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New 3D metal–organic framework isomer containing trinuclear oxo-centered mixed valence iron

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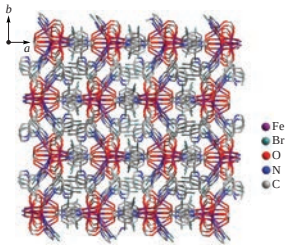
Reaction of $FeCl_2{\cdot}4H_2O$, 5-bromonicotinic acid and 4,4′-bipyridine under hydrothermal conditions produced a new isomer of $[(Fe^{III})_2Fe^{II}(\mu_3\text{-}O)(5\text{-bromonicotinato})_6]_n$, which represented 3D metal–organic covalent framework with trinuclear oxo-centered mixed valence iron clusters. Crystal structure of the isomer has been characterized by single crystal X-ray diffraction data and found distinct from the one for the known isomer with 2D structure.



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Chemical and catalytic properties, electron transfer reactions as well as magnetic couplings of trinuclear oxo-centered mixed valence transition metal complexes have been extensively studied since the earlier reports on the mixed valence compounds emerged four decades ago.[1–7] Carboxylates have been extensively investigated by our group as linkers in the synthesis of metal–organic frameworks.[8–12] The carboxylate bridges in compounds of this type influence the terminal ligand coordination, redox potential of the metal center and the solid-state polymerization process through cross-linking of the coordinating species.[1,13] The trinuclear oxo-centered carboxylate-bridged compounds such as $[M_3(\mu\text{-}O)(O_2CR)_6L_3]$, where M = Fe, Mn, Zn or Ru, have potential application in magnetochemistry,[14–16] as bioactive materials[17,18] and homogeneous catalysts.[19,20] 5-Bromonicotinic acid (HBNA) and its anion (BNA) possess one carboxylate group and one nitrogen atom as coordination sites, while their bromine atom is capable of O···Br or N···Br halogen bonding and the related Br···π and Br···Br interactions. Though several examples of transition metal carboxylate compounds derived from HBNA have been reported,[21–27] for example two-dimensional polymeric complex $[(Fe^{III})_2Fe^{II}(\mu_3\text{-}O)(BNA)_6]_n$ **1** synthesized recently by our group,[21] this ligand remains largely unexplored. Therefore, the synthesis of new metal–organic polymers containing BNA, especially trinuclear oxo-centered mixed valence transition metal complexes, for further in-depth investigations of solid state electron transfer, catalysis and magnetic coupling properties, are deemed to be promising and may have broad impact. Herein, we report the synthesis and characterization of new trinuclear oxo-centered mixed valence iron complex $[(Fe^{III})_2Fe^{II}(\mu_3\text{-}O)(BNA)_6]_n$ **2** with three-dimensional metal–organic framework as well as its comparison with the known two-dimensional isomeric counterpart **1**.[21]

Both isomers were obtained as black crystals, namely plates for compound **1**[21] and cubes for compound **2**, by reaction of $FeCl_2{\cdot}4H_2O$ with HBNA in the presence of 4,4′-bipyridine at the molar ratio of 1 : 2 : 1 and 1 : 1 : 1, respectively, under hydrothermal conditions at 140 °C for three days (complex **1**) or seven days (complex **2**). The crystals were washed with water, acetone and dried in air. A single crystal of compound **2** suitable for X-ray diffraction was employed for the data collection.†

A short consideration of the compound **1** structural features[21] is necessary here to demonstrate the difference between the two isomers. The cluster of complex **1** consists of a central oxygen atom surrounded by three iron atoms, each coordinated in slightly distorted octahedral geometry with the central μ_3-oxygen and BNA nitrogen atom (in axial positions) as well as with four carboxyl oxygen atoms from different BNA ligands (in equatorial

† *Crystal data for* **2**. $C_{36}H_{18}Br_6Fe_3N_6O_{13}$ (M = 1389.57), crystal size 0.15×0.15×0.15 mm, cubic, space group $Pa\bar{3}$, a = 20.3708(6) Å, V = 8453.3(4) Å^3, T = 223(2) K, Z = 8, d_{calc} = 2.184 g cm^{-3}, μ = 6.761 mm^{-1}, $F(000)$ = 5344, λ = 0.71073 Å, 39304 reflections collected, 2310 unique reflections, R_{int} = 0.0469, empirical absorption correction employed, max/min transmission 0.983/0.655. Final indices for $I > 4\sigma(I)$: R_1 = 0.0178, wR_2 = 0.0449, for all data R_1 = 0.0267, wR_2 = 0.0486, F^2 = 1.058, largest difference peak/hole 0.414/–0.395 e Å^{-3}.

All measurements were carried out using a Bruker DUO diffractometer equipped with a 4K CCD APEX II detector. Hemisphere of data (1519 frames at 6 cm detector distance) was collected employing a narrow-frame algorithm with scan widths of 0.30% in ω and an exposure time of 30 s per frame. The data were integrated using a Bruker-Nonius SAINT program, with the intensities corrected for Lorentz factor, polarization, air absorption and absorption due to variation in the path length through the detector faceplate. A φ-scan absorption correction was applied based on the entire data set. Redundant reflections were averaged. Final cell constants were refined using 5552 reflections having $I > 10\sigma(I)$, for details, see Online Supplementary Materials.

