Synthesis and Crystal Structure of a Mn(II) Metal-Organic Framework Based on a Polydentate Schiff Base Ligand

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A Mn(II) metal-organic framework \([MnL_2(NCS)_2](H_2O)_4\) (1) with \(L = \text{bis(pyridin-3-yl-methylene)} \text{biphenyl-2,2}'\text{-dicarbohydrazide}\) has been synthesized and characterized by IR spectroscopy, elemental analysis, UV spectroscopy, thermogravimetric (TG) analysis, powder X-ray diffraction, and single-crystal X-ray structure determination. The Mn(II) atom has a distorted octahedral coordination environment with an N\(_6\) donor set from four ligands and two NCS\(^-\) anions. The structure of 1 exhibits a layer framework containing tetranuclear metallacyclic ring units \([\text{Mn}^{\text{II}}_4L_4]\) in the chair conformation. In addition, there are multiform O–H···O, C–H···O, N–H···O, and C–H···N hydrogen bonds and C–H···π interactions in a three-dimensional supramolecular network.

Key words: Manganese(II), Metal-Organic Framework, Schiff Base, Crystal Structure

Introduction

Recently, much interest in self-assembly of metal-organic frameworks (MOFs) with intriguing topologies has grown rapidly owing to their potential applications in catalysis, molecular adsorption, magnetism, optical devices and molecular sensors [1 – 3]. In particular, the incorporation of Mn(II) into metal-organic frameworks has received increasing attention in the fields of supramolecular chemistry and crystal engineering for the remarkable performances of the products in magnetic systems, catalysis and biochemistry [4, 5]. Generally, the syntheses of MOFs are based on a self-assembly of organic ligands and metal ions or clusters, counterions, and solvent systems [6, 7]. Among them, the design of organic ligands is the most important element for assembling MOFs with novel topologies. Neutral, rigid N-donor ligands have been widely used to construct MOFs along with various anionic species to balance the electrostatic equilibrium of the networks [8 – 11]. Biphenyl-based Schiff base ligands are one type of ligands to assemble different structural frameworks [12 – 15], such as helical structures imposed by constrained rotation around the C-C bond of these otherwise flexible ligands [16, 17]. Consequently, the ligands with a twist conformation could be used as potential helical building blocks to synthesize frameworks with corresponding architectures [18 – 21]. In comparison with previously reported ligands like \(N',N'\text{-bis[1-(pyridin-4-yl)methylidene]}\text{benzyl dihydrazone (L\(^1\))}\) and \(N',N'\text{-bis[1-(pyridin-3-yl)methylidene]}\text{benzyl dihydrazone (L\(^2\))}\) [14], the ligand \(\text{bis(pyridin-3-yl-methylene)}\text{biphenyl-2,2}'\text{-dicarbohydrazide (L)}\) selected here not only possesses a longer spacer to separate the two pyridyl binding sites, but also may link metal ions via additional donor sites, viz. two pyridyl N donors, two imine N donors, two amine N donors and two carbonyl O donors, to generate multidimensional frameworks [22]. In addition, the linear triatomic pseudohalide SCN\(^-\) is a frequently used anionic auxiliary ligand, which can coordinate through either the S or N atom to a metal center [23 – 28]. In the present paper, through the assembly of the biphenyl-based Schiff base ligand L, the SCN\(^-\) anion and the Mn(II) cation, a two-dimensional MOF \([\text{MnL}_2(NCS)_2](H_2O)_4\)_\(n\) (1) was synthesized and characterized especially by single-crystal X-ray diffraction analysis.

Experimental Section

General

Materials: All chemicals were of reagent grade quality obtained from commercial sources and used without further
purification. Ligand L was synthesized and characterized by a previously reported procedure [22].

**Instrumentation:** Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240C analytical instrument. IR spectra were recorded from KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the 4000 – 400 cm\(^{-1}\) region. The UV/Vis spectrum was measured in H\(_2\)O solution with a Hitachi U-4100 spectrophotometer. Powder X-ray diffraction patterns were recorded from KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the 4000 – 400 cm\(^{-1}\) region. The thermogravimetric analysis (TGA) of coordination polymer 1 was carried out under nitrogen on a Perkin-Elmer-7 thermal analyzer at a heating rate of 10 °C min\(^{-1}\) from 25 to 700 °C.

**Synthesis**

10 mL of an acetonitrile solution of MnCl\(_2\)-4H\(_2\)O (59 mg, 0.3 mmol) and 2 mL of an aqueous solution of KSCN (90 mg, 0.9 mmol) were mixed; the solution was filtered and added to 10 mL of a methanol solution of L (45 mg, 0.1 mmol). The excess of manganese salts used here was used to improve the yield based on the ligand. The resulting mixture was stirred for 0.5 h and left to slowly evaporate at room temperature to obtain yellow block-shaped crystals suitable for single-crystal X-ray diffraction. The bulk samples were further purified by recrystallization from acetonitrile-methanol. The total yield was 60% (34 mg) based on ligand L. Anal. for C\(_{36}\)H\(_{48}\)MnN\(_{14}\)O\(_{8}\)S\(_{2}\): calcd. C 56.89, H 4.24, N 17.20; found C 57.10, H 4.17, N 17.25.

