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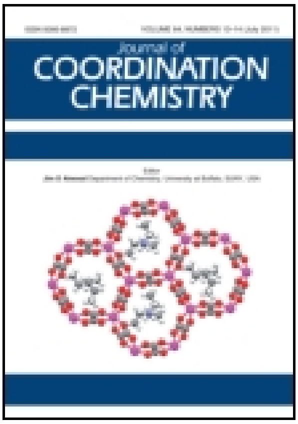

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# Synthesis, crystal structures, and properties of two heterometallic Cu(II)–M(II) (M = Zn, Ni) oxamidato-bridged coordination complexes

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Two heterometallic coordination complexes, $\{[Cu(aeop)Zn(H_2O)_3]_2 \cdot 3H_2O\}_n$ (**1**) and $[Cu(aeop)Ni(H_2O)_4] \cdot 4H_2O$ (**2**) ($H_4aeop$ = N-(2-aminoterephthalic acid)-N′-(1,3-propanediamine)oxamidate), have been synthesized and characterized by elemental analyses, IR, UV spectroscopy, thermogravimetric analysis, and X-ray crystal diffraction. Complex **1** features a 1-D chain constructed from neutral tetranuclear units. Complex **2** is a neutral binuclear complex. Through intermolecular hydrogen-bonding interactions, **2** gives a 3-D network structure. The variable temperature magnetic susceptibility measurements (2–300 K) of **2** show a pronounced antiferromagnetic interaction between the copper(II) and nickel(II), and the exchange integral $J$ is equal to $-42.7\,cm^{-1}$.

*Keywords*: Heterobimetallic complexes; Oxamidate-bridge; Crystal structure; Magnetic properties

## 1. Introduction

Design and synthesis of polynuclear complexes with predictable magnetic properties attract the interest of inorganic chemists working in the field of molecular magnetism [1–6]. In particular, the design of heterometal complexes has played an important role. A number of heterobimetallic complexes have been synthesized and their magnetic properties investigated [7–10].

One successful strategy in obtaining heterometallic complexes is the "complex as ligand" approach. Oxamato copper(II) complexes have been used for the design of heteropolynuclear complexes following this approach [11–15]. Along this line, we have recently reported three mononuclear copper(II) complexes $[CuL]^{n-}$ with the bridging ligands L = N-benzoate-N′-(2-aminoethyl)oxamido (oxbe) and 2-(2-(2-aminoethylamino)-2-oxoacetamido)terephthalic acid (aeoe) and its derivative N-(2-aminoterephthalic acid)-N′-(1,3-propanediamine)oxamidate (aeop) (figure 1) as precursors for the preparation of heterometallic complexes [16–19]. Herein, we use the mononuclear copper(II) complex $[Cu(aeop)]^{2-}$ and report the synthesis and crystal structures of

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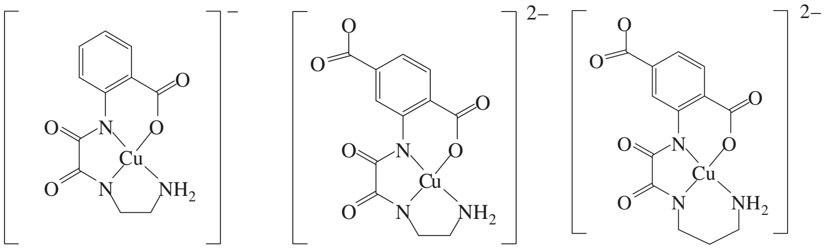

$[Cu(oxbe)]$ $[Cu(aeoe)]^2$ $[Cu(aeop)]^{2-}$

Figure 1. Mononuclear copper(II) complexes.

oxamato-bridged heterobimetallic compounds $\{[Cu(aeop)Zn(H_2O)_3]_2 \cdot 3H_2O\}_n$ (**1**) and $[Cu(aeop)Ni(H_2O)_4] \cdot 4H_2O$ (**2**). Complex **1** is a 1-D ladder-like chain, and **2** exhibits a 3-D network structure formed *via* intermolecular hydrogen bonds, and its magnetic properties are also investigated.

## 2. Experimental

### 2.1. *Materials*

All chemicals were of reagent grade and obtained commercially without purification. The ligand $H_4$aeop and copper precursor $Na_2[Cu(aeop)] \cdot 3H_2O$ were prepared as described [19].

