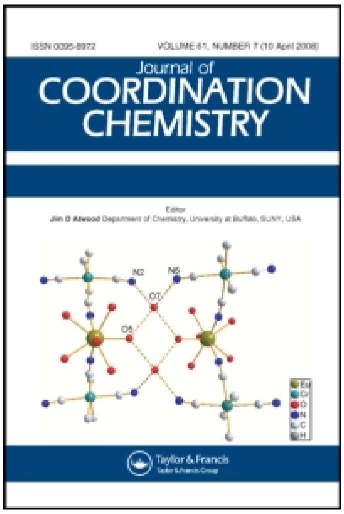

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# Synthesis, structure, spectroscopic properties, and thermal analyses of a manganese(II) complex containing oxalate, azide anion, and 1,10-phenanthroline

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# Synthesis, structure, spectroscopic properties, and thermal analyses of a manganese(II) complex containing oxalate, azide anion, and 1,10-phenanthroline

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One new metal-organic framework $[Mn(N_3)(ox)_{0.5}(phen)]_n \cdot 2H_2O$ (**1**) (ox = oxalate, $N_3^-$ = azido anion, phen = 1,10-phenanthroline) has been prepared and isolated under hydrothermal conditions. The complex has been fully characterized by elemental analysis, IR, UV-spectrum, TGA, and single-crystal X-ray diffraction. In **1** the $Mn^{2+}$ ions are linked by bridging azides and ox groups to form the zigzag Mn–$(N_3)$–Mn–ox–Mn. Zigzag chains in two directions generate a 2-D supramolecular network, stabilized by $\pi$–$\pi$ interactions between the phen ligands. IR spectra suggest that azido is an end-on bridging ligand. The thermal analysis confirms the high stability of the material, due to the infinite metal–$N_3$–metal–ox–metal arrays.

*Keywords*: Coordination polymer; Crystal structure; Infrared spectra; UV-spectrum; Supramolecular network

## 1. Introduction

Design and synthesis of functional metal-organic frameworks with potential applications in catalysis, adsorption, or separation have received much attention [1–3]. Remarkable progress has been made, but it is still difficult to prepare metal-organic frameworks with predictable topologies [4], although some fundamental aspects of coordination chemistry such as the nature, oxidation state, and coordination preference of the metal center or the relative flexibility of the organic linker can nonetheless be utilized to direct the product architecture [5]. Coordination polymers can be designed by interaction of metal ions with bridging organic ligands [6]. The azido group $N_3^-$ attracted attention because the azido anion can behave as a bidentate bridging ligand (end-on or end-to-end [7–12]) and as a tridentate bridging ligand ($\mu_{1,1,1\text{-N3}}$ [13, 14] or $\mu_{1,1,3\text{-N3}}$ [15, 16]). Both the coordinations can mediate ferromagnetic and antiferromagnetic interactions between metallic ions [17–19]. A common strategy for design of high dimensional frameworks is to incorporate a second bridging ligand with metal-azido complexes. Most second ligands are neutral organic ligands, since negatively

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charged ligands are difficult to coexist with azide due to competition in self-assembly [20]. Versatility of azido generates a variety of magnetic behaviors, difficult to achieve with other bridging ligands [21]. Recently, we extended our investigation to the complexes containing azide and carboxylate bridges. Herein we report the synthesis and crystal structure of one new compound based on azide, oxalate, and phen $[Mn(N_3)(ox)_{0.5}(phen)]_n \cdot 2H_2O$ (**1**).

