Anions Derived from Squaric Acid Form Interionic π-Stack and Layered, Hydrogen-Bonded Superstructures with Organometallic Sandwich Cations: The Magnetic Behaviour of Crystalline $[(\eta^6\text{-}C_6H_6)_2Cr]^+[HC_4O_4]^-$

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Dedicated to Professor Jean-Marie Lehn on the occasion of his 60th birthday

Abstract: Depending on the stoichiometric ratio, squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione, H_2SQA) reacts with $[(\eta^6\text{-}C_6H_6)_2Cr]$ in THF to form the crystalline material $[(\eta^6\text{-}C_6H_6)_2Cr]$-[HSQA] (**1**) and in water to yield $[\{(\eta^6\text{-}C_6H_6)_2Cr\}_2][SQA]\cdot 6H_2O$ (**3**); it also reacts with $[(\eta^5\text{-}C_5H_5)_2Co][OH]$ in water to form $[\{(\eta^5\text{-}C_5H_5)_2Co\}_2][SQA]\cdot 6H_2O$ (**4**). Compound **1** is almost isostructural with the previously reported salt $[(\eta^5\text{-}C_5H_5)_2Co]$[HSQA] (**2**); its structure is based on π–π stacks between the benzene ligands and the hydrogen squarate anionic chains (π–π distance 3.375 Å). Compounds **3** and **4** are isomorphous and have a structure in which layers of organometallic cations intercalate with layers of water molecules hydrogen bonded to squarate dianions. All crystals contain charge-assisted $C{-}H\delta^+\cdots O\delta^-$ hydrogen bonds between the organometallic and the organic components, while negative $O{-}H^{(-)}\cdots O^{(-)}$ and $O{-}H\cdots O^{(2-)}$ interactions are present in the pairs **1/3** and **2/4**, respectively. In constrast to most organic salts of $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ and $[(\eta^5\text{-}C_5H_5)_2Co]^+$ which are yellow, crystals of compounds **1–4** are orange. Reflectance spectra measured on the crystalline material **1** show the presence of an intense tail that can be assigned to a charge-transfer transition through the $[(\eta^6\text{-}C_6H_6)_2Cr]^+$/$[HSQA]^-$ π-stacking interactions, while the π stacking in **2** causes only a broadening of the band. The magnetic behaviour of **1** and **3** has been investigated by SQUID magnetometry. Both compounds are characterised by a weak antiferromagnetic interaction between the $S=1/2$ Cr centres of the $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cations, which is significantly stronger in **1** due to the π-stacking with the $HSQA^-$ anions.

Keywords: crystal engineering · hydrogen bonds · magnetic properties · super-salts

Introduction

Modern crystal engineering is the planning and utilisation of crystal-oriented syntheses and the evaluation of the physical and chemical properties of the resulting crystalline materials.[1] The leading idea is that of being able to control collective crystal properties by choosing molecular/ionic building blocks with specific molecular properties (e.g., electronic configuration, redox potential, spin, etc.) and by embedding recognition and binding sites in the building block that will lead to the target supramolecular aggregation through self-assembly.[2] The construction of molecular-based magnetic materials is one of the most attractive areas of investigation.[3]

We have devoted our efforts, in collaboration with others, to expand crystal engineering towards the field of organometallic chemistry,[4] a rather uncharted territory in which the properties of (mainly organic) ligands combine with those of metal atoms. In particular we have developed a strategy to produce mixed organic, inorganic and organometallic crystals. A number of new crystalline compounds have been obtained by combining organic/organometallic moieties that interact through $O{-}H\cdots O$ hydrogen bonds with non-coordinating organometallic cations, such as $[(\eta^5\text{-}C_5R_5)_2Co]^+$ (R = H, Me)

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and $[(\eta^6\text{-}C_6H_5R)_2Cr]^+$ (R = H, Me).[5] This strategy has been applied, for example, to the preparation of chiral organic frameworks[6] and mixed-metal mixed-valent systems.[7]

The number of groups actively involved in the development of synthetic strategies based on the simultaneous utilisation of ionic interactions and hydrogen bonds indicate the potentials of the approach. Aakeröy et al.[8] have prepared ionic materials through hydrogen-bonding interactions of the O–H···O type between partially deprotonated acid anions and through interactions of the N–H···O type between anions and cations. The strategy adopted by Hosseini and co-workers to build one-, two-, and three-dimensional networks in mixed organic crystals is also based on the interaction between acids and bases.[9] Brammer has investigated several three-centre four-electron N–H···Co hydrogen bonds formed by the carbonyl anion $[Co(CO)_4]^-$ with counterions of the NR_3H^+ type (R = Me, Et).[10a,b] Hydrogen-bonding interactions involving transition metal chlorides have also been studied.[10c] Zaworotko et al.[11] have used cubane-like molecules, such as $[M(CO)_3(OH)_4]$ (M = Mn, Re), to synthesise superdiamantoid networks with large empty spaces available for the formation of clathrates. More recently, systems based on hydrogen-bonding interactions between partially deprotonated trimesic acid have also been investigated.[11b]

