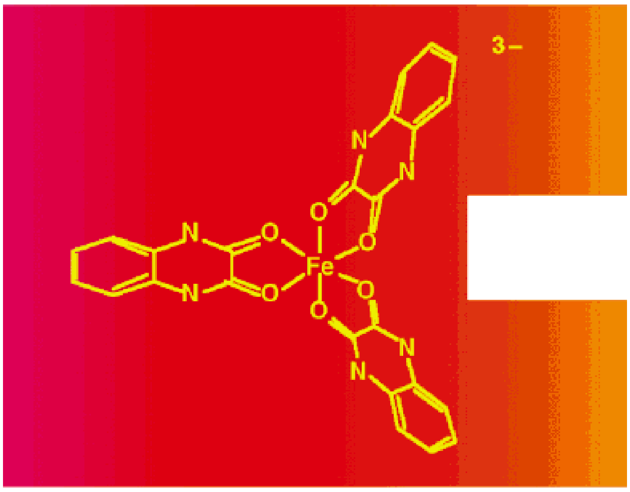
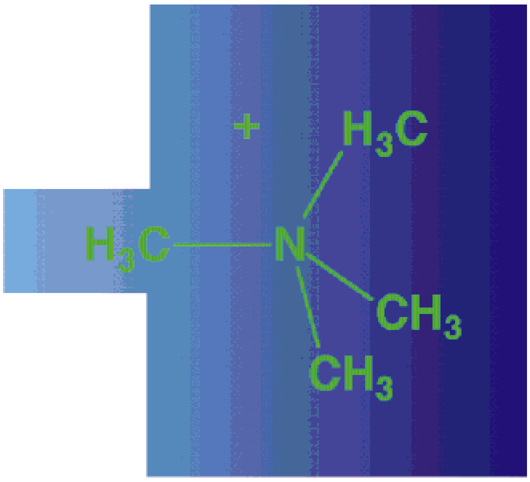
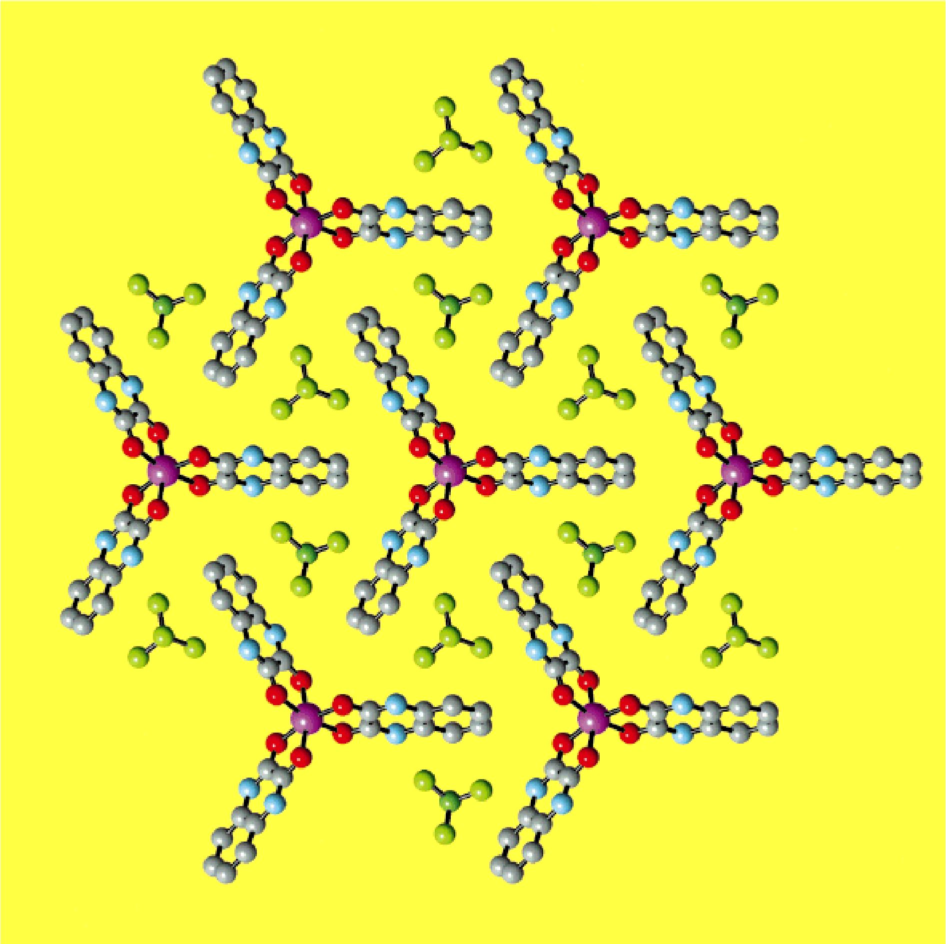






