

N,N' -(2-苯并咪唑基甲基)亚氨基甲基膦酸的双核镍化合物 $\text{Ni}_2(\text{bbimp})_2(4,4'\text{-bipy})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$ 和 $\text{Ni}_2(\text{bbimp})_2(\text{H}_2\text{O})_2[\text{Ni}(\text{bbimp})(\text{H}_2\text{O})_2]_2 \cdot 4\text{H}_2\text{O}$ 的晶体结构和磁学性质

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摘要: 该文报道了 N,N' -(2-苯并咪唑基甲基)亚氨基甲基膦酸 $\{\text{bbimpH}_2, [(\text{C}_7\text{H}_5\text{N}_2)\text{CH}_2]_2\text{NCH}_2\text{PO}_3\text{H}_2\}$ 的 2 个镍化合物 $\text{Ni}_2(\text{bbimp})_2(4,4'\text{-bipy})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$ (**1**) 和 $[\text{Ni}_2(\text{bbimp})_2(\text{H}_2\text{O})_2][\text{Ni}(\text{bbimp})(\text{H}_2\text{O})_2]_2 \cdot 4\text{H}_2\text{O}$ (**2**)。化合物 **1** 是 4,4'-联吡啶作为桥连配体的中性双核结构。化合物 **2** 含有 1 个中性的 $[\text{Ni}_2(\text{bbimp})_2(\text{H}_2\text{O})_2]$ 双核分子与 2 个中性的 $[\text{Ni}(\text{bbimp})(\text{H}_2\text{O})_2]$ 单核分子。双核分子单元中的 2 个 Ni(II) 离子被 2 个磷酸氧桥连。在化合物 **2** 中, 磷酸氧桥连的 2 个 Ni(II) 离子之间存在铁磁性相互作用。

关键词: 镍; N,N' -(2-苯并咪唑基甲基)亚氨基甲基膦酸; 4,4'-联吡啶; 晶体结构; 磁性

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Structures and Magnetic Properties of Dimeric Nickel Phosphonates Based on Bis(benzimidazol-2-ylmethyl)imino Methylenephosphonate: $\text{Ni}_2(\text{bbimp})_2(4,4'\text{-bipy})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Ni}_2(\text{bbimp})_2(\text{H}_2\text{O})_2][\text{Ni}(\text{bbimp})(\text{H}_2\text{O})_2]_2 \cdot 4\text{H}_2\text{O}$

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Abstract: This paper reports two nickel phosphonates $\text{Ni}_2(\text{bbimp})_2(4,4'\text{-bipy})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{Ni}_2(\text{bbimp})_2(\text{H}_2\text{O})_2][\text{Ni}(\text{bbimp})(\text{H}_2\text{O})_2]_2 \cdot 4\text{H}_2\text{O}$ (**2**) based on bis(benzimidazol-2-ylmethyl)imino methylenephosphonic acid $\{\text{bbimpH}_2, [(\text{C}_7\text{H}_5\text{N}_2)\text{CH}_2]_2\text{NCH}_2\text{PO}_3\text{H}_2\}$. Compound **1** has a neutral dinuclear structure in which 4,4'-bipy serves as a bridging ligand. While in compound **2**, neutral dimers of $[\text{Ni}_2(\text{bbimp})_2(\text{H}_2\text{O})_2]$, where the Ni(II) ions are doubly bridged by phosphonate oxygen atoms, are aggregated with the mononuclear species of $[\text{Ni}(\text{bbimp})(\text{H}_2\text{O})_2]$. Ferromagnetic interactions are mediated between the Ni(II) ions through the phosphonate oxygen in compound **2**. CCDC: 644282, **1**; 644283, **2**.

Key words: nickel; bis(benzimidazol-2-ylmethyl)imino methylenephosphonic acid; 4,4'-bipyridine; crystal structure; magnetic property

0 Introduction

Inorganic-organic hybrid materials based on phosphonate ligands have gained increasing attentions in recent years due to their potential applications in

catalysis, ion exchange, proton conductivity and magnetic materials etc^[1-5]. In our previous work^[6,7], we have shown that the integration of the benzimidazole moiety with the phosphonate group could not only provide additional coordination sites for the metal ions,

