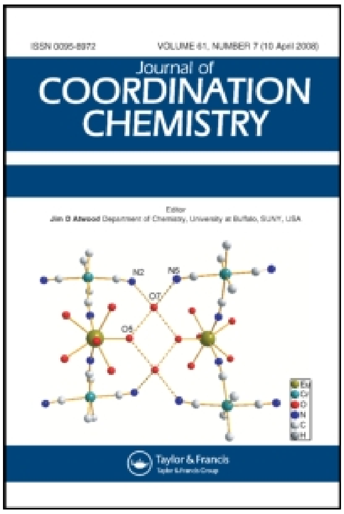

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Yong-Tao Wang[a]; Gui-Mei Tang[a]
[a] Department of Chemical Engineering, Shandong Institute of Light Industry, Jinan 250100, China

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Synthesis, structures and characterization of two new supramolecular coordination complexes with the ambidentate ligand 5-(4-pyridyl)-1,3,4-oxadiazole-2-thione (Hpot)

YONG-TAO WANG*† and GUI-MEI TANG†

†Department of Chemical Engineering, Shandong Institute of
Light Industry, Jinan 250100, China

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Two new coordination supramolecular complexes based on a versatile and unsymmetrical 5-(4-pyridyl)-1,3,4-oxadiazole-2-thione (Hpot) and Mn^{II} and Ni^{II} have been synthesized and structurally characterized by single-crystal X-ray diffraction analysis. Reaction of $MnCl_2 \cdot 4H_2O$ with Hpot afforded a neutral mononuclear complex $[Mn(pot)_2(H_2O)_4] \cdot 2H_2O$ (**1**), which exhibits a three-dimensional (3-D) supramolecule through versatile intermolecular O–H $\cdots$ X (X=O, N and S) hydrogen bond interactions. When using $NiCl_2 \cdot 6H_2O$ instead of $MnCl_2 \cdot 4H_2O$ under similar reaction conditions, a neutral mononuclear complex $[Ni(pot)_2(H_2O)_4]$ (**2**) is also obtained, which does not exhibit intermolecular hydrogen bonds and π–π stacking interactions. It is very interesting that the pot anion exhibits different coordination modes in complexes **1** and **2**. The IR spectra and the TGA for **1** and **2** have been investigated and discussed in detail.

Keywords: Supramolecular complexes; Coordination mode; 5-(4-Pyridyl)-1,3,4-oxadiazole-2-thione; Manganese complex; Nickel complex

1. Introduction

Crystal engineering with desired functions and fascinating topological architectures has been of great interest [1–3]. Considerable effort has been focused on supramolecular networks assembled by covalent [4], hydrogen bonding [5] or other intermolecular interactions [6]. Hydrogen bonding and π–π stacking play an important role in crystal packing, molecular recognition and the stability of inclusion complexes [7]. Previous studies have focused on symmetric ligands (e.g., 4,4′-bipyridine and analogues) [8, 9]; use of unsymmetrical ligands (for example, 2,3′-bipyridine, 2,4′-bipyridine, 3,4′-bipyridine and their analogues) is still rare [10]. Our research has focused on designing new unsymmetrical bridging ligands and investigating their self-assembly with metal centers.

After we have constructed coordination polymers based on unsymmetrical rigid or flexible ligands, we further attempt to investigate the design and control of

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*Corresponding author. Tel.: +86 0531 82350869. Fax: +86 0531 82350869. Email: ceswyt@sohu.com

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self-assembly to coordination polymers and supramolecular complexes [11]. In this work, we have synthesized a new unsymmetrical rigid bridging ligand 5-(4-pyridyl)-1,3,4-oxadiazole-2-thione (Hpot), which results in versatile supramolecules with desired properties. The ligand has characteristics based on the following advantages: (i) it has two possible tautomers (*thione* and *thiol*) [11d]; (ii) it has three potential binding sites; and (iii) it has the strong capability of forming hydrogen bonding interactions. This unsymmetrical multifunctional building block containing sulfide group and oxadiazole anion has rarely been used in self-assembly of supramolecular complexes, though one complex containing this ligand has recently been reported [12]. Herein, we report the synthesis, characterization and structures of two new supramolecular coordination complexes, $[Mn(pot)_2(H_2O)_4]\cdot 2H_2O$ (**1**) and $[Ni(pot)_2(H_2O)_4]$ (**2**), in which versatile coordination modes of pot were observed. Additionally, the IR spectra and TGA for complexes **1** and **2** have also been discussed in detail.

