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MS19 P16

Isostructurality and Morphotropism of Published 2,4,6-Triphenoxy-1,3,5-triazines

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Keywords: Isostructurality, morphotropism, polymorphism

The semirigid triphenoxy-1,3,5-triazine (POT) molecule and its 2X, 3X- and 4X- (mainly *halo*-) substituted derivatives enabled us to demonstrate different morphotropic links (including polymorphism) [1] between the groups of isostructural crystals hallmarked by space groups $R3c$, $P6_3/m$, $R\bar{3}$, $P\bar{3}c1$ *etc*. Since all of these structures have been published to elucidate their ability to form Piedfort complexes (PUs) *e.g.* [2], no one paid attention to those structural connections which are established between them by non-crystallographic rotations or translations. Our present (supplementary) results demonstrate the power of perception.
(i) The 2D-isostructurality of POT (space group *Ia*) and 4-FPOT ($P2_1/c$) are related by a turn of C_3-PUs through 180,º sitting on every second *c* glide plane, around axis b. (ii) Relationship between the $R3c$ and $P6_3/m$ dimorphs of 4-BrPOT, the second is isostructural with 4-ClPOT, is established by a turn of every second molecule of the C_3-PU diads through 180º perpendicular to the trigonal axis. (iii) *Mutatis mutandis*, a turn of 60º between the eclipsed molecules of 4-ClPOT linked by $3/m$ symmetry may result in a novel columnar stacking ($\bar{3}$), if X atoms migrate from para to meta positions. However, space group $R\bar{3}$ is maintained only in 3-IPOT. (iv) In case of the smaller substituents [2], every second C_{3i}-PU diad from the trigonal ($\bar{3}$) columns turns upside down which results in space group $P\bar{3}c1$. In the new columnar array the C_{3i}-PU diads are separated by D_3-PUs and *vice versa*.
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Supercooled High Spin State in Metallo-supramolecular Assemblies,

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Keywords: Molecular magnetism, supramolecular assemblies, structure analysis

In contrast to the current line of molecular magnetism to synthesize molecules or molecule clusters with large spins, the concept of designing supramolecular assemblies containing small magnetic units is most flexible and tunable. An especially versatile approach relies on metallo-supramolecular polyelectrolyte amphiphile complexes self-assembled from bis-terpyridine ligands and amphiphilic molecules hosting octahedrally coordinated Fe^{2+}- or other transition metal ions [1,3]. The Fe^{2+} ion can be induced to switch between a low-spin and a high spin electronic state near room temperature. Using experiments of x-ray scattering, x-ray magnetic circular dichroism and magnetic measurements at powdered material the spin transition has been identified as a transition from the diamagnetic $t_{2g}^6e_g^0$ low spin state to the magnetic $t_{2g}^4e_g^2$ high-spin state and is induced by a structural order-disorder transition of the amphiphilic matrix upon heating. The temperature of phase transition can be modified by the number and length of amphiphils attached. In contrast to thin organized films the induced spin transition is not reversible and can be classified as super-cooled high-spin state which might be stabilized by the disorder and interdigitation of amphiphilic molecules. Low temperature measurements may reveal possible anti-ferromagnetic spin coupling between Fe^{2+} ions. The temperature of spin transition and the amount of the magnetic moment can be tuned by mixtures of Ni^{2+} and Fe^{2+} ions [3].

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MS19 P18

A Singular Noninterpenetrating Coordination Polymer with the Pt_3O_4 Structure

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Keywords: iron complex, crystal structure, inclusion compound

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. Crystal data formula $C_{144}H_{90}Cl_{18}Fe_4N_{24}Na_{10}O_{105}$, M = 4927.18, cubic, space group $Pm3n$ (No. 223), a = 23.6270(10) Å, V = 13189.42 Å^3, Z = 2, ρcalc = 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.
The X-ray single-crystal structure revealed a cationic polymeric framework composed of mononuclear species $[Fe(\mathbf{L})_3]^{2+}$ assembled by Na^+ cations [Na(1)]. The FeII atoms lie in an almost regular octahedral environment defined by six N atoms belonging to three **L** ligands. Four $[Fe(\mathbf{L})_3]^{2+}$ units with alternating
chirality assemble, defining a pseudocubic coordination site for Na(1). The large intraframework spaces
which the Na+ ions can be considered uncoordinated.
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 Pt3O4. The Na(1) atoms and the [Fe(**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.
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 with 11 ClO4 counterions, 7 additional Na^+ClO_4 guest ion pairs, and 9 disordered H2O molecules. The H2O 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. 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 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

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The Melting Point Behaviour in the Short -Chain n-Alkan-1-ols

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Keywords: alcohols, crystal structure, melting point alternation

n-Alkanes and most of their α- and α,ω-substituted derivatives show a remarkable alternation in their melting points.[1,2] Usually, representatives with an even number of C-atoms melt relatively higher than those with an odd number. Other physical properties such as solubilities and sublimation enthalpies that are related to the solid state also exhibit an alternating pattern, whereas those related to the liquid state show monotonic behavior.[3,4-7] But there also exist exceptions. For instance the series of the 1-chloro-, 1-bromo-, and 1-thioalkanes show an inverted alternancy of the melting points[8] and the 1-alcohols are almost monotonic. It was shown that the melting points in α,ω-alkanediols are correlated to the calculated lattice energies.[5] In this study, single crystals of six members of *n*-alkane-1-ols (CH_3-$(CH_2)_n$-OH, $n = 4 - 9$) have been grown *in situ* using a miniature zone melting procedure, and their X-ray analyses have been performed. The structural similarities and differences between even and odd members could be analyzed by the packing arrangements and by the interplay between hydrogen bonding and van der Waals interaction, however the calculated packing energies exhibit a stronger alternation behavior than the melting points.

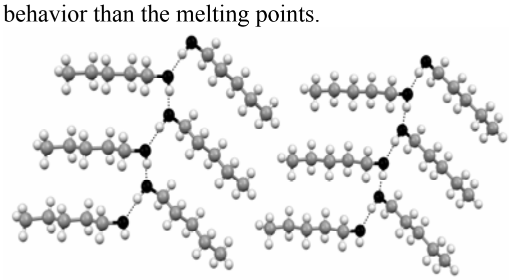

Figure 1: Crystal structure of n-pentane-1-ol

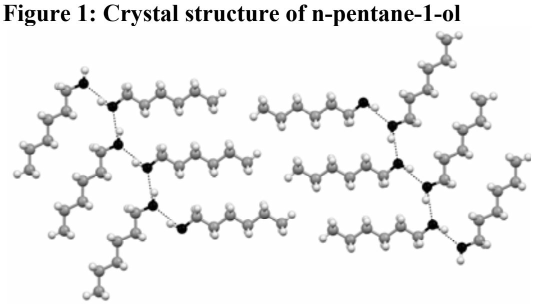

Figure 2: Crystal structure of n-hexane-1-ol

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