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but also influence the packing of the structures through weak interactions such as the aromatic stacking and the hydrogen bond interactions. Therefore, the reactions of bis (benzimidazol-2-ylmethyl)imino methylenephosphonic acid {bbimpH₂, [(C₇H₅N₂)CH₂]₂NCH₂PO₃H₂} with different metal salts result in the formation of compounds Mn₂{[(C₇H₅N₂)CH₂]₂NCH₂PO₃]₂(H₂O)₂·2H₂O and Cd₂{[(C₇H₅N₂)CH₂]₂NCH₂PO₃]₂·H₂O with dinuclear structures, Fe₂{[(C₇H₅N₂)CH₂]₂NCH₂PO₃]₂·2H₂O with a chain structure and Cu₁₂{[(C₇H₅N₂)CH₂]₂NCH₂P(OH)O₂]₂ with a two-dimensional metallomacrocyclic structure^[6]. The reactions of (benzimidazol-2-ylmethyl)imino bis(methylenephosphonic acid) [(C₇H₅N₂)CH₂N(CH₂PO₃H₂)₂] with metal salts lead to five isomorphous compounds M{[(C₇H₅N₂)CH₂N(CH₂PO₃H₂)₂] (M=Mn, Fe, Co, Cu, Cd) with chain structures^[7]. In order to explore new hybrid materials based on the same phosphonate ligands, further work is carried out by incorporating the second organic ligands such as 4,4'-bipyridine and piperazine. In this paper, we report two new nickel phosphonates, namely, Ni₂(bbimp)₂(4,4'-bipy)(H₂O)₂·2H₂O (**1**) and [Ni₂(bbimp)₂(H₂O)₂][Ni(bbimp)(H₂O)₂]₂·4H₂O (**2**). Both exhibit discrete dinuclear structures.

1 Experimental

1.1 Materials and methods

The bis(benzimidazol-2-ylmethyl)imino methylenephosphonic acid (bbimpH₂) was synthesized according to the reported method^[6]. All other starting materials were reagent grade and used as purchased. The elemental analyses were performed with a PE 240C elemental analyzer. The infrared spectra were recorded on a VECTOR 22 spectrometer with pressed KBr pellets. Thermal analyses were performed in nitrogen in the temperature range 20~800 °C with a heating rate of 10 °C·min⁻¹ on a TGA-DTA V1.1B TA Inst 2100. The powder XRD patterns were recorded on a Shimadzu XD-3A X-ray diffractometer. Variable temperature magnetic susceptibility data were obtained on microcrystalline samples (12.28 mg for **2**) from 1.8 to 300 K in a magnetic field of 2 kOe, using a Quantum Design MPMS-XL7 SQUID magnetometer. Diamagnetic corrections were made for both the sample holder and

the compound estimated from Pascal's constants^[8].

1.2 Synthesis of Ni₂(bbimp)₂(4,4'-bipy)(H₂O)₂·2H₂O (**1**)

A mixture of bbimpH₂·3H₂O (0.10 mmol, 0.042 5 g), NiSO₄·6H₂O (0.10 mmol, 0.026 3 g), 4,4'-bipy (0.10 mmol, 0.015 6 g) and 0.073 0 g 25% Me₄NOH in 8 mL H₂O (pH=5.36) was kept in a Teflon-lined autoclave at 140 °C for 24 hours. After the mixture was cooled to room temperature, cyan blocky crystals were obtained as a monophasic material because the powder X-ray diffraction pattern is consistent with the pattern simulated (according to the determined single crystal structure). Yield: 33 mg (60.9%). Anal. found (calcd) for C₄₄H₄₈N₁₂O₁₀P₂Ni₂ (%): C, 48.80 (48.70); H, 4.57 (4.43); N, 15.52 (15.49). IR (KBr, cm⁻¹): 3 632(w), 3 224~2 887(br), 1 887(w), 1 691(w), 1 664(w), 1 606(m), 1 554(w), 1 537(w), 1 487(w), 1 468(m), 1 455(s), 1 409(m), 1 352(w), 1 339(w), 1 327(w), 1 306(w), 1 271(m), 1 219(m), 1 096(s), 1 063(s), 1 037(m), 1 015(m), 973(s), 945(m), 903(w), 895(w), 837(w), 820(m), 783(w), 754(m), 743(s), 653(w), 635(w), 623(w), 597(w), 558(m), 521(w), 499(w), 483(w), 464(w), 439(w), 422(w). Thermal analysis shows that compound **1** experiences the first step of decomposition below 238 °C. The observed weight loss (6.5%) corresponds to the removal of two coordinated and two lattice water molecules (calcd. 6.6%). The decomposition above 238 °C is due to the combustion of the organic group.

1.3 Synthesis of [Ni₂(bbimp)₂(H₂O)₂][Ni(bbimp)(H₂O)₂]₂·4H₂O (**2**)

A mixture of bbimpH₂·3H₂O (0.10 mmol, 0.042 5 g), NiSO₄·6H₂O (0.10 mmol, 0.026 3 g), piperazine hexahydrate (0.10 mmol, 0.016 6 g) and 0.073 0 g 25% Me₄NOH in 8 mL H₂O (pH=9.55) was kept in a Teflon-lined autoclave at 140 °C for 24 hours. After the mixture was cooled to room temperature, green blocky crystals were obtained together with a small amount of unidentified brown powder. The crystals were manually selected and were used for physical measurements. Yield: 11 mg(25%). Anal. found (calcd) for C₆₈H₈₄N₂₀O₂₂P₄Ni₄ (%): C, 43.10 (43.12); H, 4.38 (4.44); N, 14.74 (14.80). IR (KBr, cm⁻¹): 3 611(m), 3 555(m), 3 329~2 517(s, br), 1 647(m), 1 626(m), 1 595(w), 1 556(w), 1 542

