ (30.0 mg, 0.16 mmol) was suspended in 15 ml of water and oxidized by stirring the suspension in the presence of air. Anhydrous oxalic acid (21.6 mg, 0.24 mmol) was added to the solution, which was kept under stirring for two hours. Yellow crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent. With the 1:1 and 1:2 ratios mixtures of **4** and of the excess reagent were obtained.

Synthesis of $[(\eta^5\text{-}C_5H_5)_2Co][Cl]\cdot[H_2C_2O_4][H_2O]$, 5

$[Co(\eta^5\text{-}C_5H_5)_2]$ (30.0 mg, 0.16 mmol) was suspended in 15 ml of water and oxidised by stirring the suspension in the presence of air. The hydroxide solution was neutralised by dropwise addition of HCl 0.1 M, then 14.4 mg (0.16 mmol) of anhydrous oxalic acid were added and the solution was stirred for two hours. Yellow crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent.

Table 1 Crystal data and details of measurements for compounds **1a**–**5**

Compound	**1a**	**1b**	**2**	**3**	**4**	**5**
Formula	$C_{23}H_{32}FeO_6$	$C_{23}H_{32}CoO_6$	$C_{24}H_{33}FeO_8$	$C_{14}H_{15}CrO_5$	$C_{13}H_{14}CoO_7$	$C_{12}H_{14}ClCoO_5$
M_r/g mol^{-1}	460.34	463.42	505.35	315.26	341.17	332.61
T/K	253	293	293	293	293	293
Crystal syst.	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/a$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a/Å	8.970(2)	9.007(2)	7.688(3)	6.778(6)	6.978(6)	6.821(5)
b/Å	9.976(4)	9.976(3)	16.539(5)	17.963(7)	17.143(8)	8.904(5)
c/Å	13.019(5)	12.993(4)	9.800(6)	11.030(3)	11.240(6)	11.176(6)
α/°	103.08(4)	103.41(3)	90	90	90	76.42(6)
β/°	95.36(3)	95.47(3)	96.75(4)	99.35(4)	102.94(6)	80.11(5)
γ/°	99.83(2)	99.95(2)	90	90	90	86.56(6)
U/Å^3	1107.4(7)	1107.3(5)	1238(1)	1325(1)	1310(1)	649.8(7)
Z	2	2	2	4	4	2
μ/mm^{-1}	0.717	0.811	0.654	0.879	1.342	1.538
$2\theta_{max}$/°	50	50	50	54	50	50
Collected refl.s	4070	4073	2287	2227	4512	2395
Unique refl.s	3884	3885	2158	2124	2281	2269
refined param.s	223	223	143	164	173	148
GOF on F^2	1.011	1.020	0.993	1.049	1.054	1.029
R1 (on F, $I > 2\sigma(I)$)	0.0515	0.0473	0.0512	0.0473	0.0691	0.0468
*wR*2 (on F^2, all data)	0.1576	0.1442	0.1737	0.1389	0.1804	0.1449

Crystallography. Crystal data of all compounds were collected on a Nonius CAD4 diffractometer equipped with an Oxford Cryostream liquid-N_2 device. Crystal data and details of measurements are summarised in Table 1. Common to all compounds: Mo-Kα radiation, $\lambda = 0.71073$ Å, monochromator graphite. SHELXS97 and SHELXL97[15a] were used for structure solution and refinement based on F^2. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon atoms were added in calculated positions. All the hydrogen atoms belonging to the hydrogen oxalate and oxalic acid moieties were found in the Fourier maps of **1a**, **1b** and **3**. In the case of **2** only the H_{OH} atom sitting on a crystallographic centre of inversion midway the oxalate–oxalic acid unit was observed; in compound **4**, both H-atoms of the neutral oxalic acid molecule and those of the water molecule were observed, while no H-atom could be found along the O(H)···O hydrogen bonds in the anionic chain. In the case of **5** both the oxalic acid hydrogen atoms, but only one of the two H_{water} atoms were observed. SCHAKAL99[15b] was used for the graphical representation of the results. The program PLATON[15c] was used to calculate the hydrogen bonding interactions.

CCDC reference numbers 188483–188488.

See http://www.rsc.org/suppdata/nj/b2/b205782d/ for crystallographic data in CIF or other electronic format.