We have previously communicated[12] that squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione, H_2SQA) reacts with cobalticinium hydroxide in water (or THF) to yield two different crystalline materials, namely $[(\eta^5\text{-}C_5H_5)_2Co][HSQA]$ (**2**) and $[(\eta^5\text{-}C_5H_5)_2Co][(HSQA)(H_2SQA)]$, depending on the stoichiometric ratio between cobalticinium hydroxide and squaric acid. The $[(\eta^5\text{-}C_5H_5)_2Co]^+/[H_2SQA]^-$ 1:1 system is consists of infinite ribbons $\{[HSQA]^-\}_n$ and ribbons of cobalticinium cations. The good match in size and shape between the cyclopentadienyl ligands and the $[HSQA]^-$ ions, leads to a superstructure in which the squarate ribbons *intercalate* between cobalticinium cations. The $\pi-\pi$ distance is about 3.35 Å. The oxygen atoms from the rims of the $\{[HSQA]^-\}_n$ ribbons interact with the $[(\eta^5\text{-}C_5H_5)_2Co]^+$ cations through charge-assisted $C-H\delta^+\cdots O\delta^-$ hydrogen bonds.[13] It was noted that, while the 1:1 compound is orange, the 1:2 species $[(\eta^5\text{-}C_5H_5)_2Co][(HSQA)(H_2SQA)]$ is yellow, as are all other salts of cobalticinium thus far characterised. These findings prompted us to explore the possibility of attaining a similar π-stack from the oxidation of $[(\eta^6\text{-}C_6H_6)_2Cr]$ to the paramagnetic species $[(\eta^6\text{-}C_6H_6)_2Cr]^+$. The objective was to prepare a compound that, if isomorphous or quasi-isomorphous with $[(\eta^5\text{-}C_5H_5)_2Co]^+[H_2SQA]^-$, would form an alternating A/B/A/B/ structure based on the paramagnetic $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cation.

It has been shown that the stabilisation of ferromagnetic interactions within donor/acceptor complexes requires the formation of one-dimensional D + A – D + A– structures comprised of alternating cation donors (D) and anion acceptors (A) (the so-called linear-chain paradigm).[14] Ever since the observation that various TCNQ (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane),[15] and TCNE (tetracyanoethylene)[16] salts form conducting linear chains, many organometallic materials based on this anion have been isolated and the magnetic and electrical-conductivity behaviour established. Another interesting acceptor system is hexacyanotrimethylenecyclo propanide $[C_3(C(CN)_2)_3]^-$ that has been used in conjunction with $[(\eta^5\text{-}C_5Me_5)_2Fe]^+$, $[(\eta^6\text{-}C_6H_3Me_3)_2Fe]^{2+}$ and $[(\eta^6\text{-}C_6Me_6)_2Fe]^{2+}$ to prepare extended linear-chain compounds.[17] Ward[17b] was able to show that the difference in charge-transfer absorption energies between the two complexes is equivalent to the difference in the reduction potentials of the cations in solution. A similar relationship has been observed between salts of the $[iso\text{-}C_4(CN)_6]^{2-}$.[17c]

In this paper we report the successful preparation of the π-stacked system $[(\eta^6\text{-}C_6H_6)_2Cr][HSQA]$ (**1**), which is, as desired, (almost) isostructural with $[(\eta^5\text{-}C_5H_5)_2Co][HSQA]$ (**2**). Also we have prepared the first examples of organometallic hydrated material that contain the dianion $C_4O_4^{2-}$, namely $[(\eta^6\text{-}C_6H_6)_2Cr]\}_2[SQA]\cdot 6H_2O$ (**3**) and $[(\eta^5\text{-}C_5H_5)_2Co][SQA]\cdot 6H_2O$ (**4**). In these two compounds, which are isomorphous, layers of the organometallic cations intercalate with layers of water molecules that are hydrogen bonded to fully deprotonated squarate dianions. Interestingly crystals of compounds **1**–**4** are orange, while salts of the $[(\eta^5\text{-}C_5H_5)_2Co]^+$ and $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cations are generally bright yellow. All crystals have been characterised by low-temperature X-ray diffraction experiments. The results of reflectance spectra and of magnetic-susceptibility measurements will also be discussed. The structural features of **1** will be compared with those of the cobalticinium derivative $[(\eta^5\text{-}C_5H_5)_2Co][HSQA]$ (**2**), for which preliminary data had been reported.[12] It is worth stressing that, thus far, the two pairs $[(\eta^6\text{-}C_6H_6)_2Cr][HSQA]$ **1** and $[(\eta^5\text{-}C_5H_5)_2Co][HSQA]$ **2**, and $[(\eta^6\text{-}C_6H_6)_2Cr]\}_2[SQA]\cdot 6H_2O$ **3** and $[(\eta^5\text{-}C_5H_5)_2Co][SQA]\cdot 6H_2O$ **4** are the only known cases of (*quasi*-) isomorphous salts of $[(\eta^5\text{-}C_5H_5)_2Co]^+$ and $[(\eta^6\text{-}C_6H_6)_2Cr]^+$.

Results and Discussion

Ion organisation in crystalline 1 and 2: The structure of crystalline **1** is "dissected" in Figure 1, and can be described schematically as constituted of ribbons of $[HSQA]^-$ monoanions joined through $O-H^{(-)}\cdots O^{(-)}$ hydrogen-bond interactions [O···O distance 2.467 Å]. The anions are intercalated between $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cations (or vice versa). Alternatively, the crystal can be viewed as formed of piles of alternating $[HSQA]^-$ monoanions and of $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cations extending along the *b* axis. Each $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cation is encapsulated by two cations and six $[HSQA]^-$ monoanions. These latter are placed one above, one below and four surrounding the metal atom at the equatorial level (see Figure 1b). Conversely, each $[HSQA]^-$ anion is also surrounded by six cations: one above, one below and four "clamping" the O atoms between the benzene ligands. The oxygen atoms form the outer rims of the $\{[HSQA]^-\}_n$ ribbons and interact with the $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cations on both sides through charge-assisted $C-H\delta^+\cdots O\delta^-$ hydrogen bonds. Clearly, the good match in size and shape between the $[HSQA]^-$ anions and the benzene ligands in **1** is responsible for the neat inter-mixing of the flat anions with the cylindrical cations. As the compound is built up of an alternating sequence of cations and anions, the piles