## 2. Experimental

### 2.1. *Materials and physical measurements*

All chemicals used are of reagent grade and used without purification. Infrared spectra (IR) were recorded on a BRUKER EQUINOX-55 spectrophotometer from 400–4000 $cm^{-1}$ using the samples prepared as KBr pellets. Elemental analyses were performed on a Perkin-Elmer 2400 element analyzer. The UV-Vis spectra were determined in distilled water ($1.0 \times 10^{-4}$ M) using a Hitachi UV-3310 Spectrometer with 1 cm quartz cell in the range 200–800 nm. TG analyses were performed on a Netzsch STA 449C microanalyzer under nitrogen at a heating rate of 20°C $min^{-1}$. Powder X-ray diffraction (PXRD) intensity for **1** was measured at room temperature on a Mac Scienc M18XHF22-SRA (Cu-K$\alpha$ $\lambda = 1.54056$ Å). The crushed single-crystalline powder sample was prepared by crushing crystals and scanned from 5° to 50° with steps of 0.12° $s^{-1}$.

### 2.2. *Synthesis of 1*

A mixture of sodium oxalate (0.25 mmol), sodium azide (0.5 mmol), 1,10-phenanthroline (1 mmol), $Mn(OAc)_2 \cdot 4H_2O$ (1 mmol) and 8 mL ethanol was placed in a 23 mL Teflon liner stainless steel reactor. The vessel was heated to 120°C for 3 days, then cooled at 5°C $h^{-1}$ to room temperature. Light-yellow crystals were collected by filtration. Anal. Calcd for $C_{26}H_{16}Mn_2N_{10}O_7$: C, 45.24; H, 2.34; N, 20.29. Found: C, 46.37; H, 2.43; N, 20.06. The experimental PXRD pattern agreed with the calculated one generated from single-crystal analyses for **1**, suggesting phase purity of the products (figure S1).

### 2.3. *X-ray crystallography*

Suitable single crystal of **1** was mounted on a Rigaku R-axis Spider II diffractometer equipped with graphite-monochromated Mo-K$\alpha$ ($\lambda = 0.71073$ Å) radiation. Empirical absorption corrections were applied. The unit cell parameters were determined by least squares refinements of all reflections. The structure was solved by direct methods and refined by full-matrix least squares on $F^2$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from the difference map and then added geometrically. All calculations were performed using the *SHELXTL*-97 program package [22–24]. Crystal data and experimental details for **1** are contained in table 1. Selected bond distances and angles are listed in table 2.

Table 1. Crystallographic data and processing parameters.

| | |
|---|---|
| Empirical formula | $C_{26}H_{16}Mn_2N_{10}O_7$ |
| Formula mass | 696.42 |
| System | Triclinic |
| Space group | $P\bar{1}$ |
| Crystal size (mm) | 0.35 × 0.29 × 0.09 |
| Unit cell dimensions (Å, °) | |
| $a$ | 7.9167(6) |
| $b$ | 9.7419(7) |
| $c$ | 10.6027(7) |
| $a$ | 108.077(2) |
| $\beta$ | 98.405(2) |
| $\gamma$ | 107.605(2) |
| Volume (Å$^3$) | 714.48(9) |
| Density (Calcd) (g cm$^{-3}$) | 1.619 |
| $\theta$ range for data collection (°) | 3.02 to 27.48 |
| Reflections collected | 7082 |
| Independent reflections | 3263 |
| Goodness-of-fit on $F^2$ | 1.098 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0411$, $\omega R_2 = 0.1341$ |
| $R$ indices (all data) | $R_1 = 0.0452$, $\omega R_2 = 0.1279$ |
| Parameters | 209 |