2. Experimental section

2.1. *Materials and physical measurements*

Reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with a Perkin–Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Bruker spectrometer. Thermogravimetric analysis (TGA) data were collected with a Perkin–Elmer TGS-2 analyzer in N_2 flow at a heating rate of $20^{\circ}C\,min^{-1}$.

2.2. *Synthesis of 5-(4-pyridyl)-1,3,4-oxadiazole-2-thione (Hpot)*

Hpot was prepared according to literature [11d].

2.3. *Synthesis of $[Mn(pot)_2(H_2O)_4]\cdot 2H_2O$ (1)*

Hpot (35 mg, 0.2 mmol) was dissolved in *N*,*N*-dimethylformamide (DMF) (20 mL). A dilute aqueous solution of NaOH was added dropwise with stirring to the above mixture until the pH was ca 7. To the above solution was added a dilute aqueous solution of $MnCl_2\cdot 4H_2O$ (20 mg, 0.1 mmol). The mixture was vigorously stirred under heating for ca. 30 min, and then filtered after cooling to room temperature. The pale-yellow powder of **1** was collected and washed with anhydrous methanol. The resultant pale-yellow filtrate was left to stand at room temperature. Block light-yellow single-crystals suitable for X-ray diffraction were obtained by slow evaporation of solvent within two weeks in 60% yield. Anal. Calcd for $C_{14}H_{20}MnN_6O_8S_2$: C, 32.37; H, 3.88; N, 16.18%. Found: C, 32.49; H, 3.89; N, 16.13%. IR (cm^{-1}): 3446 (br) (ν_{O-H} for H_2O), 1533 (m), 1489 (s), 1427 (s) (skeletal vibrations for pyridyl ring), 1596 (s), 1554 (m), 1200 (s), 1050 (s) (skeletal vibrations for oxadiazole ring).

2.4. *Synthesis of [Ni(pot)$_2$(H$_2$O)$_4$] (2)*

To a solution of Hpot (35 mg, 0.2 mmol) in DMF (10 mL) was slowly added a water solution (5 mL) of $NiCl_2 \cdot 6H_2O$ (24 mg, 0.1 mmol) under refluxing conditions for ca 30 min. The resultant pale-green solution was filtered and left to stand at room temperature. Block pale-purple single-crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvents within one week in 70% yield. Anal. Calcd For $C_{14}H_{16}N_6NiO_6S_2$: C, 34.52; H, 3.31; N, 17.25%. Found: C, 34.62; H, 3.32; N, 17.18%. IR (cm^{-1}): 3400 (br) ($\nu_{O\text{–}H}$ for H_2O), 1538 (m), 1492 (s), 1430 (s) (skeletal vibrations for pyridyl ring), 1580 (s), 1548 (m), 1203 (s), 1052 (s) (skeletal vibrations for oxadiazole ring).

2.5. *X-ray crystallography*

Single crystal X-ray diffraction measurements of **1** and **2** were carried out with a Bruker Smart APXII CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at 293(2) K. Data collections were performed with Mo-Kα radiation ($\lambda = 0.71073$ Å) by ω-scan mode. No evidence was found for crystal decay during data collection on **1** and **2**. All the measured independent reflections were used in the structural analysis, and semi-empirical absorption corrections were applied using the SADABS program. The program SAINT [13] was used for integration of the diffraction profiles. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL [14]. Metal atoms were located from the *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for all the non-hydrogen atoms on F^2. Except for H atoms bonded to O atoms which were freely refined with isotropic displacement parameters in compound **1**, all O-bound and C-bound H atoms were placed in geometrically idealized positions with O–H = 0.85 Å (for water H) and C–H = 0.89–0.96 Å (for aromatic H), and refined in the riding-model appproximation, $U_{iso(H)} = 1.2U_{eq}$(C, O). A summary of the crystallographic and structure refinement data is listed in table 1.

