Synthesis and Crystal Structure of a New Dinuclear Iron(III) Complex: [Fe₂O(PhCO₂)₂(2,2'-bpy)₂(N₃)₂]·H₂O

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Abstract. By using a precursor complex $[Fe_3O(PhCO_2)_6(H_2O)_3]NO_3$ as starting material and 2,2'-bpy (= 2,2'-bipyridine) as rigid chelating ligand, the new dinuclear iron-oxido complex $[Fe_2O(PhCO_2)_2(2,2'-bpy)_2(N_3)_2]\cdotH_2O$ (1) was synthesized and structurally characterized. The reaction of $[Fe_3O(PhCO_2)_6(H_2O)_3]NO_3$ with 2,2'-bpy and sodium azide in 1:3:3 ratio gave the dinuclear complex 1, whereas a 1:6:3

Introduction

Significant developments in the chemistry of oxygen-bridged polynuclear iron complexes initially resulted from discovery of the biological role of oxygen-bridged poly-iron centers [1]. Proteins containing carboxylate-bridged diiron active sites perform a variety of biochemical functions [2, 3]. The active sites in some metalloprotein systems such as hemerythrin [4, 5], methane monooxygenase [6, 7], and ribonucleotide reductase [8] may contain diiron cores, where the iron site can transfer from Fe_2^{II} to Fe_2^{III} . It is very surprising that the remarkably similar structures can exhibit various functions of these proteins. Studies on the synthesis of these model complexes to model the iron proteins were carried out and suggested how important they play a role in biological systems. As a result of these and other stimuli, a wide variety of such complexes with aesthetically pleasing structures and interesting magnetic properties were prepared and studied over the last 15 years [9-18]. The azide ligand showed a good ability to act as bridging several metals and to induce ferromagnetic exchange interactions between the paramagnetic metal atoms [19, 20]. Several polynuclear clusters with large-spin ground state were prepared in a variety of coordination modes by substituting alkoxido or hydroxido bridges with azido bridges [21, 22].

The continuing development of the above areas promotes the discovery of new synthetic procedures to obtain new structural types. One approach is to use selected chelates to encourage aggregation, while ensuring discrete products that are soluble and can be purified and crystallized. Hydrolysis of iron salts

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[a] Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education College of Chemistry and Materials Science Northwest University Xi'an 710069, P. R. China ratio reaction system only gave the complex $[Fe(2,2'-bpy)_3]^{3^+}$, which indicated that 2,2'-bipyridine plays a crucial function in the nuclear forming procedure. Meanwhile, the N₃⁻ ligands take up the chelating domain of oxygen and reduce the nucleation. Different π - π interactions exist in 1, which extend its structure to a three dimensional supramolecular framework.

in the presence of carboxylic groups, with or without other chelating ligands, proved to be a very useful method for obtaining both oxide and hydroxide containing clusters. This approach resulted in a number of complexes with diverse nucleuses and Fe_x topological arrangements [23–24].

In the last several years we have been very interested in developing 3d metal coordination cluster chemistry with oxide bridges and predominant carboxyl peripheral ligation. The presence of chelating ligands was found to have profound effects on the nucleuses and metal topology of the resultant products. Many synthetic procedures of polynuclear iron clusters rely on the reaction of $[Fe_3O(O_2CR)_6L]^+$ species with potentially chelating ligands [25-29], and we thus also explored this starting material for reactions with 2,2'-bpy, which acts as a rigid chelation ligand for the synthesis of the Fe₂O complex, $[Fe_2O(PhCO_2)_2(2,2'-bpy)_2(N_3)_2]\cdot H_2O$ (1). We have also explored the use of sodium azide in such reactions. Herein we report the synthesis and structure of complex 1.

Results and Discussion

Synthesis

The use of 2,2'-bpy in iron(III) chemistry yielded a variety of new dinuclear and hexanuclear iron complexes [30]. There was one reason to believe that stable $Fe_2O_2/PhCO_2/bpy$ complexes should be synthetically feasible if the correct procedures could be discovered. Herein we described one method to obtain stable $Fe_2O_2/PhCO_2/bpy$ complexes by introducing N_3^- to the system.

The reaction of $[Fe_3O(PhCO_2)_6(H_2O)_3]NO_3$ with 2,2'-bpy and sodium azide in a 1:3:3 ratio in MeCN gave red crystals of the new dinuclear complex **1**. The use of 2,2'-bpy drastically destroys the Fe₃O structure of the starting material for its bidentate chelating function. It indicates that 2,2'-bpy plays a determining function in the nuclear forming procedure. Meanwhile, the N₃⁻ anions take up the chelating domain of oxygen and reduce the nucleation. The reaction is shown in Scheme 1. However, a 1:6:3 ratio of $[Fe_3O(PhCO_2)_6(H_2O)_3]NO_3/2,2'$ -bpy/ NaN₃ in the reaction system gave the complex $[Fe(2,2'-bpy)_3]^{3+}$, which indicates that the ratio of reactants is very important.



Scheme 1. Formation of 1.

