



Short communication

## Bis-boron-capped tris(dioxime) cage complexes with terminal carbonyl groups

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## ABSTRACT

Three clathrochelate complexes, [(*p*-OHCC<sub>6</sub>H<sub>4</sub>B)<sub>2</sub>(chdd)<sub>3</sub>Fe<sup>II</sup>]·0.5CH<sub>2</sub>Cl<sub>2</sub> (**1**·0.5CH<sub>2</sub>Cl<sub>2</sub>, H<sub>2</sub>chdd = 1,2-cyclohexanedione-1,2-dioxime), [(*p*-OHCC<sub>6</sub>H<sub>4</sub>B)<sub>2</sub>(hmbd)<sub>3</sub>Mn<sup>II</sup>]<sub>2</sub>]·Et<sub>3</sub>NH·0.5CH<sub>3</sub>OH·0.5H<sub>2</sub>O (**2**·0.5CH<sub>3</sub>OH·0.5H<sub>2</sub>O, H<sub>3</sub>hmbd = 2-hydroxy-5-methyl-1,3-benzenedicarboxaldehyde-1,3-dioxime), and [(*p*-OHCC<sub>6</sub>H<sub>4</sub>B)<sub>2</sub>(hmbd)<sub>3</sub>Co<sup>II</sup>]<sub>2</sub>]·Et<sub>3</sub>NH·H<sub>2</sub>O (**3**·H<sub>2</sub>O), were synthesized through template macrobicyclization using metal-oximates as building blocks. These complexes contained reactive apical formyl substituents. Fe<sup>II</sup> in mononuclear complex **1** was wrapped in the cavity formed by condensation of H<sub>2</sub>chdd with 4-formylphenylboronic acid. The organic frameworks of anion unit of binuclear Mn<sup>II</sup> complex **2** and that of binuclear Co<sup>II</sup> complex **3** were combined by H<sub>3</sub>hmbd with 4-formylphenylboronic acid. Spectroscopic, electrochemical characterizations of complexes **1–3** were exploited. DFT calculation of **1** and **2** was also done for better understanding of the electronic property and charge carrier mobility.

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Metal-containing conducting polymers (MCPs) have been the subject of intense studies that are aimed at elucidating the mechanism of electron transfer (ET) which can be applied to design electronic devices and functional materials [1]. Metal centers embedded within the covalently linked polymer backbone can provide efficient charge transport [2–4]. Despite the formation of covalent bond has been a powerful tool for the construction of organic framework, in synthetic respects, the construction of such desired polymeric structures is rather difficult. In self-assembly processes, the reaction of B(OH)<sub>2</sub> group to develop novel boron system is being extensively studied now [5–10]. The investigation on boryl-capped trioximate metal complexes obtained by template condensation has been performed to reveal their properties on hydrogen-producing catalysts [11–16]. But, only a limited number of boronic acids with  $\pi$ -extended reactive substituents as monomer to access to multicomponent copolymer have been reported to date [17]. The monomers with formyl group can react with other bifunctional monomer to form infinite covalent bonded polymeric structure. At the same time, transition metal cage unit containing coordinatively saturated metal ions is ideal for electron transfer (ET) within the structure. Adjustment of structure and property of such polymer can be easily achieved by readily modifying the components.

On the basis of these aforementioned considerations, two types of 4-formylphenylboron-capped tris-dioximate metal(II) clathrochelate complexes obtained by the template condensation are described.

Synthetic approach of tris-dioximate metal based clathrochelates adopted has two steps. In the first, three dioxime molecules coordinate

metal(II) ions to form the precursor. Second, three deprotonated hydroxyl groups of dioximes are clasped together by borate ester bonds with 4-formylphenylboronic acid, giving the boron final capping complex molecules. H<sub>2</sub>chdd is a *N,N'*-bidentate chelate ligand, which can give out [1<sub>metal</sub> + 3<sub>chdd</sub> + 2<sub>boronic acid</sub>]-type monomeric iron(II) complex **1** [18]. The H<sub>3</sub>hmbd ligand with N,  $\mu_2$ -O, N coordination atoms is a typical tridentate ligand. Treatment of hydrated manganese chloride or hydrated cobaltous nitrate with H<sub>3</sub>hmbd and the substituted boronic acid in 2:3:2 (molar ratio) can perform metal-templated [2<sub>metal</sub> + 3<sub>hmbd</sub> + 2<sub>boronic acid</sub>]-type condensation reaction to produce the binuclear manganese(II) cage complex(**2**) or cobalt(II) cage complexes **3**, respectively [19,20].

