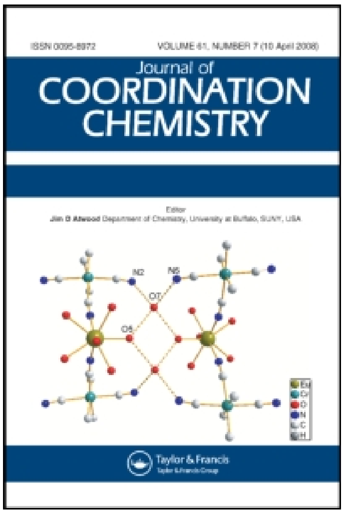

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A dinuclear nickel(II) complex with dissimilar bridges: synthesis, crystal structure, and magnetic characterization

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A dinuclear nickel(II) complex with dissimilar bridges: synthesis, crystal structure, and magnetic characterization

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Using 3,5-pyrazoledicarboxylic acid (H_3pdc), 2,2-bipyridine (2,2-bipy) and NaN_3, a dinuclear nickel(II) compound with dissimilar bridges, $[Ni_2(2,2\text{-bipy})_2(pdc)(N_3)(H_2O)_2]\cdot 2H_2O$ (**1**), has been isolated under hydrothermal conditions. Compound **1** is dinuclear, bridged by two nitrogens in the pyrazole ring of pdc^{3-} and $\mu_{1,3}-N_3^-$. The dinuclear units and lattice water molecules are further linked by extensive hydrogen bonds to form 2-D infinite planes, which are further linked through π–π stacking to construct a 3-D supramolecular structure. Variable temperature magnetic susceptibility of **1** from 2 to 300 K indicates anti-ferromagnetic interactions. The magnetic exchange coupling constants $J = -12.65\,\text{cm}^{-1}$ and $zj' = 3.34\,\text{cm}^{-1}$ for **1** can be obtained through the fit of the magnetic data.

Keywords: Dinuclear complex; Hydrothermal synthesis; 3,5-Pyrazoledicarboxylic acid; Dissimilar bridges; Magnetic property

1. Introduction

Transition metal coordination compounds have diverse magnetic properties based on different metal ions and different linkers [1, 2]. Short bridging ligands such as azido, pyrazole, and carboxylate are especially favorable because they can efficiently transfer magnetic interactions between neighboring metal ions forming magnetic materials [3–6]. Therefore, the selective combination of bridging ligands and co-ligands is an effective strategy for modulating magnetic properties and understanding magnetostructural correlations. 3,5-Pyrazoledicarboxylic acid (H_3pdc) is an efficient ligand, which contains a number of N- or O-coordination sites and rich coordination modes. Polymeric structures of H_3pdc complexes with alkaline, transition, and lanthanide metals have been reported in which H_3pdc has shown not only strong chelating ability, but bridging to form diversified structures [7–15]. A recognized linker, azido has attracted much attention because of its diversified modes in the structure and predictability in magnetism. There are two main coordination modes for azido,

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end-to-end (EE), and end-on (EO). Generally, the EE mode communicates anti-ferromagnetic couplings and the EO mode transmits ferromagnetic interactions [6].

Dinuclear copper(II) complexes with two dissimilar bridges have received considerable attention [16–22]. Orbital complementary and counter complementary effects have been proposed by Nishida *et al.* [17] and Reed *et al.* [18] to explain unusual magnetic properties in mixed-bridged copper(II) complexes. However, little work has been devoted to mixed-bridged metal complexes except copper(II) compounds [23–27]. To construct dinuclear complexes with dissimilar bridges, we chose Ni(II), H_3pdc, and azido as bridging ligands, and 2,2-bipy as terminal ligand, and synthesized $[Ni_2(2,2\text{-bipy})_2(pdc)(N_3)(H_2O)_2]\cdot 2H_2O$ (**1**). The crystal structure and magnetism of **1** are reported in table 1.

2. Experimental

2.1. *Materials and general methods*

Nickel(II) perchlorate hexahydrate was prepared by literature methods [28]. Other reagents were used as received commercially without purification. C, H, and N microanalyses were carried out with a Vario EL III elemental analyzer. Infrared spectra were recorded with a Magna-IR 750 spectrophotometer using KBr pellets. Variable-temperature magnetic susceptibilities were performed on a MPMS-7 SQUID magnetometer and were corrected for the diamagnetism of the sample (-280×10^{-6} emu M^{-1}).