(m), 1 490(w), 1 470(m), 1 452(s), 1 398(w), 1 343(m), 1 286(m), 1 257(w), 1 238(w), 1 225(w), 1 206(w), 1 157(s), 1 103(s), 1 067(s), 1 033(s), 1 021(m), 1 007(m), 982(m), 960(m), 944(m), 918(w), 898(w), 861(w), 845(w), 765(w), 748(s), 661(w), 632(w), 606(w), 569(m), 523(w), 496(w), 475(w), 442(w), 418(w). Thermal analysis reveals that compound **2** experiences two steps of decompositions below 200 °C. The observed weight loss (9.2%) corresponds to the removal of six coordination and four lattice water molecules (calcd. 9.5%). Then a plateau is observed up to 310 °C, above which the organic ligand is decomposed and the structure is collapsed.

An effort to prepare a single phase of compound **2** by changing the pH to 8.55~10.27 was not successful. Similar brown powder was also observed in the synthesis of compounds $\text{Mn}_2\{[(\text{C}_7\text{H}_5\text{N}_2)\text{CH}_2]_2\text{NCH}_2\text{PO}_3\}_2(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$, $\text{Fe}_2\{[(\text{C}_7\text{H}_5\text{N}_2)\text{CH}_2]_2\text{NCH}_2\text{PO}_3\}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Cu}^{\text{I}}_2\{[(\text{C}_7\text{H}_5\text{N}_2)\text{CH}_2]_2\text{NCH}_2\text{P}(\text{OH})\text{O}_2\}_2^{[6]}$. Further, piperazine is essential in preparing compound **2**. Without it, thin needle-like crystals of a new phase bbimp-Ni^[9] would be obtained as confirmed by the XRD measurements.

1.4 Crystal structure determination

Single crystals of dimensions 0.05 mm × 0.04 mm

× 0.03 mm for **1** and 0.10 mm × 0.05 mm × 0.04 mm for **2** were selected for diffraction data collection at 298 K on a Bruker SMART APEX CCD diffractometer equipped with graphite-monochromatized Mo $K\alpha$ ($\lambda = 0.071\,073\text{ nm}$) radiation. A hemisphere of data was collected in the θ range 1.95°~26.00° for **1** and 1.59°~26.00° for **2** using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 8 s per frame for **1** and 10 s for **2**. Numbers of measured and observed reflections [$I > 2\sigma(I)$] are 11 640 and 4 389 ($R_{\text{int}} = 0.045\,8$) for **1** and 17 998 and 7 760 ($R_{\text{int}} = 0.059\,4$) for **2**, respectively. The data were integrated using the Siemens SAINT program^[10], with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Multi-scan absorption corrections were applied. The structures were solved by direct methods, and were refined on F^2 by full matrix least squares using SHELXTL^[11]. All the non-hydrogen atoms were refined anisotropically. All H atoms were added geometrically and refined isotropically. Crystallographic and refinement details are listed in Table 1. Selected bond lengths and angles are given in Tables 2 and 3.

CCDC: 644282, **1**; 644283, **2**.

Table 1 Crystallographic data for **1** and **2**

Compound	1	2
Empirical formula	$\text{C}_{44}\text{H}_{48}\text{N}_{12}\text{O}_{10}\text{P}_2\text{Ni}_2$	$\text{C}_{68}\text{H}_{80}\text{N}_{20}\text{O}_{20}\text{P}_4\text{Ni}_4$
Formular weight	1 084.30	1 856.24
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a / nm	0.692 41(9)	1.243 1(3)
b / nm	2.898 8(4)	1.335 5(4)
c / nm	1.134 79(13)	1.371 8(4)
$\alpha / (^\circ)$		68.977(5)
$\beta / (^\circ)$	98.613(3)	81.149(6)
$\gamma / (^\circ)$		68.421(5)
V / nm^3	2.252 0(5)	1.976 2(10)
Z	2	1
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.599	1.560
$F(000)$	1 124	960
R_{int}	0.0458	0.0594
Goodness-of-fit on F^2	1.056	1.065
$R_1, wR_2 [I > 2\sigma(I)]$	0.056 1, 0.124 5	0.063 5, 0.114 1

Continued Table 1

R_1, wR_2 (All date)	0.079 7, 0.131 8	0.089 6, 0.119 6
$(\Delta\rho)_{\max}, (\Delta\rho)_{\min} / (\text{e} \cdot \text{nm}^{-3})$	305, -521	324, -634

$$R_1 = \sum |F_o| - |F_c| / \sum |F_o|, wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}.$$

