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Syntheses, structures and thermal properties of four manganese coordination polymers from imidazole-based multi-carboxylates

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ABSTRACT

By using two types of carboxylphenyl-based imidazole-4,5-dicarboxylic acids, four coordination polymers, $[Mn(o\text{-}CPhH_2IDC)(H_2O)_2]_n$ (**1**), $[Mn_3(m\text{-}CPhHIDC)_2(phen)_2]_n$ (**2**) (m-$CPhH_4IDC$ = 2-(3-carboxylphenyl)-1*H*-imidazole-4,5-dicarboxylic acid), $\{[Mn_3(o\text{-}CPhHIDC)_2(phen)_3]\cdot H_2O\}_n$ (phen = 1,10-phenanthroline) (**3**) and $\{[Mn_3(o\text{-}CPhHIDC)_2(2,2'\text{-}bipy)_3]\cdot(2,2'\text{-}bipy)_{0.5}\}_n$ (2,2′-bipy = 2,2′-bipyridine) (**4**), have been synthesized and characterized by elemental analyses, IR, thermogravimetric analyses and single-crystal X-ray diffraction. Compound **1** crystallizes as a 2-D four-connected 4^4-sql network. Polymer **2** has a 3-D architecture with a net point group of $\{4^3.8^7\}\{4^3\}\{4^6.8^4\}_2$. Complexes **3** and **4** present wave-like architectures by π–π interactions from neighboring zigzag chains. These various architectures demonstrate the versatile coordination abilities of the imidazole-based multi-carboxylate ligand. The thermal properties of the complexes have also been investigated.

1. Introduction

In chemistry and material science fields today, coordination polymers (CPs) as novel crystalline solids comprised of metal cations (or metal clusters) and organic ligands have shown promise for a wide variety of applications [1]. Since the concept of CPs was firstly reported by Robson in 1990 [2], great progress has been made in the synthetic strategies for the construction of CPs. According to the literature, one of the most effective and facile approaches for the construction of coordination frameworks with desired structural features and/or physicochemical properties is to apply organic ligands containing N and O donors, which have a great ability to adopt different coordination modes and satisfy many of the central metal coordination preferences [3].

In this context, the imidazole-4,5-dicarboxylic acid (H_3IDC) and its derivatives act as a kind of classical ligand in coordination chemistry owing to their versatile bridging coordination modes and potential hydrogen-bonding donors and acceptors [4]. Compared with H_3IDC, its 2-position substituted derivatives with diverse aromatic groups have attracted much attention now, not only owing to their electronic and steric versatilities, but also the terminal groups can easily stretch out through the coordination bonds between the donor atoms and metal centers [5]. As far as we can see, research on carboxylphenyl imidazole dicarboxylate ligands, such as 2-(2-carboxylphenyl)-1*H*-imidazole-4,5-dicarboxylic acid (o-$CPhH_4IDC$) and 2-(3-carboxylphenyl)-1*H*-imidazole-4,5-dicarboxylic acid (m-$CPhH_4IDC$), combining the virtues of both imidazole and carboxylic acid is very limited [6]. The reason for the adoption of these kinds of organic ligands is that the bulky aromatic carboxylate groups are regarded as valuable tools to tune structures, not just because bulky ligands usually lead to large pores and surface areas, but even more importantly, the carboxylate groups can show versatile bonding modes to metal ions and tend to generate metal-rich clusters, which can create a wide diversity of CPs.

Based on the above considerations, two organic ligands, o-$CPhH_4IDC$ and m-$CPhH_4IDC$, were designed [6]. To date we have reported one Mn(II) mononuclear complex, one Cd-based net-like layer structure and two Sr-based polymeric structures with these ligands. Our previous results indicate o-$CPhH_4IDC$ and m-$CPhH_4IDC$ are effective building blocks in the construction of diverse CPs [6]. To further understand the coordination features of these ligands and to prepare new Mn-based CPs, we surveyed various reaction conditions and obtained four Mn(II) CPs with different auxiliary ligands.

In this paper, four CPs, $[Mn(o\text{-}CPhH_2IDC)(H_2O)_2]_n$ (**1**), $[Mn_3(m\text{-}CPhHIDC)_2(phen)_2]_n$ (**2**), $\{[Mn_3(o\text{-}CPhHIDC)_2(phen)_3]\cdot H_2O\}_n$ (phen = 1,10-phenanthroline) (**3**) and $\{[Mn_3(o\text{-}CPhHIDC)_2$

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(2,2′-bipy)$_3$]·(2,2′-bipy)$_{0.5}$}$_n$ (2,2′-bipy = 2,2′-bipyridine) (**4**), have been hydro(solvo)thermally synthesized and structurally characterized. Their thermal properties have also been investigated. Moreover, comparisons of the polymeric structures and coordination features have been discussed in detail.

