Available online at www.sciencedirect.com
SCIENCE DIRECT®
Solid State Sciences 7 (2005) 969–982
Solid State Sciences
www.elsevier.com/locate/ssscie

Synthesis, structure and properties of Mn(II), Zn(II), Ag(I) and Cu(II) complexes with 1,3-bis(imidazole-1-ylmethyl)-5-methylbenzene

Bin Sui [a], Jian Fan [a], Taka-aki Okamura [b], Wei-Yin Sun [a,*], Norikazu Ueyama [b]

[a] *Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China*
[b] *Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan*

Received 7 July 2004; accepted 2 November 2004

Available online 22 April 2005

Abstract

Two coordination polymers with M_2L_2 type metallocyclic rings $[Mn(dimb)_2(NCS)_2]_n$ (**1**) and $[Mn(dimb)_2(N_3)_2]_n$ (**2**) were synthesized by reactions of bidentate ligand containing imidazole donors, namely 1,3-bis(imidazol-1-ylmethyl)-5-methylbenzene (dimb), with the manganese(II) salts. While the bimb ligand reacts with $Zn(NO_3)_2{\cdot}6H_2O$ and NaN_3 or $AgClO_4$, complexes $[Zn(dimb)_2(N_3)_2]_n$ (**3**) and $\{[Ag(dimb)]ClO_4\}_n$ (**4**) with one-dimensional chain structure were obtained. When the ligand dimb reacted with $Cu(NO_3)_2{\cdot}3H_2O$, a two-dimensional network $\{[Cu(dimb)_2(H_2O)_2](NO_3)_2\}_n$ (**5**) was achieved, in which the metal atoms had octahedral coordination geometry. The structures of these coordination complexes were determined by X-ray crystallography and the results revealed that both coordination geometry of metal atoms and conformation of ligand have great impacts on the structure of the supramolecular architectures. Magnetic properties of Mn(II) complexes were also investigated.

Keywords: Assembly; Coordination polymers; Crystal structure; Magnetic property

1. Introduction

In the recent years, there are great interests in the study of coordination polymers with network structures due to their possible chemical and physical properties [1]. However, the self-assembly of metal-organic frameworks (MOFs) is highly influenced by factors such as solvent [2], template[3,4], pH of solution [4], geometric requirements of metal ions and counter ions [5]. Therefore, much more works are required to extend the knowledge of the relevant structural types and established proper synthetic strategies leading to the desired species with predicted structures and properties. In the past several years, extensive works have been carried out by using rigid bridging ligands such as 4,4′-bipyridine, 2,4,6-tri(4-pyridyl)-1,3,5-triazine, etc., and a variety of 1D, 2D and 3D frameworks with novel structures and inclusion behaviors have been obtained [6,7].

On the other hand, bridging ligands with flexible spacers have not been extensively exploited except for some limited cases [8]. Comparing to the well development on the pyridyl-based bridging ligands, efforts on imidazole-based bidentate bridging ligands are rare. In our previous studies, we designed and synthesized a novel bidentate flexible ligand 1,3-bis(imidazol-1-ylmethyl)-5-methylbenzene (dimb) and obtained a 1D chain coordination polymer by reaction of dimb with $[Cu(dien)(im)](ClO_4)_2$ (dien = diethylenetriamine; im = imidazole) [9] and a 2D coordination polymer $\{[Cd(dimb)_2(MeOH)_2](ClO_4)_2\}_n$ [10] produced by reaction of dimb with cadmium(II) perchlorate hexahydrate. We herein report the syntheses, crystal structures of four 1D chain coordination polymers and one 2D corrugated coordination polymer obtained by reaction of the metal salts with dimb ligand. The results show that counter anions, geometric needs of metal atoms and conformation of the ligand

* Corresponding author. Tel.: +86-25-83593485; Fax: +86-25-83314502.
E-mail address: sunwy@nju.edu.cn (W.-Y. Sun).

1293-2558/$ – see front matter
doi:10.1016/j.solidstatesciences.2004.11.005

have significant impact on the structure of MOFs in this system.

2. Experimental

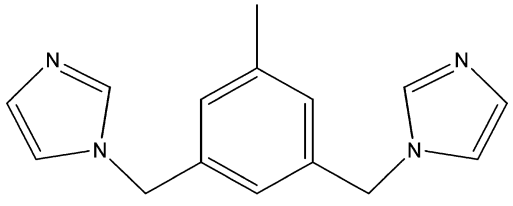
2.1. General information and materials

Ligand 1,3-bis(imidazol-1-ylmethyl)-5-methylbenzene dimb, Scheme 1 was prepared according to the literature [9]. All chemicals were of reagent grade quality obtained from commercial sources and used as received without further purification. The C, H and N analyses were carried out on a Perkin–Elmer 240C element analyzer at the analysis center of Nanjing University. IR spectra (KBr pellets) were measured on a Bruker Vector22 FT-IR. Magnetic measurements on polycrystalline samples of complexes **1** and **2** were carried out by using a SQUID susceptometer (Quantum Design, MPMS-5) in the temperature range of 2–300 K with an applied field of 2000 G. All data have been corrected for diamagnetism by using Pascal's constants.

