Full paper/Mémoire

Synthesis, crystal structure, spectroscopy and magnetism of a trinuclear nickel(II) complex with 3,5-pyrazoledicarboxylic acid as bridge ligands

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A B S T R A C T

A new complex of $[Ni_3(dcp)_2(H_2O)_{10}]$ (**1**) (H_3dcp = 3,5-pyrazoledicarboxylic acid) has been synthesized from H_3dcp and $Ni(NO_3)_2 \cdot 6H_2O$ by hydrothermal reaction. Complex **1** has the discrete trinuclear structure. Three Ni(II) ions are bridged by two dcp^{3-} ligands, with 10 coordinated water molecules as terminal ligands. The molecules of $[Ni_3(dcp)_2(H_2O)_{10}]$ extend into three-dimensional supramolecular architectures by intermolecular O–H···O hydrogen bonds as well as π-π stacking interactions. Magnetic susceptibility measurement shows that a weak antiferromagnetic interaction is operative between nickel(II) ions and an excellent simulation of the experimental data gives $D = 5.27$ cm^{-1}, $J = -2.19$ cm^{-1} and $g = 2.05$.

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1. Introduction

Multinuclear transition metal complexes have attracted much interest because of their interesting molecular architecture, intriguing magnetic properties [1–4], fascinating biological activities [5–7], potential applications as functional materials in catalysis [8–10], and so on. For a multinuclear transition metal complex, it contains a variety of forces, including some strong interactions (i.e. metal–ligand coordination bonds) and other weak interactions such as hydrogen bonds [11–13] and π-π stacking interactions [10,14,15]. Although these weak interactions are relatively weak, they play critical roles in the construction of high-dimensional supramolecular networks [10]. Hence, research on weaker interactions is vital to the development of supramolecular chemistry [16].

Ligand H_3dcp (H_3dcp = 3,5-pyrazoledicarboxylic acid) is a versatile ligand, which contains a number of N or O

coordination sites and rich coordination modes [17,18]. The deprotonated anion of dcp^{3-} could provide six donor sites from two carboxylate groups and one pyrazole ring [19]. The carboxylate groups of dcp^{3-} have a strong ability to bond various metal ions and influence the coordinated configurations, even change the dimensional number [20–24]. Till now, some H_3dcp complexes with alkaline, transition, and lanthanide metals have been reported [25–28]. Moreover, ligand H_3dcp contains abundance N or O atoms, thus the coordinated structural motifs of H_3dcp complexes readily form hydrogen-bonded networks [29,30]. Herein, we reported a new trinuclear nickel(II) complex $[Ni_3(dcp)_2(H_2O)_{10}]$ (**1**) with dcp^{3-} as bridge ligands. The crystal structure and magnetic properties of complex **1** have also been investigated.

2. Experimental

2.1. Materials and instrumentations

All chemicals and solvents used for synthesis were purchased from Alfa, were of reagent grade and used without

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further purification. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 C analyzer and the FT-IR spectra were recorded with a Bruker Tensor 27 Fourier transform infrared spectroscopy device in the 4000–400 cm^{-1} regions on KBr disks. Variable-temperature magnetic susceptibilities were measured on a Quantum Design MPMS-7 SQUID magnetometer from 2 to 300 K in a magnetic field of 2000 G. Diamagnetic contributions of all constituent atoms were made with Pascal's constants [31].