Table 2 Selected bond lengths (nm) and angles ($^\circ$) for 1^a

Ni(1)-O(3)	0.204 4(2)	Ni(1)-N(4)	0.217 0(3)	P(1)-O(2)	0.152 2(3)
Ni(1)-O(1W)	0.209 5(3)	Ni(1)-N(6)	0.207 3(3)	P(1)-O(3)	0.151 1(3)
Ni(1)-N(1)	0.213 9(3)	P(1)-C(1)	0.180 9(4)		
Ni(1)-N(2)	0.2077(3)	P(1)-O(1)	0.1514(3)		
O(3)-Ni(1)-N(1)	87.07(11)	N(2)-Ni(1)-N(4)	94.05(12)	C(3)-N(1)-Ni(1)	107.0(2)
O(3)-Ni(1)-N(2)	91.91(11)	N(2)-Ni(1)-O(1W)	175.35(12)	C(4)-N(2)-Ni(1)	111.4(2)
O(3)-Ni(1)-N(4)	163.73(11)	N(6)-Ni(1)-N(4)	103.47(12)	C(10)-N(2)-Ni(1)	142.4(3)
O(3)-Ni(1)-O(1W)	87.42(12)	N(6)-Ni(1)-N(2)	98.13(12)	C(11)-N(4)-Ni(1)	107.4(2)
O(3)-Ni(1)-N(6)	90.63(11)	N(6)-Ni(1)-O(1W)	86.48(12)	C(17)-N(4)-Ni(1)	147.6(2)
N(1)-Ni(1)-N(2)	82.52(11)	O(1W)-Ni(1)-N(4)	85.42(12)	C(18)-N(6)-Ni(1)	123.0(2)
N(1)-Ni(1)-N(4)	78.73(11)	P(1)-O(3)-Ni(1)	116.60(14)	C(22)-N(6)-Ni(1)	121.3(3)
N(1)-Ni(1)-N(6)	177.64(12)	C(1)-N(1)-Ni(1)	107.7(2)		
N(1)-Ni(1)-O(1W)	92.85(11)	C(2)-N(1)-Ni(1)	108.8(2)		

^aSymmetry code: A: $-x, -y+1, -z+1$.

Table 3 Selected bond lengths (nm) and angles ($^\circ$) for 2^a

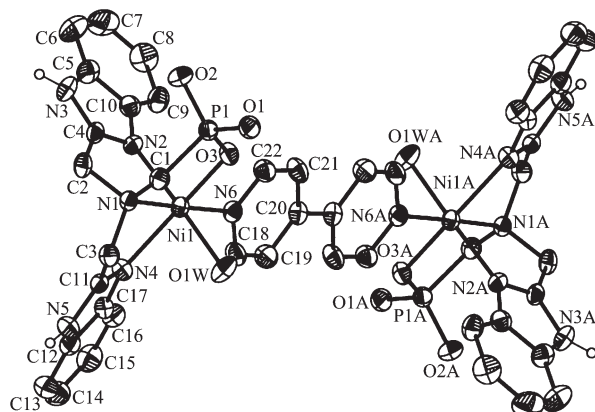
Ni(1)-O(1)	0.210 9(3)	Ni(2)-O(4)	0.205 0(3)	P(1)-O(1)	0.154 2(3)
Ni(1)-O(1A)	0.205 2(3)	Ni(2)-N(6)	0.215 5(4)	P(1)-O(2)	0.149 5(3)
N(1)-Ni(1)	0.216 2(3)	Ni(2)-N(7)	0.204 5(4)	P(1)-O(3)	0.151 0(3)
N(2)-Ni(1)	0.202 5(3)	Ni(2)-N(9)	0.210 0(3)	P(2)-O(4)	0.151 9(3)
N(4)-Ni(1)	0.207 8(3)	Ni(2)-O(2W)	0.208 6(3)	P(2)-O(5)	0.151 0(3)
Ni(1)-O(1W)	0.216 9(3)	Ni(2)-O(3W)	0.201 1(3)	P(2)-O(6)	0.151 6(3)
O(1)-Ni(1)-N(1)	85.96(12)	P(1)-O(1)-Ni(1A)	141.19(18)	O(2W)-Ni(2)-N(6)	91.94(13)
O(1)-Ni(1)-N(2)	96.34(13)	P(1)-O(1)-Ni(1)	116.90(16)	O(2W)-Ni(2)-N(7)	88.80(13)
O(1)-Ni(1)-N(4)	162.12(12)	C(1)-N(1)-Ni(1)	106.0(2)	O(2W)-Ni(2)-N(9)	172.43(12)
O(1)-Ni(1)-O(1W)	86.29(11)	C(2)-N(1)-Ni(1)	110.3(2)	O(3W)-Ni(2)-O(2W)	91.68(12)
O(1A)-Ni(1)-N(1)	164.24(12)	C(3)-N(1)-Ni(1)	108.9(2)	O(3W)-Ni(2)-O(4)	93.96(11)
O(1A)-Ni(1)-N(2)	100.09(12)	C(4)-N(2)-Ni(1)	114.7(3)	O(3W)-Ni(2)-N(6)	176.23(12)
O(1A)-Ni(1)-O(1)	78.30(10)	C(10)-N(2)-Ni(1)	139.1(3)	O(3W)-Ni(2)-N(7)	100.30(14)
O(1A)-Ni(1)-O(1W)	90.54(11)	C(11)-N(4)-Ni(1)	110.7(3)	O(3W)-Ni(2)-N(9)	95.02(12)
O(1A)-Ni(1)-N(4)	115.15(12)	C(17)-N(4)-Ni(1)	143.2(3)	P(2)-O(4)-Ni(2)	118.49(16)
N(1)-Ni(1)-O(1W)	89.30(13)	O(4)-Ni(2)-N(6)	85.27(13)	C(18)-N(6)-Ni(2)	105.8(2)
N(1)-Ni(1)-N(4)	80.43(13)	O(4)-Ni(2)-N(7)	164.71(14)	C(19)-N(6)-Ni(2)	107.8(3)
N(1)-Ni(1)-N(2)	80.62(14)	O(4)-Ni(2)-N(9)	97.73(12)	C(20)-N(6)-Ni(2)	108.5(3)
N(2)-Ni(1)-N(4)	92.83(15)	N(6)-Ni(2)-N(7)	80.84(15)	C(21)-N(7)-Ni(2)	112.4(3)
N(2)-Ni(1)-O(1W)	169.35(13)	N(7)-Ni(2)-N(9)	86.54(13)	C(27)-N(7)-Ni(2)	140.4(3)
N(4)-Ni(1)-O(1W)	82.04(13)	N(9)-Ni(2)-N(6)	81.44(13)	C(28)-N(9)-Ni(2)	111.9(3)
Ni(1A)-O(1)-Ni(1)	101.70(10)	O(4)-Ni(2)-O(2W)	85.29(12)	C(34)-N(9)-Ni(2)	141.2(3)