3. Results and discussion

3.1. *Preparation of compounds 1 and 2*

Compounds **1** and **2** were obtained as neutral complexes in water by combination of Hpot with different metal salts. Compound **1** could also be isolated according to the same synthetic procedure, however, using $MnSO_4$ or $Mn(OAc)_2$ as the source of manganese (confirmed by X-ray diffraction, IR spectra and elemental analyses). Similar cases were also observed for Ni^{II} complex, which indicates that the final products are independent of the counter-anions of the metal salts. Complexes **1** and **2** have the 2 : 1 ligand/metal compositions. Indeed, in these specific self-assembled processes, the products do not depend on the ligand-to-metal ratio (the results were confirmed by X-ray diffraction, IR spectra and elemental analyses).

Table 1. Crystallographic data and structure refinements for **1** and **2**.

	1	**2**
Chemical formula	$C_{14}H_{20}MnN_6O_8S_2$	$C_{14}H_{16}N_6NiO_6S_2$
Fw	519.44	487.16
T (K)	298	298
λ (Mo-Kα) (Å)	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic
Space group (Å, °, Å^3)	$P\bar{1}$	*Pbca*
a	7.004(6)	12.787(18)
b	8.095(8)	8.629(12)
c	9.842(5)	18.74(3)
α	89.17(8)	90
β	89.85(7)	90
γ	73.58(8)	90
V	535.2(8)	2067(5)
Z	1	4
μ (Mo-Kα) (mm^{-1})	0.866	1.184
ρ (g cm^{-3})	1.612	1.565
GOF	1.053	1.057
$R_1{}^{a}$ ($I > 2\sigma(I)$)	0.0257	0.0449
$wR_2{}^{b}$ (all data)	0.0743	0.1376

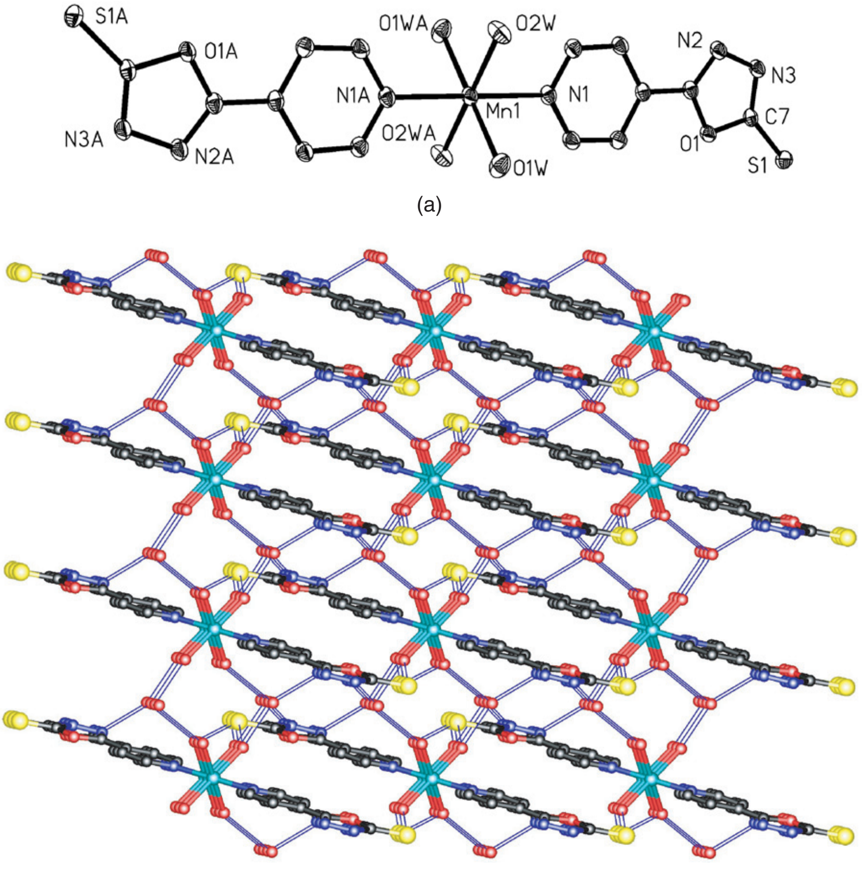
$^{a}R_1 = F_o - F_c/F_o$. $^{b}wR_2 = [[w(F_o^2 - F_c^2]/[wF_o^2))^2]]^{1/2}$.