Table 1. Crystallographic data and structure refinement information for **1**.

Complex	**1**
Empirical formula	$C_{25}H_{25}N_9Ni_2O_8$
Formula weight	696.96
Temperature (K)	291(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*C2/c*
Unit cell dimensions (Å, °)	
a	24.134(10)
b	9.047(4)
c	17.085(13)
β	131.637
Volume (Å^3), *Z*	2788(3), 2
Calculated density (kg m^{-3})	1.661
Absorption coefficient (mm^{-1})	1.417
F(000)	1432
θ range for data collection (°)	2.39–25.50
Independent reflections	2498
Observed reflections	9730
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2498/0/200
Goodness-of-fit on F^2	1.019
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0549$, $wR_2 = 0.1315$
R indices (all data)	$R_1 = 0.0768$, $wR_2 = 0.1449$
Largest difference peak and hole (e Å^{-3})	1.176–0.587

2.2. *Synthesis of [Ni_2(2,2-bipy)$_2$(pdc)(N_3)(H_2O)$_2$]•$2H_2O$ (1)*

A mixture of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.3 mM, 110 mg), H_3pdc (0.2 mM, 47 mg), 2,2-bipy (0.2 mM, 31 mg), NaN_3 (0.4 mM, 23 mg), and deionized water (18 mL) in the molar ratio of 3 : 2 : 2 : 4 : 10,000 was sealed in a 25 mL stainless steel reactor with Teflon liner and heated to 120°C. After keeping at 120°C for 3 days, it was cooled to room temperature at $4^{\circ}C\,h^{-1}$. Green block crystals were obtained by filtration and washed with water and ethanol. Yield: 38%. Anal. Calcd for $C_{25}H_{25}N_9Ni_2O_8$ (%): C, 43.04; H, 3.59; N, 18.08. Found (%): C, 42.79; H, 3.71; N, 17.91. IR spectra (KBr pellet, cm^{-1}): 3325 m, 2056 vs, 1621 vs, 1605 m, 1581 s, 1441 s, 1352 s, 768 m.

Caution: Perchlorate salts of transition metals and their complexes are potentially explosive; only a small amount should be prepared and handled with care.

2.3. *X-ray crystallography*

The room temperature (294 ± 1 K) single-crystal X-ray experiments were performed on a Bruker SMART 1000 CCD diffractometer equipped with graphite monochromated Mo-Kα radiation. Data collection and reduction were performed using SMART and SAINT [29]. An empirical absorption correction (SADABS) was applied to the raw intensities [30]. The structure was solved by direct methods and refined by full-matrix least-squares based on F^2 using the SHELXTL program package. Non-hydrogen atoms were subjected to anisotropic refinement [31]. The hydrogens were assigned with common isotropic displacement factors. Crystallographic data for **1** is listed in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Synthetic aspects*

Our synthetic strategy succeeded through rational assembly with bidentate bipy, a terminal ligand and a chelate pdc^{3-} bridge holding two Ni(II) centers at proper distance so that azido could bridge EE.

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

Ni(1)–N(5)	2.065(4)	Ni(1)–O(2)	2.077(3)
Ni(1)–N(1)	2.086(4)	Ni(1)–N(2)	2.088(4)
Ni(1)–O(1)	2.108(3)	Ni(1)–N(3)	2.111(4)
O(2)–C(11)	1.294(6)	O(3)–C(11)	1.248(6)
N(5)–Ni(1)–O(2)	79.43(14)	N(5)–Ni(1)–N(1)	167.50(15)
O(2)–Ni(1)–N(1)	91.72(14)	N(5)–Ni(1)–N(2)	92.94(16)
O(2)–Ni(1)–N(2)	93.66(15)	N(1)–Ni(1)–N(2)	78.72(16)
N(5)–Ni(1)–O(1)	91.80(14)	O(2)–Ni(1)–O(1)	90.36(13)
N(1)–Ni(1)–O(1)	97.12(14)	N(2)–Ni(1)–O(1)	174.28(16)
N(5)–Ni(1)–N(3)	97.50(16)	O(2)–Ni(1)–N(3)	175.37(14)
N(1)–Ni(1)–N(3)	91.83(16)	N(2)–Ni(1)–N(3)	89.95(17)
O(1)–Ni(1)–N(3)	86.25(16)	N(3)–N(4)–N(3A)	179.8(7)

Symmetry transformations used to generate equivalent atoms for **1**: A = $-x$, y, $-z + 1/2$.