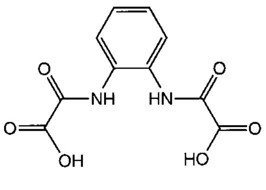
An esthetically pleasing trigonal network, formed by self-assembly in the crystalline phase from NMe_4^+ cations and enantiomerically pure Δ and Λ isomers of the anionic iron(III) complex presented above on the left, is described by Y. Journaux, M. C. Muñoz, J. R. Pedro, and co-workers on the following pages.

Sheets of Alternating Chirality in the Structure of a Novel Iron(III) Complex with a Cyclic Oxamide Ligand[**]

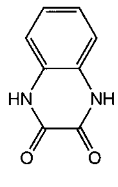
M. Carmen Muñoz,* Rafael Ruiz, Maria Traianidis, Ally Aukauloo, Joan Cano, Yves Journaux,* Isabel Fernández, and José R. Pedro*

When neutral molecules or ions approach each other to form ordered solid-state structures, highly selective interactions occur between the building blocks which determine the crystal packing. Supramolecular chemistry provides us with a plethora of terms and concepts to describe the basic features of these interactions in the solid state.[1, 2] In this sense one can speak of supramolecular solid-state chemistry or, equivalently, crystalline supramolecules. Empirical methods are entirely valid in this relatively young area of science, and they often provide the sole approach to crystal engineering.[3]

Recently we initiated an investigation to assess the possible use of bis-*N*-substituted oxamato ligands such as $H_4[\mathbf{1}]$ in the preparation of iron–amide complexes.[4] Intriguingly, our results indicate that in basic medium in the presence of ferric ion the ligand $Et_2H_2[\mathbf{1}]$ (the diethyl ester of $H_4[\mathbf{1}]$) cyclizes to form the cyclic oxamide ligand $H_2[\mathbf{2}]$, which is present in the resulting iron(III) complex in the form of the bidentate 2,3-quinoxalinedionate ligand $[\eta^2\text{-}\mathbf{2}]^{2-}$.[5] We report here the synthesis, crystal structure, and general physical characteristics of this new species **3**, one of the rare iron compounds in which an amido ligand is bound to the iron center through an oxygen atom.



$H_4[\mathbf{1}]$



$H_2[\mathbf{2}]$

$(NMe_4)_2(H_3O)[Fe(\eta^2\text{-}\mathbf{2})_3]\cdot 14\,H_2O$ **3**

The crystal structure of **3** consists of discrete mononuclear $[Fe(\eta^2\text{-}\mathbf{2})_3]^{3-}$ complex anions together with tetramethylammonium and oxonium cations and water molecules (Figure 1). Interestingly, parallel planar layers of $[Fe(\eta^2\text{-}\mathbf{2})_3]^{3-}$ anions and NMe_4^+ cations alternate in regular fashion in the crystal lattice. Within the anionic layers the iron complex ions are arranged according to a triangular pattern in the *ab* plane (the distance between two iron centers is 12.2 Å; Figure 2, top). The aromatic rings of the ligands associated with one complex anion are arrayed between those of the neighboring molecules such that the edge of each ring interacts with the faces of two aromatic rings from a neighboring molecule. Each phenyl ring projects two of its hydrogen atoms toward the nitrogen atoms of the heteroatom rings from neighboring molecules in such a way that the coulombic attraction $H^{\delta+}\cdots N^{\delta-}$ establishes both the directionality of the interaction and most of the energy of attraction. This leads to small tetrahedral cavities with C-H$\cdots$N distances that range from 3.63 to 5.24 Å and in which the NMe_4^+ cations reside. They are located alternately above and below the anionic layers, whereby one of the methyl groups points toward the center of the cavity. Thus, the anionic voids function as a sort of "open hosts." However, host and guest appear to be held together only by electrostatic attractions in addition to van der Waals forces (the C-H$\cdots$N distances range from 3.88 to 4.34 Å).