**X-Ray crystallographic study**

A suitable single crystal of size 0.34 \times 0.23 \times 0.10 mm\(^3\) was chosen for the crystallographic study and then mounted on a Bruker Smart APEX II CCD diffractometer with omega and phi-scan mode in the range of 1.91 \leq \theta \leq 25.00'. All diffraction measurements were performed at room temperature using graphite-monochromatized MoK\(_\alpha\) radiation (\(\lambda = 0.71073\) Å). The structure was solved by Direct Methods and refined on \(F^2\) by using full-matrix least-squares methods with SHELXS/L-97 [29, 30]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques. All hydrogen atoms were geometrically fixed to allow riding on the parent atoms to which they are attached, except those disordered hydrogen atoms which were added to the molecular formula according to the electroneutrality principle. To assist the refinement, the water oxygen atom O2W was taken as rotationally disordered over three orientations in the refined ratio 0.5 : 0.25 : 0.25. Space group, lattice parameters and other relevant information are listed in Table 1, and selected bond lengths and angles are given in Table 2.

**Results and Discussion**

**IR and UV/Vis spectra**

In the IR spectrum of polymer 1, the absorption bands at 1652 and 1613 cm\(^{-1}\) are assigned to...
the C=O and C=N group, respectively, which are shifted slightly to higher wavenumbers compared with L (1651 and 1593 cm\(^{-1}\)). The sharp and strong absorption band at 2053 cm\(^{-1}\) should be attributed to ν(\(\text{SCN}\)), indicating nitrogen coordination of the NCS\(^-\)group [31–34]. These assignments were finally confirmed by X-ray crystallography (see below). The UV spectrum of 1 in aqueous solution displays two absorption peaks at 196 and 284 nm, respectively, which can be assigned to the \(\pi-\pi^*\) and \(n-\pi^*\) transitions of ligand.

**Crystal and molecular structure**

In the solid state the title compound forms a 2D coordination polymer. The asymmetric unit consists of one half Mn(II) atom which lies on an inversion center, one ligand L, one NCS\(^-\)ion and two H\(_2\)O molecules. As shown in Fig. 1, the coordination sphere around the manganese atom is distorted octahedral made up of four \(N_{\text{pyridyl}}\) donor atoms from four ligands and two N\(_{\text{NCS}}\) donor atoms. The axial Mn(II)–N\(_{\text{NCS}}\) bond length of 2.169(3) Å is shorter than the equatorial Mn(II)–N\(_{\text{pyridyl}}\) distances of 2.303(3) and 2.319(3) Å. Through two \(N_{\text{pyridyl}}\) donors the bidentate ligand bridges two Mn(II) centers with a separation of 16.121(2) Å for Mn(1)···Mn(1D) (symmetry code: D: \(x, y + 1, -z\); E: \(-x + 1, y - 1/2, -z - 1/2\); F: \(-x + 1, y + 1/2, -z - 1/2\)). These H\(_2\)O molecules are tightly fitted into the large macrocycles through multiform hydrogen bonds. As shown in Fig. 2, one large macrocycle \([\text{Mn}^{III}_{4}\text{L}_4]\) is in the chair conformation with one large Mn–Mn separation of 29.733(3) Å and one shorter Mn–Mn separation of 12.472(2) Å (Fig. 2). Compared to the similar tetranuclear metallacyclic structure in \([\text{ZnL}_{1.2}(\text{NCS})_2\text{H}_2\text{C}_2\text{N}]_n\) (L\(_1\) = \(N',N'-\text{bis[1-(pyridin-4-yl)methylidene]benzyl dihydrazone}\)), the separations of metal centers in four zeniths of the metallacycle \([\text{Mn}^{III}_{4}\text{L}_4]\) are longer owing to the longer spacer in L [20]. These macrometallacyclic units are further extended to form a layer network. In the solid state, H\(_2\)O molecules are tightly fitted into the tetranuclear metallacyclic rings through multiform O–H···O, C–H···O and N–H···O hydrogen bonds (Table 3). These H\(_2\)O molecules also link adjacent sheets by O(1W)–H(1WA)···O(1) hydrogen bonds forming a 3D supramolecular structure (Fig. 3).