### 2.2. *Preparation of $\{[Cu(aeop)Zn(H_2O)_3]_2 \cdot 3H_2O\}_n$ (1)*

$Na_2[Cu(aeop)] \cdot 3H_2O$, 0.1 mmol (0.0469 g), was dissolved in 20 mL water to give a violet solution. $Zn(OAC)_2 \cdot 2H_2O$, 0.1 mmol (0.044 g), was dissolved in 20 mL of methanol. The violet $Na_2[Cu(aeop)] \cdot 3H_2O$ aqueous solution (5 mL), 10 mL 2 : 1(V : V) methanol–water solution, and 5 mL $Zn(OAC)_2 \cdot 2H_2O$ methanol solution were carefully added in order to a 30-mL test tube from bottom to top. Purplish red single crystals suitable for X-ray crystal analysis were obtained in 2 months. Anal. Calcd for $C_{26}H_{40}Cu_2N_6O_{21}Zn_2$ (%): C, 30.30; H, 3.91; and N, 8.15. Found: C, 30.24; H, 3.79; and N, 8.21. IR (KBr, $cm^{-1}$): $\nu_{NH2}$ 3417(s); $\nu_{C=O}$ 1627(s).

### 2.3. *Preparation of $[Cu(aeop)Ni(H_2O)_4] \cdot 4H_2O$ (2)*

In this study, 0.1 mmol (0.0469 g) $Na_2[Cu(aeop)] \cdot 3H_2O$ was dissolved in 20 mL of water to give a violet solution, and 20 mL of DMF solution containing 0.1 mmol (0.025 g) $Ni(CH_3COO)_2 \cdot 4H_2O$ was added. The resulting solution was stirred for 1 h and then filtered, and finally well-shaped violet single crystals suitable for X-ray crystal analysis were obtained by the slow diffusion of methanol into the solution. Anal. Calcd for

Table 1. Crystal data and structure refinement for **1** and **2**.

| | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{26}H_{40}Cu_2N_6O_{21}Zn_2$ | $C_{13}H_{27}CuN_3NiO_{14}$ |
| Formula weight | 1030.46 | 571.63 |
| Temperature (K) | 296(2) | 296(2) |
| Wavelength (nm) | 0.071073 | 0.071073 |
| Crystal system | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_1/n$ |
| Unit cell dimensions (Å, °) | | |
| $a$ | 9.5907(6) | 14.9037(6) |
| $b$ | 9.6499(6) | 7.4465(3) |
| $c$ | 10.9814(6) | 19.2457(8) |
| $\alpha$ | 69.684(1) | 90 |
| $\beta$ | 81.143(1) | 98.441(1) |
| $\gamma$ | 80.141(1) | 90 |
| Volume (Å$^3$), $Z$ | 934.10(10), 1 | 2112.76(15), 4 |
| Calculated density (g cm$^{-3}$) | 1.832 | 1.797 |
| Absorption coefficient (mm$^{-1}$) | 2.484 | 1.975 |
| Crystal size (mm$^3$) | 0.27 × 0.18 × 0.16 | 0.29 × 0.15 × 0.13 |
| $\theta$ range for data collection (°) | 1.99–25.00 | 1.87–24.99 |
| Independent reflection | 3274 [$R$(int) = 0.0182] | 3713 [$R$(int) = 0.0219] |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0330$, $wR_2 = 0.1133$ | $R_1 = 0.0392$, $wR_2 = 0.1111$ |
| $R$ indices (all data) | $R_1 = 0.0377$, $wR_2 = 0.1166$ | $R_1 = 0.0483$, $wR_2 = 0.1161$ |

$C_{13}H_{27}CuN_3NiO_{14}$ (%): C, 27.54; H, 4.74; and N, 7.31. Found: C, 27.52; H, 4.83; and N, 7.26. IR (KBr, cm$^{-1}$): $\nu_{NH2}$ 3409(s); $\nu_{C=O}$ 1621(s).