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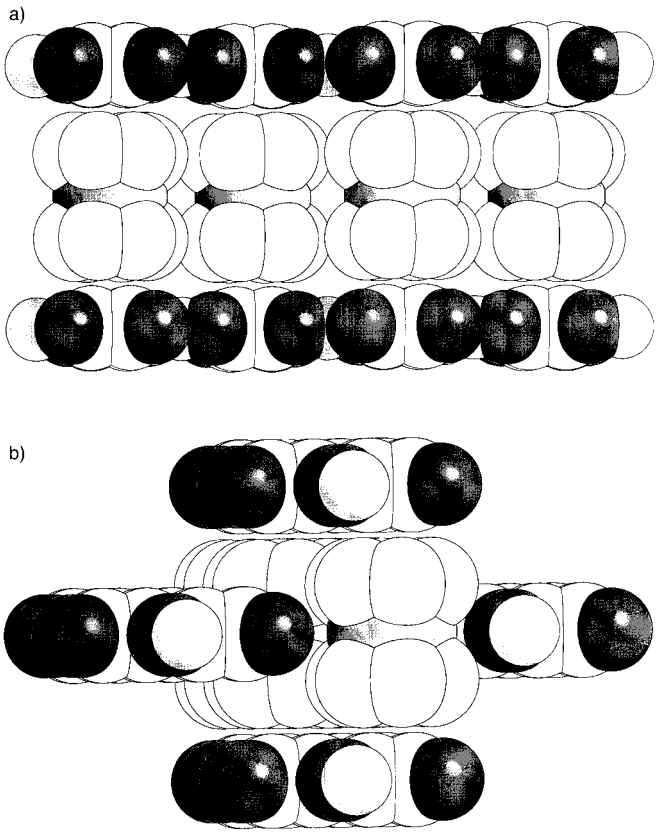

Figure 1. "Dissection" of the packing arrangement in crystalline **1**: a) space-filling representation of a row of cations encapsulated between two $\{[HSQA]^-\}_n$ ribbons. b) Space-filling representation of the distribution of anionic $\{[HSQA]^-\}_n$ chains around the $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cations. H atoms of the cations omitted for clarity.

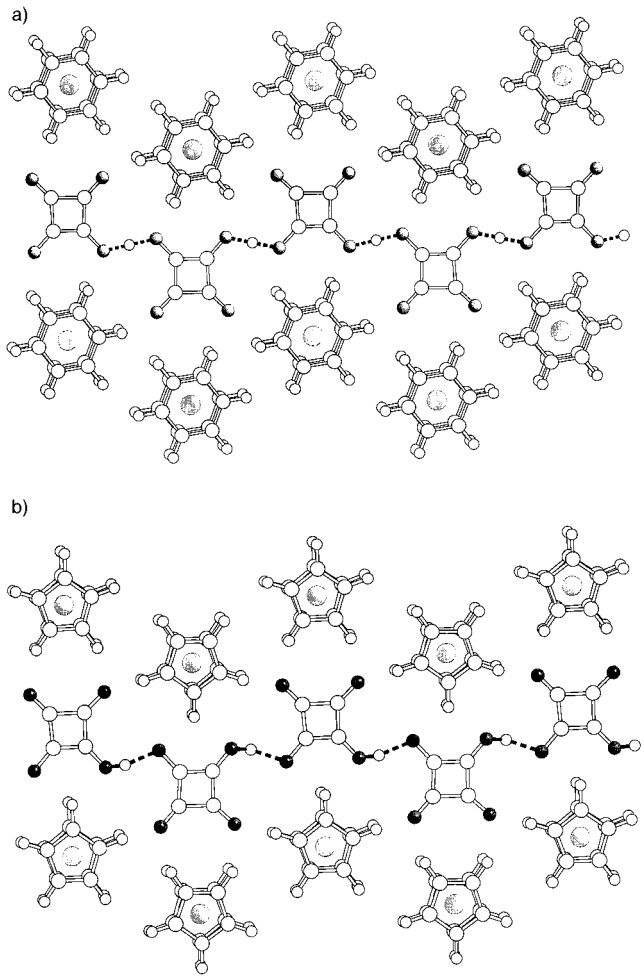

Figure 2. Comparison of alternating rows of cations and anions in crystalline a) **1** and b) **2**. Note the $O{-}H^{(-)}\cdots O^{(-)}$ hydrogen-bond interactions (broken bonds) along the $\{[HSQA]^-\}_n$ chains and also how the C–H systems of the benzene and cyclopentadienyl rings are directed towards the oxygen atoms along the chain to form a profusion of charge assisted $C{-}H\delta^+\cdots O\delta^-$ interactions (not shown for sake of clarity).

of ions are stabilised by Coulombic interactions, while interaction between the piles is guaranteed by the H atoms that bridge the anions in the $\{[HSQA]^-\}_n$ chains.

A comparison of some relevant intra- and intermolecular structural parameters for **1** and **2** is reported in Table . The substitution of the bis-benzene chromium for the cobalticinium cation on going from **1** to **2** appears to require some small "adjustment" of the structure in order to accommodate the slightly smaller cobalticinium cation. As a matter of fact, the hydrogen squarate chains in **1** are "stretched" with respect to those in compound **2**. This is reflected in two aspects of the structure: i) the O ··· O distances along the chain are longer in **1** than in **2** (2.467 and 2.473 versus 2.446 Å) and ii) the ribbon of hydrogen squarates is completely flat in **1**, while it is slightly puckered in **2** (see Figure 2). This is also reflected in the cation–cation separation along the ribbons, which allows slightly longer next-neighbour H ··· H contacts in **1** than in **2**.

Table 1. Comparison between some intermolecular structural parameters in **1** and **2** (distances in Å, angles in degrees).

	(O–H) ··· O	O ··· O	O–H ··· O	π–π
1[a]	1.23	2.47	180.0	3.350
	1.24	2.47	180.0	
2[b]	1.634	2.446	149.3	3.375

[a] Esd (1) for **1**. [b] Esd (8) for **2**.