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

| | | | |
|---|---|---|---|
| Mn–N(3$^i$) | 2.174(2) | Mn–N(2) | 2.230(2) |
| Mn–O(2$^{ii}$) | 2.1842(17) | Mn–N(1) | 2.266(2) |
| Mn–O(1) | 2.2054(17) | Mn–N(3) | 2.222(2) |
| Mn$^{ii}$–O(2) | 2.1842(17) | Mn$^i$–N(3) | 2.174(2) |
| N(3$^i$)–Mn–O(2$^{ii}$) | 94.47(7) | N(3$^i$)–Mn–O(1) | 163.99(7) |
| O(2$^{ii}$)–Mn–O(1) | 75.32(6) | N(3$^i$)–Mn–N(3) | 81.44(9) |
| N(2)–Mn–N(1) | 74.04(7) | N(3$^i$)–Mn–N(1) | 98.33(8) |
| N(3)–Mn–N(1) | 171.02(8) | N(3)–Mn–N(2) | 97.23(8) |
| O(1)–Mn–N(1) | 93.99(7) | O(1)–Mn–N(2) | 89.67(7) |
| O(2$^{ii}$)–Mn–N(1) | 89.78(7) | O(2$^{ii}$)–Mn–N(2) | 157.24(7) |
| N(3$^i$)–Mn–N(2) | 103.49(8) | O(1)–Mn–N(3) | 87.97(7) |
| O(2$^{ii}$)–Mn–N(3) | 99.19(7) | Mn$^i$–N(3)–Mn | 98.56(9) |

Symmetry codes: (i): 0z, 0, 0; (ii): 0, 0, 0.

## 3. Results and discussion

### 3.1. *Structural description of 1*

X-ray crystal structure analysis reveals that **1** consists of 1-D polymeric chains. The asymmetric unit contains one manganese, one azido ligand, half an oxalate, a phen, and two disordered water molecules (figure 1a). The extended structure results from growth about two different crystallographic centers of inversion, one at the center of the oxalate and one between the azides (figure 1b). The Mn(II) is octahedrally coordinated with two oxygens and four nitrogens; two oxygens from ox, two nitrogens from phen, and two nitrogens from end-on (EO) azides. The apical positions are occupied by N1 and N3 and the equatorial plane formed by O1, O2A, N2, and nitrogen of another end-on azide (figure 1a). The mean equatorial plane deviation is about 0.2472 Å. The deviation (−0.0449 Å) from the equatorial plane indicates manganese does not lie in the plane. The N(3)–Mn–N(1) angle is 171.02°. The Mn(AA) links to Mn(B) *via* two end-on azides at 3.332 Å (figure 1b). The Mn–N$_{\text{azido}}$–Mn angle of 98.56° and distances [Mn–N(3B) = 2.174(2) Å, Mn–N(3A) = 2.222(2) Å] are similar to those in other Mn–N$_{\text{bridge}}$ complexes [25–27]. The Mn(AA) and Mn(A) are connected by ox bridging at 5.708 Å. Adjacent Mn components are connected by bridging azido and ox groups to form a 1-D