2.2. Preparation of $[Ni_3(dcp)_2(H_2O)_{10}]$ 1

Complex **1** was synthesized by reaction of $Ni(NO_3)_2 \cdot 6H_2O$ with H_3dcp via hydrothermal reaction. A mixture of $Ni(NO_3)_2 \cdot 6H_2O$ (0.0206 g, 0.1 mmol), H_3dcp (0.0112 g, 0.1 mmol), NaOH (0.004 g, 0.1 mmol), 3 mL acetonitrile and 8 mL aqueous solution was sealed in a 25 mL stainless steel Teflon liner reactor. The reaction mixture was directly heated to 140 °C and kept for three days, and then cooled to room temperature at a rate of 6 °C per hour. The resulting green rectangular-shaped crystals were filtered off, washed with distilled water and dried at ambient temperature. (Yield: 78% based on Ni.) Anal. Calc. for $C_5H_{11}N_2Ni_{1.5}O_9$ (331.22): C, 18.13%; H, 3.35%; N, 8.46%; Found: C, 18.20%; H, 3.12%; N, 8.37%. IR data (KBr, cm^{-1}): 3369 (vs), 2363 (m), 1567 (m), 1368 (vs), 1236 (m), 1119 (w), 857 (w), 783 (s), 738 (w), 678 (w).

2.3. X-ray structure determination and refinement

A crystal of dimensions 0.22 mm × 0.32 mm × 0.12 mm for complex **1** was mounted on a Bruker Smart 1000 area detector using graphite monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) at 293(2) K. The ω-φ scan technique was employed. Structure of the crystal was solved primarily by direct method followed by Fourier difference techniques (SHELXS-97) and refined by the full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97) [32]. Crystallographic data and experimental details for structural analyses are summarized in Table 1.

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the

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

Empirical formula	$C_5H_{11}N_2Ni_{1.5}O_9$
Formula weight	331.22
Temperature/K	293(2)
Crystal system	Monoclinic
space group	$C2/c$
Unit cell dimensions	a = 12.183(3) Å
	b = 8.8520(3) Å, β = 103.23(3)°C
	c = 19.674(4) Å
V	2065.4(7) Å³
Z	8
Calculated density	2.130 Mg/m³
Absorption coefficient	2.809 mm^{-1}
$F(000)$	1352
Crystal size (mm)	0.32 × 0.22 × 0.12
θ range for data collection	3.33 to 24.99°
Limiting indices	$-14 \leq h \leq 12, - 0 \leq k$
	$\leq 10, - 23 \leq l \leq 21$
Reflections collected/unique	4843/1742 [R_{int} = 0.1565]
Completeness to θ = 27.89	95.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7292 and 0.4668
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1742/64/172
Goodness-of-fit on F^2	1.116
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0937$, $wR_2 = 0.1369$
R indices (all data)	$R_1 = 0.1715$, $wR_2 = 0.1600$
Largest diff. peak and hole	0.672 and $-$ 0.633 e Å^{-3}

Cambridge Crystallographic Data Centre as supplementary publication No. 826001. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 1223 336 033; e mail: deposit @ccdc cam ac uk).

3. Results and discussion

3.1. Description of crystal structure

Single-crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the monoclinic space group $C2/c$. The crystal structure consists of centrosymmetric $[Ni_3(pd-c)_2(H_2O)_{10}]$ molecules. Selected bond lengths and angles are given in Table 2 and the perspective view of the compound with atomic numbering scheme is shown in

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

Ni(1)–N(1)	2.0514(6)	Ni(1)–O(2)	2.0220(3)
Ni(1)–O(3)	2.0692(3)	Ni(1)–O(4)	2.0814(3)
Ni(1)–O(5)	2.0766(6)	Ni(1)–O(6)	2.0004(3)
Ni(2)–O(7)	2.0786(3)	Ni(2)–O(8)	2.0646(6)
Ni(2)–N(2)	2.0280(3)		
O(6)–Ni(1)–N(1)	105.367(7)	O(2)–Ni(1)–N(1)	80.352(6)
O(6)–Ni(1)–O(3)	87.713(6)	O(2)–Ni(1)–O(3)	89.787(6)
N(1)–Ni(1)–O(3)	91.147(7)	O(6)–Ni(1)–O(5)	86.488(6)
O(2)–Ni(1)–O(5)	87.713(6)	N(1)–Ni(1)–O(5)	167.947(13)
O(3)–Ni(1)–O(5)	87.106(7)	O(6)–Ni(1)–O(2)	173.773(6)
O(6)–Ni(1)–O(4)	91.587(6)	O(2)–Ni(1)–O(4)	90.751(5)
O(3)–Ni(1)–O(4)	177.718(7)	O(5)–Ni(1)–O(4)	90.700(6)
N(2)–Ni(2)–N(2)#1	180.000	N(2)–Ni(2)–O(8)	80.316(6)
N(2)–Ni(2)–O(8)#1	99.684(6)	Ni(1)–O(4)–H(4A)	125.680(11)
Ni(1)–O(3)–H(3A)	131.892(12)	N(2)–Ni(2)–O(7)	87.316(5)
O(8)–Ni(2)–O(7)	90.047(6)	O(7)–Ni(2)–O(7)#1	180.000