### 2.4. *Physical measurements*

Elemental analyses for C, H, and N were carried out on a Perkin Elmer 2400II analyzer. Infrared spectra were recorded on an Avatar-360 spectrometer using KBr pellets from 400 to 4000 cm$^{-1}$. UV-Vis spectra were taken on a UV-540 spectrometer from 400 to 800 nm. Thermogravimetric analysis (TGA) was carried out on a TGA/SDTA851$^e$ analyzer in nitrogen, and the complexes were heated to 600°C at a heating rate of 10°C min$^{-1}$. Magnetic measurement was carried out on polycrystalline samples with a MPMS-7SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all atoms.

### 2.5. *X-ray analysis*

The single crystals used for data collection were selected and mounted on a Bruker Smart APEX diffractometer with a CCD detector using graphite monochromated Mo-K$\alpha$ radiation ($\lambda = 0.071073$ nm). Lorentz and polarization factors were made for the intensity data and absorption corrections were performed using SADABS [20]. The crystal structures were solved using SHELXTL and refined using full matrix least-squares [21]. Hydrogen positions were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbons. Crystal data collection and refinement parameters are given in table 1.

## 3. Results and discussion

### 3.1. *IR spectra and UV-Vis*

IR spectra of the complexes show strong $\nu_{C=O}$ (oxamido) bands at 1627 cm$^{-1}$ in **1** and 1621 cm$^{-1}$ in **2**. In addition, $\nu_{as(COO-)}$ and $\nu_{s(COO-)}$ exhibit two intense absorptions at 1405 and 1432 cm$^{-1}$ for **1** and 1398 and 1430 cm$^{-1}$ for **2**, respectively, which may be attributed to the bidentate coordinated carboxyl groups; these results are in accord with the literature [22–24].

UV-Vis absorptions of **1** and **2** (Supplementary material) exhibit broad absorptions at *ca* 563 and 568 nm, which were attributed to d–d transition of Cu(II) [25].

### 3.2. *Thermal properties*

TGA shows that **1** loses 10.8% of total weight from 25°C–145°C, corresponding to the loss of three crystal waters and three coordinated waters (expected: 10.1%). Compound **2** loses 24.3% (expected: 25.2%) at 25°C–175°C, corresponding to the loss of four crystal waters and four coordinated waters. Complex **1** decomposes at about 375°C and **2** at about 340°C, indicating that they are more stable than the copper precursor (Supplementary material).

### 3.3. *Description of the structures*

X-ray single crystal structure analysis reveals that **1** crystallizes in the triclinic system, space group $P\bar{1}$. Selected bond lengths and angles are listed in table 2. As shown in figure 2, **1** consists of a binuclear unit and three coordination waters. In the binuclear unit, Cu1 is in the form of a distorted square pyramid, coordinated by one oxygen and three nitrogens from oxamidate bridges, and the apical position is occupied by another carboxylic oxygen (O5#2) with a bond length of 2.531 Å. This value is significantly longer than those complexes reported [17–19]. Zn1 has a distorted octahedral geometry

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

| | | | |
|---|---|---|---|
| Cu(1)–O(3) | 1.923(2) | Cu(1)–N(2) | 1.930(3) |
| Cu(1)–N(1) | 1.974(2) | Cu(1)–N(3) | 2.012(3) |
| Zn(1)–O(6)#1 | 2.040(2) | Zn(1)–O(2) | 2.050(2) |
| Zn(1)–O(2W) | 2.093(2) | Zn(1)–O(3W) | 2.110(3) |
| Zn(1)–O(1) | 2.163(2) | Zn(1)–O(1W) | 2.185(2) |
| O(3)–Cu(1)–N(2) | 169.49(11) | O(3)–Cu(1)–N(1) | 92.77(9) |
| N(2)–Cu(1)–N(1) | 85.21(11) | O(3)–Cu(1)–N(3) | 87.03(11) |
| N(2)–Cu(1)–N(3) | 94.61(12) | N(1)–Cu(1)–N(3) | 177.92(13) |
| O(6)#1–Zn(1)–O(2) | 177.12(9) | O(6)#1–Zn(1)–O(2W) | 88.26(9) |
| O(2)–Zn(1)–O(2W) | 89.87(9) | O(6)#1–Zn(1)–O(3W) | 86.96(11) |
| O(2)–Zn(1)–O(3W) | 95.01(11) | O(2W)–Zn(1)–O(3W) | 174.54(11) |
| O(6)#1–Zn(1)–O(1) | 103.86(9) | O(2)–Zn(1)–O(1) | 78.35(8) |
| O(2W)–Zn(1)–O(1) | 90.73(10) | O(3W)–Zn(1)–O(1) | 87.86(11) |
| O(6)#1–Zn(1)–O(1W) | 93.70(9) | O(2)–Zn(1)–O(1W) | 83.98(9) |
| O(2W)–Zn(1)–O(1W) | 86.08(10) | O(3W)–Zn(1)–O(1W) | 96.85(11) |
| O(1)–Zn(1)–O(1W) | 162.05(9) | Cu(1)–O(5)#2 | 2.531(3) |

