

Polynuclear Carboxylato-Bridged Iron(II) Clusters: Synthesis, Structure, and Host–Guest Chemistry

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Introduction

Inorganic analogues of crown ethers called metallacrowns, which are macrocycles composed of heteroatoms such as nitrogen, oxygen, and main group or transition metal ions have recently been identified by Pecoraro and co-workers.¹ When combined with paramagnetic metal centers, such inorganic host–guest complexes can have potentially important applications in analytical chemistry, catalysis, magnetic imaging chemistry, mesogenic materials, and magnetic materials,¹ but the field of inorganic host–guest chemistry is still in its infancy. The general synthetic routes for the preparation of the metallacrowns reported so far are self-assembly reactions where the host complex was not first isolated. In the course of exploring the coordination chemistry of the tripodal ligand BPG (H-BPG = bis(2-pyridylmethyl)glycine), we have assembled a neutral trinuclear carboxylato-bridged iron(II) complex, [Fe₃(O₂CCH₃)₃(BPG)₃] (**1**), that can bind a fourth metal ion to form the tetranuclear complex [Fe₄(O₂CCH₃)₃(BPG)₃](ClO₄)₂ (**2-OAc**). A comparison of the two structures suggests that **1**, after minor structural rearrangement, acts as a host for the added Fe(II). This pair of structures represents one of a few instances of a metallacrown wherein both the neutral host and a corresponding host–guest complex can be isolated and structurally characterized.²

Experimental Section

Materials. All manipulations were done using Schlenk techniques or in a Vacuum Atmospheres glovebox. Unless otherwise stated, all materials were used as received from commercial sources without further purification. 2-Aminomethylpyridine, 2-pyridinecarboxaldehyde, bromoacetic acid, and Fe(ClO₄)₂·6H₂O were purchased from Aldrich Chemical Co. Fe(O₂CCH₃)₂ was prepared according to the literature method. Solvents used in this work were of analytical grade.

Synthesis of the Ligand K⁺BPG⁻. A high-yield synthesis of the ligand was achieved by modifying the procedure published several years ago from this laboratory.³ Equimolar amounts of bis(2-pyridylmethyl)amine, potassium bromoacetate, and KOH (as the base) in H₂O were stirred for 2 days under an atmosphere of dinitrogen. Evaporation of the solvent afforded a solid, which was then redissolved in methanol to separate KBr through filtration. Upon evaporation of the methanol, the solid was washed with CH₃CN and recrystallized from methanol, affording the potassium salt of the ligand in 80% yield.

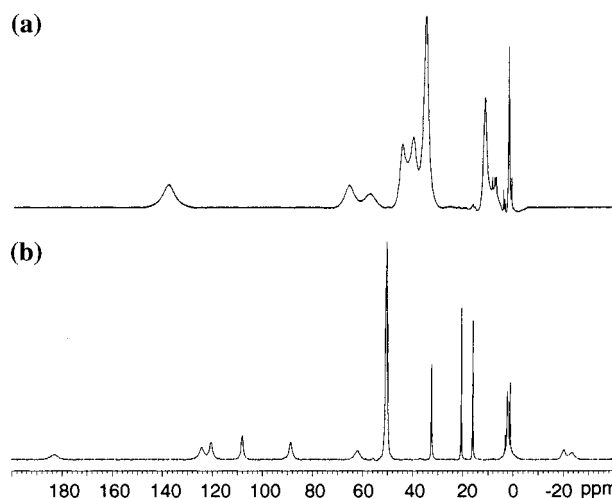


Figure 1. ¹H NMR spectra of (a) [Fe₃(OAc)₃(BPG)₃] (**1**) and (b) **1** + 1.0 equiv Fe(O₂SCF₃)₂ in CD₃CN.

Synthesis of [Fe₃(O₂CCH₃)₃(BPG)₃] (1**).** Fe(OAc)₂ (87 mg, 0.5 mmol) was added to a methanolic solution (10 mL) of K⁺BPG⁻ (150 mg, 0.5 mmol). After the solution was stirred for 10 min, a clear-yellow solution was obtained from which a golden-yellow solid precipitated upon addition of ether. Recrystallization by vapor diffusion of ether into an acetonitrile solution of **1** afforded needle-shaped crystals in 70% yield. Elemental analysis for [Fe₃(O₂CCH₃)₃(BPG)₃]·3K⁺O₂-CCH₃·CH₃CN: C₅₆H₆₃Fe₃K₃N₁₀O₁₈ (MW 1449). Anal. Calcd (found): C, 46.41 (46.09); H 4.38 (4.14); N, 10.01 (9.66). The same complex was also obtained using H-BPG instead of K⁺BPG⁻, from which crystals for X-ray diffraction studies were obtained.