Crystal Structure

Single-crystal X-ray analysis reveals that complex 1 crystallizes in monoclinic system, space group C2/c, with one Fe³⁺ cation, one O²⁻ anion, one PhCO₂⁻ anion, one azide anion, one 2,2'-bpy molecule, and one lattice water molecule in the asymmetric unit. As shown in Figure 1, the neutral molecule contains a $[Fe_2O]^{4+}$ core bridged by two PhCO₂⁻ groups. Each Fe^{III} atom coordinates to three nitrogen atoms from one bidentate chelating 2,2'-bpy ligand and one azide anion and three oxygen atoms from two benzoate and one central O²⁻ anion with distorted octahedral arrangement. The Fe–O bond lengths range from 1.785 to 2.123 Å. It is noteworthy that the bond length of



Figure 1. ORTEP drawing of 1 with thermal ellipsoids at 30 % probability level, hydrogen atoms are omitted for clarity.

the bridged atom O3 with Fe^{III} is the shortest. The Fe--Fe distance (3.120 Å) is similar to those of the typical distances of dinuclear species with one oxido and two carboxylic bridges [31]. In the crystal structure of 1 there are three types of $\pi \cdots \pi$ stacking interactions: (1) $\pi(2,2'-bpy)\cdots\pi(2,2'-bpy)^i$ (i = 1/2-x, 1/ 2-v, 1-z), centroid–centroid distance = 3.814 Å, dihedral angle = 3.45°; (2) π (2,2'-bpy)ⁱⁱ··· π (2,2'-bpy)ⁱⁱⁱ (ii = -x, y, 1/2-z; iii = x-1/2, 1/2-v, z-1/2), plane-plane distance = 3.54 Å; (3) $\pi(C12-17)\cdots\pi(C12-C17)^{iv}, \pi(C12-17)^{v}\cdots\pi(C12-C17)^{vi}, (iv =$ x, -y, 2-z; v = -x, y, 3/2-z; vi = x, -y, z-1/2), plane-plane distance = 3.152 Å and one type of C–H··· π interaction: C9– H9... π (C12–17)^{vii} (vii = -x, y, 2.5–z), H... π distance = 2.882 Å, C–H··· π angle = 151.96°. The molecules are packed together through the first type of $\pi \cdots \pi$ stacking interactions to form 1D infinite chains (Figure 2). The adjacent chains are parallel to each other and further linked by the second type of π ... π stacking interactions and the C-H··· π interactions to form a sheet along the b axis (Figure 3a). The sheet shows butterfly-shaped chains along the a axis (Figure 3b) and bowl-shaped chains



Figure 3. Perspective view of the 2D sheet formed by π - π stacking interactions and the C-H··· π interactions along the *b* axis (a), the *a* axis (b) and the *c* axis (c).



Figure 2. The 1D infinite chain forming through the π - π stacking interactions.



along the *c* axis (Figure 3c). These sheets are parallel to each other and further linked by the third type of $\pi \cdots \pi$ stacking interactions along the *a* axis to form a 3D supramolecular structure (Figure 4a). Another interesting feature of the structure of **1** is that the bowls of the adjacent sheets are arrange top to top along the *c* axis to produce a grid pore with a size of 5.732×17.202 Å and bottom to bottom to produce a grid pore with a size of 3.558×7.938 Å (Figure 4b). There are some intermolecular interactions in the crystal structure of **1**: C1–H1···O3, 3.060 Å, 115.4°; C10–H10A···O2, 3.120 Å, 118.1°; O4W···N3, 2.941 Å; C7–H7···N4ⁱ, 3.477 Å, 151.9°; C4–H4···N3ⁱ, 3.536 Å, 148.0° (i = 1/2–*x*, 1/2–*y*, 1–*z*). These hydrogen bonds are helpful to stabilize the crystal packing in **1**.



Figure 4. Perspective view of the 3D supramolecular structure through the π - π interactions between the phenyl rings along the *a* axis (a) and the *c* axis with two kinds of pores (b).

IR Spectrum

The band at 3447 cm⁻¹ in the IR spectrum of 1 may be assigned to the O–H stretching vibrations of the lattice water molecules. The band at 2053 cm⁻¹ may be assigned to the stretching vibrations of the azide anions. The bands at 1597 and 1492 cm⁻¹ belong to the azide anions [32, 33]. The v_{as} (COO) vibration is identified by the strong band at 1547 cm⁻¹, the band at 1443 cm⁻¹ is assigned to the v_s (COO) vibration. The separation between the v_{as} (COO) and v_s (COO) band in 1 amounts 104 cm⁻¹, which confirms the bridging mode of the carboxyl groups in 1 [34]. The strong absorption band at 834 cm⁻¹ may be assigned to the v_{as} (Fe–O–Fe) stretching vibrations of the oxido-bridged dinuclear iron complexes [35, 36].

Conclusions

In summary, the appropriate ratios of the ligands 2,2'-bpy and N_3^- proved to be a very useful route to form a Fe₂O complex from a Fe₃O complex. The results presented in this work further illustrate the values of 2,2'-bpy and N_3^- in reactions with Fe^{III} reagents as tools to induce the nucleation. The use of the ligand 2,2'-bpy and sodium azide in iron(III) carboxyl chemistry continues to provide access to interesting supramolecular assemblies of dinuclear units. Both the present and previous results thus suggest that the well-defined polynuclear iron carboxyl complexes may serve as models for lower nucleation species in both synthetic and biological systems.

