Journal of Molecular Structure 1155 (2018) 687–694

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Four unprecedented 2D trinuclear Mn(II)-complexes with adenine nucleobase controlled by solvent or co-ligand: Hydrothermal synthesis, crystal structure and magnetic behaviour

Hongkun Zhao*, Hongming He, Xiuguang Wang, Zhongyi Liu, Bo Ding, Hanwen Yang

Key Laboratory of Inorganic-Organic Hybrid Functional Material Chemistry, Ministry of Education, Tianjin Key Laboratory of Structure and Performance for Functional Molecules, College of Chemistry, Tianjin Normal University, Tianjin 300387, PR China

ARTICLE INFO

Article history:
Received 25 September 2017
Received in revised form
16 November 2017
Accepted 16 November 2017
Available online 17 November 2017

Keywords:
Adenine
Mn^{II}_3 SBUs
Magnetic behaviors
Hydrothermal synthesis

ABSTRACT

Four unique infinite 2D Mn(II) aggregates, $[Mn_3(\mu_3\text{-ade})_2(OAc)_4X]_n$ (X = DMF for **1**, DMA for **2** and $C_2H_5O^-$ for **3**), $[Mn_3(\mu_3\text{-ade})_2(ap)_2DMF]_n$ (**4**) (Hade = adenine; DMF = *N*,*N*-dimethylformamide; DMA = *N*,*N*-dimethylacetamide, OAc^- = acetate ion, H_2ap = adipic acid) with trinuclear Mn(II) as secondary building units (SBUs), have been successfully synthesized by the assembly of Hade nucleobase and manganese acetate under solvothermal conditions. The resultant complexes can be applied to explore the influence of solvent or co-ligands on the self-assembly and properties of metal complexes based on adenine. The Hade represent tridentate μ_3-N3, N7, N9 bridging coordination modes. The acetate anions exhibit $\mu_2\text{-}\eta^1\text{:}\eta^1$ bidentate, $\mu_2\text{-}\eta^1\text{:}\eta^2$ tridentate mode, and $\mu_2\text{-}\eta^0\text{:}\eta^2$ bidentate mode. The adipate anions in complex **4** adopt two coordination modes: one is $\mu_4\text{-}\eta^2\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1$ pentadentate mode, the other one is $\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{:}\eta^1$ hexadentate mode. Their magnetic behaviors exhibit interesting variations, in which the local net magnetization at low temperature increases from **1** to **3**. The Mn^{II}_3 SBUs in **1**–**3** are symmetric with an inversion center, whereas that in **4** has three crystallographically independent Mn^{II} atoms. Thus, the magnetic behaviors of **4** are different from complex **1**–**3**.

1. Introduction

It is understandable that the ligand disposition around metal ions and the nature of the bridging groups influence magnetic-exchange interactions [1–5]. Thereinto, acetates [4] are commonly used as bridging groups and adipic acids contain plenty of carboxylate groups providing more coordination sites to construct new molecular magnetic materials [6–8]. Besides, long aliphatic chain of adipic acid has been applied to construct functional coordination polymers as auxiliary ligands [9,10]. Anionic carboxylates are highly flexible ligands which modulate its reactivity and coordination behaviour to result in a series of coordination modes such as monodentate chelating, bidentate bridging, monoatomic bridging, and chelating bridging [11]. During the past decades, adenine (Hade) and its diverse derivatives have already drawn interest because of their biological importance of metal-nucleobase bonds and potential applications in many applications, including magnetic behaviour [12], CO_2 adsorption [13,14], N_2 adsorption [15] and advanced functional materials [16–19]. Up to data, lots of Cu^{II}– [16,17], Co^{II}– [18,19], and Zn^{II}– [20–24] containing complexes with adenine have been widely prepared and investigated. To the best of our knowledge, numerous Hade-based metal complexes have been reported in recent years, whereas only a few adenine (ade)-based manganse(II) complexes have been investigated by far [25–29]. The Danuta Dobrzyńska's group has synthesized the first ade-Mn cocrystals of $[Mn(quin\text{-}2\text{-}c)_2(H_2O)_2]\cdot 2Ade$, in which the extensive systems of hydrogen bonds and π-π interactions result in supramolecular [25]. Pascual Román [26] reported two 1D zig-zag chains $[Mn(\mu\text{-}ox)(H_2O)(7H\text{-}pur\text{-}\kappa N^9)]_n$ (pur = purine) and $\{[Mn(\mu\text{-}ox)(H_2O)_2]\cdot(7H\text{-}ade)\cdot(H_2O)\}_n$, in which the adenine nuclebase remains free and the coordination polyhedron is filled by two water molecules. Mononuclear $[Mn(H_2O)_4\cdot(ade)_2\cdot(ClO_4)_2]$ and binuclear $[Mn_2(H_2O)_6\cdot(ade)_2\cdot(NO_3)_4\cdot 2H_2O]$ represent the first example of direct binding between the Mn(II) ion and the adenine molecule in 2007 [27]. Crystal packing of $[1H, 9H\text{-}ade][3H, 7H\text{-}ade][ML_2]\cdot 3H_2O$ can be regarded as a lamellar inorganic-organic hybrid network in which adeninium cations generate cationic ribbons with the aid of

---

* Corresponding author.
E-mail address: hongkun82@163.com (H. Zhao).

https://doi.org/10.1016/j.molstruc.2017.11.069

intermolecular hydrogen bonding interactions.