Both **1** and **2** contain anionic $\{[HSQA]^-\}_n$ chains. We have argued[18] that the stability of $O{-}H^{(-)}\cdots O^{(-)}$ chains, such as in hydrogen oxalate salts and in hydrogen squarates, can not be attributed to, albeit favourable, hydrogen bonding $O{-}H^{(-)}\cdots O^{(-)}$ interactions because of the electrostatic repulsions between neighbouring anions, but to the overcompensation arising from stabilising anion–cation Coulombic interactions. Along anionic chains, the $O{-}H^{(-)}\cdots O^{(-)}$ interaction acts essentially as a *supramolecular organiser* which minimises electrostatic repulsions. It is interesting to observe that the O ··· O separation in **1** and **2** is considerably shorter than that found in crystals of neutral squaric acid (2.55 Å) and neutral carboxylic acids. This apparent contradiction between length and strength of the O–H ··· O interaction in neutral and charged systems has been explained with the "electrostatic compression" effect,[18a,b] which arises from the presence of the electrostatic field generated by anions and cations. Similar reasoning applies to other types of non-covalent interactions, such as π–π stacking.[18c,d] In the cases of **1** and **2**, the separations between benzene or cyclopentadienyl planes and the squarate planes are 3.375 and 3.35 Å, respectively, both

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appreciably shorter than in graphite. Although it would be reasonable to think that the close approach is favoured by the alternating ionic charge along the chains, it has been observed that short $\pi-\pi$ separations are attained also by systems carrying the *same* ionic charge, for example, alkali hydrogen squarate salts; hence the same rationale as in the case of $O-H^{(-)}\cdots O^{(-)}$ interactions applies.

Ion organisation in crystalline 3 and 4: As mentioned in the Introduction, compounds **3** and **4** are, at least at the time of this publication, the only other *pair* of isostructural systems obtained from the same organic moiety and $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ and $[(\eta^5\text{-}C_5H_5)_2Co]^+$, respectively, in the family of organic-organometallic *supersalts*.[5] When the stoichiometric molar ratio of squaric acid/bis-benzene chromium or squaric acid/cobaltocene is 1:2, complete deprotonation of the acid with formation of the dianion $C_4O_4^{2-}$ is achieved. As previously noted in the course of our crystal engineering studies,[5] the acid moieties are completely deprotonated every time, hence there is an "excess" of acceptor with respect to donor sites in $O-H\cdots O$ interactions; water molecules are brought in the crystal to compensate for the lack of donors. This is also the case of species **3** and **4**, in which six water molecules are co-crystallized with the dianions forming a hydrogen-bonded web which joins the squarate dianions together (see Figure 3). While in crystalline **3** only three hydrogen atoms bonded to the oxygen atoms were located from the Fourier map, in crystalline **4** all the hydrogen atoms of the water molecules were directly localised from the Fourier map. If only C and O atoms are considered there are three motifs that can be distinguished: an hexagonal ring formed by five water molecules and one squarate oxygen, the seven-membered ring formed by half of a squarate anion and three water molecules and a more complex ten-member ring (excluding the H-atoms) formed by two halves of two squarate anions and two water molecules. This web gives the two-dimensional motif of the puckered anionic layers that alternate with layers of $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ or $[(\eta^5\text{-}C_5H_5)_2Co]^+$ cations, as shown in Figure 4. The stacking present in crystalline **3** (and **4**) is reminiscent of that observed[19] in crystals of the hydroxide $[(\eta^6\text{-}C_6H_6)_2Cr]^+[OH^-]\cdot 3H_2O$ (compare Figures 4a and 4b with 4c). The layers in this last crystal consist of a slightly puckered hexagonal network that contains three water molecules and one OH^- group per formula unit. A comparison of some relevant intermolecular structural parameters in **3** and **4** is reported in Table 2. $O_{anion}\cdots O_{water}$ and $O_{water}\cdots O_{water}$ distances in **3** and **4** are comparable in length. The interaction between the organometallic cations and the $O-H\cdots O$ network is attained through a profusion of charge-assisted $C-H\delta^+\cdots O\delta^-$ interactions involving both the squarate and the water oxygen atoms. The quality of the X-ray data for compound **4** allowed location in the Fourier maps of *all* hydrogen atoms bound to the water molecules, thus enabling us to completely characterise the hydrogen-bond network. In this case, it is worth noting the absence of disorder that usually accompanies extended hydrogen-bonded networks involving water molecules. In the case of **4** (and, logically, of **3**) this is easy to rationalise: there are in fact *two types* of structural water molecules, those which are directly linked directly to the dianions, and hence can only act as donors towards the squarate oxygen atoms, and those in between. Since the orientation of the outer molecules is fixed, there is only one distribution of possible inter-water $O-H\cdots O$ hydrogen bonds for the remaining molecules (see Figure 3b).