However, increasing the metal-to-ligand ratio results in a somewhat higher yield and crystal quality. Complexes **1** and **2** are air stable and retain their structural integrity at room temperature for a considerable length of time.

3.2. *Description of crystal structures*

In the centrosymmetric mononuclear compound **1**, each Mn^{II}, located at the inversion center, coordinates to two pyridyl nitrogen atoms from two distinct pot moieties (Mn–N distance: 2.262(2) Å) and four water molecules (Mn–O lengths: 2.196(2) and 2.183(3) Å) as shown in figure 1(a), adopting an approximate octahedral geometry (MnN2O4). Pot behaves as a monodentate ligand (scheme 1a), coordinating to Mn^{II} with only the N_{py} atom, and thus results in this unexpected mononuclear structure.

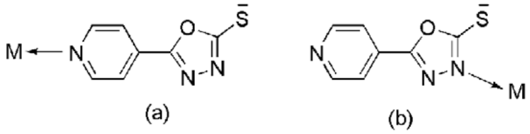
The S–C (the bond length is 1.6869(17) Å) bond of coordinated pot is obviously longer than that of free pot [11d], whereas, N3–C7 (1.311(2) Å) of the pot anion is shorter than that of free pot (table 2), in agreement with its structural geometry. Analysis of the crystal packing of **1** reveals the existence of intermolecular O–H $\cdots$ O hydrogen bonds, including O(2w)–H(2A) $\cdots$ O(3w)^{i} ($i = -x, 2-y, 2-z$), between oxygen from one of water O(1w) ligands and oxygen from one lattice water. Two intermolecular O–H $\cdots$ S hydrogen bonds between the sulfur atoms and two O(1w) water ligands from adjacent complex molecules. In addition, two intermolecular O–H $\cdots$ N hydrogen bonds between an oxygen atom from lattice water and two nitrogen atoms of oxadiazole groups from adjacent complex molecules [15]. The O $\cdots$ O separations are in the 2.782 and 2.961 Å range with H $\cdots$ O distances of 2.04–2.07 Å, and the bond angles are 167–178°. Additionally, the O $\cdots$ S separations are in the 3.246 and 3.256 Å range with H $\cdots$ S distances of 2.47 and 2.46 Å, and the bond angles are 170 and 173°. Similarly, the O $\cdots$ N separations are 2.779 and 2.924 Å with H $\cdots$ N



(a)

(b)

Figure 1. (a) View of the mononuclear structure of **1** (hydrogen atoms are omitted for clarity). (b) 3-D supramolecular network extended by hydrogen bonds along *b*-axis in **1** (all hydrogen atoms are omitted for clarity). Thin blue lines stand for hydrogen bonds.



Scheme 1. Coordination modes of pot anion in **1** and **2**.

distances of 1.99 and 2.09 Å; bond angles are in the region of 175 and 177° (table 3), being in the normal range of such non-covalent interactions [16].

