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Unusual solvent influence of formamide on the structural variations of chiral and achiral Mn(II) complexes based on tetrachlorophthalate

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ABSTRACT

Using an achiral ligand 3,4,5,6-tetrachloro-1,2-benzenedicarboxylic acid (1,2-H_2BDC-Cl_4), a short series of chiral or achiral manganese(II) complexes with the formulae $[Mn(1,2\text{-}BDC\text{-}Cl_4)(MF)_2(H_2O)_2]_n$ (**1**), $[Mn(1,2\text{-}BDC\text{-}Cl_4)(DMF)(H_2O)_2]_n$ (**2**) and $[Mn_2(1,2\text{-}BDC\text{-}Cl_4)_2(DEF)_2(H_2O)_6]\cdot 2H_2O$ (**3**) (MF = *N*-methylformamide; DMF = *N*,*N*-dimethylformamide and DEF = *N*,*N*-diethylformamide) have been spontaneously obtained through the alteration of formamide solvent media, and characterized by single-crystal X-ray diffraction, elemental analysis, IR, thermal gravimetric analyses (TGA) and powder X-ray diffractions (PXRD). Complex **1** crystallizes in the monoclinic $P2_1/c$ space group and shows a one-dimensional fishbone chain structure, complex **2** crystallizes in the orthorhombic $P2_12_12_1$ space group and has a chiral double-stranded helical chain consisting of two single-stranded helices of the same right-handness, and complex **3** crystallizes in the triclinic $P1$ space group and possesses a dinuclear $[Mn(1,2\text{-}BDC\text{-}Cl_4)]_2$ metallomacrocycle directing a two-dimensional hydrogen-bonded water layer based on both coordinated and lattice water molecules. This remarkable structural difference displays the significant influence of formamide solvents on the formation of such chiral and achiral Mn(II) complexes. The spectroscopic, thermal stability and luminescence properties of **1**–**3** have also been investigated briefly.

1. Introduction

The field of discrete or polymeric metal–organic coordination complexes has undergone explosive growth due to their intriguing variety of architectures and potential applications as functional materials [1–3]. Of higher interest is the exploration of new chiral materials because of their fundamental importance in the area of asymmetric catalysis and chiral recognition [4]. The synthesis of chiral materials can be constructed by employing chiral ligands, chiral templates, and/or chiral solvents, or by using achiral components via spontaneous resolution in the absence of any chiral sources [5–7]. Among these, the spontaneous resolution is a peculiar phenomenon and usually results in an optically inactive conglomerate (racemic mixture of chiral crystals) [8], which has been proved as a constructive approach for the synthesis of individual homochiral microporous crystalline solids. However, the controllable generation of such chiral solids from totally achiral precursors is still of a great challenge since it may be significantly governed by several factors such as the flexibility of organic ligand [8e,9], coordination geometry of the metal center [10], counteranion [11], reaction temperature [12], and pH value of the solution [13].

It was realized that solvents play an important role in the design and synthesis of coordination networks and supramolecular assemblies. Solvents with different sizes and coordination abilities not only facilitate the crystallization of well-defined molecular architectures such as macrocycles and cages, interlocked species, helical assemblies and other metal–organic frameworks, but also trigger physicochemical properties such as adsorption, magnetism, catalysis, and chirality, etc. [14]. In particular, the solvent-dependent structural assemblies of chiral coordination compounds based on achiral ligands have been recently reported, although they are very rare. For instance, Aoyama et al. showed the importance of solvent in tuning the chiral Cd(II) coordination polymers from an achiral anthracene-pyrimidine derivative 5-(9-anthracenyl)pyrimidine [15]. The tuning effect of the solvents on the conformation of an achiral flexible ligand in the generation of the heterochiral or homochiral Ag(I) coordination polymers was nicely demonstrated

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by Mak's group [8b]. Tzeng et al. presented the coordinated-solvent induced assembly of Cd(II) ions and achiral 4,4′-dipyridylsulfide, affording a novel chiral self-entangled framework [16].

