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A Singular Noninterpenetrating Coordination Polymer with the Pt_3O_4 Structure Containing Naked $[Na^+]_4$ Units

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The homoleptic low-spin complex $[Fe(L)_3]^{2+}$, where L is the bisbidentate ligand 1,10-phenanthroline-5,6-dione, coordinates Na^+ ions via exo-oriented dione groups defining a three-dimensional cationic network $\{[Fe(\mathbf{L})_3]_4Na_3\}^{11+}\}_n$ with Pt_3O_4 topology. The large volume generated by the network is filled with 11 perchlorate ions, 7 "$NaClO_4$" ionic pairs, and 9 H_2O molecules. Singular $[Na^+]_4$ units, in which the Na^+ ions are practically uncoordinated, are formed.

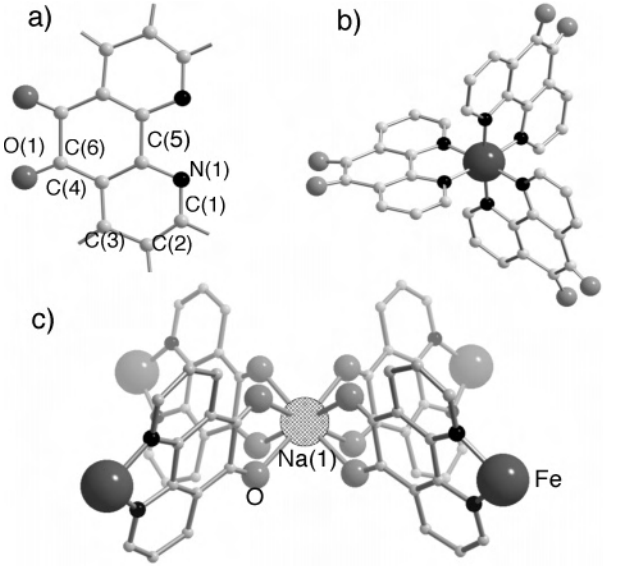

Figure 1. (a) Molecular structure of **L** with the corresponding atom numbering. (b) Molecular structure of $[Fe(\mathbf{L})_3]^{2+}$. (c) Fragment of polymer **1** emphasizing the $[Na(1)O_8]$ coordination core.

The versatility of metal−organic chemistry offers a unique opportunity to construct new functional materials based on the assembly of molecular building blocks. Such an approach can lead to the design of coordination polymers with specific network topologies and potentially interesting properties.[1−3] An important number of relevant supramolecular architectures have been designed from the assembly of triangular exodentate moieties. The orientation in space of the donor atoms fixed at 120° can be achieved either from specifically designed rigid organic structures[4−7] or by use of metal complexes as ligands[8] able, in suitable cases, to form propeller-like coordination monomers.[9] The latter building block approach adds helical chirality as a further aspect related with molecular topology. To construct new coordination polymers, we have chosen 1,10-phenanthroline-5,6-dione (**L**), a neutral bisbidentate redox-active ligand that incorporates both the orthoquinone (−OC−CO−) and the α-diimine (−NC−CN−) functionalities having distinct affinities for metal ions (Figure 1a).

Our propeller-like motive is the very stable and kinetically inert low-spin Fe^{II} complex $[Fe(\mathbf{L})_3]^{2+}$ (Figure 1b). Two

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intense and large absorption bands at 368 and 472 nm (molar absorption coefficients 7700 and 9500 M^{-1} cm^{-1}, respectively) characterize the visible spectrum of $[Fe(\mathbf{L})_3]^{2+}$ and account for its deep-brown color.[10] These bands correspond to the intramolecular metal-to-ligand charge-transfer absorption characteristic of most tris(α-diimine)iron(II) compounds. However, the redox potential of the $[Fe(\mathbf{L})_3]^{3+}/[Fe(\mathbf{L})_3]^{2+}$ pair is positive and high enough to prevent spontaneous oxidation in $[Fe(\mathbf{L})_3]^{2+}$.[10] In this complex, the O atom pairs of **L** remain uncoordinated because they cannot compete against the N atoms of the α-diimine moiety for the Fe^{II} ion.[11]