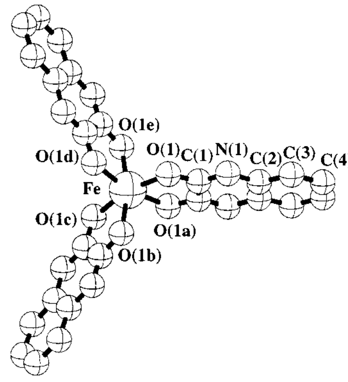


Figure 1. Perspective view of the anionic mononuclear $[Fe(\eta^2\text{-}\mathbf{2})_3]^{3-}$ unit of **3** (hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: Fe–O(1) 2.011(4); O(1)-Fe-O(1a) 80.4(3), O(1)-Fe-O(1b) 90.7(2), O(1)-Fe-O(1c) 166.3(3), O(1)-Fe-O(1d) 90.7(2), O(1)-Fe-O(1e) 99.8(3) [symmetry operations: (a) $2-x$, $1-x+y$, $1/2-z$, (b) $2-y$, $1+x-y$, z; (c) $1+x-y$, $2-y$, $1/2-z$, (d) $1-x+y$, $2-x$, z; (e) y, x, $1/2-z$].

The layer organization and topology found in crystals of **3**, where one sheet of $\{[Fe(\eta^2\text{-}\mathbf{2})_3]^{3-}\}$ octahedra is surrounded by two sheets of $\{NMe_4^+\}$ tetrahedra, are reminiscent of those in the phyllosilicate minerals, which belong to the important class of clays. In the latter case, layers of corner-sharing $\{SiO_4\}$ tetrahedra are linked with layers of edge-sharing $\{M(O,OH)_6\}$ octahedra (M = Mg, Al), with alternating tetrahedral–octahedral–tetrahedral layers.

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[*] Dr. M. C. Muñoz
Departamento de Física Aplicada
Universidad Politécnica de València
E-46071 València (Spain)

Dr. Y. Journaux, Dr. R. Ruiz, M. Traianidis, Dr. A. Aukauloo,
Dr. J. Cano
Laboratoire de Chimie Inorganique, URA 420, CNRS
Université de Paris-Sud
F-91405 Orsay (France)
Fax: (+33) 169157436
E-mail: jour@icmo.u-psud.fr

Dr. J. R. Pedro, Dr. I. Fernández
Departament de Química Orgànica, Facultat de Química
Universitat de València
E-46100 Burjassot, València (Spain)

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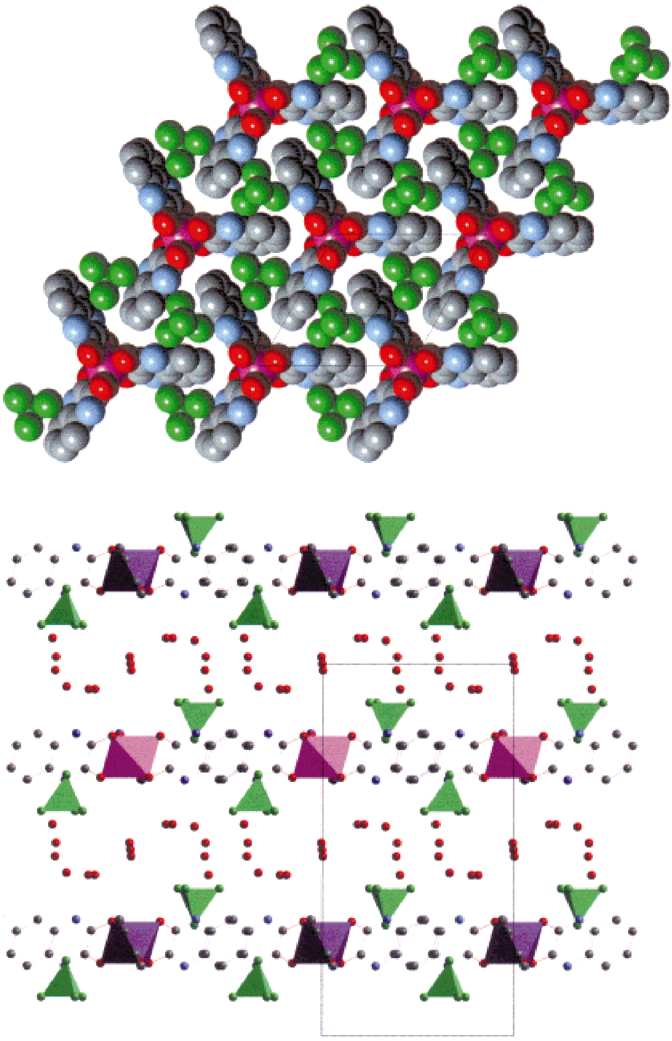

Figure 2. Top: Space-filling model of a portion of the crystal structure of **3**, projected along the *c* axis. Atoms are represented by spheres of arbitrary diameters; iron: violet, oxygen: red, nitrogen: blue, carbon: gray or green. Bottom: Projection of the structure of **3** along the *a* axis. The tetrahedrally arranged carbon atoms of the tetramethylammonium ions are depicted in green, and iron octahedra from the distinctive chiral layers are in dark and light violet.