Symmetry transformations used to generate equivalent atoms: #1: $-x+2$, $-y+1$, $-z+1$; #2: $-x+1$, $-y+1$, $-z+1$.

with two oxygens from one oxamido, three oxygens from water, and one oxygen from another carboxylic oxygen. The Zn–O distances vary from 2.040(2) to 2.185(2) Å. The Cu–Zn distance through the oxamidate bridge is 5.384(8) Å, similar to the value reported [18]. The binuclear molecules are linked by coordination bonds between carboxylic oxygen and Zn to give a tetranuclear neutral loop. These tetranuclear neutral loops are further associated by coordination bonds between carboxylic oxygen and Cu to form a new 1-D ladder-like chain structure (figure 3).

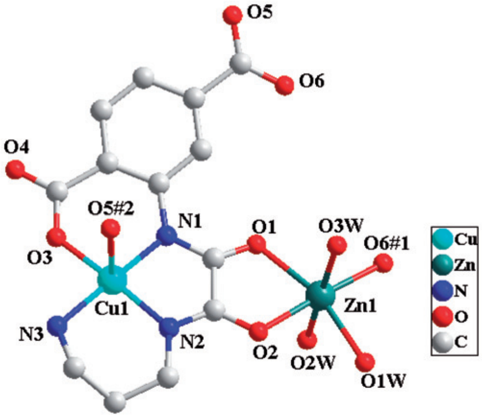

Figure 2. Molecular structure of **1**; hydrogens and crystallization waters are omitted for clarity. Symmetry codes: #1: $-x+2$, $-y+1$, $-z+1$; #2: $-x+1$, $-y+1$, $-z+1$.

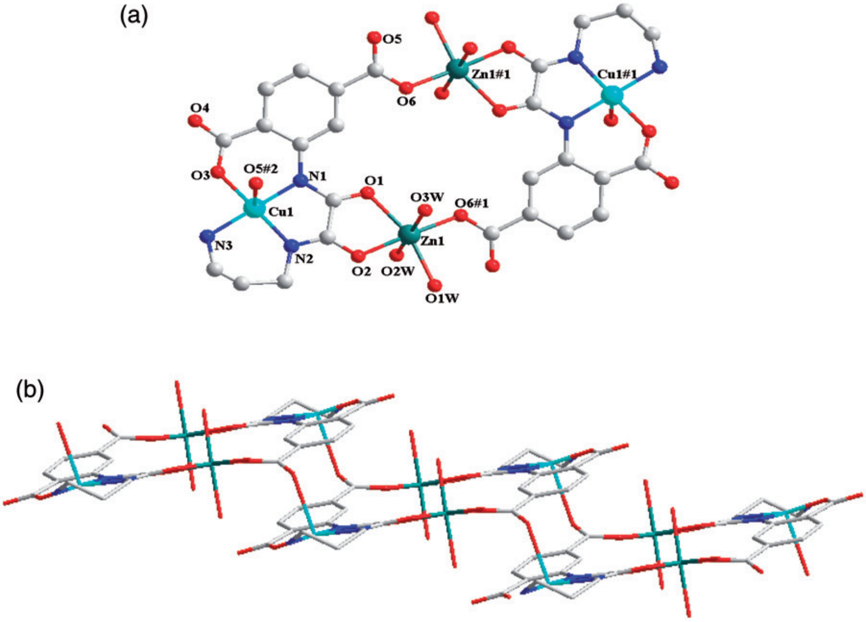

Figure 3. (a) The tetranuclear unit structure of **1**; (b) 1-D ladder-like chain structure of **1**; hydrogens and crystallization waters are omitted for clarity.