2. Experimental

2.1. Materials and measurements

All chemicals were of reagent grade quality, obtained from commercial sources and used without further purification. The organic ligands *o*-CPhH$_4$IDC and *m*-CPhH$_4$IDC were prepared according to literature procedures [6].

The C, H and N microanalyses were carried out on a FLASH EA 1112 analyzer. IR spectra were recorded on a Nicolet NEXUS 470-FTIR spectrophotometer as KBr pellets in the 400–4000 cm^{-1} region. Thermal gravimetric (TG) measurements were performed by heating a crystalline sample from 20 to 850 °C at a rate of 10 °C min^{-1} in air on a Netzsch STA 409PC differential thermal analyzer. Fluorescence spectra were characterized at room temperature by an F-4500 fluorescence spectrophotometer. X-ray powder diffraction (PXRD) measurements were recorded on a PANalytical X'pert PRO X-ray diffractometer.

2.2. Preparation of [Mn(*o*-CPhH$_2$IDC)(H$_2$O)$_2$]$_n$ (**1**)

A mixture of MnCl$_2$·4H$_2$O (19.8 mg, 0.1 mmol), *o*-CPhH$_4$IDC (27.6 mg, 0.1 mmol), CH$_3$CN/H$_2$O (3/4, 7 mL) and Et$_3$N (0.042 mL, 0.3 mmol) was sealed in a 25 mL Teflon-lined bomb and heated at 150 °C for 72 h. The reaction mixture was then allowed to cool to room temperature at a rate of 10 °C/h. Colorless flake-shaped crystals of **1** were collected, washed with distilled water and dried in air (67% yield based on Mn). *Anal.* Calc. for C$_{12}$H$_{10}$N$_2$O$_8$Mn: C, 39.43; H, 2.74; N, 7.67. Found: C, 39.40; H, 2.59; N, 7.58%. IR (cm^{-1}, KBr): 3415 (m), 1624 (m), 1384 (m), 1288 (s), 1222 (w), 1089 (w), 954 (m), 864 (m), 847 (s), 790 (w), 777 (m), 728 (s), 699 (m), 673 (s), 634(m), 570 (s), 437 (m).

2.3. Preparation of [Mn$_3$(*m*-CPhHIDC)$_2$(phen)$_2$]$_n$ (**2**)

A mixture of MnCl$_2$·4H$_2$O (19.8 mg, 0.1 mmol), *m*-CPhH$_4$IDC (27.6 mg, 0.1 mmol), phen (19.8 mg, 0.1 mmol), CH$_3$OH/H$_2$O (3/4, 7 mL) and Et$_3$N (0.084 mL, 0.6 mmol) was sealed in a 25 mL Teflon-lined bomb and heated at 150 °C for 96 h, and then cooled to room temperature. Colorless cubic crystals of **2** were isolated, washed with distilled water and dried in air (59% yield based on Mn). *Anal.* Calc. for C$_{48}$H$_{26}$N$_8$O$_{12}$Mn$_3$: C, 53.75; H, 2.43; N, 10.45. Found: 53.92; H, 2.61; N, 10.35%. IR (cm^{-1}, KBr): 3438 (m), 3075 (m), 1927 (w), 1590 (m), 1549 (m), 1471 (w), 1426 (w), 1382 (m), 1264 (m), 1222 (w), 1044 (w), 990 (m), 837 (s), 793 (s), 726 (s), 660 (w), 639 (m), 540 (m).

2.4. Preparation of {[Mn$_3$(*o*-CPhHIDC)$_2$(phen)$_3$]·H$_2$O}$_n$ (**3**)

A mixture of MnCl$_2$·4H$_2$O (19.8 mg, 0.1 mmol), *o*-CPhH$_4$IDC (27.6 mg, 0.1 mmol), phen (19.8 mg, 0.1 mmol), CH$_3$CH$_2$OH/H$_2$O (4/3, 7 mL) and Et$_3$N (0.056 mL, 0.4 mmol) was sealed in a 25 mL Teflon-lined bomb and heated at 160 °C for 96 h. The reaction mixture was then allowed to cool to room temperature at a rate of 10 °C/h. Light yellow crystals of **3** were collected, washed with distilled water and dried in air (72% yield based on Mn). *Anal.* Calc. for C$_{60}$H$_{36}$N$_{10}$O$_{13}$Mn$_3$: C, 56.70; H, 2.84; N, 11.03. Found: C, 56.92; H, 2.69; N, 11.22%. IR (cm^{-1}, KBr): 3446 (s), 3069 (m), 1942 (w), 1564 (m), 1515 (w), 1478 (w), 1422 (m), 1269 (s), 1140 (s), 1101 (m), 953 (m), 865 (m), 846 (s), 793 (w), 776 (w), 768 (m), 742 (w), 728 (s), 638 (s), 543 (m), 480 (m).