^aSymmetry code: A: $-x+1, -y+1, -z+2$.

2 Results and discussion

2.1 Description of the structures

Compound **1** crystallizes in space group $P2_1/c$. It has a centrosymmetrically related dinuclear structure (Fig.1). The Ni atom is six-coordinated with a distorted octahedral environment. Four of the six bonding sites are occupied by the phosphonate oxygen (O3) and three nitrogen atoms (N1, N2 and N4) from the same bbimp²⁻ ligand. The remaining sites are filled with N6 from the 4,4'-bipy and the water molecule (O1W). The Ni1-N bond lengths [0.207 3(3)~0.217 0(3) nm] are in agreement with those in compounds $[\text{Ni}(\text{timpt})_2](\text{ClO}_4)_2$ 0.209 7(5)~0.215 1(4) nm [timpt=2,4,6-tris[4-(imidazol-1-ylmethyl)phenyl]-1,3,5-triazine]^[12]. The distances of Ni1-O3 and Ni1-O1W are 0.204 4(2) and 0.209 5(3) nm, respectively. Each bbimp²⁻ ligand serves a tetradentate ligand and chelates to the Ni atom through one amino nitrogen atom (N1), two benzimidazol nitrogen atoms (N2 and N4) and one phosphonate oxygen (O3), forming three adjacent five-member rings (Fig.1). The 4,4'-bipy serves as a bridge and links two equivalent Ni atoms into a dimer with Ni···Ni distance of 1.124 1 nm.



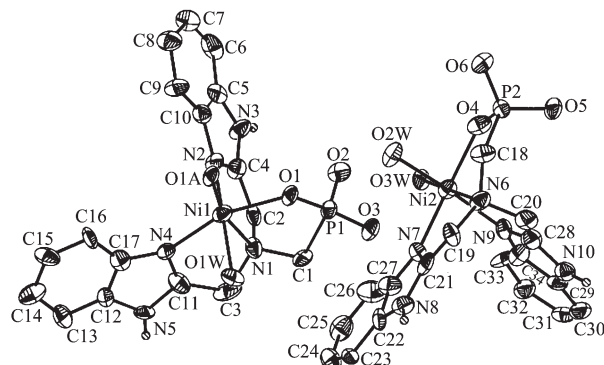
Two lattice waters were omitted. All the H atoms except the H3A, H3AA, H5A and H5AA were also omitted for clarity

Fig.1 Binuclear structure of **1** with the atomic labeling scheme (50% probability)

The noncoordinated phosphonate oxygens (O1, O2) and benzimidazol nitrogen atoms (N3, N5) in compound **1** are involved in intra- or inter-molecular hydrogen bond network together with the water molecules (O1W, O2W), and form five sets of hydrogen bonds $\text{N5} \cdots \text{O1}^a$ 0.258 6(4) nm, $\text{N3} \cdots \text{O2W}^b$ 0.272 2(5) nm, $\text{O2W} \cdots \text{O1}^c$

0.275 4(4) nm, $\text{O2W} \cdots \text{O2}$ 0.276 6(5) nm and $\text{O1W} \cdots \text{O2}^d$ 0.258 9(4) nm (symmetric codes: ^a $x+1, -y+1/2, z+1/2$; ^b $x+1, y, z$; ^c $-y+1/2, z-1/2$; ^d $x, -y+1/2, z+1/2$). Therefore a three-dimensional supramolecular structure is built up.