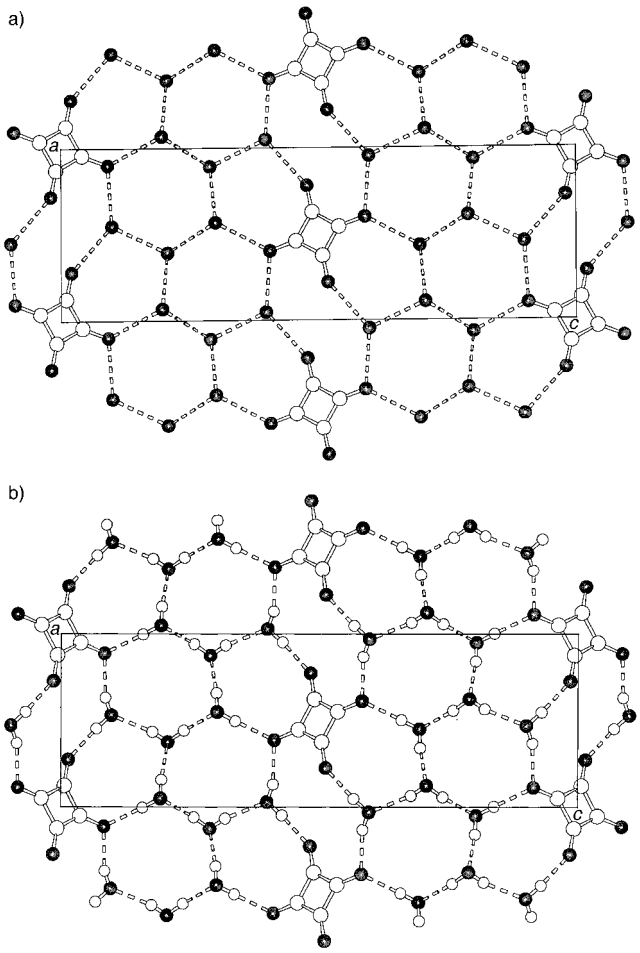


Figure 3. The corrugated layers formed by the dianions $C_4O_4^{2-}$ and water molecules in the *ac* plane of a) **3** and b) **4**, showing the presence of 6-, 7- and 10-membered hydrogen-bonded rings (excluding the H atoms) formed by the O–H donors belonging to the water molecules and the O-acceptors on the water molecules and the dianions. In compound **4** all H-atoms were located from the Fourier maps; the absence of disorder is noteworthy.

The pairs **1/2** and **3/4** permit a geometrical comparison between squarate monoanions $HC_4O_4^-$ and dianions $C_4O_4^{2-}$. As shown in the Table 3, while the monoanion retains the difference between C–C and C=C and between C=O and C–O bond lengths characteristic of the neutral molecule squaric acid,[20] the bonding in the dianions becomes fully delocalised with four equivalent C–C and four equivalent C–O bond lengths; the values for these bond lengths are intermediate between those of single and double bonds observed in **1** and **2**.

Reflectance measurements on 1–4: Reflectance spectra were measured on crystalline samples of compounds **1**–**4** in order to understand the nature and degree of the electronic interactions among the ionic building blocks in the structures. The spectrum of the cobalticinium salt **2** shows a broadening of the band in the 350–500 nm region. In relation to the spectrum measured for cobalticinium hexafluorophosphate,

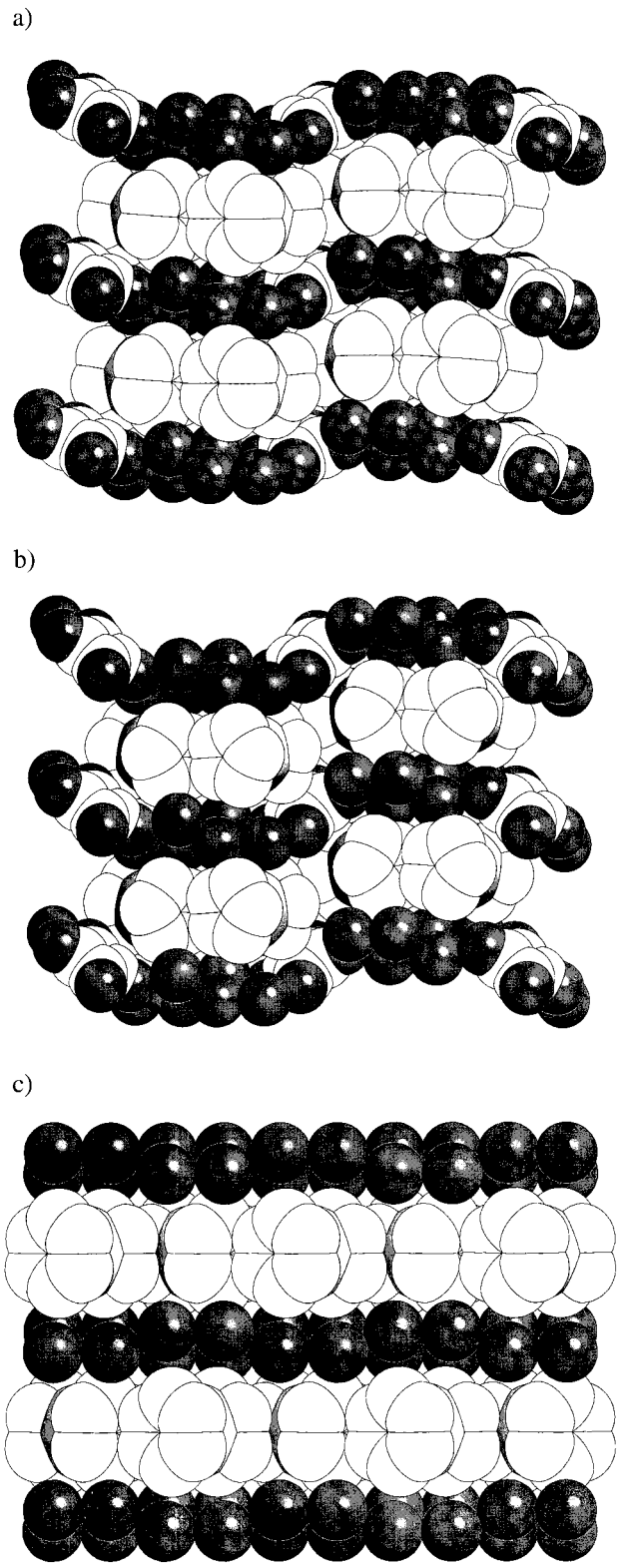


Figure 4. Space-filling representation of the stacking sequence of alternating layers of hydrated squarate dianions and a) $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ or b) $[(\eta^5\text{-}C_5H_5)_2Co]^+$ cations piled along the *a* axis. c) Space-filling model of the same stacking sequence present in crystalline $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ $[OH^-]\cdot 3H_2O$.[9]

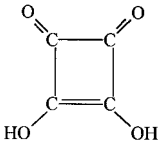
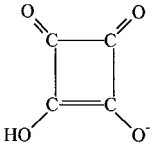
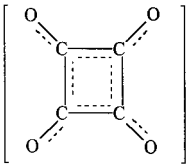
this behaviour appears to be consistent with the presence of a π-stacking interaction. This broadening is not observed in the spectrum of **4**, in accordance with the absence of such π stack as shown by the X-ray structure. Much stronger perturbations

Table 2. Comparison between O···O distances [Å] in **3** and **4**.