The lattice of **1**·0.5CH<sub>2</sub>Cl<sub>2</sub> [21] consists of a mononuclear Fe<sup>II</sup> unit and a half of dichloromethane molecule of crystallization. The {[(*p*-OHCC<sub>6</sub>H<sub>4</sub>B)<sub>2</sub>(chdd)<sub>3</sub>Fe<sup>II</sup>]} molecule (Fig. 1) contains chelate three dioximate fragments, in which the Fe(II) ion is in encapsulated coordination environment. Each divalent Fe(II) center is in a coordination center of six nitrogen atoms. The FeN<sub>6</sub>-coordination polyhedron with the distortion angle  $\varphi = 20.77^\circ$  is between trigonal prismatic (TP,  $\varphi = 0^\circ$ ) and trigonal antiprismatic (TAP,  $\varphi = 60^\circ$ ) geometry, as reported elsewhere. These two triangular planes are almost parallel, with the dihedral angle of  $0.3^\circ$ . The average Fe–N distance is 1.906 Å, which is comparable to that observed Fe<sup>II</sup> ion in distorted trigonal prismatic coordination geometry [22–24]. In the clathrochelate framework, the distances of Fe(1)⋯B(1)(3.029 Å) and Fe(1)⋯B(2)(3.006 Å) are almost identical. The B(1)–Fe(1)–B(2) bond angle is 179.83°.

The structure of **2**·0.5CH<sub>3</sub>OH·0.5H<sub>2</sub>O [25] is shown in Fig. 2. The lattice consists of a discrete monoanion binuclear Mn<sup>II</sup><sub>2</sub> unit, a triethylamine cation, a half of methanol molecule and a half of water molecule on crystallography.

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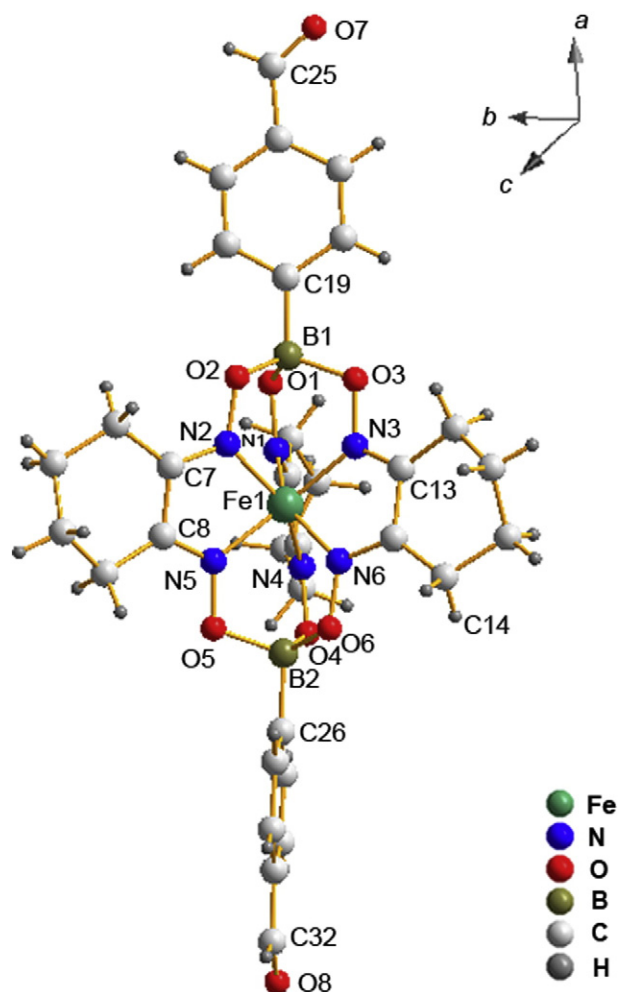


Fig. 1. General representation of the structure of complex 1.