Compound **2** crystallizes in triclinic space group $P\bar{1}$. It contains two kinds of distinct neutral moieties: $[\text{Ni}_2(\text{bbimp})_2(\text{H}_2\text{O})_2]$ dinuclear unit and $[\text{Ni}(\text{bbimp})(\text{H}_2\text{O})_2]$ mononuclear unit. The asymmetric unit contains two different surrounding Ni(II) ions, and two bbimp²⁻ ligands, three coordinated and two lattice water molecules (Fig.2). The Ni1 atom adopts distorted octahedral coordination geometry. Four of the six bonding sites are occupied by the phosphonate oxygen (O1) and three nitrogen atoms (N1, N2 and N4) from the same bbimp²⁻ ligand. The remaining sites are filled with the phosphonate oxygen atom (O1A) from the other equivalent bbimp²⁻ ligand and the water molecule (O1W). Ni2 atom also adopts a distorted octahedral coordination geometry. Four of the six positions are occupied by the phosphonate oxygen (O4) and three nitrogen atoms (N6, N7 and N9) from the same bbimp²⁻ ligand. The remaining two sites are filled with two molecules (O2W and O3W). The Ni-N 0.202 5(3)~0.216 2(3) nm and Ni-O bond lengths 0.205 0(3)~0.216 9(3) nm are comparable to those in **1**.

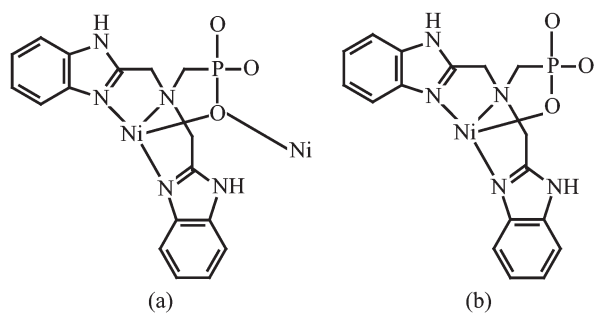


Lattice waters (O4W and O5W) and the H atoms except the H5A, H3C, H8A, and H10A are omitted for clarity

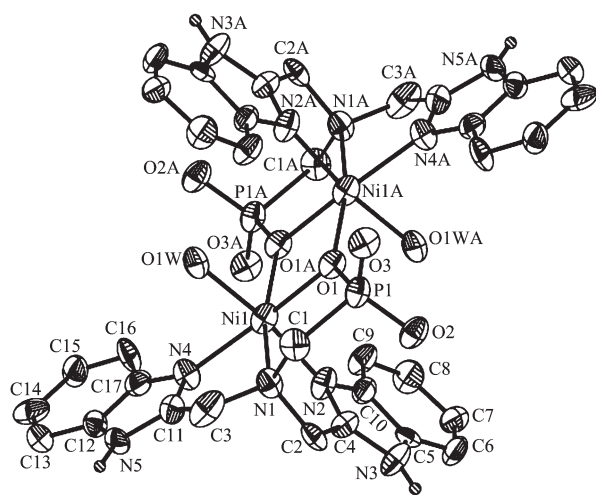
Fig.2 Moieties of **2** with the atomic labeling scheme (50% probability)

Although each of the two bbimp²⁻ ligands in **2** acts as a tetra-dentate ligand and chelates to one Ni atom using one phosphonate oxygen, one imino nitrogen and two benzimidazol nitrogen atoms (O1, N1, N2 and N4

for Ni1; O4, N6, N7 and N9 for Ni2), their coordination fashions are quite different. The phosphonate oxygen atom O1 in one bbimp²⁻ serves as μ_3 -O and bridges the two equivalent Ni atoms into a neutral dimer of $[\text{Ni}_2(\text{bbimp})_2(\text{H}_2\text{O})_2]$ similar to $\text{Mn}_2\{[(\text{C}_7\text{H}_5\text{N}_2)\text{CH}_2]_2\text{NCH}_2\text{PO}_3\}_2(\text{H}_2\text{O})_2\cdot 2\text{H}_2\text{O}$ ^[6] (Scheme 1a, Fig.3). The Ni1-O1-Ni1A bond angle is $101.7(1)^\circ$, slightly lower than that in the later $102.8(1)^\circ$. The Ni1...Ni1A distance 0.322 7 nm is also shorter than the Mn...Mn distance 0.335 8 nm. While the phosphonate oxygen atom O4 in the other bbimp²⁻ acts as a μ_2 -O and coordinates to one Ni atom forming a neutral monomer of $[\text{Ni}(\text{bbimp})(\text{H}_2\text{O})_2]$ (Scheme 1b).