Synthesis of [Fe₄(O₂CCH₃)₃(BPG)₃](ClO₄)₂ (2-OAc**).** To an acetonitrile solution (10 mL) of **1** (134 mg, 0.12 mmol) was added Fe(ClO₄)₂·6H₂O (45 mg, 0.12 mmol) dissolved in 5 mL of acetonitrile with stirring. The solution became light-yellow in color, and a yellow solid was obtained upon evaporation of the solvent. Recrystallized product was obtained by vapor diffusion of ether to an acetonitrile solution of the solid. Yield: 95%. Elemental analysis for [Fe₄(O₂-CCH₃)₃(BPG)₃](ClO₄)₂: C₄₈H₅₁Cl₂Fe₄N₉O₂₀ (MW 1368). Anal. Calcd (found): C, 42.10 (41.93); H 3.73 (3.96); N, 9.21 (9.43).

Results and Discussion

The reaction of Fe(O₂CCH₃)₂ with the ligand K⁺BPG⁻ in a 1:1 ratio in methanol under strict anaerobic conditions afforded a golden-yellow solid after removal of the solvent; analytically pure needle-shaped crystals of **1** were obtained upon recrystallization from CH₃CN/Et₂O. The ¹H NMR spectrum of **1** (Figure 1a) in CD₃CN shows well-resolved paramagnetically shifted proton resonances that range from 0 to 141 ppm. The signals have been assigned on the basis of their relative intensities, relaxation time (*T*₁) values, and comparisons with other high-spin iron(II)–tripodal pyridine complexes.⁴ The number of resonances observed for pyridine protons indicates that all BPG ligands are in similar environments. The py α protons, which are closest to the metal centers, are assigned to the 141 ppm peak. The β protons on each pyridine are resolved from each other and assigned to the features at 45 and 40 ppm. The py γ protons are found at 12 ppm. The remaining two features at 72 and 62 ppm are assigned to the methylene protons.

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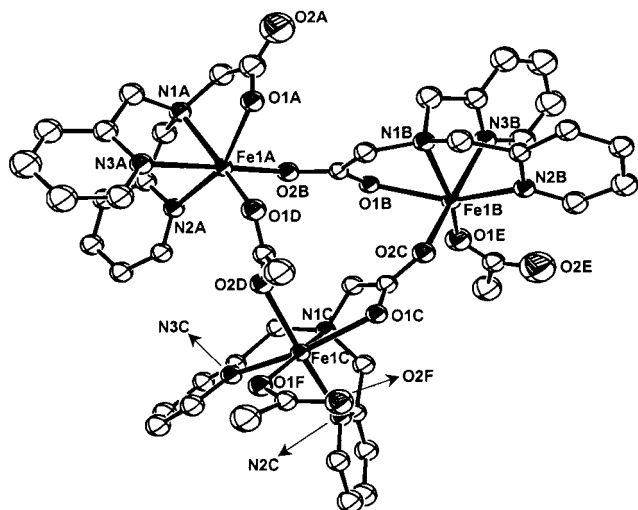


Figure 2. Crystal structure of $[\text{Fe}_3(\text{OAc})_3(\text{BPG})_3]$ (**1**) showing the 50% probability thermal ellipsoids. For clarity, hydrogen atoms are omitted. Selected interatomic distances (Å) and angles (deg) are as follows: Fe(1A)–O(ID) 2.032(2), Fe(1A)–O(1A) 2.117(2), Fe(1A)–O(2B) 2.141(2), Fe(1A)–N(3A) 2.210(3), Fe(1A)–N(2A) 2.231(3), Fe(1A)–N(1A) 2.241(3), Fe(1B)–O(1E) 2.017(3), Fe(1B)–O(2C) 2.156(2), Fe(1B)–O(1B) 2.192(2), Fe(1B)–N(2B) 2.209(3), Fe(1B)–N(3B) 2.221(3), Fe(1B)–N(1B) 2.264(3), Fe(1C)–O(1F) 2.024(2), Fe(1C)–O(1C) 2.138(2), Fe(1C)–O(2D) 2.179(2), Fe(1C)–N(3C) 2.213(3), Fe(1C)–N(2C) 2.218(3), Fe(1C)–N(1C) 2.286(3); O(ID)–Fe(1A)–O(1A) 95.57(9), O(ID)–Fe(1A)–O(2B) 99.74(9), O(1A)–Fe(1A)–O(2B) 93.40(9), N(3A)–Fe(1A)–N(2A) 81.55(10), N(3A)–Fe(1A)–N(1A) 78.49(11), N(2A)–Fe(1A)–N(1A) 77.10(10), O(1E)–Fe(1B)–O(2C) 99.81(11), O(1E)–Fe(1B)–O(1B) 90.57(10), O(2C)–Fe(1B)–O(1B) 91.79(9), N(2B)–Fe(1B)–N(3B) 79.90(10), N(2B)–Fe(1B)–N(1B) 76.61(10), N(3B)–Fe(1B)–N(1B) 77.26(11), O(1F)–Fe(1C)–O(1C) 122.29(9), O(1F)–Fe(1C)–O(2D) 95.32(9), O(1C)–Fe(1C)–O(2D) 84.03(9), N(3C)–Fe(1C)–N(2C) 84.25(10), N(3C)–Fe(1C)–N(1C) 76.14(10), N(2C)–Fe(1C)–N(1C) 77.45(10).