2.5. Preparation of {[Mn$_3$(*o*-CPhHIDC)$_2$(2,2′-bipy)$_3$]·(2,2′-bipy)$_{0.5}$}$_n$ (**4**)

A mixture of MnCl$_2$·4H$_2$O (19.8 mg, 0.1 mmol), *o*-CPhH$_4$IDC (27.6 mg, 0.1 mmol), 2,2′-bipy (15.6 mg, 0.1 mmol), H$_2$O (7 mL) and Et$_3$N (0.056 mL, 0.4 mmol) were sealed in a 25 mL Teflon-lined bomb and heated at 160 °C for 96 h. The reaction mixture was then allowed to cool to room temperature at a rate of 10 °C/h. Colorless crystals of **4** were collected, washed with distilled water and dried in air (58% yield based on Mn). *Anal.* Calc. for C$_{59}$H$_{38}$N$_{11}$O$_{12}$Mn$_3$: C, 56.29; H, 3.02; N, 12.24. Found: C, 56.52; H, 2.96; N, 12.22%. IR (cm^{-1}, KBr): 3424 (m), 3107 (w), 3073 (m), 1939 (w), 1560 (m), 1473 (m), 1362 (m), 1313 (m), 1269 (s), 1151 (m), 1092 (m), 1059 (s), 1016 (s), 951 (m), 856 (s), 794 (m), 778 (s), 539 (s), 480 (s), 430 (m).

2.6. Crystal structure determinations

Single-crystal data for **1**–**4** were obtained on a Bruker smart APEXII CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). All data were collected at room temperature using the ω–2θ scan technique and corrected for Lorenz-polarization effects. Furthermore, a correction for secondary extinction was applied.

The four structures were solved by direct methods and expanded using the Fourier technique. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included but not refined. The final cycle of full-matrix least squares refinement was based on 3047 observed reflections and 242 variable parameters for **1**, 7366 observed reflections and 894 variable parameters for **2**, 13479 observed reflections and 778 variable parameters for **3**, 12673 observed reflections and 826 variable parameters for **4**, All calculations were performed using the SHELX-97 crystallographic software package [7]. The crystallographic data of the four complexes are given in Table 1. Selected bond lengths and angles are listed in Table 2.

3. Results and discussion

3.1. Synthesis

Previously, we have obtained useful information on the *o*-carboxylphenyl and *m*-carboxylphenyl effect in *o*-CPhH$_4$IDC and *m*-CPhH$_4$IDC ligands by theoretical calculations [6]. The optimized geometry and natural bond orbital (NBO) charge distributions of *o*-CPhH$_4$IDC and *m*-CPhH$_4$IDC have been calculated at the B3LYP/6-311 ++G(d, p) level [8]. Clearly, it is to be pointed out that the introduced carboxylate group in the ligands *o*-CPhH$_4$IDC and *m*-CPhH$_4$IDC exhibit a strong coordination ability and also can show various coordination modes. It is interesting to compare the coordination modes of the *o*-CPhH$_{4\text{-}n}$IDC^{n-} and *m*-CPhH$_{4-n}$IDC^{n-} species in **1**–**4**. In **1**, two hydrogen atoms of imidazole COO-*H* and phenyl COO-*H* are removed from the ligand *o*-CPhH$_4$IDC to form the *o*-CPhH$_2$IDC^{2-} unit, which connects Mn ions in the mode μ_3-*k*N,O:*k*O:*k*O′ (Scheme 1a), while three hydrogen atoms of one imidazole COO-*H*, one phenyl COO-*H* and one imidazole-*H* are triply deprotonated in **3** and **4**, leading to *o*-CPhHIDC^{3-} (Scheme 1d and e). The hydrogen atoms are triply deprotonated in **2** leading to the *m*-CPhHIDC^{3-} unit and showing two kinds of coordination modes (Scheme 1b and c). These findings further confirm our previous views about the coordination ability of *o*-CPhH$_4$IDC and *m*-CPhH$_4$IDC, that they can afford various coordination modes to meet the coordination requirements of