3.2. *Description of crystal structure*

As shown in figure 1, **1** comprises one dinuclear Ni(II) unit and two lattice waters with N4 and C13 located on a two-fold rotation axis and one half of the fundamental unit related to the other by the crystallographic axis of rotation. In the dinuclear unit, two Ni(II)s are bridged by one pdc^{3-} and one N_3^-, and bipy is a terminal ligand. Each Ni(II) is six-coordinate by one carboxylic oxygen (O2) and one nitrogen (N5) from the same pdc^{3-}, two nitrogens (N1, N2) from 2,2′-bipy, one nitrogen (N3) from N_3^- and one oxygen (O1) from coordinated water, forming a slightly distorted octahedral geometry. The *trans* bond angles N5–Ni1–N1, N2–Ni1–O1, and O2–Ni1–N3 are 167.50(15), 174.28(16), and 175.37(14), respectively. The Ni–N bond distances range from 2.065(4) to 2.111(4) Å and the Ni–O bond distances are 2.077(3) and 2.108(3) Å, close to that of the literature [32, 33]. The imino-hydrogen in H_3pdc is deprotonated, so the coordination ability of nitrogen is enhanced. Pdc^{3-} bridges two Ni(II) ions in the (N, N) bridging coordination mode with the Ni1–Ni1A distance of 4.472 Å.

Extensive hydrogen bonds assemble the dinuclear units and lattice water into a 2-D plane (figure 2 and table 3). Three types of complementary hydrogen bonds are found: the first one between lattice water and uncoordinated carboxylic oxygen, the second one between lattice water and coordinated water, and the third between coordinated water and coordinated carboxylic oxygen in a neighboring dinuclear Ni(II) unit. The pyridyl rings of neighboring planes are parallel to each other with face-to-face π–π stacking interactions between the parallel pyridyl rings at 3.652 Å. Through the weak bonds, a 3-D network is formed from the 2-D planes (figure 3).

3.3. *IR spectrum*

In the IR spectrum of **1**, a very strong band at 2056 cm^{-1} is assigned to N_3^- stretch. Strong peaks at 1621, 1581 cm^{-1} are attributed to ν(C=O) and 1441, 1352 cm^{-1}

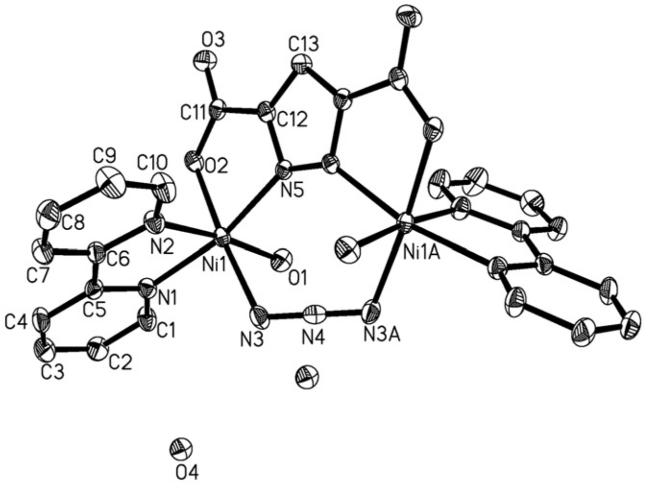

Figure 1. ORTEP diagram of $[Ni_2(2,2\text{-bipy})_2(pdc)(N_3)(H_2O)_2]\cdot 2H_2O$ (**1**) showing the crystallographic numbering scheme; all hydrogens are omitted for clarity.

to ν(C–O). A weak peak at $1605\,\text{cm}^{-1}$ is assigned to C=N [34]. A broad, medium band at *ca* $3325\,\text{cm}^{-1}$, attributed to O–H stretching vibrations, suggests hydrogen-bonding interactions [35]. All these results are in agreement with the X-ray analysis.