Magnetometry. The temperature dependence of the magnetisation of microcrystalline samples of **1a**, **2**, and **3** was measured with a Cryogenic M600 SQUID magnetometer. The data were corrected for the diamagnetic contribution, evaluated from Pascal's constants. The experimentally determined M/H ratio was assumed to coincide with the magnetic susceptibility $\chi = \partial M/\partial H$ as the linearity of M *vs.* H was verified. In the case of **3** the comparison between measured and calculated powder diffractograms (see also below) did not show the presence of another phase. However, even a small oxidation of Cr^{I} to Cr^{III} could alter the magnetic measurements.

Results and discussion

Description of the supramolecular arrangements. Because of their close structural relationship compounds [Fe(η^5-$C_5Me_5)_2$][HC_2O_4]·[$H_2C_2O_4$]$_{0.5}$, **1a**, [Co(η^5-$C_5Me_5)_2$][HC_2O_4]·[$H_2C_2O_4$]$_{0.5}$, **1b**, [Fe(η^5-$C_5Me_5)_2$][HC_2O_4]·[$H_2C_2O_4$], **2**, [Cr(η^6-$C_6H_6)_2$][HC_2O_4]·[H_2O], **3**, and [Co(η^5-$C_5H_5)_2$][HC_2O_4]·[$H_2C_2O_4$]$_{0.5}$[H_2O], **4** and of the chloride salt [Co(η^5-$C_5H_5)_2$][Cl]·[$H_2C_2O_4$][H_2O], **5**, will be discussed together. Essential structural information is reported in Table 2. Beside the data on the hydrogen bonding interactions, the interplanar separations (ID) between carbocyclic ligands along the cationic stacks (see below) are reported together with the distance between ring centroids (CD) and the shift between ring centroids in projection. These parameters, illustrated in Scheme 3, are essential to understand fully the relative disposition in space of the rings and will be of practical use in the interpretation of the magnetic behaviours.

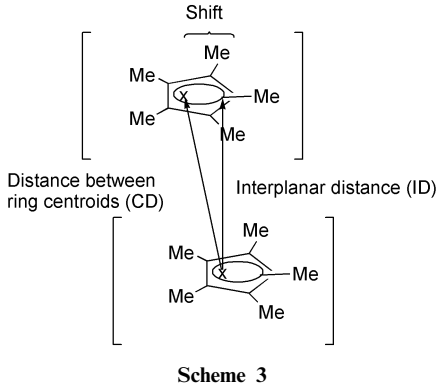
The stoichiometry deserves a preliminary comment. All compounds described herein contain either oxalic acid molecules or water molecules, or both. Crystallization in the presence of an excess of oxalic acid leads to co-crystallisation of $[HC_2O_4]^-$ and $H_2C_2O_4$ in 1:1 ratio, smaller ratios leads invariably to a $[HC_2O_4]^-$ *versus* $H_2C_2O_4$ ratio of 2:1. In only one case, in spite of the number of efforts, has it been possible to isolate/crystallize compounds in which the neutral acid is absent; compound **3** is only apparently an exception: the smaller size of the cation allows in fact the exclusion of the acid moiety, but co-crystallisation of water cannot be avoided. As observed previously we ascribe this feature to the relative size of the ions: the small hydrogen oxalate anion cannot *on its own* satisfy the two requirements for efficient packing and cohesion, namely density and optimisation of hydrogen bonding interactions. This latter feature, in particular, can only be satisfied by other molecules/ions carrying hydrogen bonding donor–acceptor groups, such as oxalic acid itself or water.

The difference in stoichiometry between compounds **1a,b** and **2** has important consequences on the organisation of the hydrogen oxalate anions in the solid state: while in compounds **1a,b** the hydrogen oxalate anions aggregate in chains of alternating dianionic rings (see below) and neutral molecules, in **2** a two-dimensional network is observed containing oxalic acid and *twisted* hydrogen oxalate anions. In both crystals, however, the paramagnetic cations form one-dimensional arrangements with interplanar distances of 3.67, 3.84 Å and 3.42 Å, respectively, between C_5Me_5 ligands belonging to different cations.

