

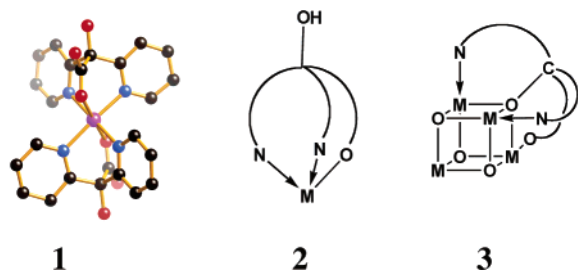
Highly Symmetric Networks Derived from Cubane-Related Octametallc Complexes of a New Oxyanion of Carbon, $C_4O_7^{4-}$, Each Molecule Attached to Eight Neighbors by 24 Equivalent Hydrogen Bonds

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2,2'-Pyridoin, $(C_5H_4N)C(OH)=C(OH)(C_5H_4N)$, upon reaction with nickel acetate in the presence of air generates the nickel(II) bis-pyridilate complex, $Ni[(C_5H_4N)_2C(OH)(CO_2)]_2$, **1**.¹ The pyridilate ligand present in this complex is generated by initial air oxidation of pyridoin to pyridil, $(C_5H_4N)CO \cdot CO(C_5H_4N)$, which was shown long ago to undergo metal-promoted benzylic acid-type rearrangement to pyridilate.² We have discovered³ that the pyridilate system, when deprotonated at the OH group, can be "turned inside out", as in the imaginary conversion of **2** to **3**, to form a cubane-related product in which each alkoxo ligand provides three chelating "straps".⁴ We propose that appropriately trisubstituted methoxide ligands, related to that represented in **3**, may show a general strong predisposition to form cubane-like metal complexes, a proposition supported by the results presented below. Dihydroxyfumaric acid, $HOOC \cdot C(OH)=C(OH) \cdot COOH$ is a close relative of pyridoin in that both are ene-diols carrying potentially metal-binding terminal substituents. We report here that dihydroxyfumaric acid, in the presence of certain divalent metal ions, undergoes a similar sequence of oxidation and benzylic acid rearrangement to produce the trisubstituted methoxide ion $^-OC(CO_2^-)_3$, a previously undocumented oxyanion of carbon, which generates the cubane-like core of a highly symmetrical octa-metallic complex.



Crystals, of composition $[(M^{II})_8(C_4O_7)_4(H_2O)_{12}] \cdot 24H_2O$ ($M = Zn, Co, Fe, \text{ and } Mg$), suitable for single-crystal X-ray diffraction studies, are obtained extremely simply from aqueous reaction mixtures at room temperature containing dihydroxyfumaric acid and $M^{II}(OAc)_2$ (or in the case of $M = Fe$, $FeSO_4$ plus sodium acetate).⁵ All four compounds crystallize in the body-centered cubic space group $I\bar{4}3m$ with cell dimensions $a \approx 15.0 \text{ \AA}$.⁶ Discrete electrically neutral $[(M^{II})_8(C_4O_7)_4(H_2O)_{12}]$ molecules are present, having the structure shown in Figure 1. At the center of the highly symmetrical molecule is a cubane-related core⁷ consisting of four M^{II} centers, $M(1)$ in Figure 1, and four μ_3 -alkoxo centers from separate $C_4O_7^{4-}$ ligands. The structural role of the $C_4O_7^{4-}$ ligands, all of which are equivalent, can be appreciated by focusing on the upper ligand unit in Figure 1; besides providing the μ_3 component of the cubane core the $C_4O_7^{4-}$ provides a carboxy donor for each of the three metal centers bridged by its alkoxo center, i.e. it acts as a "three-strap cubane-generating ligand" similar to that repre-

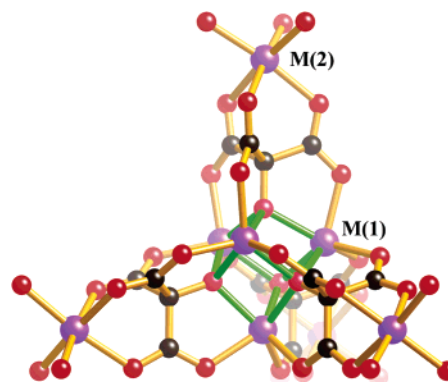


Figure 1. Structure of the $[(M^{II})_8(C_4O_7)_4(H_2O)_{12}]$ molecule. The cubane unit is highlighted in green.