Although both coordination ability and steric requirement of solvent are usually considered as of primary importance for the mentioned spontaneous processes, synergistic noncovalent interactions (including hydrogen bonding, halogen bonding and $\pi\cdots\pi$ stacking) between solute and solvent often prove to be a useful, sometimes deciding factor [17]. Incorporation of hydrogen bonding functionalities in the achiral ligand is important in studying the effect of solvent on the structural assembly and prediction of chiral and/or helical supramolecular architectures since most of the solvents can act as excellent hydrogen bonding donor/acceptor. Nangia and co-workers demonstrated that weak halogen···halogen (Cl, Br and I) interactions can also direct the handedness of guest water helix [17b].

Along with our work in exploring the design and synthesis of new functional coordination polymers with perhalogenated ligands [18], we have illustrated the fluorine-induced chiral coordination arrays based on an achiral perfluorinated Schiff-base ligand [18c]. In this contribution, we selected tetrachlorophthalic acid (1,2-H_2BDC-Cl_4) as a new candidate to react with $Mn(OAc)_2\cdot 4H_2O$, and one new achiral and two homochiral Mn(II) compounds, namely [Mn(1,2-BDC-Cl_4)$(MF)_2(H_2O)_2]_n$ (**1**), [Mn(1,2-BDC-Cl_4)(DMF)$(H_2O)_2]_n$ (**2**) and [Mn_2(1,2-BDC-Cl4)$_2$(DEF)$_2(H_2O)_6]\cdot 2H_2O$ (**3**) were spontaneously resolved by simply alternating a short series of mixed formamide/H_2O systems, including MF/H_2O, DMF/H_2O, and DEF/H_2O (MF = *N*-methylformamide; DMF = *N*,*N*-dimethylformamide and DEF = *N*,*N*-diethylformamide) (see Scheme 1). Notably, X-ray structural analyses indicate that complexes **1**–**3** crystallize in different space groups $P2_1/c$, $P2_12_12_1$ and $P1$, respectively. Compound **1** displays a 1-D coordination chain structure, **2** features a double-stranded helical chain structure possessing two single-stranded helices of the same right-handness, while **3** shows a discrete dinuclear metallomacrocyclic structure directing a unique 2-D water aggregation. Remarkably, their structural difference only originates from the subtle variation of the size of formamide solvents, which can significantly affect the final formation of achiral and homochiral complexes in the present system. In addition, the spectroscopic, thermal, and luminescence properties of **1**–**3** will also be discussed in detail as described below.

2. Experimental

2.1. Materials and general methods

All reagents and solvents for synthesis and analysis were commercially available and used as received. The Fourier transform (FT) IR spectra (KBr pellets) were recorded on a Nicolet ESP 460 FT-IR spectrometer. Elemental analyses of carbon, hydrogen and nitrogen were performed on a PE-2400II (Perkin-Elmer) analyzer. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV and 100 mA for a Cu-target tube (λ = 1.5406 Å). The calculated PXRD patterns were obtained from the single-crystal diffraction data using the PLATON software [19]. Thermogravimetric analysis (TGA) experiments were carried out on a Dupont thermal analyzer from room temperature to 800 °C at a heating rate of 10 °C min^{-1} under nitrogen stream. Luminescent spectra of the crystalline samples in solid state were recorded with a Varian Cary Eclipse spectrometer.