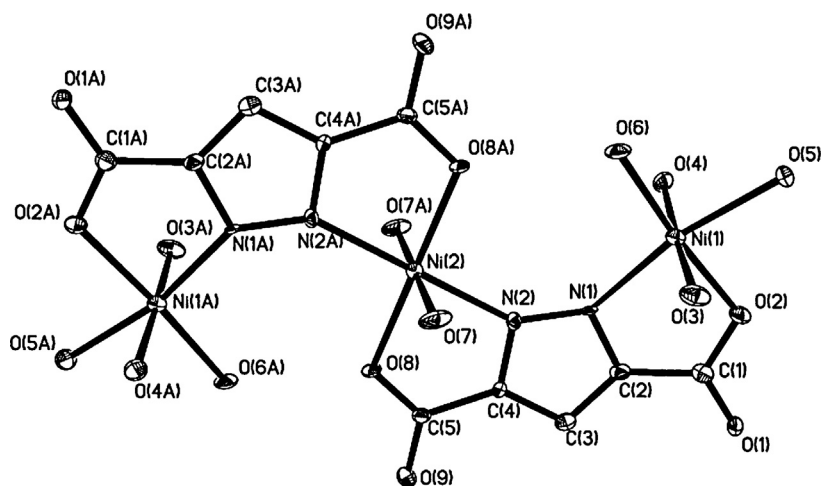Symmetry transformations used to generate equivalent atoms: #1 $-x+3/2, -y+1/2, -z+2$

Fig. 1. Molecular structure for $[Ni_3(pdc)_2(H_2O)_{10}]$ with the atomic numbering scheme.

Fig. 1. In complex **1**, two pdc^{3-} ligands behave as bis(bidentate) ligands binding three Ni ions (Ni(1), Ni(1A) and Ni(2)), forming a trinuclear unit. The intramolecular Ni(1)···Ni(2) separations are 4.472 Å. The trinuclear unit consists of two crystallographically independent Ni atoms, namely, Ni(1) and Ni(2). All Ni(II) ions have slightly distorted octahedral geometries. However, there are two sets of coordination environments around the Ni atoms. The Ni(1) or Ni(1A) atom is coordinated to one L^{3-} and four H$_2$O

molecules, giving a slightly distorted octahedral geometry with an O$_5$N donor set, while Ni(2), located at the center of the trinuclear unit, has an O$_4$N$_2$ donor set originating from two L^{3-} ligands and two H$_2$O molecules. The average Ni–O and Ni–N distances are 2.058(0) and 2.039(8) Å, respectively, which are all within the normal range.