Table 2 Essential structural information on the hydrogen bonding interaction and on the relative disposition of the carbocyclic ligands. See Scheme 3 for an explanation of the parameters

Complex		O(H)···O Å	Interplanar distance (ID)	Centroid distance (CD)	Shift
$[Fe(\eta^5\text{-}C_5Me_5)_2][HC_2O_4]\cdot[H_2C_2O_4]_{0.5}$	**1a**	O1...O3 2.664(6)	3.67	3.69	0.40
		O6...O4 2.569(6)	3.84	4.28	1.88
$[Co(\eta^5\text{-}C_5Me_5)_2][HC_2O_4]\cdot[H_2C_2O_4]_{0.5}$	**1b**	O1...O3 2.661(4)	3.75	3.75	0.00
		O6...O4 2.566(5)	3.90	4.42	2.07
$[Fe(\eta^5\text{-}C_5Me_5)_2][HC_2O_4]\cdot[H_2C_2O_4]$	**2**	O1...O1 2.456(5)	3.42	4.67	3.18
		O2...O3 2.741(5)			
$[Cr(\eta^6\text{-}C_6H_6)_2][HC_2O_4]\cdot[H_2O]$	**3**	O100...O300 2.522(8)	3.39	3.66	1.38
		O300...O201 2.699(7)			
		O300...O200 2.683(7)			
$[Co(\eta^5\text{-}C_5H_5)_2][C_2O_4]_{0.5}[H_2C_2O_4]\ [H_2O]$	**4**	O1...O5 2.577(8)	3.68	3.72	0.49
		O3...O7 2.527(7)			
		O7...O6 2.690(8)			
		O7...O6 2.726(8)			
$[Co(\eta^5\text{-}C_5H_5)_2][Cl]\cdot[H_2C_2O_4]\cdot[H_2O]$	**5**	O2...O6 2.623(5)	3.52	3.61	0.78
		O3...Cl1 2.994(4)			
		O6...Cl1 3.155(5)			
		O6...Cl1 3.212(5)			

In crystalline compounds **1a,b** the hydrogen oxalate anions and the neutral oxalic acid molecules form linear chains (see Fig. 1a). The chains run parallel to the columns formed by the $[Fe(\eta^5\text{-}C_5Me_5)_2]^+$ and $[Co(\eta^5\text{-}C_5Me_5)_2]^+$ cations and are composed of two $[HC_2O_4]^-$ anions in a deca-atomic dimer formed by two hydrogen oxalate anions joined together *via* $^{(-)}O\text{–}H\cdots O^{(-)}$ interactions. Hence, contrary to what has thus far been observed, the anions do not form the "usual" head-to-tail chain, *i.e.* a **C(4)** in graph set terminology,[12] nor the carboxylic ring $\mathbf{R_2^2(8)}$, but rather adopts a side-to-side arrangement, which allows a double hydrogen bonding interaction to be established. The dimers are bridged together by one molecule of oxalic acid. The hydrogen oxalate–oxalic acid chain can thus be described as a $(H_2C_2O_4)$—$[(HC_2O_4)\text{-}(HC_2O_4)]^{2-}$—$(H_2C_2O_4)$—$[(HC_2O_4)(HC_2O_4)]^{2-}$ sequence of ions and molecules (see Fig. 1b). These chains form the backbone of the crystal structure and allow the cations to pile up as shown in Fig. 1a. This ring dimer motif between mono-hydrogen oxalate anions has been previously observed only in the organic salt $[DABCO][HC_2O_4]_2$.[13] It is interesting to note that, while in this latter case, two ring dimers are linked to a dication *via* $O_{(CO)}\cdots H\text{–}N^{(+)}$ hydrogen bonding interactions (see Fig. 1c), the role of the cationic linker is played by a neutral moiety in compounds **1a**,**b**. The good quality of the diffraction data allowed location of the hydrogen atoms and unambiguous attribution of the charges: it is noteworthy that the O···O distance between the dimer $[(HC_2O_4)(HC_2O_4)]^{2-}$ and the neutral molecule of $H_2C_2O_4$ is shorter than the intra-dimer one [O4···O6 2.569(6) *versus* O1···O3 2.664(6) Å]. The intra-dimer distance is much longer than the average $^{(-)}O(H)\cdots O^{(-)}$ distance along chains of hydrogen oxalate anions, but on average it is comparable to the intra-dimer values observed in $[DABCO][HC_2O_4]_2$ (OH···O 2.618 and 2.742 Å) and in the squarate–squaric acid system present in $[Co(\eta^5\text{-}C_5H_5)_2][HSQA]\cdot[H_2SQA]$[7b] [OH···O distances in the range 2.539–2.574 Å].