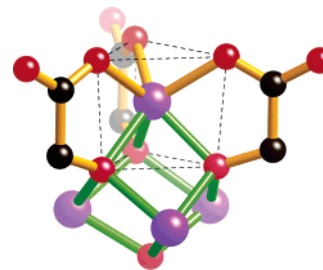


Figure 2. The trigonal prismatic coordination environment of the metal centers in the cubane unit, $M(1)$.

sented in **3**. The five-membered chelate rings formed in this way are internally planar and are so oriented that the central point of the cubane unit lies within the planes of all 12 chelate rings that surround it. Thus, the four metal centers, $M(1)$, in the cubane core, which are located on sites of $3m$ symmetry, have trigonal prismatic coordination environments as shown in Figure 2. The three carboxy oxygen centers from each $C_4O_7^{4-}$ ligand not attached to $M(1)$ are then beautifully placed to provide a facial tridentate ligand system for a second type of metal, $M(2)$ in Figure 1. The octahedral coordination environment of $M(2)$ is completed by a facial arrangement of three aqua ligands. The equilateral triangle formed by the oxygen atoms of these three aqua ligands is effectively identical in size to the equilateral triangle of carboxy oxygen atoms coordinated to $M(1)$ that can be seen in Figure 2. A trio of aqua ligands in one molecule, therefore, is very nicely set up to act as a triple hydrogen bond donor to a trio of carboxy oxygen atoms coordinated to $M(1)$ in an adjacent molecule. Since each molecule has four sets of aqua trios and four sets of carboxy oxygen trios, it is able, because of its high symmetry, to form 12 donor H-bonds to four neighbors and, simultaneously, 12 acceptor H-bonds to four other neighbors. Figure 3 represents a central molecule acting as a triple H-bond donor to one neighbor and as a triple H-bond acceptor

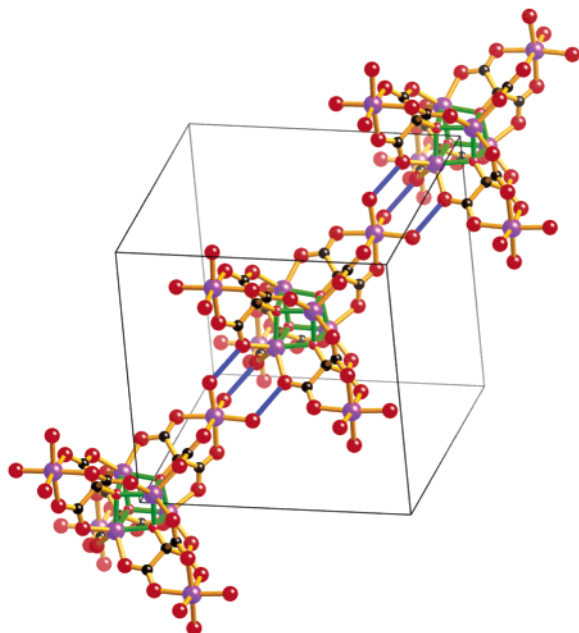


Figure 3. A central molecule acting as a triple H-bond donor to one neighbor and as a triple H-bond acceptor from another neighbor arranged along one solid diagonal of the cube. Similar interactions occur along the other three diagonals to give a body-centered cubic arrangement.

from another neighbor, all three molecules being located along one of the four solid diagonals of the cube. The central molecule is involved in similar pairs of triple H-bonds along the other three solid diagonals to give a body-centered cubic arrangement in which every molecule is bonded to eight neighbors by 24 equivalent hydrogen bonds⁸ ($O\cdots O$ 2.708(5) Å in the case of $Zn_8(C_4O_7)_4(H_2O)_{12}$)—an extreme example of self-complementarity. The water molecules occupying the framework voids are ill-defined and highly disordered.⁹ The $C_4O_7^{4-}$ system described here has not, to the best of our knowledge, been documented previously; the reason for this may be that, upon protonation, it is likely to become very prone to decarboxylation. Presumably the organic components of the reaction mixture are chaperoned by metal centers throughout the various phases of their lives, including the metamorphosis to the fragile $C_4O_7^{4-}$ stage and the final entombment within the crystal.