It is worth pointing out that polymer 1 contains infinite \(2_1\) helical chains through the bridging of Mn(II) centers by the helical ligands. The helical pitch, given by one full rotation around the \(2_1\) helical axis, is 12.472(2) Å (the unit cell length along the crystallographic \(b\) axis). The axis of the helix runs at \((0, y, 1/4)\). Complex 1 crystallizes in the centrosymmetric space group \(P2_1/\text{c}\), and the metal ion occupies the crystallographic inversion center. Consequently, one \(P\) helicate and one \(M\) helicate are alternating in the layers (Fig. 4). The dihedral angle between two benzene rings of the twisted ligand is 74.4(2)\(^o\). The torsion angles about C(7)–N(3)–N(4)–C(8) and C(21)–N(5)–N(6)–C(22) bonds are 172.6(6) and 171.7(6)\(^o\), respectively. Two types of C(2)–H(2A)···N(3) and N(4)–H(4B)···O(2) intramolecular hydrogen bonds are found in the ligand, especially N(4)–H(4B)···O(2) from two arms of one ligand stabilizing the helical structure.

In addition, there is a C–H···N hydrogen bond between C(27) of the pyridyl ring and N(1) of the NCS\(^-\)
Table 3. Hydrogen bond interactions (Å and deg) of the title compound.

<table>
<thead>
<tr>
<th>D-H···A</th>
<th>d(D-H)</th>
<th>d(H···A)</th>
<th>d(D···A)</th>
<th>∠(DHA)</th>
<th>Symm. codes of atom A</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1W)-H(1WA)···O(1)</td>
<td>0.85</td>
<td>2.56</td>
<td>3.392(5)</td>
<td>165</td>
<td>-x, 1/2+y, -1/2-z</td>
</tr>
<tr>
<td>O(1W)-H(1WB)···O(2W)</td>
<td>0.85</td>
<td>2.11</td>
<td>2.911(7)</td>
<td>157</td>
<td>1-x, -y, -z</td>
</tr>
<tr>
<td>O(1W)-H(1WB)···O(1)</td>
<td>0.85</td>
<td>2.43</td>
<td>2.957(5)</td>
<td>121</td>
<td>1-x, -y, -z</td>
</tr>
<tr>
<td>N(4)-H(4B)···O(2)</td>
<td>0.86</td>
<td>2.01</td>
<td>2.845(3)</td>
<td>164</td>
<td>x, 1/2-y, -1/2+z</td>
</tr>
<tr>
<td>N(5)-H(5B)···O(1W)</td>
<td>0.86</td>
<td>2.22</td>
<td>3.065(5)</td>
<td>168</td>
<td>1-x, 1-y, -z</td>
</tr>
<tr>
<td>C(2)-H(2A)···N(3)</td>
<td>0.93</td>
<td>2.55</td>
<td>2.863(4)</td>
<td>100</td>
<td>x, 1/2+y, -1/2-z</td>
</tr>
<tr>
<td>C(4)-H(4A)···O(1W)</td>
<td>0.93</td>
<td>2.54</td>
<td>3.464(5)</td>
<td>173</td>
<td>1-x, 1-y, -z</td>
</tr>
<tr>
<td>N(1)-H(1W)···O(2)</td>
<td>0.93</td>
<td>2.57</td>
<td>3.391(7)</td>
<td>147</td>
<td>1-x, -y, -z</td>
</tr>
<tr>
<td>C(27)-H(27A)···N(1)</td>
<td>0.93</td>
<td>2.61</td>
<td>3.199(5)</td>
<td>122</td>
<td>1-x, 1/2+y, -1/2-z</td>
</tr>
</tbody>
</table>

Thermogravimetric analysis

Thermogravimetric experiments were conducted to examine the thermal stability of the metal-organic compound. The curve of 1 suggests that the weight loss in the range from 36 to 115 °C is 6.22%, corre-
Fig. 5. The powder X-ray diffraction pattern calculated from the single-crystal data (top) and that obtained from the experiment (bottom) for 1.

Corresponding to the loss of four H$_2$O molecules (calcd. 6.32\% (Fig. 6), which is in agreement with the formula $\{[\text{MnL}_2(\text{NCS})_2](\text{H}_2\text{O})_x]\}_n$ with $x = 4$ proposed above. Two ligands and two NCS$^-$ anions are lost in a continuous fashion above 212 °C, and the decomposition of the framework backbone is still progressing even at the upper limit of measurement range.

Conclusions

In summary, we have presented a 2D coordination polymer $\{[\text{MnL}_2(\text{NCS})_2](\text{H}_2\text{O})_4]\}_n$ (1) based on the Schiff base ligand bis(pyridin-3-ylmethylene)biphenyl-2,2′-dicarbonyldrazide (L). The crystal and molecular structure of 1 has been determined on single crystals. The complex was also characterized by IR spectroscopy, UV spectroscopy, PXRD and thermogravimetric (TG) analysis. The polymer shows a layer containing two types of $2_1$ helical chains (P and M helices) formed by the bridging interactions of the twisted ligands with the Mn(II) centers.

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