Scheme 3

When the hydrogen oxalate:oxalic acid stoichiometric ratio is raised to 1:1 on passing to **2**, the one-dimensional aggregate

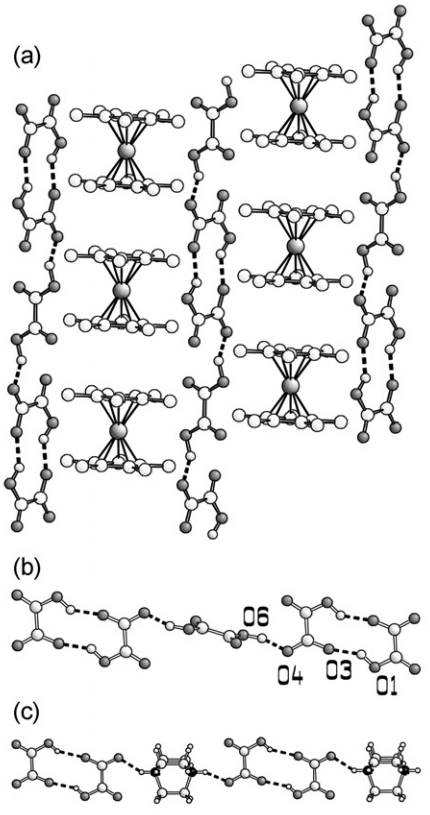


Fig. 1 The ion arrangement in crystalline $[Fe(\eta^5\text{-}C_5Me_5)_2][HC_2O_4]\cdot[H_2C_2O_4]_{0.5}$, **1**. (a) Note how the cations pile up, at inter-planar separations of 3.67 and 3.84 Å. (b) The hydrogen oxalate anions and the neutral oxalic acid molecules form $(H_2C_2O_4)$—$[(HC_2O_4)(HC_2O_4)]^{2-}$—$(H_2C_2O_4)$—$[(HC_2O_4)(HC_2O_4)]^{2-}$ linear chains interactions. (c) An analogous motif is present in the organic salt $[DABCO][HC_2O_4]_2$,[13] where the ring dimers are connected *via* the dicationic counterion.