Scheme 1

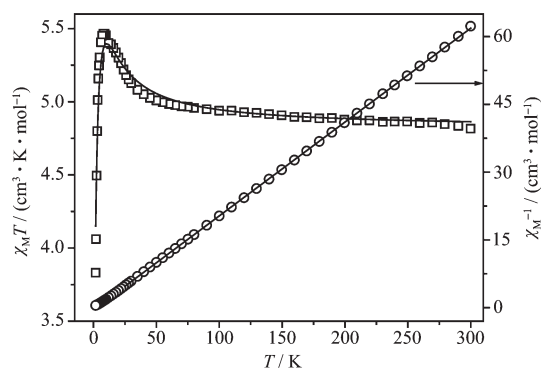
Fig.3 $[\text{Ni}_2(\text{bbimp})_2(\text{H}_2\text{O})_2]$ dinuclear unit in **2**

Extensive hydrogen bonding interactions are observed among the imidazole nitrogen, phosphonate oxygen and water molecules, leading to a three dimensional supramolecular structure. The N8...O5W, O2...O2W, O2W...O4^a, O3W...O6^a, N3...O5^a, N5...O6^b, N10...O5^c, and O3W...O4W^d distances are 0.291 0(7), 0.266 2(4), 0.275 3(4), 0.267 2(4), 0.284 4(5), 0.272 4(4), 0.266 3(5) and 0.297 8(6) nm, respectively (symmetry

codes: ^a $-x+1, -y+2, -z+1$; ^b $x, y-1, z$; ^c $-x+2, -y+2, -z+1$; ^d $x, y+1, z$).

2.2 Magnetic property

The temperature dependent molar magnetic susceptibilities of compound **2** was measured at 2 kOe in the temperature range 1.8~300 K. Fig.4 shows the $\chi_M T$ and χ_M^{-1} vs T plots for compound **2**. The room temperature effective magnetic moment per Ni ($3.10\mu_B$) is close to the expected spin only value ($2.83\mu_B, S=1$). Upon cooling, compound **2** shows the typical features of ferromagnetic behavior. The $\chi_M T$ value increases until it reaches a maximum of $5.46 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 9 K, then decreases to $3.83 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 1.8 K, which could be due to the inter-molecule interactions as well as the zero-field splitting of the ground state. The magnetic susceptibility above 25 K obeys the Curie-Weiss law with Curie constant $4.81 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ and Weiss constant $+2.29 \text{ K}$. The positive Weiss constant further indicates a ferromagnetic interaction between the magnetic centers.

Fig.4 $\chi_M T$ (\square) and χ_M^{-1} (\circ) vs T plots for **2**

Compound **2** contains one dinuclear unit of $[\text{Ni}_2(\text{bbimp})_2(\text{H}_2\text{O})_2]$ where two Ni (II) ions are doubly bridged by phosphonate oxygen atoms O1 plus two mononuclear units of $[\text{Ni}(\text{bbimp})(\text{H}_2\text{O})_2]$. Thus the magnetic susceptibility data can be analyzed by the following expression based on a Heisenberg Hamiltonian $\hat{H} = -2J\hat{S}_1\hat{S}_2$ ^[8].

$$\chi_M' = \frac{2Ng^2\beta^2}{kT} \frac{\exp(2J/(kT)) + 5\exp(6J/(kT))}{1 + 3\exp(2J/(kT)) + 5\exp(6J/(kT))} + \frac{4Ng^2\beta^2}{3kT}$$

$$\chi_M = \frac{\chi_M'}{1 - (zj'/(Ng^2\beta^2))\chi_M'}$$

where $2J$ is the coupling constant and N, g, β and k have their usual meanings. zj' accounts for the inter-

molecule exchange. As shown in Fig.4, the best fit results in parameters $g=2.20$, $2J=7.04 \text{ cm}^{-1}$, and $zj'=-0.17 \text{ cm}^{-1}$. The magnetization measured at 2 K is $2.04N\beta$ at 70 kOe, slightly lower than the value of $2.20N\beta$ anticipated for a spin $S=1$ with $g=2.20$ (Fig.5). Weak ferromagnetic interactions were also found in a few phenoxo bridged Ni(II) compounds such as $[\text{Ni}_2(\text{Dabox})_2(\text{H}_2\text{O})_2]$ ($\text{DaboxH}_2=2,6\text{-bis}(\text{acetoximato})\text{-4-tert-butylphenol}$, $2J=5.1 \text{ cm}^{-1}$)^[13] and $[\text{Ni}_2(\text{L}^{3,3})(\text{OAc})_2] \cdot 0.5\text{CH}_3\text{OH}$ ($J=2.1 \text{ cm}^{-1}$)^[14]. It is noted that compound $\text{Mn}_2\{[(\text{C}_7\text{H}_5\text{N}_2)\text{CH}_2]_2\text{NCH}_2\text{PO}_3\}_2(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$ in which the Mn(II) ions are bridged by phosphonate oxygen atoms also shows a weak ferromagnetic interaction with $2J=0.72 \text{ cm}^{-1}$.