2.2. Syntheses of complexes

$[Mn(dimb)_2(NCS)_2]_n$ **1**. Complex **1** was synthesized by the laying method. A solution of dimb (25.2 mg, 0.1 mmol) in methanol (5 ml) was carefully layered over a solution of $MnSO_4$ (15.1 mg, 0.1 mmol) and KSCN (19.4 mg, 0.2 mmol) in water (5 ml). Single crystals of $[Mn(dimb)_2(NCS)_2]_n$ suitable for X-ray analysis were obtained as colorless blocks at room temperature for several days. Yield: 65%. Anal. calc. for $C_{32}H_{32}N_{10}MnS_2$: C, 56.88; H, 4.77; N, 20.73%. Found: C, 56.85; H, 4.84; N, 20.59%. IR (KBr, cm^{-1}): 3441m, 3101m, 2070vs, 1607m, 1518s, 1233s, 1106s, 1088s, 932m, 838m, 741s, 662s.

$[Mn(dimb)_2(N_3)_2]_n$ **2**. The synthesis was carried out using the same method as in **1** by using $MnCl_2{\cdot}4H_2O$ (19.8 mg 0.1 mmol) and sodium azide (NaN_3) (13.0 mg, 0.2 mmol), instead of $MnSO_4$ and KSCN. After several days single crystals suitable for X-ray analysis were collected. Yield: 50%. Anal. calc. for $C_{30}H_{32}N_{14}Mn$: C, 55.98; H, 5.18; N, 30.47%. Found: C, 55.90; H, 5.18; N, 30.22%. IR (KBr, cm^{-1}): 3441w, 3349m, 3120m, 3107m, 2039vs, 1605m, 1515s, 1449m, 1241s, 1112m, 1091m, 931m, 754m, 739m, 666m, 659m.



dimb

Scheme 1.

$[Zn(dimb)_2(N_3)_2]_n$ **3**. An acetonitrile (5 ml) solution of dimb (25.2 mg, 0.1 mmol) was carefully layered over a solution of $Zn(NO_3)_2{\cdot}6H_2O$ (29.7 mg, 0.1 mmol) and NaN_3 (13.0 mg, 0.2 mmol) in water (5 ml). Colorless crystals were isolated in 56% yield by filtration after several days at room temperature. Anal. calc. for $C_{15}H_{16}N_{10}Zn$: C, 44.85; H, 4.01; N, 34.86%. Found: C, 44.60; H, 4.12; N, 34.62%. IR (KBr, cm^{-1}): 3376m, 3143m, 3121m, 2090vs, 2061vs, 1606m, 1521s 1443m, 1333m, 1285m, 1108s, 1094s, 951m, 834m, 744s, 656s, 639m.

$\{[Ag(dimb)]ClO_4\}_n$ **4**. A methanol solution (5 ml) of dimb (25.2 mg, 0.1 mmol) was carefully layered over an aqueous solution (5 ml) of $AgClO_4$ (20.7 mg, 0.1 mmol). Colorless crystals were appeared within one week at 4 °C. Yield: 63%. Anal. calc. for $C_{15}H_{16}AgClN_4O_4$: C, 39.20; H, 3.51; N, 12.19%. Found: C, 39.48: H, 3.69; N, 12.15%. IR (KBr, cm^{-1}): 3447w, 3123m, 1607m, 1519s, 1441m, 1287m, 1237s, 1117vs, 1080vs, 950m, 830m, 745s, 653m, 621s.

$\{[Cu(dimb)_2(OH_2)_2](NO_3)_2\}_n$ **5**. A methanol solution (5 ml) of dimb (25.2 mg, 0.1 mmol) was carefully putted over an aqueous solution (5 ml) of $Cu(NO_3)_2{\cdot}3H_2O$ (24.1 mg, 0.1 mmol). Light blue crystals were obtained after several days. Yield: 70%. Anal. calc. for $C_{30}H_{36}CuN_{10}O_8$: C, 49.48; H, 4.98; N, 19.23%. Found: C, 49.53; H, 4.78; N, 19.14%. IR (KBr cm^{-1}): 3425s, 3115m, 1606m, 1524s, 1384vs, 1245m, 1108s, 1097s, 747s, 657m.

2.3. Single crystal structure determination

Single crystal suitable for X-ray determination was mounted and data collection was carried on a Rigaku RAXIS-RAPID Imaging Plate diffractometer at 200 K, using graphite-monochromated Mo-K radiation (λ = 0.71069 Å). The structures were solved by direct method using SIR92 [11], and expanded using Fourier techniques [12]. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. The hydrogen atoms were generated geometrically. All calculations were carried out on a SGI workstation using the teXsan crystallographic software package of Molecular Structure Corporation [13]. Details of the crystal parameters, data collection and refinement for the compound are summarized in Table 1, and selected bond lengths and angles with their estimated standard deviations are listed in Table 2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-243904 (**1**), CCDC-243905 (**2**), CCDC-243906 (**3**), CCDC-243907 (**4**) and CCDC-243908 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).