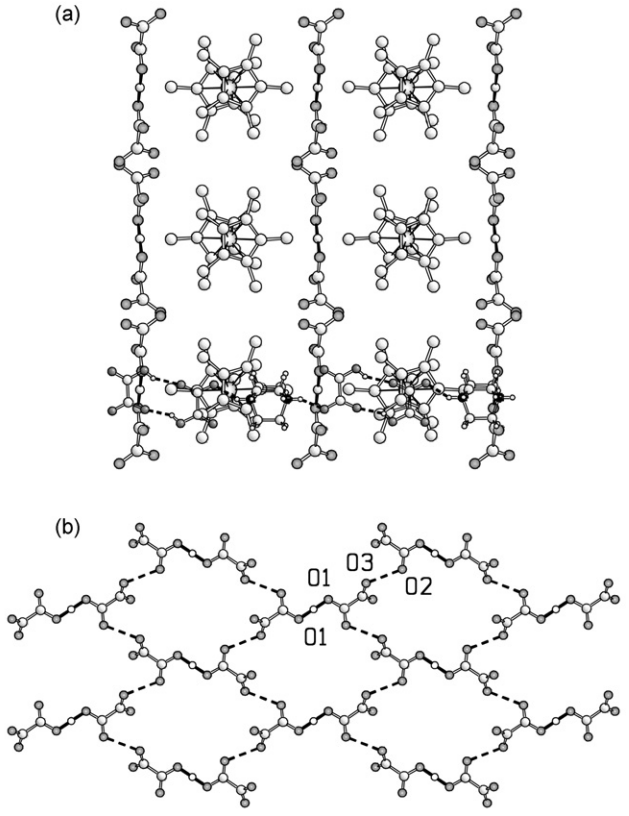


Fig. 2 The ion arrangement in crystalline $[Fe(\eta^5\text{-}C_5Me_5)_2][HC_2O_4]\cdot[H_2C_2O_4]$, **2**. (a) The two-dimensional networks of hydrogen oxalate anions form anionic layers, with parallel rows of $[Fe(\eta^5\text{-}C_5Me_5)_2]^+$ cations sandwiched in between. (b) The network is composed of dimeric units which are best described as the type $[(HC_2O_4)\cdots H\cdots(HC_2O_4)]^-$, with O···O separations of 2.456(5) and 2.741(5) Å for the intra-anion and inter-anions hydrogen bonding interactions, respectively.

''evolves'' towards a two-dimensional network. The cations do not form stacks as in compounds **1** but are arranged side-on in the structure (see Fig. 2a). The network is composed of dimeric units, but, contrary to **1**, it is no longer possible to distinguish between the neutral oxalic acid molecule and the hydrogen oxalate anion. As a matter of fact the building block is best described as a supramolecular monoanion of the type $[(HC_2O_4)\cdots H\cdots(HC_2O_4)]^-$ formed by the association of the two subunits. The inner $^{(-)}O\text{–}H\cdots O^{(-)}$ interaction is very short, 2.456(5) Å, with the H atom located on the centre of inversion, as often observed.[16] The hydrogen oxalate network is two-dimensional with very large rings composed of 28 atoms, with six $^{(-)}O\text{–}H\cdots O^{(-)}/O\text{–}H\cdots O^{(-)}$ interactions, and can thus be described as $\mathbf{R_6^6(28)}$ in graph-set terminology.

The two-dimensional network forms a layer and the crystal structure can be described as an alternating sequence of anionic layers formed by the hydrogen bridged anions in which parallel rows of $[Fe(\eta^5\text{-}C_5Me_5)_2]^+$ cations are sandwiched. A further noticeable aspect of the hydrogen bridged network in **2** is the non-planar conformation of the hydrogen oxalate anions, with the –COO groups adopting a twisted conformation (dihedral O–C–C–O angle 69.8°). Although much less frequent than the ''normal'' flat geometry, this conformation has been observed in other cases. A search has been run with the October 2001 version of the CSD,[17] and torsion angles for the O–C–C–O system have been retrieved. The search has been limited to systems containing only the free (*i.e.* not coordinated to a metal) $[HC_2O_4]^-$ anion; compounds in which the monoanion had been crystallised with either the $H_2C_2O_4$ or

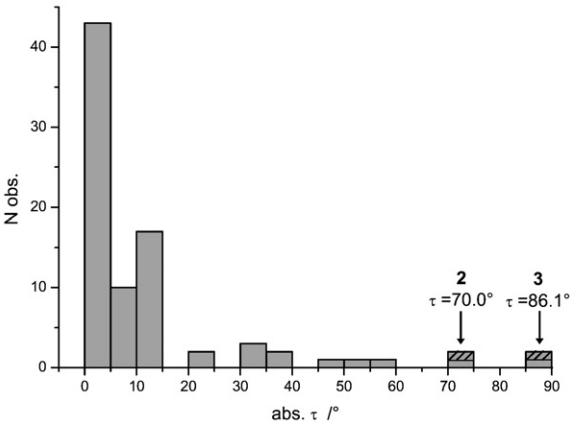


Fig. 3 The histogram shows the distribution in the CSD (October 2001) of torsion angle values for the free $[HC_2O_4]^-$ anion (73 hits, 82 observations); the values for compounds **2** and **3** have been added and evidenced by arrows.

$[C_2O_4]^{2-}$ moieties were excluded. The search yielded 73 compounds, and a total of 82 observations. Fig. 3 shows the distribution of the torsion angles: it can be seen that the favourite conformation is planar or slightly twisted, although a certain spread is observed towards wider angles. The torsion angle values observed in compounds **2** and **3** are evidenced in the highest values region of the histogram. When an analogous search is run including the $H_2C_2O_4$ and $[C_2O_4]^{2-}$ systems, one obtains a total of 198 hits and 250 observations. Although most neutral molecules and dianions have a planar geometry, there are a few cases of high torsion angles; in particular there are at least two dianions with an O–C–C–O angle larger than 30° and one oxalic acid molecule with an O–C–C–O angle of *ca.* 75°.