Fig. 2 shows the packing diagram of complex **1**. There are two kinds of O-H···O hydrogen bonds in the title complex (Table 3). The first one is a hydrogen bond
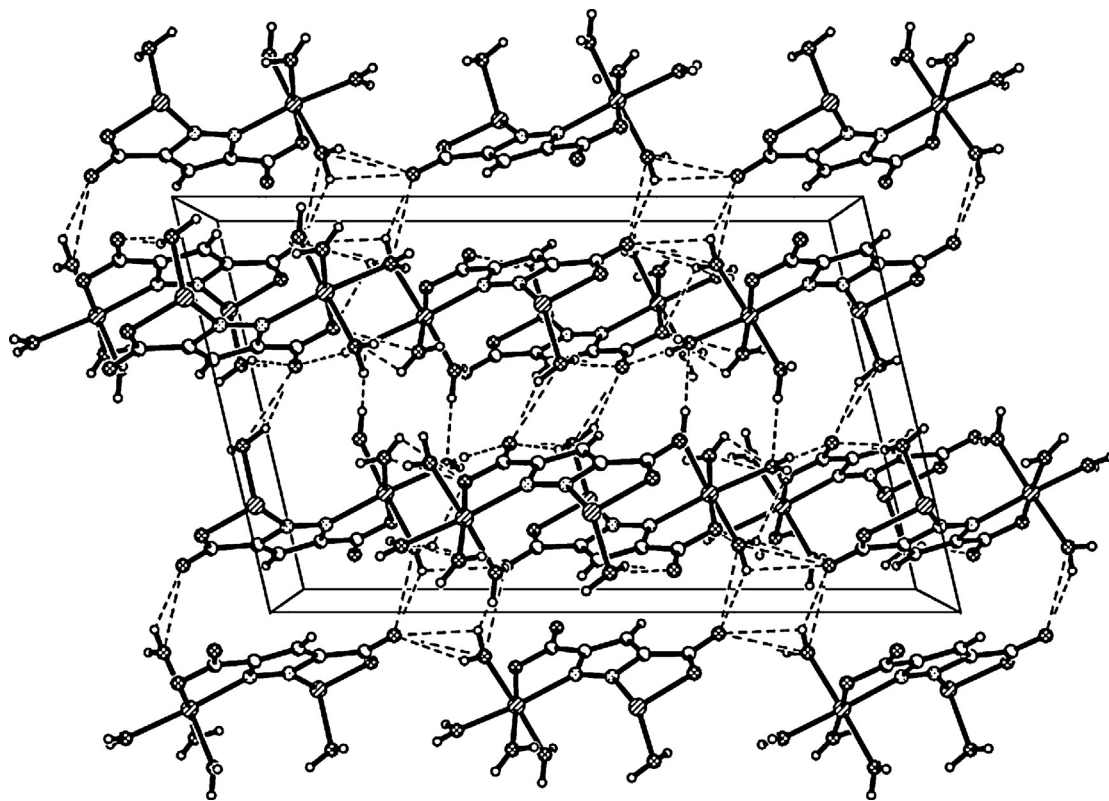

Fig. 2. A view of intermolecular O–H···O hydrogen bonding interactions between adjacent molecules that lead to the 3D network (black dashed lines present the H–bond).

Table 3
Hydrogen bonds (Å and°) in complex **1**.

D–H–A	D–H	H–A	D–A	< DHA	Symmetry code on A
O(3)–H(3A)–O(5)	0.8658(2)	2.0905(5)	2.956	178.216(13)	−0.5+x,1.5−y,−0.5+z
O(3)–H(3B)–O(9)	0.8692(2)	1.9507(4)	2.791(2)	162.252(9)	1.5−x,−0.5+y,1.5−z
O(4)–H(4A)–O(9)	0.8635(1)	2.4289(5)	2.812(6)	107.556(15)	−0.5+x,0.5+y,−1+z
O(4)–H(4A)–O(2)	0.8635(1)	2.4508(7)	3.088(4)	131.171(11)	−0.5+x,0.5+y,z
O(4)–H(4A)–O(5)	0.8635(1)	2.4731(5)	3.004(4)	120.447(8)	−0.5+x,0.5+y,z
O(4)–H(4B)–O(9)	0.8706(1)	2.1218(7)	2.767(1)	130.452(12)	1.5−x,0.5+y,1.5−z
O(5)–H(5A)–O(1)	0.8483(2)	1.8470(3)	2.689(1)	171.558(13)	−0.5+x,0.5+y,z
O(5)–H(5B)–O(4)	0.8467(1)	2.3200(4)	3.004(4)	138.171(9)	1−x,1−y,1−z
O(6)–H(6A)–O(2)	0.8606(2)	2.4230(6)	2.731(9)	101.789(13)	−0.5+x,0.5+y,z
O(6)–H(6B)–O(8)	0.8555(1)	1.7957(3)	2.651(1)	178.484(13)	1−x,1+y,1−z
O(7)–H(7A)–O(1)	0.8501(3)	2.0787(7)	2.863	153.158(15)	−0.5+x,1.5−y,−0.5+z
O(7)–H(7B)–O(1)	0.8480(1)	1.9538(3)	2.751(7)	156.347(11)	1.5−x,−0.5+y,1.5−z