2.2. Syntheses of the Mn^{II} complexes

2.2.1. [Mn(1,2-BDC-Cl_4)$(MF)_2(H_2O)_2]_n$ (1)

A mixture of equal molar 1,2-H_2BDC-Cl_4 (91.2 mg, 0.3 mmol), $Mn(OAc)_2\cdot 4H_2O$ (73.5 mg, 0.3 mmol) was dissolved in the MF/H_2O mixed solvents (v/v, 1:1, 12 mL) with stirring for *ca*. 30 min. The resulting solution was filtered and left to stand at room temperature. Colorless block crystals of **1** suitable for X-ray single-crystal diffraction were obtained by slow evaporation of the solvents after three weeks in about 70% yield based on 1,2-H_2BDC-Cl_4. *Anal.* Calc. for $C_{12}H_{14}Cl_4MnN_2O_8$ (**1**): C, 28.21; H, 2.76; N, 5.48. Found: C, 28.37; H, 2.79; N, 5.36%. IR (cm^{-1}): 3266 br, 3091 m, 2946 m, 2926 m, 1656 s, 1602 vs 1529 s, 1426 s, 1396 s, 1372 s, 1342 s, 1269 m, 1205 m, 1156 w, 1128 w, 932 w, 913 m, 831 w, 780 m, 655 s, 616 m, 572 m.

2.2.2. [Mn(1,2-BDC-Cl_4)(DMF)$(H_2O)_2]_n$ (2)

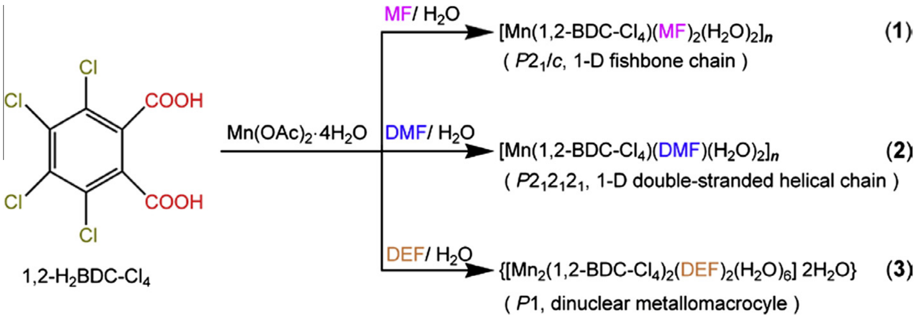
The same synthetic procedure as that for **1** was used except that MF was replaced by DMF, affording colorless block crystals of **2** in about 30% yield based on 1,2-H_2BDC-Cl_4. *Anal.* Calc. for $C_{11}H_{11}Cl_4MnNO_7$ (**2**): C, 28.35; H, 2.38; N, 3.01. Found: C, 28.12; H, 2.36; N, 3.25%. IR (cm^{-1}): 3311 br, 2958 m, 2930 m, 1671 s, 1604 s, 1526 m, 1426 s, 1384 s, 1342 s, 1253 m, 1202 w, 1125 m, 1095 m, 1060 w, 925 w, 913 m, 828 m, 652 s, 612 m, 541 m.

2.2.3. [Mn_2(1,2-BDC-Cl_4)$_2$(DEF)$_2(H_2O)_6]\cdot 2H_2O$ (3)

The procedure was the same as that for **1** except that the solvent MF was replaced by DEF, affording colorless block crystals of **3** in about 40% yield based on 1,2-H_2BDC-Cl_4. Elemental analysis calcd for $C_{26}H_{38}Cl_8Mn_2N_2O_{18}$: C, 29.46; H, 3.61; N, 2.64. Found: C, 30.12; H, 3.59; N, 2.68%. IR (KBr, cm^{-1}): 3419 br, 3078 s, 2933 s, 1657 vs 1614 s, 1566 s, 1449 s, 1371 vs 1312 m, 1251 m, 1110 m, 1061 w, 968 m, 807 m, 781 s, 728 s, 680 m.

2.3. X-ray crystallography

Single-crystal X-ray diffraction measurements of **1**–**3** were performed on a Bruker APEX II CCD diffractometer at the ambient temperature with Mo Kα radiation (λ = 0.71073 Å). In each case, a semiempirical absorption correction was applied using SADABS [20], and the program SAINT was used for integration of the diffraction



Scheme 1. Solvent-regulated synthetic routes of **1**–**3**.