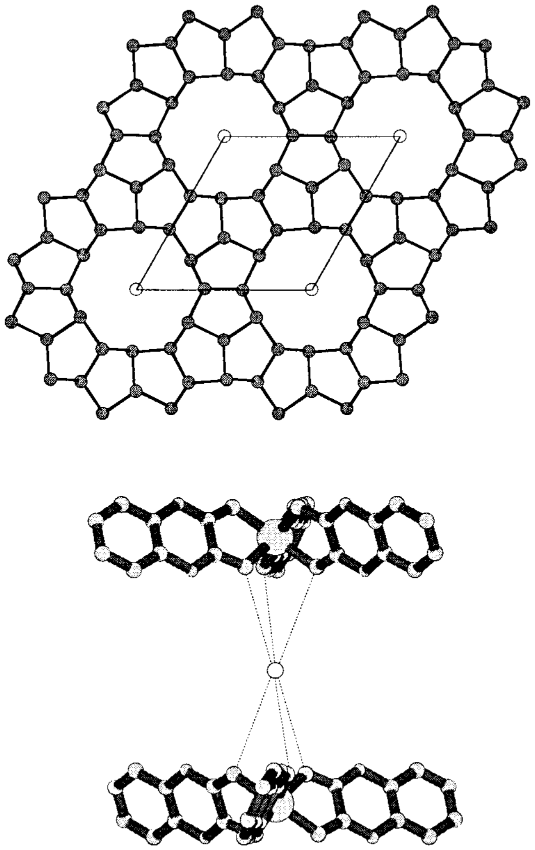

Figure 3. Top: Projection along the *c* axis of oxygen atoms from water molecules involved in the hydrogen-bonding network of **3**. The approximate positions of the hydrogen bonds are indicated. Oxygen atoms from water molecules and oxonium ions are represented by gray and white circles, respectively. Bottom: Perspective view of the octahedral polyhedra around the oxonium ion.

The superposition of mixed layers along the *c* axis results in a large interplanar separation of 10.3 Å because of the presence of charge-balancing oxonium cations and a significant number of water molecules in the space between the layers (Figure 2, bottom). A very unusual two-dimensional framework of hydrogen bonds is apparent between the solvent water molecules themselves, with O ··· H distances ranging from 2.76 to 2.83 Å. Surprisingly, there are no hydrogen bonds to the oxonium ions (Figure 3, top). The oxygen atoms of the water molecules form a puckered network of edge-sharing, bent, five-membered rings interrupted by twelve-membered rings in the form of large pores (average radius 4.65 Å). The oxonium ions lie at the centers of these rings composed of twelve hydrogen-bonded water molecules. The layers can therefore be viewed as a two-dimensional model of the three-dimensional clathrates that contain the oxonium ions as guests. The oxonium ions are in turn stabilized by relatively weak electrostatic interactions with six negatively charged amido oxygen atoms from two distinct iron complex anions in adjacent layers (see below). This leads to an elongated octahedral polyhedron (O–O distances of 4.32 Å) in which the oxonium ion is encapsulated and thus not avalaible to interact with the H_2O molecules (i.e., it is not solvated; Figure 3, bottom).

The iron center is coordinated to six amido oxygen atoms from the bidentate $[\eta^2\text{-}\mathbf{2}]^{2-}$ ligands in a geometry that is approximately trigonally distorted octahedral. A segregated distribution of Δ and Λ isomers occurs between neighboring layers (i.e., alternate layers display opposite chirality), as is nicely shown in the lower part of Figure 2. The angles around the iron center deviate significantly from ideal octahedral geometry as a result of constraints imposed by the five-membered chelate rings (e.g., O(1)-Fe-O(1a) 80.4°). The faces of the triangles, which are perpendicular to the threefold rotational axis, are twisted relative to one another by 51.6° (60° in an ideal octahedron). The iron center of the octahedron displays six equivalent $Fe-O_{amide}$ bond lengths of 2.011 Å, which is surprisingly shorter than that for the only reported iron(III) complex with amido ligands coordinated through oxygen (2.165 Å), where the amido groups are present in neutral form.[6] The distances are, however, comparable to those of the Fe–O bonds in iron(III) catecholato complexes (2.015 Å),[7] which suggests an alternative description for H_2[**2**] as a 2,3-quinoxalinediolate after substitution of an amido proton by a metal ion.[8]

Further developments are suggested by the present study with respect to the synthesis of solid-state materials with ordered structures. First, the role played by tetramethylammonium cations in the stabilization of this highly sophisticated structure must be thoroughly examined through the use of other cations of different size and geometry. Second, the question also arises as to whether the mononuclear iron complex anions are able to bind other cations of greater chemical or physical significance than the oxonium ion, such as alkali metal or transition metal cations. We are currently exploring both of these avenues.