In a previous report, we demonstrated the suitability of the outer-sphere coordination of the complex $[Fe(\mathbf{L})_3]^{2+}$ to generate supramolecular entities affording the compound $[Fe(\mathbf{L})_3]_2[Fe(H_2O)_6](ClO_4)_6$, a two-dimensional noncovalent array made up of $[Fe(\mathbf{L})_3]^{2+}$ species assembled by $[Fe(H_2O)_6]^{2+}$ cations encapsulated in pseudohexagonal cages. The cages are sustained by 12 H bonds established between the coordinated H_2O molecules and the exo-oriented dione groups of six alternating Δ, Λ chiral $[Fe(\mathbf{L})_3]^{2+}$ moieties.[11]

This singular result is a consequence of the poor donor capacity of the hard O atoms of the dione moiety and its low affinity toward a borderline Lewis acid like Fe^{II}. In contrast, although hard alkali metal ions form labile and not very stable complexes, their affinity for O-containing ligands is well-known, as exemplified by natural and synthetic ionophores.[12] In pursuit of novel frameworks built by the homoleptic complex $[Fe(\mathbf{L})_3]^{2+}$, we have obtained an unprecedented non-interpenetrated cationic coordination polymer with the rare topology of Pt_3O_4. Single crystals of $\{[Fe(\mathbf{L})_3]_4Na_3\}(ClO_4)_{11}\cdot 7NaClO_4\cdot 9H_2O$ (**1**) were formed from acidic water/methanol solutions ($HClO_4$, pH ≈ 1−2) containing $[Fe(\mathbf{L})_3]^{2+}$ and a large excess of $NaClO_4$.[13]

The X-ray single-crystal structure of **1** revealed a cationic polymeric framework composed of mononuclear species $[Fe(\mathbf{L})_3]^{2+}$ assembled by Na^+ cations [Na(1)].[14] The Fe^{II} atoms lie in an almost regular octahedral environment defined by six N atoms belonging to three **L** ligands [Fe−N bond distance of 1.965(3) Å]. Four $[Fe(\mathbf{L})_3]^{2+}$ units with alternating chirality (Λ−Δ−Λ−Δ) assemble, defining a pseudocubic coordination site for Na(1) [Na(1)−O bond distance of 2.524(3) Å] (Figure 1c). The large intraframework spaces are filled with ClO_4^- anions, H_2O molecules, and Na^+ cations. The latter form a singular cationic entity $[Na^+]_4$ in which the Na^+ ions can be considered uncoordinated.

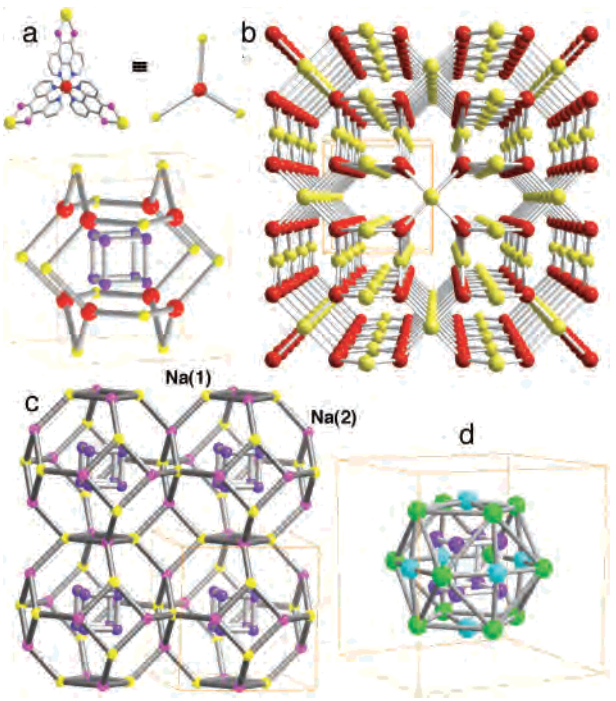

Figure 2. Three-dimensional architecture of **1**: (a) Schematic view of the unit cell defined by $\{[Fe(\mathbf{L})_3]_4Na_3\}^{11+}$ and loaded with the $[Na^+]_8$ units with 50% occupancy factor per Na^+ ion [violet, Na(3)]. The perchlorate and H_2O molecules have been omitted for clarity. (b) Fragment of the "guest-free" Pt_3O_4-type (red and yellow correspond to Fe and Na(1) sites, respectively). (c) View of the sodalite arrangement defined by Na(1) (yellow) and Na(2) (pink), together with the enclathrated $[Na^+]_8$ units. (d) View of the polyhedron defined by the Cl atoms of the perchlorate(1) (green) and perchlorate(2) (blue) groups wrapping the $[Na^+]_8$ units. Rods connecting ClO_4^- and Na^+ ions are depicted just for visualization of the defined polyhedrons.