CCDC 1870136 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

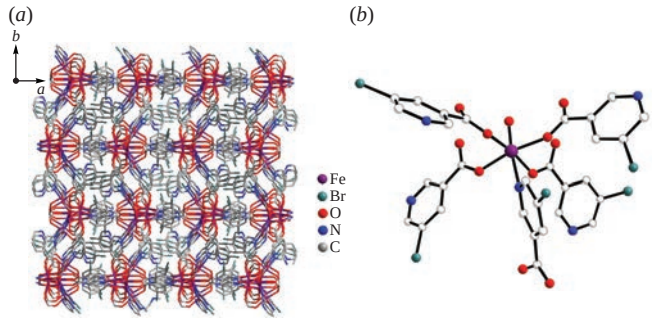

Figure 1 Structure of complex **2**: (*a*) three-dimensional network; (*b*) complete coordination around the iron atom.

positions). Half of the BNA nitrogen atoms in complex **1** are bound to the iron ones, while others are non-coordinated (*i.e.*, dangling). Thus, further coordination in the third dimension is stopped by the dangling nitrogen atoms along *a* axis, which results in two-dimensional layer in *bc* plane. For detailed description of the structure of compound **1**, see ref. 21. BNA ligands in complex **1** demonstrate two different coordination patterns, namely μ_2-κ*O*:κ*O′* bidentate mode and the μ_3-κ*O*:κ*O′*;κ*N* tridentate one, the latter connects adjacent iron clusters. In addition, there exist additional non-classic hydrogen bonding interactions, which play important role for further stabilization of the structure.

While polymer **1** displays two-dimensional layered structure, its newly synthesized isomer **2** represents three-dimensional covalent network [Figure 1(*a*)].

The cluster of complex **2** in a similar manner consists of a central oxygen atom surrounded by three iron atoms, each coordinated with the central μ_3-oxygen and BNA nitrogen atoms as well as with four carboxyl oxygen atoms from different BNA ligands, which represent bridges between iron atoms of the same cluster [Figures 1(*b*), 2].

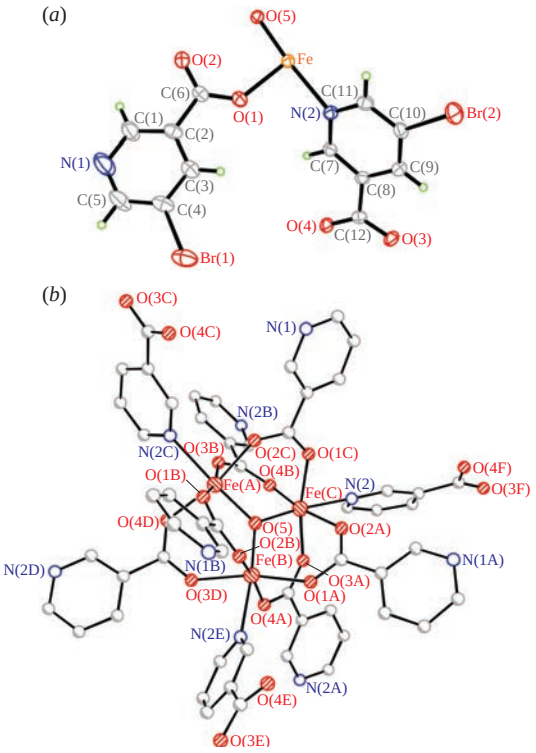

Figure 2 (*a*) Asymmetric unit of complex **2** with the atom numbering scheme, thermal ellipsoids are depicted at 60% probability with hydrogen atoms as spheres of arbitrary diameter. (*b*) Complete coordination in complex **2** around the trinuclear iron cluster with oxo-center and coordinating atoms shaded. Bromine and hydrogen atoms are omitted for clarity.

Three BNA ligands in each trinuclear cluster have non-coordinated (dangling) nitrogen atoms [see Figure 2, ligands with N(1), O(1) and O(2)]. Each of another three BNA ligands in the trinuclear cluster has nitrogen atom coordinated with the iron one of this same cluster and two carboxyl oxygen atoms coordinated with iron atoms of another cluster [see Figure 2, ligands with N(2), O(3) and O(4)]. Finally, three ligands in each cluster have nitrogen atom coordinated with the iron one of another cluster and two carboxyl oxygen atoms coordinated with iron atoms of this same cluster [see Figure 2(*b*), ligands with N(2), O(3) and O(4)]. The two last types of BNA ligands form the three-dimensional structure.

Similar to complex **1**,[21] BNA ligands in complex **2** display the coordination patterns with μ_2-κ*O*:κ*O′* bidentate mode and the μ_3-κ*O*:κ*O′*;κ*N* tridentate one. The three-dimensional structure of compound **2** has more complicated connection pattern and spatial structure compared with the two-dimensional network of isomeric polymer **1**.

In summary, we have synthesized a new isomer of the three-dimensional covalent metal–organic framework with BNA ligands and iron coordination centers, which represents trinuclear oxo-centered mixed valence iron polymer. Its lustrous black metallic crystals may have promising physical properties, including magnetic coupling ones, due to the mixed valence state of iron in the network. Further research of this system may offer insight into the synthesis and properties for a series of new similar materials.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.09.012.

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