Experimental Section

3: A solution of Et_2H_2[**1**] (1.54 g, 5 mmol) in methanol (100 mL) was treated with a 25 % solution of tetramethylammonium hydroxide in methanol (10 mL, 25 mmol), and the resulting light yellow solution was stirred at 60 °C for 30 min. A methanolic solution (50 mL) of $Fe(ClO_4)_3 \cdot H_2O$ (1.77 g, 5 mmol) was then added dropwise through a dropping funnel while the reaction mixture was stirred. The resulting intensely red solution was filtered to eliminate a white precipitate of NH_4ClO_4, and its volume was reduced to 10 mL with a rotary evaporator. The concentrated solution was treated successively with Et_2O and acetone to give a very hygroscopic product (solid or oil), which was diluted with acetonitrile (300 mL). The resulting suspension was gently heated for 5 h with vigorous stirring and then filtered to eliminate residual solid particles. A polycrystalline red solid precipitated almost immediately when the solution was allowed to cool to room temperature; this was collected by filtration and dried under air (yield: 60.0 %). Well-shaped, large, hexagonal prisms of **3** suitable for X-ray structural analysis were obtained by recrystallization from acetonitrile. Complex **3** gave satisfactory elemental analyses (C, H, N, Fe). IR (KBr): $\tilde{\nu} = 3424$ and 1639 (O–H; H_2O and H_3O^+), 1513 and 1462 (C=O), 1379 and 1244 (C–O), 947 cm^{-1} (N–C; NMe_4^+); UV/Vis (CH_3CN): λ_{max}[nm] (ε[$L\,mol^{-1}\,cm^{-1}$]) = 230 (107000), 318 (43000), 330 (sh), 365 (12000), 460 (8000); magnetic moment (298 K): 5.9 μ_B; electrochemical measurements (CH_3CN, 25 °C, 0.1 mol dm^{-3} NEt_4ClO_4): $E_p(Fe^{III}/Fe^{II})$ [V vs. SCE] (ΔE_p[mV]): −1.38(70).

Crystal structure analysis for **3**: Enraf-Nonius CAD-4 diffractometer, $Mo_{K\alpha}$ radiation, $\lambda = 0.71069$ Å, graphite monochromator, 293 K. Data collection and refinement: $\omega - 2\theta$, corrections for Lorentzian and polarization effects, but no absorption correction ($\mu = 3.58$ cm^{-1}). The structure was solved with standard Patterson methods and subsequent full-matrix least-squares method refinement. SHELX86, SHELX93.[9] $C_{32}H_{67}FeN_8O_{21}$, trigonal, space group $P3c1$, $a = b = 12.205(3)$, $c = 20.545(3)$ Å, $V = 2650(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.20$ g cm^{-3}, $2 \leq 2\theta \leq 50°$, crystal dimensions 0.10 × 0.10 × 0.10 mm^3. Of 1568 unique reflections, 1491 were regarded as observed with $I > 2\sigma(I)$. The hydrogen atoms from the water molecules were not located. Furthermore, charge-balance considerations dictate that there be one proton present per Fe atom attached to a water molecule of the solvent (the alternative formulation as iron(IV) is inconsistent with the magnetic measurements). In light of the reported occupancy factors of O(2), O(3), O(4), and O(5) (two, six, six, and one, respectively, for each Fe atom) the proton is unambiguously assigned to the O(5) center (which also occupies a special position in the crystal lattice) rather than integrated into the network of water molecules. The disorder found for the tetramethylammonium and oxonium ions as well as for some of the water molecules is probably enforced by the threefold symmetry of the crystal lattice. Refinement of 103 variables with anisotropic thermal parameters for all atoms except the O(5) atom, which was refined isotropically, resulted in $R = 0.094$, $R_w = 0.108$, $S = 1.2$. Crystal drawings were prepared with the program CRYSTAL MAKER.[10] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100457. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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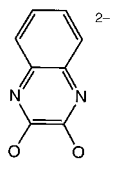

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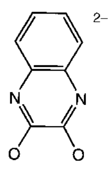

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