The cationic covalent network $\{[Fe(\mathbf{L})_3]_4Na_3\}^{11+}$ constitutes a rare example of a (3,4)-connected non-interpenetrated coordination polymer based on the structure of the binary oxide Pt_3O_4.[15] The Na(1) atoms and the $[Fe(\mathbf{L})_3]^{2+}$ units play the role of the 4-connected Pt atoms and the 3-connected O atoms of the Pt_3O_4 net, respectively (Figure 2a,b). A first example of a non-interpenetrated coordination polymer with Pt_3O_4 topology was recently reported for the compound $[\{Cu_4(C_2O_4)_4(Me_4bpz)_4\}_3\cdot\{Cu_3(C_2O_4)_3(Me_4bpz)_6\}_2\cdot 3(Me_4bpz)\cdot 25H_2O]_n$ (Me_4bpz = 3,3′,5,5′-tetramethyl-4,4′-bipyrazole), which is made up of neutral three-dimensional coordination frameworks $\{Cu_4(C_2O_4)_4(Me_4bpz)_4\}_n$ constituted of heteroleptic hexacoordinated copper $[Cu(C_2O_4)_2(Me_4bpz)_2]$ moieties.[16] Prior to this compound, the double interpenetrated coordination polymer with Pt_3O_4 topology $Cu_3(BTB)_2(H_2O)_3(DMF)_9(H_2O)$ (MOF-14) (BTB represents the deprotonated form of the 4,4′,4″-benzene-1,3,5-triyltribenzoic acid) was reported.[7]

The void defined by $\{[Fe(\mathbf{L})_3]_4Na_3\}^{11+}$ corresponds to 60.4% of the total unit cell volume (ca. 8475 $Å^3$). It is filled

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(13) Synthesis of **1**: The starting material $[Fe(\mathbf{L})_3]^{2+}$ was synthesized according to the literature method (see ref 11). To prepare complex **1**, a H_2O solution of $NaClO_4$ (1.7 mmol, 30 mL) was added to a deep-brown water/methanol (1:1) solution of $[Fe(\mathbf{L})_3]^{2+}$ (0.17 mmol, 30 mL) under gentle stirring. The resulting solution was adjusted to ca. pH 1−2 by adding an aqueous solution of $HClO_4$. The final solution was allowed to evaporate at room temperature. After several weeks, cubed-shaped black single crystals of **1** suitable for X-ray analysis were formed. Yield: 10%. Anal. Calcd for $C_{144}H_{90}Cl_{18}Fe_4N_{24}Na_{10}O_{105}$: C, 35.07; H, 1.83; N, 6.82. Found: C, 35.12; H, 1.87; N, 6.91. The crystals of **1** are slightly insoluble in water and stable in air at room temperature.

(14) Crystal data for **1**: formula $C_{144}H_{90}Cl_{18}Fe_4N_{24}Na_{10}O_{105}$, $M = 4927.18$, cubic, space group $Pm\bar{3}n$ (No. 223), $a = 23.62700(10)$ Å, $V = 13189.42$ $Å^3$, $Z = 2$, $\rho_{calcd} = 1.236$ g cm^3, $F(000) = 5028$, μ(Mo Kα) = 5 cm^{-1}; 2387 reflections observed [$I > 2\sigma(I)$]; R1 = 0.0656, wR2 = 0.1688.

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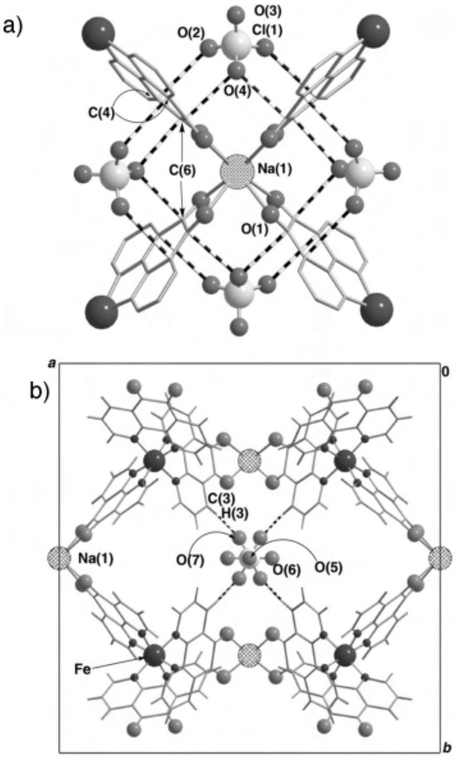