	O···O_{water}	O_{water}···O_{water}
3[a]	2.758	2.712
	2.737	2.767
	2.752	2.783
4[b]	2.745	2.737
	2.755	2.770
	2.773	2.700

[a] Esd (6) for **3**. [b] Esd (4) for **4**.

Table 3. Comparison between intramolecualar structural parameters [Å] in for squaric acid the squarate mono- and dianions.

	C–C	C–O		
	C–C 1.497[a] 1.464[a] 1.461[a] C=C 1.414[a]	C–O(H) 1.290[a] 1.286[a] C=O 1.232[a] 1.228[a]		
	**1**[b] C–C 1.53 1.49 1.52 C=C 1.40	**2**[c] C–C 1.522 1.462 1.469 C=C 1.425	**1**[b] C–O(H) 1.28 C–O⁻ 1.29 C=O 1.19 1.21	**2**[c] C–O(H) 1.280 C–O⁻ 1.280 C=O 1.237 1.218
	**3**[d] C:C 1.449 1.469	**4**[e] C:C 1.449 1.468	**3**[d] C:O 1.257 1.232	**4**[e] C:O 1.261 1.251

[a] Ref. [20] neutron crystal structure of squaric acid at 15 K. [b] Esd (1). [c] Esd (6–8). [d] Esd (6–8). [e] Esd (3–4).

with respect to the spectra of the components [bis-benzene chromium(I) hexafluorophosphate and sodium squarate] are instead observed in the spectrum of **1** (see Figure 5), in which an intense tail is present in the 400–500 nm region. This new feature can be assigned to a charge-transfer transition between the bis-benzene chromium cations and the squarate anions in the $\{[HSQA]^-\}_n$ chains. This interpretation is supported by the possibility for the bis-benzene chromium(I)

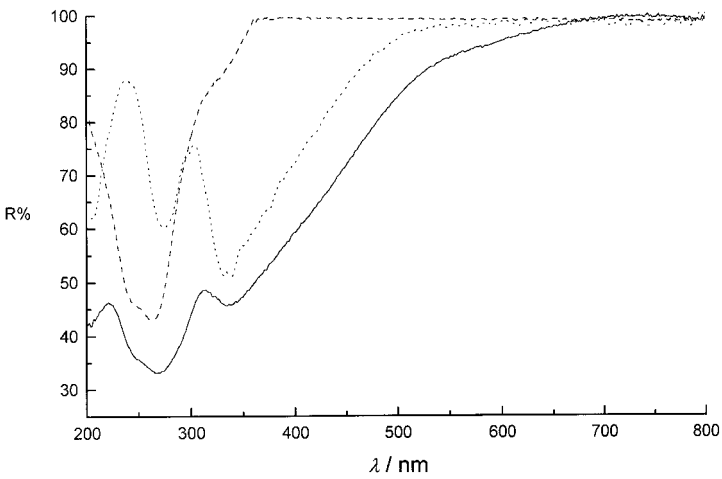


Figure 5. Reflectance spectra of $NaHC_4O_4$ (dashed line), $[(\eta^6\text{-}C_6H_6)_2Cr]PF_6$ (dotted line) and **1** (solid line).

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ion to undergo further oxidation at accessible potentials (E_p = 1.14 V vs. SCE in DMF),[21] a possibility not presented by the cobalticinium ion. The presence of such a new absorption is a clear indication of the existence of an appreciable electronic interaction between the two ions.[22] This new band is not observed in **3**, again in accordance with the X-ray structure, which indicates a much lower degree of electronic interaction.

Magnetic properties of 1 and 3: The raw data of **1** are characterised by a room-temperature value of the product of the magnetic susceptibility with temperature (χT) of about 0.5 emu K mol^{-1}, which is significantly higher than that expected for one unpaired electron of the $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cation. Due to the air sensitivity of the compound we also measured the oxidised product and found it to be strongly paramagnetic, due to the presence of Cr^{III}, with relatively strong antiferromagnetic interactions. The data of **1** has been corrected by taking into account about 3% in weight of the oxidised form in order to obtain the correct high-temperature value of the χT product. The corrections do not significantly affect the low-temperature values of χ, reported in Figure 6, which do not diverge on lowering T, but level off around 4 K. The data have been fitted by using two different models that take into account the antiferromagnetic interaction of the S = 1/2 extending over one[23a] or two dimensions, respectively.[23b] The one-dimensional model better reproduces the experimental data and provides an estimation of the coupling constant J/k_B = 4.7 K, for which the Hamiltonian is written as $H = J\chi_i \mathbf{S}_i\mathbf{S}_{i+1}$; however further experimental data, like single-crystal EPR spectra, are necessary to quantify the two-dimensional character. This sizeable antiferromagnetic interaction, taking into account that the Cr–Cr separation exceeds 6 Å and dipolar interactions are therefore of the order of 0.05 K, can be justified by the π-stack interaction between the benzene ring and the $[HSQA]^-$ anions, which extends along the b axis. This hypothesis is confirmed by the reflectance spectra and by the comparison with the magnetic behaviour of **3**, in which such a strong π-stacking interaction is not present. In Figure 6 the temperature dependence of the magnetic susceptibility of **3** is also reported, but in this case the susceptibility diverges at low temperature, suggesting that only weaker AF interactions are present.[24] Even if, in principle, we cannot exclude the contribution of H-bonds in transmitting the magnetic interaction, thus providing a two-dimensional character, the electronic interactions between the $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cation and the $[HSQA]^-$ anion through the π stack is the principal one. In fact, the magnetic interaction due to a charge-transfer mechanism in one-dimensional system originated by π stack of $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ with stable organic radicals like $TCNE^{\bullet-}$ has been already observed and widely investigated and found to be ferromagnetic when the radicals are not dimerized, while a weak antiferromagnetic interaction is observed when the pairs of $TCNE^{\bullet-}$ are in the singlet ground state.[25] The magnetic properties of compound **2** have also been investigated and the compound revealed to be diamagnetic in the whole temperature range, as expected.