A twisted conformation (O–C–C–O dihedral angle 86.1°) is adopted by the hydrogen oxalate anion in the chromium salt $[Cr(\eta^6\text{-}C_6H_6)_2][HC_2O_4]\cdot[H_2O]$, **3**, while the cobalticinium derivative $[Co(\eta^5\text{-}C_5H_5)_2][HC_2O_4]\cdot[H_2C_2O_4]_{0.5}[H_2O]$ **4** presents a layered structure as in **2**. A projection of compound **3** along the cationic stack is shown in Fig. 4a with the benzene ligands in close contact. The anionic chain develops parallel to the cationic piles and contains twisted hydrogen oxalate units as in **2**. The distance between the centroids in **3** is 3.66 Å (ID 3.39, shift 1.38 Å). The chain is shown in Fig. 4b. It can be noticed that the twisted hydrogen oxalate anions do not interact with each other but are linked in the chains by means of water bridges, which form complex 14-membered rings based on four hydrogen bonding interactions $\mathbf{R_4^4(14)}$.

The crystal structure of $[Co(\eta^5\text{-}C_5H_5)_2][HC_2O_4]\cdot[H_2C_2O_4]_{0.5}[H_2O]$, **4**, can be described as formed by piles of $[Co(\eta^5\text{-}C_5H_5)_2]^+$ cations lying next to each other so as to form a layer of cations (Fig. 5a). The cationic layer alternates with anionic layers. There are two types of chains in **4**, the first is formed exclusively by hydrogen oxalate anions, while the second chain is formed by oxalic acid molecules and water (Fig. 5b). Hydrogen atoms along the hydrogen oxalate chain could not be observed. They are very likely disordered along the O···O interaction because the anions lie on inversion centres. The water molecules provide the intra-chain and inter-chain bridges.

Compound **5** is reported mainly for the sake of completeness. Its structure is analogous to the structure **4**, where cationic layers alternate with anionic layers. The $[Co(\eta^5\text{-}C_5H_5)_2]^+$ piles up with a plane distance of 3.52 Å (similar to **4**). In the anionic layer each oxalic acid molecule interacts both with a water molecule and with a Cl^- anion. Each chloride anion accepts hydrogen bonds from two water molecules and one oxalic acid unit as shown in Fig. 6.

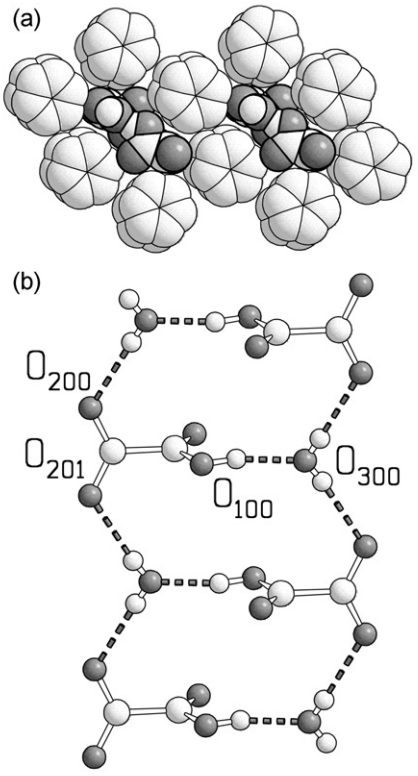


Fig. 4 (a) A projection of compound $[Cr(\eta^6\text{-}C_6H_6)_2][HC_2O_4]\cdot[H_2O]$, **3**, along the cationic pile showing the anionic chain in between the cationic piles. (b) The twisted hydrogen oxalate anions do not interact with each other but are linked in the chains by means of water bridges.