between the oxygen atoms from carboxylate groups and coordinated water molecules (O(3)···O(9), O(4)···O(9), O(5)···O(1), O(6)···O(8), O(4)···O(2) and O(7)···O(1)), in which the coordinated water molecules act as hydrogen donors to form hydrogen bonds with oxygen atoms of carboxylate moieties. The second one is the O–H···O hydrogen bond between coordinated water molecules (O(3)···O(5), O(4)···O(5)). As a result, these hydrogen bonds extend the trinuclear structure into a three-dimensional network. Moreover, Fig. 3 shows that the plane-to-plane distance of pyrazole rings are 4.205 Å and 3.902 Å, respectively, indicating the possible existence of π-π stacking interactions in the system. These O–H···O hydrogen bonds and π-π stacking interactions are likely to play an important role in the stabilization of the crystal system [24].

3.2. IR spectra

The FT-IR spectra for complex **1** is consistent with other pyrazoledicarboxylic compounds [19,33,34]. A band at 3369 cm^{-1} can be assigned to the O–H stretching

frequency of the water molecule, which is approximately close to the value of 3359 cm^{-1} in the extended water tapes [35]. Bands at 1567 cm^{-1} can be assigned to the pyrazole ring C=N bond stretching modes. The strong absorptions at 1368 cm^{-1} [$\upsilon_{asym}(CO_2)$] and 1236 cm^{-1} [$\upsilon_{sym}(CO_2)$] are attributable to the characteristic of the carboxylate group [24,36,37]. Additional characteristic bending vibrations can be identified in the region 857–678 cm^{-1}.

3.3. Magnetic properties

The temperature dependence of χ_M and $\chi_M T$ for complex **1** in the range of 2–300 K is shown in Fig. 4 (χ_M is the molar magnetic susceptibility per Ni$_3$ unit). As shown in Fig. 4, the value of $\chi_M T$ for complex **1** at room temperature is 3.07 cm^{3}K mol^{-1}, which is very close to the spin-only value (3.00 cm^{3}K mol^{-1}) for three isolated nickel(II) ions ($S = 1$, $g = 2.0$). When decreasing the temperature, the $\chi_M T$ plot decreases very slowly till 55 K and then begins to drop down sharply and reaches a minimum
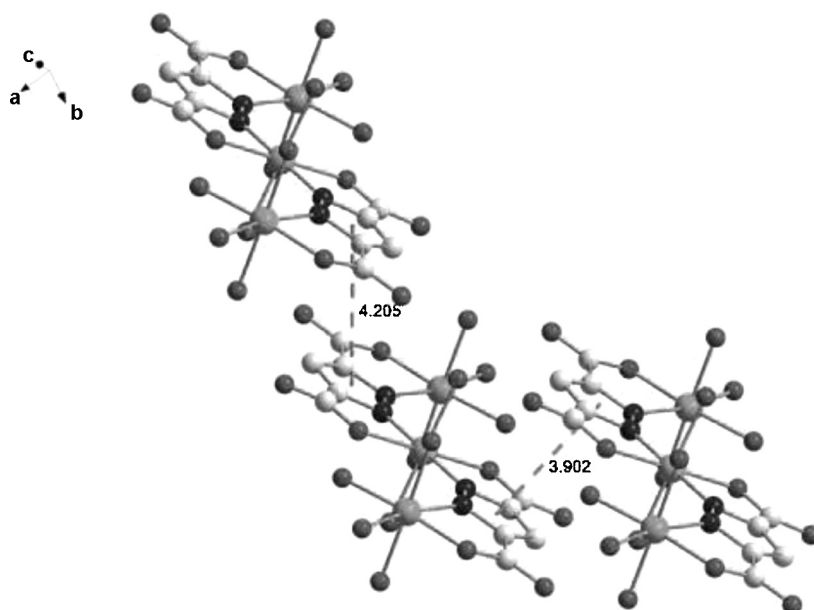