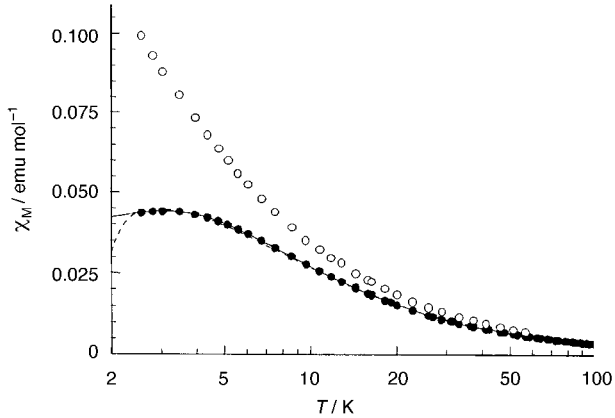

Figure 6. Temperature dependence of the magnetic susceptibility (per mole of $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cation) of **1** (●) and **3** (○). The lines correspond to the calculated for antiferromagnetically interaction S = 1/2 Cr centres that best reproduce the observed behaviour values by using the one-dimensional model with J/k_B = 4.7 K (solid), and the two-dimensional model with J/k_B = 3.0 K (broken line).

Conclusion

In this paper we have discussed the synthesis, structural characterisation and evaluation of the magnetic properties of two crystalline *supersalts* obtained by treating bis-benzene chromium (or cobaltocene) with squaric acid in the presence of oxygen. The crystal synthesis process has been discussed previously and we only need to recall the basic sequence of steps through which self-assembly of the organometallic cations and organic anions in the solid state is achieved.[5] The sequence is initiated by a redox process that, in the presence of oxygen, leads from neutral bis-benzene chromium to the paramagnetic cation $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ (or from neutral cobaltocene to the diamagnetic cation $[(\eta^5\text{-}C_5H_5)_2Co]^+$) with consequent formation of the strongly basic species O_2^-, which then deprotonates the acid. The hydrogen squarate monoanion or squarate dianion are formed according to the stoichiometric ratio. The characteristics of the aggregates depend on the choice of medium. If an anhydrous material is sought the reaction ought to be carried out in THF and the insoluble ionic precipitate needs to be recrystallised from anhydrous nitromethane (as in the case of **1**). If water is used, the insoluble neutral organometallic sandwich compound utilised as starting material is carried in solution in its oxidised form (as in the cases of **3** and **4**) and hydrated crystals are formed on evaporating the solvent.

On the basis of the similarity in shape and redox properties of $[(\eta^6\text{-}C_6H_6)_2Cr]$ and $[(\eta^5\text{-}C_5H_5)_2Co]^+$, we have successfully planned the construction of the anhydrous species **1** which is *almost* isomorphous and isostructural with the previously characterised species $[(\eta^5\text{-}C_5H_5)_2Co][HSQA]$, but contains the paramagnetic cation $[(\eta^6\text{-}C_6H_6)_2Cr]^+$. In view of the paramagnetism of the cation and of the features of the ion organisation, compound **1** has been subjected to magnetic measurements revealing a one-dimensional character with significant antiferromagnetic interactions, which are probably associated with the electronic interaction between the

$[HSQA]^-$ anion and the π-stacked cation $[(\eta^6\text{-}C_6H_6)_2Cr]^+$. The squarate monoanion has, therefore, the double function of providing the structural framework and that of transmitting the magnetic interaction between the paramagnetic cations. This conclusion is supported by the reflectance measurements on crystalline **1** that show the presence of a charge-transfer transition through the $[(\eta^6\text{-}C_6H_6)_2Cr]^+/[HSQA]^-$ π-stacking interactions.

Compounds **3** and **4**, on the other hand, represent the only other examples of isomorphous organometallic salts of the squarate dianions. Their crystalline structures are reminiscent of that of the hydroxide $[(\eta^6\text{-}C_6H_6)_2Cr][OH]\cdot 3H_2O$ and consist of stacking sequences of layers of hydrated anions and cations. In all these crystals O–H···O hydrogen bonds are confined within the anionic layers, while the inter-layer interactions are based on charge-assisted C–H···O bonds between cyclopentadienyl and benzene C–H systems belonging to the cations, and the oxygen atoms in the anionic layers.

The utilisation of noncovalent bonding is the paradigm of supramolecular chemistry,[26] while periodicity and symmetry are the paradigms of the crystalline state, hence molecular crystal engineering can be regarded as the way to obtain *periodical (solid) supermolecules*. The collective properties of such solid supermolecules, though different from those of the components, result from the way the components (ionic or molecular building blocks) interact among themselves. Organometallic building blocks permit the inclusion in the design strategy of the topological, redox, and spin properties of transition metal atoms (a rather large portion of the Periodic Table!) and promise interesting discoveries in materials chemistry. The more we learn on the deliberate design, preparation and characterisation of crystalline materials, and on the resulting physical and chemical properties, the closer we get to grasping the basic factors that control recognition, aggregation and nucleation of crystalline solids.

Experimental Section

3,4-Dihydroxycyclobut-3-ene-1,2-dione was purchased from Aldrich, $[(\eta^6\text{-}C_6H_6)_2Cr]$ and $[(\eta^5\text{-}(C_5H_5)_2Co]$ were purchased from Strem.

Synthesis of $[(\eta^6\text{-}C_6H_6)_2Cr][HSQA]$ (1): $[(\eta^6\text{-}C_6H_6)_2Cr]$ (58.0 mg, 0.279 mmol) was added to a well-stirred suspension of squaric acid (32.4 mg, 0.279 mmol) in anhydrous THF (20 mL) at 35 °C. An orange precipitate formed immediately. The precipitate was filtered and then dried under vacuum. Crystals suitable for single-crystal X-ray diffraction were obtained by dissolving part of the powder in nitromethane and allowing slow evaporation of the solvent in a watch glass at room temperature. Both single crystals and crystalline powder were stored under Ar at low temperature, because traces of impurities, not detectable with powder diffraction, were found to catalyse the decomposition of compound **1**.