3.4. *Magnetic properties*

The variable temperature magnetic susceptibility of **1** was measured at 10 kOe in the temperature range 2–300 K. Plots of χ_M and $\chi_M T$ *versus* T for **1** are shown in figure 4. At room temperature $\chi_M T$ is $2.37\,\text{cm}^3\,\text{M}^{-1}\,\text{K}$, typical for two non-interacting pseudo-octahedral high spin Ni(II) ions ($g > 2.0$) [36]. On lowering the temperature, the $\chi_M T$ slowly decreases to $0.98\,\text{cm}^3\,\text{M}^{-1}\,\text{K}$ at 10 K, after which the values rapidly decrease to $0.28\,\text{cm}^3\,\text{M}^{-1}\,\text{K}$ at 2.0 K. This is indicative of anti-ferromagnetic interactions between the Ni(II) centers in **1**. The variable temperature susceptibility of Ni(II) dimers can be described using an isotropic exchange Hamiltonian, $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$ [37, 38]:

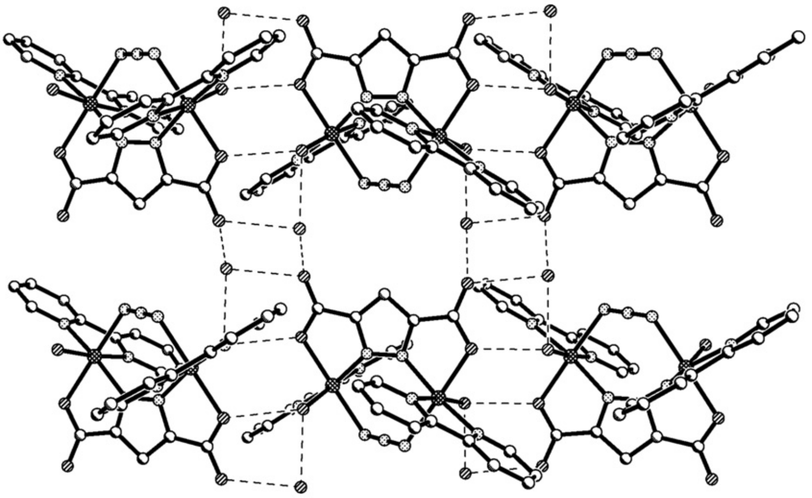

Figure 2. Packing view of the 2-D structure built by intermolecular hydrogen bonds in **1**.

Table 3. Hydrogen bonding lengths (Å) and angles (°) for **1**.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O(4)–H(4W)···O(3)#1	0.830(10)	2.025(17)	2.825(5)	162(3)
O(4)–H(3W)···O(3)#2	0.83	1.97	2.784(5)	166.5
O(1)–H(2W)···O(4)#3	0.83	1.91	2.711(5)	162.0
O(1)–H(1W)···O(2)#1	0.83	2.07	2.836(5)	153.2

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y+2$, $-z+1$; #2 x, $y-1$, z; #3 $-x$, $-y+1$, $-z+1$.