In addition, the nonbonding S(1)···S(1) distance between two adjacent 1-D frameworks is 3.601(3) Å, less than the sum of the van der Waals' radii of two S atoms and indicating a weak S···S interaction [17]. Therefore, mononuclear subunits are connected through hydrogen bonds and S(1)···S(1) interactions to form a three-dimensional supramolecular network (figure 1b).

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

1^{i}			
Mn(1)–O(2W)	2.183(3)	S(1)–C(7)	1.687(2)
Mn(1)–O(1W)	2.196(2)	N3–C7	1.311(2)
Mn(1)–N(1)	2.262(2)		
O(2W)–Mn(1)–O(2W)^{a}	180.0	O(1W)^{a}–Mn(1)–N(1)^{a}	92.04(9)
O(2W)–Mn(1)–O(1W)^{a}	89.67(9)	O(1W)–Mn(1)–N(1)^{a}	87.96(9)
O(1W)^{a}–Mn(1)–O(1W)	180.0	O(2W)–Mn(1)–N(1)	93.36(9)
N(1)^{a}–Mn(1)–N(1)	180.0		
2^{ii}			
Ni(1)–O(1W)	2.117(3)	S(1)–C(1)	1.681(3)
Ni(1)–N(1)^{a}	2.131(3)	N1–C1	1.319(4)
Ni(1)–O(2W)^{a}	2.143(4)		
O(1W)–Ni(1)–O(1W)^{a}	180.00(5)	N(1)^{a}–Ni(1)–O(2W)^{a}	92.77(8)
O(1W)–Ni(1)–N(1)	89.86(11)	O(1W)^{a}–Ni(1)–O(2W)	89.53(11)
N(1)^{a}–Ni(1)–N(1)	180.00(12)	O(2W)^{a}–Ni(1)–O(2W)	180.0

^{i}Symmetry code for **1**: $^{a}-x+1, -y+2, -z+2$.
^{ii}Symmetry code for **2**: $^{a}-x+2, -y, -z+1$.

Table 3. Hydrogen bond geometries in the crystal structure of **1**.

Complex	D–H···A	D···A (Å)	H···A (Å)	D–H···A (°)
1^{i}	O1W–H1A–S1^{a}	3.246(4)	2.47(3)	170(3)
	O1W–H1B–O3W	2.782(3)	2.07(2)	167(2)
	O2W–H2A–O3W^{b}	2.794(3)	2.04(3)	178(3)
	O2W–H2B–S1^{c}	3.256(3)	2.46(2)	173(2)
	O3W–H3A–N2^{d}	2.924(3)	2.09(3)	177(3)
	O3W–H3B–N3^{e}	2.779(3)	1.99(2)	175(2)

^{i}Symmetry codes for **1**: $^{a}x, -1+y, -1+z$; $^{b}-x, 2-y, 2-z$; $^{c}x, y, -1+z$; $^{d}x, -1+y, z$; $^{e}-x, 3-y, 3-z$.

X-ray single-crystal determination indicates that complex **2** is a neutral mononuclear complex. As shown in figure 2(a), Ni^{II} is located on the inversion center. Each Ni^{II} center is coordinated by two distinct N_{oz} atoms (oz = oxadiazole, Ni-N distances: 2.131(3) Å) and four water molecules (Ni–O lengths: 2.117(3) and 2.143(4) Å). The coordination geometry of the six-coordinate Ni^{II} center (NiN_2O_4) can be described as an almost perfect octahedron (table 2). The structure of complex **2** is mononuclear, similar to that of complex **1**, though pot adopts different coordination modes when coordinating to the metal ions (scheme 1b).

There are neither hydrogen bonds nor weak S···S intermolecular interactions in the crystal packing of **2** (figure 2b).

According to the above description, it is obvious that coordination of pot is quite different to different metal centers, a critical factor in determining the solid structures of its metal complexes.