The crystal structure of **1**⁵ (Figure 2) shows a trinuclear complex with an unprecedented triangular structural motif that is held together with carboxylate bridges. Compound **1** is a neutral species containing three Fe^{2+} ions, three acetates, and three monoanionic BPG ligands. There are three bridging carboxylate groups, two of them from the carboxylate arms of two BPG ligands and the third being an acetate group. The pentadentate ligation mode for BPG has been noted for a similar ligand in a dinuclear complex.⁶ The bridging carboxylate moieties from the BPG ligands bind more symmetrically (the four Fe–O distances range from 2.138(2) to 2.192(2) Å) than the bridging acetate group (the Fe–O distances are 2.032(2) and 2.179(2) Å). This difference is reflected in the intramolecular distances between the iron centers that vary from

(5) Crystal data for **1**: formula, $\text{C}_{48}\text{H}_{51}\text{Fe}_3\text{N}_9\text{O}_{12}$; molecular weight = 1113.53; crystal system monoclinic; space group $C2/c$ (no. 15); temperature 173K; lattice parameters $a = 23.4347(9)$ Å, $b = 9.4689(4)$ Å, $c = 49.145(2)$ Å, $\beta = 95.234(1)^\circ$; unit cell volume = 10859.9(8) Å³; $\rho_{\text{calc}} = 1.362$ g/cm³; $Z = 8$; $\mu(\text{Mo K}\alpha) 8.56$ cm⁻¹; Mo $\text{K}\alpha$ graphite-monochromated radiation on a Siemens platform CCD diffractometer; 27 308 total reflections collected in the range of $1.66^\circ \leq 2\theta \leq 50.0^\circ$; 9446 merged reflections with $R_{\text{int}} = 0.0517$; 8437 reflections with $I > 2\sigma(I)$. Semiempirical absorption correction yielded minimum and maximum transmission factors of 0.481 and 0.504; 695 parameters were refined to $R1 = 0.0506$ and $wR2 = 0.1085$. Hydrogen atoms were placed in ideal riding positions. Platon (Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34) located a region of disordered solvent equal to 1290.1 Å³, or 11.8% of the total unit cell volume. Final calculations were done after processing the data with the SQUEEZE function of Platon. Additional information can be found in Supporting Information.

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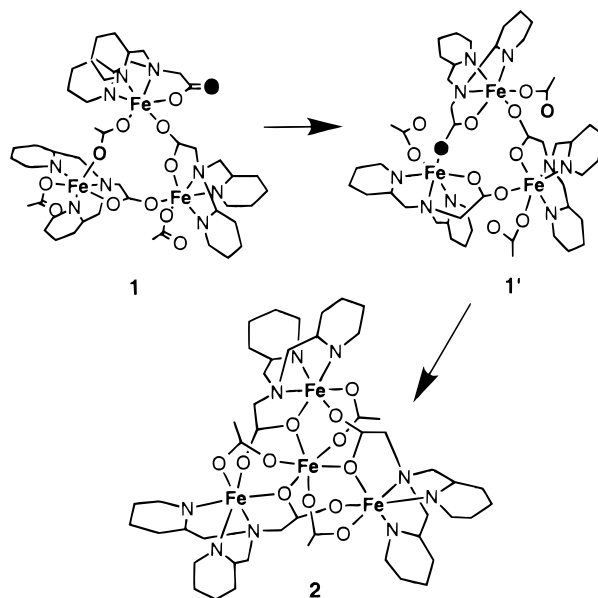


Figure 3. Proposed rearrangement of **1** in solution to its structural isomer **1'** in preparation for binding the guest metal ion to form **2**.