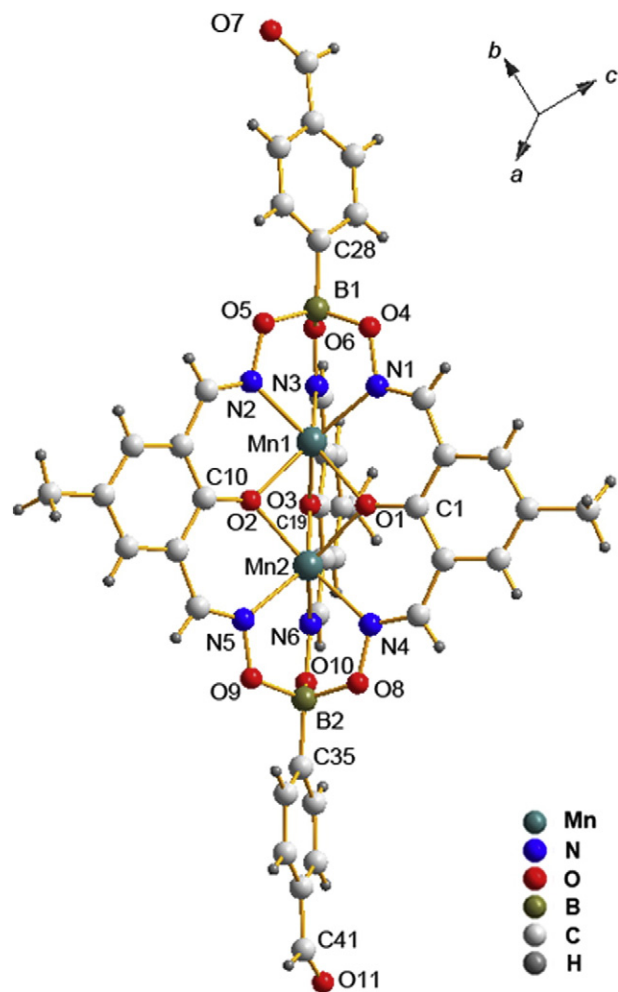


Fig. 2. General representation of the structure of the anion in complex 2.

Each divalent Mn(II) center is in a hexacoordination center, which is embedded in the cavity of the clathrochelate ligand. Geometry of the  $MnN_3O_3$  coordination polyhedron is a slightly distorted trigonal prism (TP), which may be caused by the rigid of  $hmbd^{3-}$ . Owing to the  $\mu_2$ -bridging mode of phenoxy oxygen atoms, O(1), O(2), and O(3), a face-shared bi-trigonal prism structure for the dimanganese(II) is formed with the Mn(1)⋯Mn(2) separation of 2.898(2) Å. The average distortion angle  $\varphi$  of the trigonal prism containing Mn(1) is equal to 1.86°, while that value is 1.52° for Mn(2) involving coordination polyhedron. The distance between Mn(1) and the plane formed by N(1), N(2), and N(3) is 1.34 Å and that between Mn(1) and the plane formed by O(1), O(2), and O(3) is 1.45 Å. Mn(2) to the O(1)O(2)O(3) plane is 1.45 Å and to the N(4)N(5)N(6) plane is 1.33 Å, which is in full agreement with that of Mn(1). The B(1)⋯B(2) separation is 9.126(10) Å. No obvious distortion of the clathrochelate framework is observed in the direction of the B(1)⋯B(2) axis. The atoms of B(1), Mn(1), Mn(2), and B(2) are nearly linear. The average Mn–O distance (2.126 Å) and Mn–N (2.170 Å) distance around Mn(1) are comparable to that around Mn(2) (Mn–O 2.130 Å and Mn–N 2.167 Å, respectively). The bond lengths around the manganese center are in agreement with a high-spin  $d^5$  electron configuration [10].

The structure of **3** [26] is similar to that of **2** (Fig. S1). The Co–O bond lengths are in the range of 2.077(4)–2.124(4) Å and Co–N bond lengths are in the range of 2.081(5)–2.103(6) Å. The average distortion angle  $\varphi$  of the trigonal prism containing Co(1) is equal to 2.60°, while that value is 6.87° for Co(2) involving coordination polyhedron. The

Co(1)⋯Co(2) separation is 2.959(2) Å and the B(1)⋯B(2) separation is 9.138(10) Å.

The Fe(II) complex **1** has an intensive metal-to-ligand  $Fed \rightarrow L\pi^*$  charge transfer (MLCT) bands at  $\lambda_{max} = 449$  nm (Fig. S2). The manganese(II) complex **2** has a MLCT bands at  $\lambda_{max} = 372$  nm. Complex **3**, the homologue of complex **2**, exhibits similar MLCT band appears at  $\lambda_{max} = 385$  nm. The differences in the UV–vis spectrometry are caused by the different structures of the cages of complexes. As it shows in the UV–vis spectrometry, complex **2** and complex **3** have similar UV–vis spectrometry behaviors, owing to the similar cages structure of them. Because the structure of complex **1** is different from structures of complexes **2** and **3**, it behaves differently in UV–vis spectrometry.

The electrochemical properties of **1**, **2** and **3** are studied by CV (Fig. 3). As it shows in CV data, **1** showed a pair of oxidation and reduction peaks, in the potential range of 1.00 to 1.25 V, the one-electron wave demonstrates that the metal-centered Fe(II)/Fe(III) redox process is a quasi-reversible process. Because it's a mononuclear complex, in the stable potential range (–1.75 V to 1.5 V), Fe(II) to Fe(III) is a most stable process, and in this process there is no other ligand redox peaks in Fig. 3, which also prove its stability in this range. That is in accordance with the reference [27]. Complex **2** tends to show more than a pair of redox peaks, which are in agreement with the reference [10]. The CV of **2** exhibits consecutive oxidation and reduction processes, which proves a good reversibility of complex **2** in the redox process. The first pair of redox peaks appears at 0.697 V and 0.775 V and the second pair appears at 1.043 V and 1.160 V, respectively. The first pair of

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