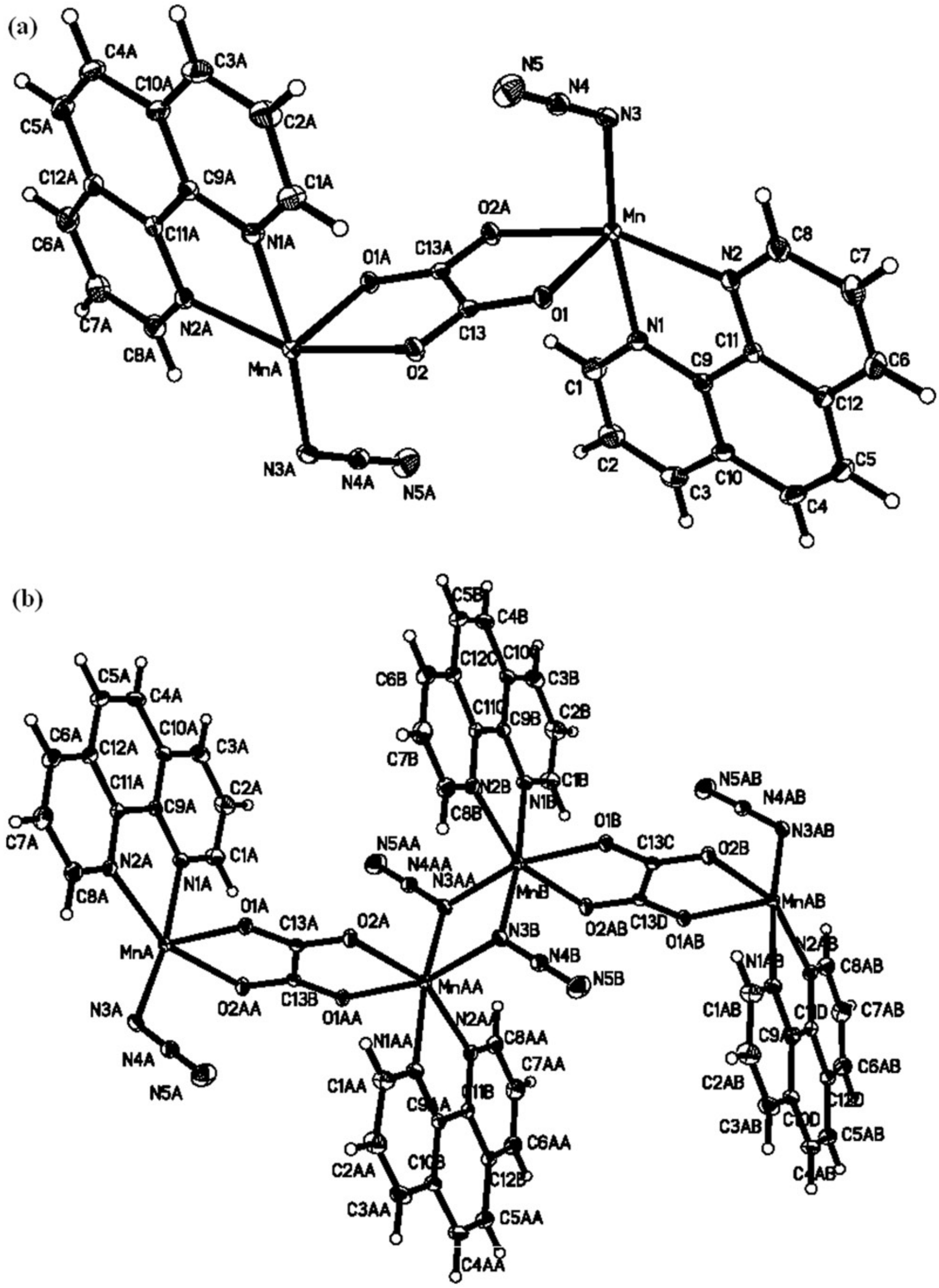

Figure 1. (a) Crystal structure of **1** with the coordination environment around Mn(II) (ellipsoids at 30% probability). (b) A view of the extended structure of **1**. The $H_2O$ groups are omitted.

zigzag coordination polymer. Weak intermolecular interaction between the zigzag coordination polymers are *π–π* interactions between adjacent phen ligands with separation of *ca*. 3.740 Å and 4.314 Å forming 2-D sheet within the *ab*-plane, as shown in figure 2.

### 3.2. *Spectroscopic properties*

Infrared spectra of **1** exhibit a very strong split band at 2103 and 2068 cm$^{-1}$, corresponding to the asymmetric stretch of azide, consistent with end-on azido bridging ligands [28]. A strong band at 1631 cm$^{-1}$ is a characteristic of $\upsilon_{(CO_2-)}$ symmetric vibrations of the ox [29]. In addition, phen-based absorptions appear at 1576, 1514, 1423, 788, and 726 cm$^{-1}$ [30].

The UV-Vis absorption spectrum (Supplementary material) displays bands centered at 226 and 236 nm, with the latter broader, assigned to the *π–π** of the phen groups [31].