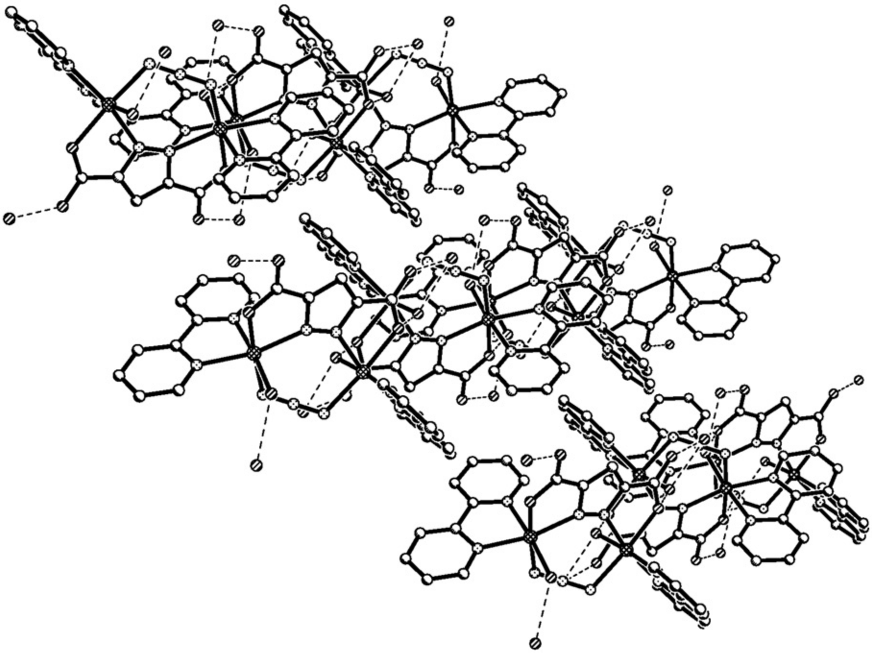

Figure 3. Packing view of the 3-D structure built by π–π stacking interactions between layers in **1**.

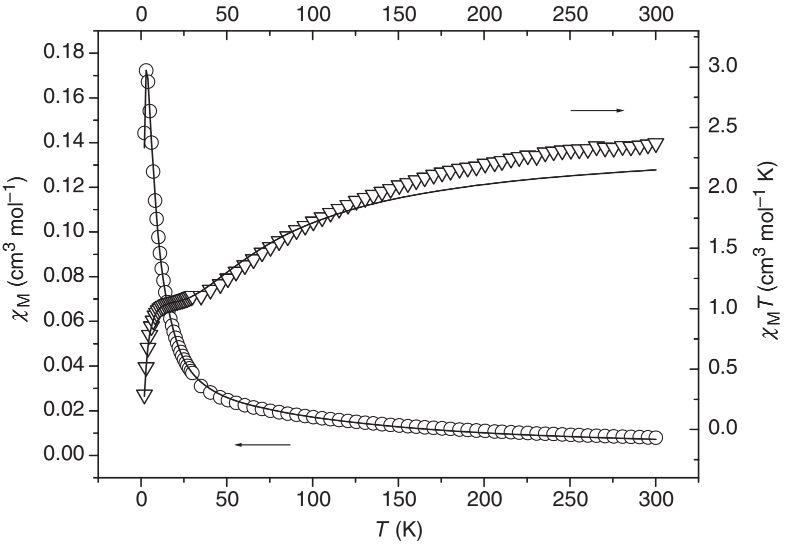

Figure 4. χ_M (○) *vs.* T and $\chi_M T$ (▽) *vs.* T plot for **1**; the solid lines represent the best-fit curve.

$$\chi_M = \frac{\chi_d}{1 - (2zj'/Ng^2\beta^2)\chi_d}$$
$$\chi_d = \left(\frac{2N\beta^2 g^2}{kT}\right)\left(\frac{e^{2J/KT} + 5e^{6J/KT}}{1 + 3e^{2J/KT} + 5e^{6J/KT}}\right) \qquad (1)$$

where N, β, and g have their usual meaning, J is the exchange coupling constant describing magnetic interaction between two adjacent Ni(II) ions and zj' accounts for the inter-dimer interaction. The fitted values are in good agreement with the experimental data giving the parameters $J=-12.65\,\mathrm{cm}^{-1}$, $zj'=3.34\,\mathrm{cm}^{-1}$, $g=2.19$ and $R=3.24\times10^{-4}$ $(R=\sum(\chi_{\mathrm{Obsd}}-\chi'_{\mathrm{Calcd}})^2/\sum(\chi_{\mathrm{Obsd}})^2)$, which further confirms the anti-ferromagnetic exchange coupling within the dimer. In general, the dinickel(II) complexes with pyrazolate bridges show anti-ferromagnetic coupling [39], same as the $\mu_{1,3}$-N_3 bridge [6]. Herein, anti-ferromagnetic coupling for **1** would be expected and is observed.

4. Conclusion

A dinuclear nickel(II) compound with dissimilar bridges, $[Ni_2(2,2\text{-bipy})_2(pdc)(N_3)(H_2O)_2]\cdot H_2O$, has been obtained under hydrothermal conditions. The complex has a discrete dinuclear structure, bridged by pdc^{3-} and azido. The magnetic susceptibility of **1** at 5–300 K exhibits anti-ferromagnetic interactions. The magnetic exchange coupling constants $J=-12.65\,\mathrm{cm}^{-1}$ and $zj'=3.34\,\mathrm{cm}^{-1}$ correspond to similar pyrazole ring or N_3^- bridged Ni(II) complexes.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 641758. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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