Experimental Section

Materials and General Methods

 $[Fe_3O(PhCO_2)_6(H_2O)_3]NO_3$ was synthesized according to the literature [37]. Sodium azide and solvents were commercially available and used as received without further purification. 2,2'-bpy was purchased from Alfa Aesar and used without further purification. Elemental analyses (C, H, N) were determined with a Vario EL III elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm⁻¹ with a Bruker EQUINOX-55 spectrometer.

Synthesis

[Fe₂O(PhCO₂)₂(2,2'-bpy)₂(N₃)₂]·H₂O (1): To a stirred solution of 2,2'-bpy (0.0519 g, 0.33 mmol) in MeCN (5 mL) was added [Fe₃O(PhCO₂)₆(H₂O)₃]NO₃ (0.103 g, 0.1 mmol) and sodium azide (0.0215 g, 0.33 mmol). After being stirred under aerobic conditions at ambient temperature for 8 hours, the reaction mixture was left overnight at room temperature and afterwards filtered. The filtrate was left undisturbed by slowly evaporation. The block red crystals of 1 formed after one week, they were collected by filtration and air dried. Yield 0.0392 g, ca. 50 % (based on Fe). Anal. $C_{34}H_{28}Fe_2N_{10}O_6$: calcd. C 52.06; H 3.60; N 17.86 %; found: C 52.01; H 3.63; N 17.88 %. **FT-IR** (KBr): $\tilde{v} = 3447$ (w), 2053 (s), 1597 (s), 1547 (s),1492 (s), 1443 (m), 834 (s) cm⁻¹.

X-ray Crystallography

Intensity data for complex 1 were collected with a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo- K_a radiation ($\lambda = 0.71073$ Å) at room temperature. Empirical absorption corrections were applied by the SADABS program. The structure was solved by direct methods and refined by the full-matrix least-squares based on F^2 using the SHELXTL-97 program [38]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms of organic ligands were generated geometrically. Crystallographic data and other details on the refinements are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

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Table 1. Crystal data and structural refinement parameters for 1.

Complex	1	
Empirical formula	C ₃₄ H ₂₈ Fe ₂ N ₁₀ O ₆	
Formula weight	784.36	
Crystal system	Monoclinic	
Crystal size /mm	$0.18 \times 0.12 \times 0.10$	
Space group	C2/c	
a/Å	16.463(2)	
b /Å	26.660(2)	
c /Å	9.542(3)	
α /°	90.00	
β /°	101.669(2)	
γ /°	90.00	
$V/\text{\AA}^3$	4101.4(13)	
Ζ	4	
$D / Mg \cdot m^{-3}$	1.270	
μ / mm^{-1}	0.759	
F(000)	1608	
λ (Mo- K_{α}) /Å	0.71073	
Reflections collected	10203	
Unique reflections	3626	
Parameters	234	
$R_1^{a}, w R_2^{b}$ $[I > 2\sigma(I)]$	0.0624, 0.1741	
R_1^{a} , wR_2^{b} (all data)	0.1175, 0.2078	
S on F^2	1.027	
$\Delta \rho$ max and min /e·Å ⁻³	0.578 and -0.419	

a) $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$ for $F_0 \ge 4\sigma(F_0).b$) $wR_2 = \{\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_c^2)^2] \}^{1/2}$.

Table 2. Selected bond len	igths /Å and bond angles /° for	1
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Fe(1)-O(3)	1.785(2)	Fe(1)-O(2)#1	2.034(3)
Fe(1) - N(3)	2.039(5)	Fe(1) - O(1)	2.123(4)
Fe(1) - N(1)	2.149(4)	Fe(1) - N(2)	2.211(4)
O(3)-Fe(1)-O(2)#1	101.81(14)	O(3) - Fe(1) - N(3)	96.46(18)
O(2)#1-Fe(1)-N(3)	92.90(18)	O(3)-Fe(1)- $O(1)$	95.70(13)
O(2)#1-Fe(1)-O(1)	84.36(15)	N(3)-Fe(1)-O(1)	167.83(18)
O(3) - Fe(1) - N(1)	94.03(15)	O(2)#1-Fe(1)-N(1)	162.37(15)
N(3)-Fe(1)-N(1)	92.95(19)	O(1)-Fe(1)-N(1)	86.43(15)
O(3) - Fe(1) - N(2)	167.96(15)	O(2)#1-Fe(1)-N(2)	89.99(15)
N(3)-Fe(1)-N(2)	85.19(18)	O(1)-Fe(1)-N(2)	82.96(14)
N(1)-Fe(1)-N(2)	73.96(16)	Fe(1)-O(3)-Fe(1)#1	121.9(3)

Symmetry transformations used to generate equivalent atoms: #1 (-x, y, -z+3/2).

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Copies of the data can be obtained on quoting the depository number CCDC-765318 (1) (http:// www.ccdc.cam.ac.uk/conts/retrieving.html; Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

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