Synthesis of $[(\eta^6\text{-}C_6H_6)_2Cr]_2[SQA]\cdot 6H_2O$ (3): $[(\eta^6\text{-}C_6H_6)_2Cr]$ (42.2 mg, 0.203 mmol) was suspended in doubly distilled (20 mL) water at room temperature in air and stirred until a clear, bright yellow solution of $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ was obtained. Squaric acid (11.6 mg, 0.102 mmol) was added to the solution. The solution was dried in rotary evaporator and the resulting orange powder was recrystallised from nitromethane at room temperature. Red/orange crystals suitable for single-crystal X-ray diffraction were obtained and kept under inert gas atmosphere.

Synthesis of $[(\eta^5\text{-}C_5H_5)_2Co]_2[SQA]\cdot 6H_2O$ (4): $[(\eta^5\text{-}C_5H_5)_2Co]$ (100 mg, 0.53 mmol) was suspended in doubly distilled water (20 mL) and stirred at room temperature in air until a clear, bright yellow solution of $[(\eta^5\text{-}C_5H_5)_2Co]^+[OH]^-$ (pH of the solution >10) was obtained. Squaric acid (30.2 mg, 0.265 mmol) was added to the solution of cobaltocenium hydroxide. The solution (ca. pH 5) was dried in rotary evaporator and the powder was recrystallised from nitromethane at room temperature. Hygroscopic and low-melting orange crystals were obtained.

Crystallography: Crystal data for **2** were previously deposited with the CSD and will not be reported again.[12] Crystal data for species **1**, **3** and **4** and details of measurements are reported in Table 4. Common to all compounds: $Mo_{K\alpha}$ radiation, $\lambda = 0.71069$ Å, monochromator graphite, psi-scan absorption correction. All non-hydrogen atoms were refined anisotropically. (O)H atoms were directly located from Fourier maps and not refined. H atoms bound to C atoms were added in calculated positions. The computer program SHELX-97[27a] was used for structure solution and refinement. The computer program SCHAKAL-97[27b] was used for all graphical representations. In order to evaluate the C–H···O bonds, the C–H bond lengths were normalised to the neutron derived value of 1.08 Å and the program PLATON was used.[27c] In spite of the similarities between the primitive unit cells of **1** and **2** initial attempts to treat structure **1** in space group $P2_1$ failed to give satisfactory refinement; this resulted, in particular, in the presence of several short H···H contact distances between neighbouring cations. Reconsideration of the structural model showed that the bis-benzene chromium cations adopted a slightly different distribution over the hydrogen squarate chains. Refinement in space group *C2/m* gave satisfactory results and no unreasonable H···H contacts. Hence, crystals of compounds **1** and **2** are quasi-isomorphous. In contrast, compounds **3** and **4** are isomorphous and crystallise in space group *Pbca*. Data for **4** were of sufficient quality to allow location of all oxygen-bound hydrogen atoms, hence permitting a complete description of the hydrogen-bond network (see above). H atoms were kept in observed positions and were not refined, all other H atoms were added in calculated positions and allowed to ride on the corresponding C atom. Some rotational disorder was observed for the benzene and cyclopentadienyl rings in **3** and **4** (occupancy ratios 6:4 and 7:3, respectively) In all cases, correspondence between the structures determined by single-crystal X-ray diffraction and that of the bulk materials precipitated from solution was confirmed by comparing the experimental powder diffractograms obtained from the bulk material with those calculated on the basis of the single-crystal structures. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-132876, CCDC-132877 and CCDC-132878. Copies of the data can be obtained free of charge on

Table 4. Crystal data and details of measurements for compounds **1**, **3** and **4**.

	1	**3**	**4**
formula	$C_{16}H_{13}CrO_4$	$C_{28}H_{36}Cr_2O_{10}$	$C_{24}H_{32}Co_2O_{10}$
M_w	321.26	636.57	598.36
T [K]	150(2)	223(2)	193(2)
crystal system	monoclinic	orthorhombic	orthorhombic
space group	*C2/m*	*Pbca*	*Pbca*
a [Å]	11.47(1)	7.490(6)	7.403(4)
b [Å]	9.95(1)	16.75(1)	16.089(3)
c [Å]	11.139(5)	22.46(2)	22.19(1)
α [°]	90	90	90
β [°]	91.06(6)	90	90
γ [°]	90	90	90
V [Å^3]	1271(2)	2818(4)	2643(2)
Z	4	4	4
$F(000)$	660	1328	1240
max/min transmission	1.00/0.47	1.00/0.75	1.00/0.68
$\mu(Mo_{K\alpha})$ [mm^{-1}]	0.913	0.828	1.308
measured reflections	1469	2849	2598
unique reflections	1343	2475	2250
parameters	98	169	142
GOF on F^2	1.071	1.040	0.692
$R1$ [$I > 2\sigma(I)$]	0.0884	0.0780	0.0338
$wR2$ (on F^2,all data)	0.2698	0.2355	0.1445

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application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Reflectance measurements: The reflectance spectra were measured with a Perkin–Elmer (Lambda 9) UV/VIS/NIR, equipped with an integrating sphere. $MgSO_4$ was used as matrix for dilution of the compound.

Magnetic measurements: The temperature dependence of the magnetic susceptibility of microcrystalline powders **1**, **2**, and **3** was measured with a Metronique Ing. MS02 SQUID magnetometer. Data was corrected for the sample holder and the diamagnetism by using Pascal's constants. Due to the air sensitivity of **1**, the data were found to be affected by a partial oxidation of the sample. The magnetism of the green oxidation product of **1** was also investigated.

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