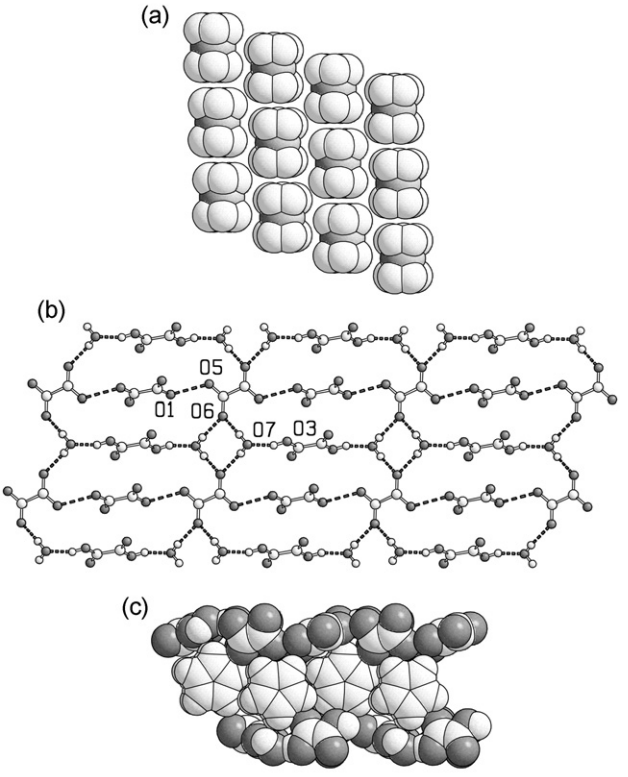


Fig. 5 (a) The cationic piles in $[Co(\eta^5\text{-}C_5H_5)_2][HC_2O_4]\cdot[H_2C_2O_4]_{0.5}[H_2O]$, **4**. (b) The two types of chains in **4**; one chain is formed exclusively by the hydrogen oxalate anions, while the second chain is formed by oxalic acid molecules and water. The water molecules also provide the intra-chain and inter-chain bridges. (c) A projection along the cationic pile showing how the cationic layers alternates with the anionic layers.

Magnetic behaviour of compounds 1a, 2 and 3. In order to check if the different crystal organisation of the hydrogen oxalate–oxalic acid hydrogen bonded structure influences the magnetic properties, the temperature dependence of the magnetic susceptibility of **1a** and **2** were measured. Both compounds at room temperature have a χT value (0.89 and 0.84 emu K mol^{-1} for **1a** and **2** respectively) in good agreement with the literature values for ferricinium ions.[18] The χT product decreases smoothly on decreasing the temperature (see Fig. 7), as previously observed and justified with a splitting of the ground $^2T_{2g}$ state by low symmetry components of the crystal field and spin-orbit coupling effects. Slight modifications of the surrounding of the ferricinium ion usually result in small modification of the χT values but the curves have very similar trends. On the contrary, below 30 K **1a** and **2** show a significantly different behaviour with a more pronounced decrease of χT for **1a**, which reaches *ca.* 0.40 emu K mol^{-1} at 2 K against 0.56 emu K mol^{-1} for **2**. The $1/\chi$ at low temperature (inlet in Fig. 7) has been fitted with the Curie–Weiss law and the results are $C = 0.70$ and 0.65 emu K mol^{-1} for **1a** and **2**, respectively with $\theta = -1.60$ K and -0.41 K. In both cases the negative θ suggests the presence of antiferromagnetic interactions, which are significantly stronger in **1a**.

The temperature dependence of the magnetic susceptibility of **3** has also been measured and found to be around 0.6 emu K mol^{-1} at room temperature, a value significantly larger than that expected for a species with one unpaired electron. This value has also been found to vary sensibly from sample to sample and suggests the occurrence of partial oxidation to chromium(III). The strong paramagnetic contribution of chromium(III) affects the data in the entire temperature range, hence does not allow to attribute the magnetic features of **3** to a specific type of intermolecular interaction.