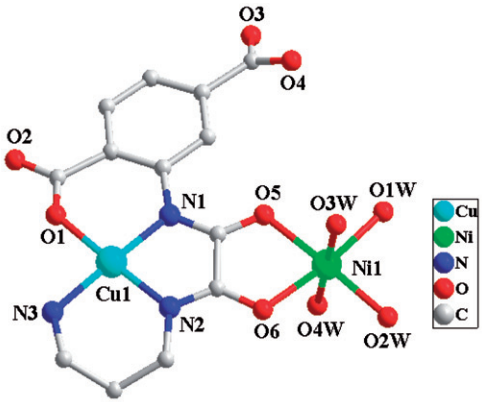

Figure 4. Molecular structure of **2**; hydrogens and solvent waters are omitted for clarity.

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

| | | | |
|---|---|---|---|
| Cu(1)–O(1) | 1.910(3) | Cu(1)–N(2) | 1.942(3) |
| Cu(1)–N(1) | 1.964(3) | Cu(1)–N(3) | 1.994(3) |
| Ni(1)–O(3W) | 2.030(3) | Ni(1)–O(1W) | 2.040(3) |
| Ni(1)–O(2W) | 2.036(3) | Ni(1)–O(5) | 2.039(3) |
| Ni(1)–O(6) | 2.062(3) | Ni(1)–O(4W) | 2.072(3) |
| O(1)–Cu(1)–N(2) | 177.93(13) | O(1)–Cu(1)–N(1) | 92.88(11) |
| N(2)–Cu(1)–N(1) | 85.47(12) | O(1)–Cu(1)–N(3) | 87.29(12) |
| N(2)–Cu(1)–N(3) | 94.44(13) | N(1)–Cu(1)–N(3) | 175.93(14) |
| O(3W)–Ni(1)–O(1W) | 86.70(14) | O(3W)–Ni(1)–O(2W) | 89.13(12) |
| O(1W)–Ni(1)–O(2W) | 89.27(12) | O(3W)–Ni(1)–O(5) | 92.45(12) |
| O(1W)–Ni(1)–O(5) | 92.57(11) | O(2W)–Ni(1)–O(5) | 177.64(11) |
| O(3W)–Ni(1)–O(6) | 90.95(13) | O(1W)–Ni(1)–O(6) | 172.20(12) |
| O(2W)–Ni(1)–O(6) | 98.14(10) | O(5)–Ni(1)–O(6) | 80.09(10) |
| O(3W)–Ni(1)–O(4W) | 179.47(13) | O(1W)–Ni(1)–O(4W) | 92.78(13) |
| O(2W)–Ni(1)–O(4W) | 90.97(12) | O(5)–Ni(1)–O(4W) | 87.47(12) |
| O(6)–Ni(1)–O(4W) | 89.55(12) | | |

The structure of **2** is shown in figure 4. Selected bond lengths and angles are listed in table 3. Complex **2** consists of a binuclear neutral molecule and four waters. The coordination geometry around Cu1 is distorted square planar, composed of one oxygen and three nitrogens from oxamato. The Ni1 is in a distorted octahedral environment, coordinated by two oxygens from the oxamidate bridge and four oxygens from water. The oxamato group bridges Cu and Ni with distance of 5.309(6) Å, similar to the literature [17]. Inside the $[Cu(aeop)Ni(H_2O)_4]\cdot 4H_2O$ framework, the N–H···O and O–H···O hydrogen bonds organize the binuclear molecules into a 3-D supramolecular framework, as illustrated in figure 5.

### 3.4. *Magnetic properties*

The magnetic susceptibility of **2** has been measured from 2–300 K. The curves of $\chi_M$ and $\mu_{eff}$ *versus* $T$ are shown in figure 6 (where $\mu_{eff}$ is the effective magnetic moment).

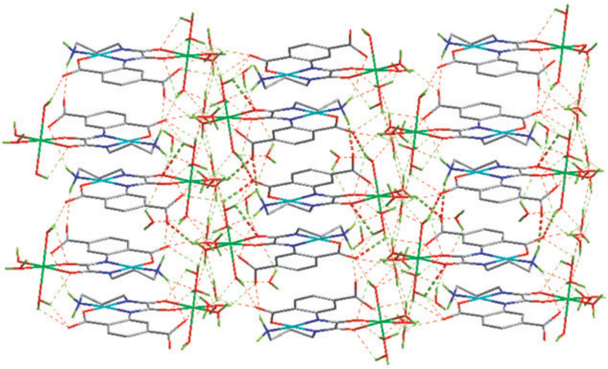

Figure 5. 3-D supramolecular structure through intermolecular hydrogen bonds.