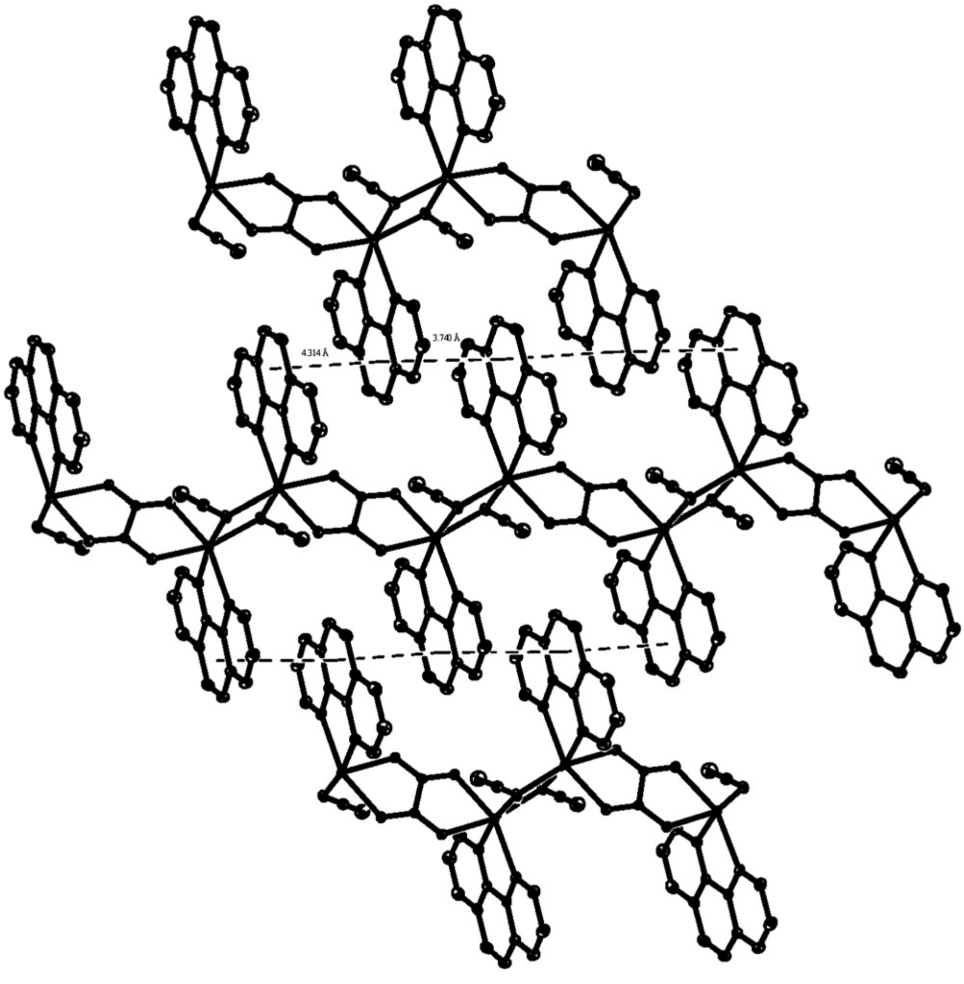

Figure 2. View of the 2-D framework of **1** in the *ab* plane. Hydrogens and $H_2O$ groups are omitted for clarity.

### 3.3. *Thermal analysis*

Azido complexes display explosive decomposition and only a small amount of azido complex should be handled with care. TGA was carried out for powder sample of **1** from 30–500°C (Supplementary material). TG-DTG curves demonstrate two main mass loss stages. The first from 260 to 320°C was attributed to loss of phen, 51.25% (Anal. Calcd 56.11%). The second mass loss from 320 to 350°C was attributed to loss of ox and $N_3^-$, 26.66% (Anal. Calcd 26.79%), and the framework of the coordination polymer collapsed. The final residue is $Mn_2O_3$ (found 25.24%, Anal. Calcd 24.58%).

## 4. Conclusion

We have synthesized and characterized a new manganese(II) coordination polymer which exhibits a 2-D supramolecular network constructed by $\pi$–$\pi$ interactions between adjacent 1-D Mn–$(N_3)_2$–Mn–ox–Mn zigzag coordination polymers. The complex displays strong absorptions at 226 and 236 nm in distilled water at room temperature.

## Supplementary material

CCDC reference number: 694536. 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). A comparison of simulated with experimental PXRD patterns with this article can be found in the online version.

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