Figure 3. Relative disposition of the perchlorate groups and **L** ligands: (a) dotted rods indicating strong intermolecular C···O interactions between $Cl(1)O_4$ groups and the ligands **L**; (b) disorder along a 6-fold pseudorotation axis passing through the O(5)−Cl(2) bond and strong C−H···$OCl(2)O_3$ hydrogen bonds (dotted rods).

with 11 ClO_4^- counterions, 7 additional $Na^+ClO_4^-$ guest ion pairs, and 9 disordered H_2O molecules. The H_2O molecules interact with each other via weak H bonds [d(O···O) = 2.939(3) Å] and form well-separated, ca. 7 Å, $[H_2O]_4$ square units. The additional Na^+ cations belong to two different crystallographic sites, namely, Na(2) and Na(3). The Na(2) atoms define, together with Na(1), a regular truncated octahedron [d(Na(1)···Na(2)) = 8.353(3) Å], with the Fe^{II} atoms placed at the center of the hexagonal faces (Figure 2c). The space inside this sodalite-like, positively charged surface is filled with a symmetrical negatively charged "cage", made up of two nonequivalent perchlorate groups. The cage may be described as the interpenetration of a cuboctahedron [perchlorate(1)] and an octahedron [perchlorate(2)] (Figure 2d). Interestingly, each perchlorate(1) group is located between two ligands **L** so that two O atoms, O_3Cl−O(2) and O_3Cl−O(4), are separated by a distance of only 3.090(3) Å to C(4) and 2.939(3) Å to C(6), respectively (Figure 3a). This is well within the van der Waals contact limit and indicates some kind of interaction of the perchlorate(1) groups with the π-electronic cloud of ligand **L**. This fact has already been observed for a related compound.[11] The perchlorate(2) groups present orientation disorder along a 6-fold pseudorotation axis passing through the O(5)−Cl(2) bond and form strong H bonds with the H(3)−C(3) unit of four **L** ligands [d(O_3Cl−O(7)···C(3)) = 2.794(3) Å, ∠(O_3Cl−O(7)···H(3)···C(3)) = 132.1(1)°, d(O_3Cl−O(7)····H(3)) = 2.085(3) Å, and d(C(3)−H(3)) = 0.930(3) Å] (Figure 3b).

The room defined by this negatively charged cage is occupied by the Na(3) cations, which are arranged in a regular cubic fashion with a half-occupation factor. The edge of this formal $[Na^+]_8$ cube, 5.675(3) Å, is comparable to that of the unit cell of the halite (NaCl), 5.630 Å. The remarkable difference is the lack of stabilizing counterions in between the Na^+ atoms in the former. Notably, the shortest distances between these cations and the O atoms, which belong to either H_2O molecules or perchlorate ions, are unusually large [d(Na(2)···Ow) ≈ 3.649 Å and d(Na(3)···$OClO_3$) ≈ 4.934 Å]. Thus, the Na(2) and Na(3) ions can be considered as free.

Half-occupancy for the Na(3) atoms means that there are twice as many available positions as Na(3) atoms; consequently, the holes and Na(3) atoms are uniformly and randomly distributed in the crystal. A possible static picture of this singularity would correspond to the occupation of a tetrahedron ($[Na^+]_4$ units) of the cube while the complementary tetrahedron would define the holes. In many solids, this feature, together with the lack of coordination for the Na(2) and Na(3) atoms, is connected with a low activation energy for ion diffusion and fast ion conductivity.[17] This conjecture is currently under investigation.

In summary, we have synthesized a new non-interpenetrating three-dimensional coordination polymer with Pt_3O_4 topology from assembling $[Fe(\mathbf{L})_3]^{2+}$ and Na^+ cations. The polymer is loaded with 14 $Na^+ClO_4^-$ guest pairs and 18 H_2O molecules per unit cell, which stabilize its structure. Interestingly, the charge distribution in the unit cell is rather singular because it can be described like a "Russian nested doll": the positively charged sodalite-like cage "enclathrate", a negative surface defined by the interpenetration of a cuboctahedron and an octahedron generated by 18 ClO_4^- groups. Finally, this negative surface is filled with an unprecedented $[Na^+]_8$ structure in which the corresponding site has half-occupation.

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Supporting Information Available: Crystallographic information file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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