Recently [28], our intention was in expanding dimension of the complexes containing Mn(II) metal directly linked to adenine and magnetic behaviour by changing the solvent and co-ligands. As a result, four new Mn-ade complexes, three $[Mn_3(\mu_3\text{-ade})_2(OAc)_4X]_n$ cluster-based 2D layers (X = DMF for **1**, DMA for **2** and $C_2H_5O^-$ for **3**) and one scarcely $[Mn_3(\mu_3\text{-ade})_2(ap)_2DMF]_n$ (**4**) consisting three crystallographically independent Mn^{II} atoms, were synthesized under solvothermal conditions. Significantly depending on the solvent systems, the former three complexes exhibit interesting variations of magnetic behaviors, in which the local net magnetization at low temperature increases gradually from **1** to **3**. The acetate anions exhibit μ_2-η^1:η^1 bidentate, μ_2-η^1:η^2 tridentate mode, and μ_2-η^0:η^2 bidentate mode in complex **1**–**3**. The adipate anions in complex **4** adopt two coordination modes: one is μ_4-η^2:η^1:η^1:η^1 pentadentate mode, the other one is μ_3-η^1:η^2:η^2:η^1 hexadentate mode. All complexes have been analyzed by infrared spectroscopy, elemental analysis, simulated powder X-ray diffraction (SPXRD) and powder X-ray diffraction analyses (PXRD). Additionally, the compositional stability and magnetic behaviour of the four complexes were also measured and discussed in detail.

2. Experimental

2.1. Materials and physical measurements

All of the starting materials employed were commercially purchased (Hade were from Acros and other analytical-grade reagents were from Tianjin Chemical Reagent Factory) and used as received without further purification. Elemental analyses of carbon, hydrogen and nitrogen were carried out with a CE-440 (Leeman-Labs) analyzer. Fourier transform (FT) IR spectra (KBr pellets) were taken on an Avatar-370 (Nicolet) spectrometer in the range 4000–400 cm^{-1}. Thermogravimetric analysis (TGA) experiments were carried out on Shimadzu simultaneous DTG-60 A compositional analysis instrument from room temperature to 800 °C under N_2 atmosphere at a heating rate of 5 °C/min. PXRD patterns were obtained with a Bruker D8 ADVANCE diffractometer at 40 kV and 40 mA for Cu Kα radiation (λ = 1.5406 Å), with a scan speed of 0.1 s/step and a step size of 0.01° in 2θ. The SPXRD pattern was calculated using single-crystal X-ray diffraction data and processed by the free Mercury v1.4 program provided by the Cambridge Crystallographic Data Center. Magnetic susceptibilities were acquired on a Quantum Design MPMS-XL-7 (SQUID) magnetometer with crystalline samples, in which the phase purity of the samples was determined by PXRD experiments. The diamagnetic corrections were calculated using Pascal's constants. In addition, an experimental correction for the sample holder was applied.

2.2. Synthesis of the complexes

All the complexes were successfully synthesized by a hydrothermal method. Solvothermal reactions of $Mn(OAc)_2\cdot4H_2O$ and Hade ligand in the presence of different solvents, DMF/CH_3OH, DMA or C_2H_5OH, led to three unique infinite 2D Mn(II) aggregates with trinuclear Mn(II) as secondary building units: $[Mn_3(\mu_3\text{-ade})_2(OAc)_4X]_n$ (X = DMF for **1**, DMA for **2** and $C_2H_5O^-$ for **3**). Replacement of $Mn(OAc)_2\cdot4H_2O$ in **1**–**3** by $MnCl_2$ and adipic acid generated complex $[Mn_3(\mu_3\text{-ade})_2(ap)_2DMF]_n$ **4**.