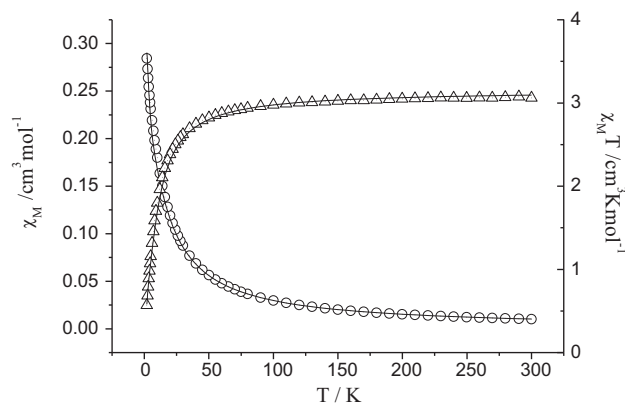**Fig. 3.** The plane-to-plane distance of pyrazole rings.

Fig. 4. Experimental and calculated variations of $\chi_M(\text{O})$ and $\chi_M T(\Delta)$ versus T for complex **1**.

value of $0.57\ \text{cm}^3\text{K mol}^{-1}$ at 2 K, suggesting that the dominant antiferromagnetic interactions are propagated between nickel(II) ions. There is no peak in the χ_M vs T plot. Therefore, no long-range magnetic ordering is found.

In order to analyze the experimental data, we tried to simulate the data by taking into account zero-field splitting of Ni(II) ions by parameter D, and treating exchange interaction (J) between Ni(II) ions in the following Hamiltonian given in eq. (1):

$$\hat{H} = -2J[\widehat{S_1}\widehat{S_2} + \widehat{S_2}\widehat{S_3}] + D\sum_{i=1}^{3}\widehat{S}_{iz}^{2} + g\mu_B H\sum_{i=1}^{3}\widehat{S}_i \qquad (1)$$

By using the computational program of MAGPACK [38,39], we have obtained an excellent simulation of the experimental data from the following parameters $D = 5.27\ \text{cm}^{-1}$, $J = -2.19\ \text{cm}^{-1}$ and $g = 2.05$, where $\hat{S}_{iz}$ is the z component of the $\hat{S}_i$ operator, J is the magnetic coupling constant between Ni(II) ions in the trimer, D is zero-field splitting parameter, g is the Landé factor of the Ni(II) ion. The small negative value of J also indicates that a weak antiferromagnetic interaction is operative between the nickel(II) ions. The obtained D parameter is close to previously reported values in similar nickel(II) complexes [40].

4. Conclusions

In this paper, we have presented the synthesis, spectroscopy, crystal structure and magnetic properties of a new nickel(II) compound [Ni$_3$(dcp)$_2$(H$_2$O)$_{10}$] **1** (H$_3$dcp = pyrazoledicarboxylic acid). The crystal structure indicates that three Ni(II) ions exist in a line arrangement, with two dcp^{3-} as bridge ligands and ten coordinated water molecules as terminal ligands. Complex **1** is further packed into a three-dimensional structure via intermolecular hydrogen bonds and π-π stacking interactions. Magnetic susceptibility measurements show that a weak antiferromagnetic interaction is operative in this nickel(II) complex.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.crci.2013.01.001

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