5.597(2) to 6.053(2) Å. Each Fe^{II} ion in **1** has a distorted octahedral geometry with an N_3O_3 donor set (at all three iron centers, each Fe–N bond is trans to an Fe–O bond) with three nitrogen atoms from the BPG ligand, one oxygen from a monodentate carboxylate group, and two oxygens from the bidentate bridging carboxylate moieties. The amine nitrogen atoms of BPG ligands are trans to one of the oxygen atoms of the acetate groups; N(1A) is trans to the bridging acetate group, while N(1B) and N(1C) are trans to the monodentate acetate groups, affording Fe–O distances (ave 2.024 Å) that are the shortest in **1**. The average Fe(II)– N_{amine} distance (2.263 Å) is longer than the average Fe(II)– N_{py} distance (2.217 Å), which is typical of Fe(II) complexes with pyridylamine ligands.⁷ All but one of the other discrete carboxylate-bridged trinuclear Fe(II) complexes thus far reported in the literature have a linear triiron motif,⁸ with the sole exception being a complex with a triangular basic metal acetate arrangement with a μ_3 -hydroxo bridge.⁹ Thus, the trinuclear arrangement found here is unique.

The composition of **1** differs from that of a previously reported tetranuclear species, $[\text{Fe}_4(\text{O}_2\text{CC}_6\text{H}_5)_3(\text{BPG})_3](\text{ClO}_4)_2$ (**2-OBz**)¹⁰ by $\text{Fe}(\text{ClO}_4)_2$, allowing the interchange of acetate and benzoate. Complex **2-OBz** was prepared directly from a mixture of $\text{Fe}(\text{ClO}_4)_2$, $\text{C}_6\text{H}_5\text{CO}_2\text{H}$, H-BPG, and an appropriate amount of NEt_3 (as a base) in methanol. Its crystal structure⁸ (Figure 3) shows a tetrairon aggregate consisting of three crystallographically identical $\{\text{Fe}(\text{BPG})(\text{O}_2\text{CCH}_3)\}$ units coordinated to a central Fe^{II} ion. The compositional difference between **1** and **2-OBz** suggested that **1** may be converted to the acetate analogue of **2** by the addition of an equivalent of Fe^{II} . Indeed, addition of an equivalent of $\text{Fe}^{\text{II}}\text{X}_2$ ($\text{X} = \text{ClO}_4$ or CF_3SO_3) to the golden-

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yellow solution of **1** in CH₃CN under an atmosphere of argon changed it to light-yellow. Evaporation of solvent afforded a yellow solid in quantitative yield. The ¹H NMR spectrum of this yellow solid (Figure 1b) in CD₃CN shows a number of well-resolved and narrow signals ranging from -22 to 186 ppm. These features are more paramagnetically shifted than those of **1** and match those of **2**-OBz.

Comparison of the structures of **1** and **2** shows that the metallacrown core in **2** is constructed with three BPG ligands connected through three high-spin iron(II) ions, where BPG acts as a pentadentate ligand with three nitrogen and two oxygen atoms. The triangular periphery around the central iron is composed of three {M-O-C-O-} units forming a 12-membered ring that can be considered as an analogue of 12-crown-6. Prior to the formation of **2** from **1**, a structural rearrangement between the acetate group that bridges Fe(1A) and Fe(1C) and the carboxylate arm of the BPG ligand that is bonded only to Fe(1A) must occur to bind the guest cation. Such a rearrangement requires the replacement of O(2D) by O(2A) at the Fe(1C) center and would lead to **1'**, a 3-fold symmetric structural isomer of **1** (Figure 3). The guest Fe^{II} binds

to three of the six ether-like oxygen atoms of the metallacrown ring and three oxygen atoms of acetates that now act as bidentate bridges between the guest iron and the irons in the host. The guest Fe(II) ion is displaced by 1.33 Å above the best least-squares plane defined by the three oxygen atoms of the ring.

In conclusion, we have prepared for the first time a neutral trinuclear carboxylato-bridged iron(II) compound that acts as a host for a fourth metal ion, forming a tetranuclear host-guest complex. Both host and host-guest complex have been crystallographically characterized, and ¹H NMR spectroscopy indicates that the host-guest complex remains intact in CD₃CN solution. This pair may serve as the prototype for a new class of inorganic host-guest complexes.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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