2.2.1. Synthesis of complex $[Mn_3(\mu_3\text{-ade})_2(OAc)_4DMF]_n$ (**1**)

$Mn(OAc)_2\cdot4H_2O$ (24.5 mg, 0.1 mmol) and Hade (13.5 mg, 0.1 mmol) in a mixed *N*,*N*-dimethylformamide (DMF 7 mL)/methanol (1 mL) solvent were placed in a 15 mL vial, and then sealed. The mixture was heated to 80 °C for 12 h, maintained at this temperature for 3 days under autogenous pressure, and cooled to room temperature slowly. After they were washed with methanol and dried in air, pale-yellow block crystals suitable for X-ray analysis were obtained directly. Yield: 68% on the basis of Mn^{II} salt. Anal. calcd for $C_{21}H_{27}Mn_3N_{11}O_9$: C 39.88 36.33, H 4.30, N 24.36%; Found: C 39.76, H 4.25, N 24.89%. FT-IR (cm^{-1}): 3319(m), 1655(m), 1608(m), 1575(s), 1394(m), 1338(w), 1262(w), 1213(m), 1149(m), 1043(m), 669(m), 613(m).

2.2.2. Synthesis of complex $[Mn_3(\mu_3\text{-ade})_2(OAc)_4DMA]_n$ (**2**)

$Mn(OAc)_2\cdot4H_2O$ (29.7 mg, 0.1 mmol) and Hade (13.5 mg, 0.1 mmol) were mixed in *N*,*N*-dimethylacetamide (DMA 7 mL)/ethanol (3 mL) solvent. Then the mixture was transferred into a Teflon-lined stainless steel vessel (20 mL) and heated at 140 °C for 72 h under autogenous pressure. After cooling to room temperature at the rate of 1.5 $°C\cdot h^{-1}$, yellow block crystals suitable for X-ray analysis were obtained directly, and washed by ethanol and air-dried. Yield: 56% on the basis of Mn^{II} salt. Anal. calcd for $C_{22}H_{29}Mn_3N_{11}O_9$: C 34.94, H 3.86, N 20.37%; Found: C 34.85, H 3.79, N 20.25%. FT-IR (cm^{-1}): 3317(m), 3118(m), 1677(m), 1607(m), 1578(s), 1391(m), 1262(w), 1212(m), 1149(m), 655(m), 614(w).

2.2.3. Synthesis of complex $[Mn_3(\mu_3\text{-ade})_2(OAc)_4\cdot C_2H_5O^-]_n$ (**3**)

Yellow block-shaped single crystals of **3** were obtained by adopting the same synthetic procedures as **2** only using ethanol instead of DMA. Yield: 68% on the basis of Mn^{II} salt. Anal. calcd for $C_{11}H_{16}Mn_{1.5}N_5O_5$: C 34.71, H 4.24, N 18.40%; Found: C 34.63, H 4.12, N 18.34%. FT-IR (cm^{-1}): 3317(m), 3099(m), 1673(m), 1610(m), 1571(s), 1424(m), 1396(m), 1342(w), 1268(w), 1218(m), 1147(m), 1044(m), 661(m), 615(m).

2.2.4. Synthesis of complex $[Mn_3(\mu_3\text{-ade})_2(ap)_2DMF]_n$ (**4**)

A mixed DMF/methanol (v:v = 7:3) solution (10 mL) containing $MnCl_2$ (19.7 mg, 0.1 mmol), adeH (13.5 mg, 0.1 mmol) and H_2ap (7.3 mg, 0.05 mmol) was placed in parr Teflon-lined stainless steel vessel (23 mL) with the maximum pressure supported up to 3 MPa, which was heated to 140 °C for 24 h and kept for 72 h under autogenous pressure, and then cooled to room temperature at a rate of 5 $°C\cdot h^{-1}$. The colorless block-shaped single crystals suitable for X-ray analysis were obtained directly in a 65% yield based on adeH, which were further washed with ethanol and air-dried. Yield: 72% on the basis of Mn^{II} salt. Anal. calcd for $C_{25}H_{31}Mn_3N_{11}O_9$: C 37.80, H 3.93, N 19.40%; Found: C 37.72, H 3.85, N 19.31%. FT-IR (cm-1): 3311(m), 3103(m), 1684(m), 1599(m), 1542(s), 1406(m), 1355(w), 1320(w), 1227(m), 1148(m), 1040(m), 782(m), 639(m), 588(m).

2.3. Crystallographic data

Single-crystal X-ray diffraction analyses of complexes **1**–**4** were collected on Bruker APEX-II CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation with radiation wavelength 0.71073 Å by using the φ-ω scan technique at 296(2) K. There was no evidence of crystal decay during the data collection process. Semiempirical absorption corrections were applied (SADABS), and the program SAINT was used for integration of the diffraction profiles [30]. The structures were solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs [31]. All the hydrogen atoms of the ligands were found in the difference Fourier Map and refined with isotropic temperature factors. No attempts have been performed to locate hydrogen atoms of the splitting water molecules. The crystallographic data is given in Table 1. Selected bond distances and angles are given in Table S1 (see the Supporting Information). CCDC-1574698(**1**), CCDC-1574699(**2**), CCDC-1574700 (**3**)