As discussed above, the crystal structures of **1a** and **2** differ both in the packing of the $[Fe(\eta^5\text{-}C_5Me_5)_2]^+$ units and of the oxalic anions. These differences could be responsible for the different magnetic behaviours. In **1a** the $[Fe(\eta^5\text{-}C_5Me_5)_2]^+$ units are arranged in pairs, relatively close (ID = 3.67, CD = 3.69 Å) with the centroids that are shifted by only 0.40 Å. These pairs are arranged in columns with inter-pairs larger distances and shift (ID = 3.84, CD = 4.28, shift = 1.88 Å). In **2** a much larger shift is observed (3.18 Å) combined with a slightly reduced ID of 3.42 Å and a significantly larger CD (4.67 Å). The $[Fe(\eta^5\text{-}C_5Me_5)_2]^+$ are here arranged in columns. Also, the oxalate anions could be responsible for the weak antiferromagnetic interactions observed here. In fact, in **1a**, the two oxygen atoms of the carboxylate group belonging to the hydrogen oxalate are at relatively short contact distance from the methyl carbon atoms of the C_5Me_5 groups of different $[Fe(\eta^5\text{-}C_5Me_5)_2]^+$ units (O···C = 3.138 and 3.309 Å). In the case of **2** the shortest contact between a methyl group of $[Fe(\eta^5\text{-}C_5Me_5)_2]^+$ unit and an oxygen atom of the supramolecular monoanion $[(HC_2O_4)\cdots H\cdots(HC_2O_4)]^-$ is 3.44 Å. Since both the distance between centroids and the oxygen carbon contacts are shorter in **1a** than in **2**, it is not

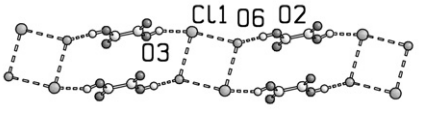


Fig. 6 In $[Co(\eta^5\text{-}C_5H_5)_2][Cl]\cdot[H_2C_2O_4][H_2O]$, **5**, each oxalic acid molecule interacts both with a water molecule and with a Cl^- anion. Each chloride ion accepts hydrogen bonds from two water molecules and one oxalic acid unit.

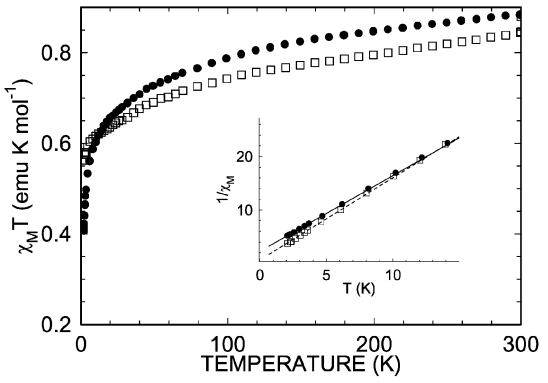


Fig. 7 Temperature dependence of the product of the magnetic susceptibility with temperatures measured for **1a** (solid circles) and **2** (empty squares) with an applied field of 10 kOe. In the inset the inverse of susceptibility is reported. The linear fit of the data, corresponding to the Curie–Weiss law, is reported as lines (see text).

possible to discriminate which exchange pathway dominates. Moreover the exchange interaction is too weak, compared to the temperature range investigated, to allow discrimination through the goodness of fitting procedures based on different models (mean-field, dimer, chain, *etc*.).

Conclusions

In this study, we have shown that the small hydrogen oxalate anion is a versatile building block for the construction of crystalline materials with predefined architectures. Clearly, with respect to larger anions derived from polycarboxylic acids,[4] the packing of the hydrogen oxalate anions has to compromise between two not necessarily converging factors: (i) the size of the anion which is small with respect to that of the sandwich cations and (ii) the need to preserve inter-anion hydrogen bridges in the absence of competing hydrogen bonding units on the cations.

The small dimensions of the oxalic acid unit do not allow intercalation of the anions between the C_5Me_5 rings as observed in the cases of TCNE and TCNQ and also for other anions, such as chloranilic acid.[19] It seems that preservation of the maximum number of O–H···O interactions is the driving force which thus favours the alternative $C^{(+)}$–$C^{(+)}$–$C^{(+)}$–$C^{(+)}$ cation organisation over the $A^{(-)}$–$C^{(+)}$–$A^{(-)}$–$C^{(+)}$ sequence. Another example of cationic piles of the type observed in **1**, **3** and **4** had been previously obtained with another small acid anion, the methoxychromate anion in the mixed valence crystalline salt $[Cr(\eta^6\text{-}C_6H_6)_2][CrO_3OMe]$.[20] Even if the $C^{(+)}$–$C^{(+)}$–$C^{(+)}$–$C^{(+)}$ organisation leads to sizeable magnetic interactions, these are much weaker than those observed in the charge transfer salts with TCNE and TCNQ, and, contrary to the latter,[21] no bulk magnetic behaviour is observed above 2 K.

Acknowledgements

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