We note the two different types of metal center in the octanuclear molecule—the four unexceptional terminal tri-aqua octahedral ones and the four metals within the cubane unit with trigonal prismatic geometry; perhaps if the system is provided with a choice of two different metal cations, there will be a preference for a specific mixed metal structure to be formed. Given the unusual coordination geometry of the metal centers in the core, the magnetic interactions in such mixed metal systems and also in the Fe and Co systems reported above may be interesting. We note in addition that the

$[(M^{II})_4(C_4O_7)_4]^{8-}$ core (or the $[(M^{III})_4(C_4O_7)_4]^{4-}$ core if it were possible to use trivalent cations) has the perfect geometry to form an infinite coordination network with the diamond topology, if each of the four O_3 donor sets from one such tetranuclear unit could be attached to an O_3 donor set from another unit by octahedral connecting metal centers. These are possibilities we are exploring.

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Supporting Information Available: Synthesis details, X-ray powder diffraction spectra; X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (4) Some related cubane-like metal derivatives of 2,2'-dipyridyl ketone have been reported recently: Tong, M.-L.; Zheng, S.-L.; Shi, J.-X.; Tong, Y.-X.; Lee, H. K.; Chen, X.-M. *J. Chem. Soc., Dalton Trans.* **2002**, 1727.
- (5) Preparation of $[M^{II}_8(C_4O_7)_4(H_2O)_{12}] \cdot 24H_2O$: $M = Zn$; A solution of $Zn(OAc)_2 \cdot 6H_2O$ (742 mg, 3.4 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (603 mg, 3.4 mmol) in water (100 mL) was added to a stirred solution of dihydroxyfumaric acid (500 mg, 3.4 mmol) in water (100 mL). The solution was stirred overnight. The colorless crystals of $[Zn_8(C_4O_7)_4(H_2O)_{12}] \cdot 24H_2O$ that separated were collected, washed with water, and dried in a stream of air (305 mg, 0.7 mmol, 21%). Analysis calculated for $Zn_8C_{16}H_{56}O_{64}$: C 10.6, H 4.0, Zn 28.8. Found: C 10.4, H 3.6, Zn 28.0. For $M = Co$, Mg, and Fe similar procedures were used (see Supporting Information for details). Analysis calculated for $Co_8C_{16}H_{56}O_{64}$: C 10.69, H 4.1. Found: C 10.8, H 3.8. X-ray powder diffraction patterns for $M = Zn$, Co, and Mg were in agreement with those calculated on the basis of the single-crystal diffraction studies and indicated the products were homogeneous. The crystals of all four of the derivatives typically adopted a rhombic dodecahedral morphology. The rhombic dodecahedral crystals of $[Fe_8(C_4O_7)_4(H_2O)_{12}] \cdot 24H_2O$, easily identified and easily selectively removed by hand picking, were accompanied by an unidentified fine solid which predominated.
- (6) Crystal data for $[Zn_8(C_4O_7)_4(H_2O)_{12}] \cdot 24H_2O$: $M_r = 1811.70$, space group $I43m$, $a = 15.0161(11)$ Å, $V = 3385.8(5)$ Å³, $Z = 2$, $T = 293$ K, $\mu(Cu K\alpha) = 4.209$ mm⁻¹, 3105 reflections measured, 680 unique ($R_{int} = 0.0184$) which were used in all calculations. The final values for $wR2$ (all data) and $R1$ [$I > 2\sigma(I)$] were 0.0653 and 0.0248, respectively. The crystal structure was solved and refined using SHELX-97.¹⁰ See Supporting Information for crystal data of $M = Co$, Mg, and Fe.
- (7) For other examples of cubane-like metal complexes see ref 4.
- (8) Hydrogen-bonded networks of coordination complexes are reviewed in Beatty, A. M., *CrystEngComm* **2001**, 51. A more general review of hydrogen-bonded networks can be found in Sherrington, D. C.; Taskinen, K. A. *Chem. Soc. Rev.* **2001**, *30*, 83.
- (9) Preliminary thermogravimetric analysis of $Zn_8C_{16}H_{56}O_{64}$ indicated gradual endothermic weight loss of approximately 35% throughout the range from room temperature to approximately 180 °C with maximum rate at approximately 120 °C.; calculated weight loss for removal of water = 35.8%. Crystals of $Zn_8C_{16}H_{56}O_{64}$ suspended in water (in which the compound is extremely insoluble) heated to 120 °C for 24 h in a sealed tube survived unscathed, indicating the thermal stability of the $C_4O_7^{4-}$ unit when it is secured in the crystalline phase by zinc ions. Detailed TG analysis of all four compounds, when completed, will be reported elsewhere.
- (10) SHELX-97, Program for Crystal Structure Analysis (Release 97-2), G. M. Sheldrick, 1997. Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Gottingen, Germany, 1998.

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