3.3. *Thermogravimetric analysis*

To investigate the high thermal stability of **1** and **2**, thermogravimetric analyses (TGA) were conducted. TGA of **1** and **2** were performed under a flow of nitrogen from room

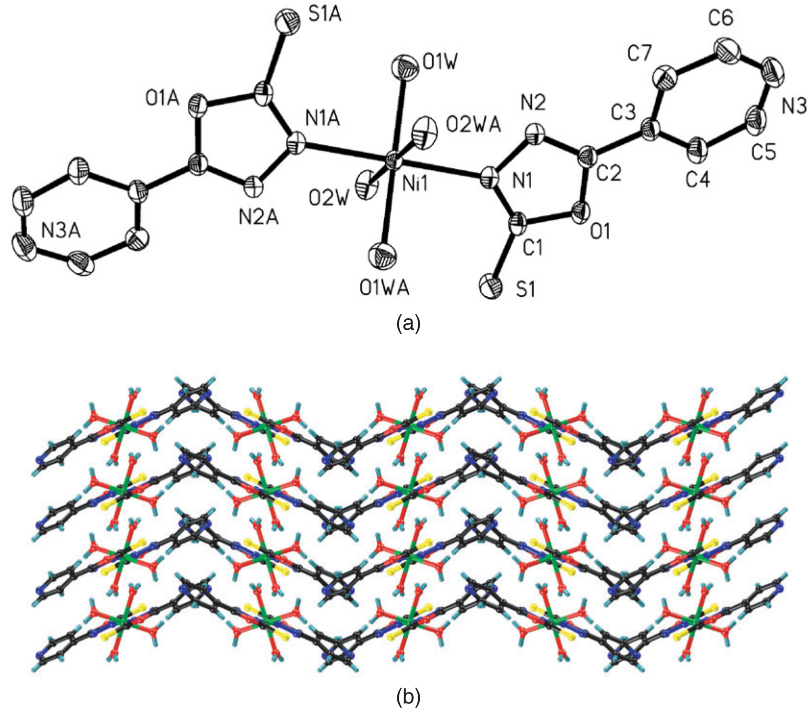


Figure 2. (a) Local coordination environment around the metal atom for **2** (hydrogen atoms are omitted for clarity). (b) The packing perspective along *a* axis for **2**.

temperature to 700°C at a heating rate of $20^\circ\mathrm{C\,min^{-1}}$. TGA curve for **1** shows that the first weight loss of 6.80% (Calcd: 6.93%) from 50 to 125°C corresponds to the loss of two lattice water molecules per formula unit. Subsequently, the second weight loss of 13.74% (Calcd: 13.86%) from 125 to 170°C corresponds to the loss of four coordinated water molecules per formula unit. The final weight 79.00% (Calcd: 79.21%) corresponds to a framework of $[\mathrm{Mn(pot)_2}]$. Decomposition of the complex begins at 200°C and ends at 365°C. The final decomposed product hardly loses any weight upon further heating from 365 to 700°C. For **2**, the first weight loss of 14.70% (Calcd: 14.78%) from 50 to 170°C corresponds to the loss of four coordinated water molecules per formula unit. The final weight 85.01% (Calcd: 85.22%) corresponds to $[\mathrm{Ni(pot)_2}]$. Decomposition of the complex begins at 220°C and ends at 380°C. The final decomposed product hardly loses any weight upon further heating from 380 to 700°C.

4. Conclusions

An inorganic–organic coordination supramolecular complex has been generated from Hpot and $\mathrm{Mn^{II}}$. A $\mathrm{Ni^{2+}}$ complex shows no supramolecular interactions. This work demonstrates that the rigid and unsymmetrical pot anion is capable of coordinating to metal centers with N_{py} or N_{oz} donors. The versatile ligand pot in **1** and **2** is coordination unsaturated, and may be used as a "complex ligand" to construct supramolecular compounds with other metal ions or complexes. This work is being investigated.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, 267656 for **1** and 267657 for **2**. Copies of this information may be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK]. Fax: C44 1223 336 066. Email: deposit@ccdc.cam.ac.uk

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