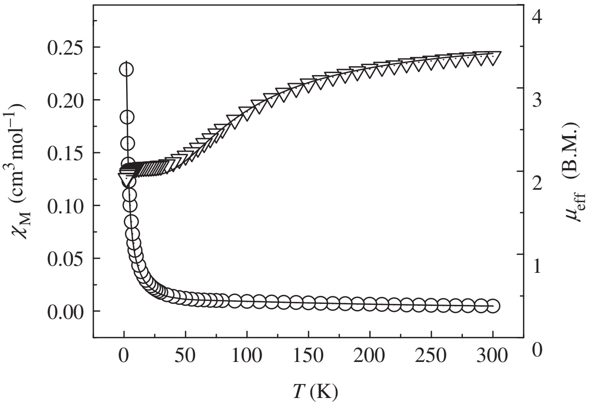

Figure 6. $\chi_M$ *vs.* $T$ and $\mu_{eff}$ *vs.* $T$ plots for **2**.

At room temperature, the $\mu_{eff}$ value of **2** is 3.41 BM, a little higher than the spin-only value, expected for uncoupled $Cu^{II}$–$Ni^{II}$ binuclear system (3.32 BM). Upon cooling, the $\mu_{eff}$ value decreases regularly, approaching a minimum around 2 K with $\mu_{eff} = 1.95$ BM, which is similar to the value reported in the literature [17].

The magnetic analysis was carried out using the theoretical expression of the magnetic susceptibility deduced from the spin Hamiltonian $\hat{H} = -2J\hat{S}_{Cu}\hat{S}_{Ni}$. The expression of the magnetic susceptibility for the Cu–Ni system is

$$\chi_M = \frac{Ng^2\beta^2}{4KT}\left[\frac{10+\exp(-3J/KT)}{2+\exp(-3J/KT)}\right] + N_\alpha, \quad N_\alpha = 200 \times 10^{-6}\,\text{cm}^3\,\text{mol}^{-1}$$

where $J$ is the exchange integral between Cu(II) and Ni(II) and $N_\alpha$ the temperature-independent paramagnetism. The best fitting for the experimental data gives $J = -42.7\,\text{cm}^{-1}$, $g = 2.25$. The agreement factor $R = \sum(\chi_{obsd} - \chi_{calcd})^2/\sum\chi_{obsd}{}^2$ is $1.98 \times 10^{-3}$, which corresponds to a good agreement, as seen in figure 6. The negative $J$ value suggests that the interaction between Cu(II)–Ni(II) ions is antiferromagnetic.

## 4. Conclusion

Through the ''complex as ligand'' approach, we have synthesized several heterometallic coordination polymers. Using the mononuclear copper(II) complexes $[Cu(aeoe)]^{2-}$ and $[Cu(aeop)]^{2-}$, we have obtained five 1-D ladder-like chain structure coordination polymers and a cyclic neutral tetranuclear complex, $\{[Cu(aeoe)M(H_2O)_3 \cdot 2H_2O]_2\}_n$ $(M = Mn(II), Co(II), Ni(II))$ [17], $\{[Cu(aeoe)Zn(H_2O)_3 \cdot 1.5H_2O]_2\}_n$ [18], $\{[Cu(aeop) Mn(H_2O)_3]_2\}_n$ [19], and $[Cu(aeoe)Ni(H_2O)_3]_2$ [17]. In the study mentioned in this article, we synthesized two new oxamido-bridged complexes with $Na_2[Cu(aeop)] \cdot 3H_2O$. Complex **1** is a 1-D ladder-like chain coordination polymer. Complex **2** is a 3-D supramolecular framework formed *via* intermolecular hydrogen bonds. Complex **2** shows weak antiferromagnetic exchange between the adjacent metal centers. Currently, we are trying to exploit the reaction of these precursors with 3d–4f heterometallic cations to provide unique 3d–4f heterometallic coordination polymers.

## Supplementary material

CCDC-802492 (**1**) and 802493 (**2**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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