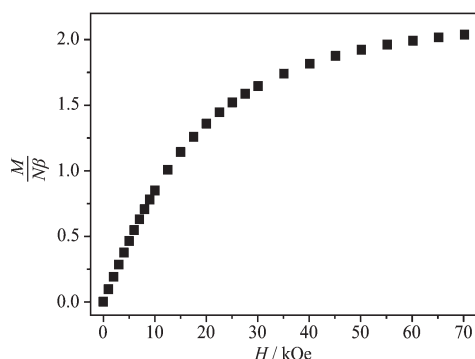


Fig.5 Field dependent magnetization for **2**

3 Conclusions

Hydrothermal reactions of bis(benzimidazol-2-yl-methyl)imino methylenephosphonic acid $\{[(\text{C}_7\text{H}_5\text{N}_2)\text{CH}_2]_2\text{NCH}_2\text{PO}_3\text{H}_2, \text{bbimpH}_2\}$ and NiSO_4 in the presence of a second organic ligand (4,4'-bipy or piperazine) result in two nickel phosphonates. Compound $\text{Ni}_2(\text{bbimp})_2(4,4'\text{-bipy})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$ (**1**) has a dinuclear structure in which 4,4'-bipy bridges two Ni(II) ions trapped inside three five-membered chelate rings of the bbimp^{2-} ligands. Compound $[\text{Ni}_2(\text{bbimp})_2(\text{H}_2\text{O})_2][\text{Ni}(\text{bbimp})(\text{H}_2\text{O})_2]_2 \cdot 4\text{H}_2\text{O}$ (**2**) is composed of neutral dimers of $[\text{Ni}_2(\text{bbimp})_2(\text{H}_2\text{O})_2]$ and monomers of $[\text{Ni}(\text{bbimp})(\text{H}_2\text{O})_2]$ which are interco-

nected through hydrogen bond interactions. Although piperazine is not involved in the product, it is essential in the formation of compound **2**. Further work is in progress to build up new clusters or polymeric compounds based on the same ligand.

References:

- [1] Hu A, Ngo H L, Lin W. *Angew. Chem. Int. Ed.*, **2003**,**42**:6000~6003
- [2] Wang Z, Heising J M, Clearfield A. *J. Am. Chem. Soc.*, **2003**, **125**:10375~10383
- [3] Alberti G, Casciola M. *Solid State Ionics*, **2001**,**145**:3~16
- [4] Maheswaran S, Chastanet G, Teat S J, et al. *Angew. Chem. Int. Ed.*, **2005**,**44**:5044~5048
- [5] Clearfield A. *Prog. Inorg. Chem.*, **1998**,**47**:371~510
- [6] Cao D K, Xiao J, Tong J W, et al. *Inorg. Chem.*, **2007**,**46**:428~436
- [7] Cao D K, Xiao J, Li Y Z, et al. *Eur. J. Inorg. Chem.*, **2006**: 1830~1837
- [8] Kahn O. *Molecular Magnetism*. New York: VCH Publishers, **1993**.
- [9] IR (KBr, cm^{-1}): 3 611(w), 3 581(m), 3 386~2 534(s, br), 1 627(m), 1 594(w), 1 561(w), 1 491(w), 1 472(m), 1 453(s), 1 400(w), 1 337(w), 1 279(m), 1 226(w), 1 206(w), 1 158(m), 1 121(m), 1 084(m), 1 041(s), 1 024(s), 1 000(m), 950(m), 935(m), 897(w), 851(w), 766(w), 745(s), 655(w), 596(w), 558(w), 517(w), 486(w), 438(w).
- [10] SAINT, *Program for Data Extraction and Reduction*, Siemens Analytical X-ray Instruments, Madison, WI 53719, **1994** ~ **1996**.
- [11] SHELXTL (version 5.0) Reference Manual, Siemens Industrial Automation, Analytical Instrumentation, Madison, WI, **1995**.
- [12] Wan S Y, Huang Y T, Li Y Z, et al. *Microporous and Mesoporous Materials*, **2004**,**73**:101~108
- [13] Nanda K K, Addison A W, Paterson N, et al. *Inorg. Chem.*, **1998**,**37**:1028~1036
- [14] Aratake Y, Ohba M, Sakiyama H, et al. *Inorg. Chim. Acta*, **1993**,**212**:183~190