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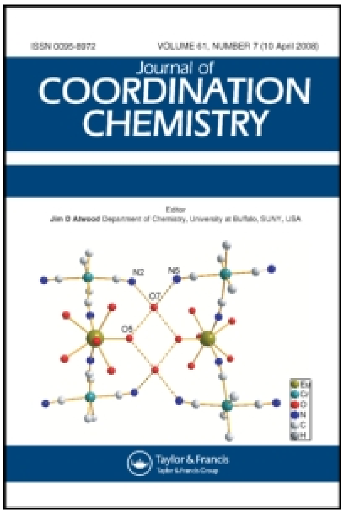

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Synthesis and characterization of a nickel metavanadate complex: $Ni(pz)(V_2O_6)$ (pz = pyrazine)

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A nickel metavanadate complex $Ni(pz)(V_2O_6)$ (pz = pyrazine) (**1**) was hydrothermally synthesized and characterized by elemental analysis, IR spectroscopy and thermal analysis. The complex was also investigated by single crystal X-ray diffraction analysis. The three-dimensional extended structure in the crystal is constructed by corner sharing $\{VO_3\}_n$ chains running along the b axis and two types of $\{Ni(pz)\}_n$ chains oriented in [0 1 1] and [0 1 −1] directions, respectively. Ni is coordinated by two N atoms from two pyrazines and four O atoms from three metavanadates in a distorted octahedral geometry. The variable-temperature magnetic susceptibility of **1** was measured. The magnetic coupling parameter indicates an antiferromagnetic interaction within the $\{Ni(pz)\}_n$ chain.

Keywords: Nickel complexes; Pyrazine; Polyoxovanadates; X-ray analysis; Magnetic properties; Thermal analysis

1. Introduction

Considerable effort has been devoted to inorganic-organic hybrid materials because of their fascinating structures and potential applications in catalysis and material sciences [1, 2]. Since vanadium can adopt varied coordination environments (octahedral, square pyramidal, trigonal bipyramidal and tetrahedral) and oxidation states (5+, 4+, 3+) [3], hydrothermal assembly of inorganic-organic hybrid materials based on polyoxovanadium oxides has been extensively explored and many promising architectures have been constructed. Previous reports include discrete species such as $[V_4O_{12}]^{4-}$ and $[V_2O_6]^{2-}$ [7], cluster species such as $[V_{16}O_{38}]^{5-}$ [4], layered species such as $[V_6O_{14}]^{2-}$ and $[V_6O_{17}]^{2-}$ [5, 6] and infinite metavanadate chains in $Co(pz)(VO_3)_2$, $\{[Co(phen)_2]_2V_6O_{17}\}_n$, and $Cu(dpa)VO_3$ [8–10]. Although more than 50 accessible structures of polyoxovanadates provide a rich background for understanding the relationship of structure and property, how to combine substructures, such as chains or layers, of different metal-oxides to obtain a composite solid that possesses a combination of individual physical properties (optical or magnetic) remains a great challenge.

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Our synthetic effort on the assembly of metavanadates and coordination complexes has uncovered a new complex, Ni(pz)(V_2O_6) (**1**), which has high thermal stability. Its magnetic properties have also been studied.

2. Experimental

2.1. *Materials and methods*

$NiSO_4 \cdot 6H_2O$, NH_4VO_3, malonic acid and pyrazine were purchased from Alfa Aesar. All reagents and solvents were analytical grade and used as received. Infrared measurement was carried out on a Nicolet FT-IR360 spectrometer with the sample prepared as a KBr pellet. Thermogravimetric analysis (TG) was performed under nitrogen atmosphere with a heating rate of 10°C per minute using a NETZSCH TG-209 F1 thermal analyzer. Magnetic susceptibility data were obtained on polycrystalline sample (35 mg) from 2 to 300 K in a magnetic field of 5 KG using a SQUID magnetometer. Elemental analyses were carried out on a Vario EL III CHN elemental analyzer.

2.2. *Synthesis*

A mixture of $NiSO_4 \cdot 6H_2O$ (0.26 g, 1 mmol), NH_4VO_3 (0.12 g, 1 mmol), pyrazine (0.24 g, 3 mmol), malonic acid (0.10 g, 1 mmol) and H_2O (15 ml) was sealed in a Teflon-lined autoclave and heated under autogenous pressure at 170°C for 5 days. Green rod-like crystals were obtained as a major phase together with very small amount of unidentified black microcrystalline phase. Yield: ca. 57% based on vanadium. Anal. Calcd for $C_4H_4N_2O_6V_2Ni$: C, 14.27, H, 1.20, N, 8.32; Found: C, 14.19, H, 1.24, N, 8.12.

2.3. *Crystal data collection and refinement*

A green rod-like single crystal with dimensions of 0.26 mm × 0.04 mm × 0.04 mm was selected and mounted on a Bruker CCD area-detector diffractometer equipped with graphite-monochromated Mo K radiation ($\lambda = 0.71073$ Å) at 298 K. A total of 6759 reflections including 1060 independent ones ($R_{\text{int}} = 0.0538$) were collected in the range $3.31 \leq \leq 28.35^\circ$ by using the φ and ω scan mode, of which 1041 reflections with $I \geq 2\sigma(I)$ observed. An empirical absorption correction based on symmetry equivalent reflections was applied with SADABS [11], giving the minimum and maximum transmission factors 0.3966 and 0.8613, respectively. All calculations for data reduction, structure solution and refinement were done by standard procedures (WINGX) [12]. The structure was solved by the direct method using SHELXLS97 [13]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques on F^2 with SHELXL97 [13]. The C-bound H atoms were generated geometrically and constrained with a riding model, subject to C–H = 0.93 Å, and their displacement parameters were set to 1.2 times those of their parent atoms. The final geometrical calculations and the graphical manipulations were carried out with ORTEPII [14] and DIAMOND [15]. The final refinement converged at $R = 0.0328$, $wR = 0.0742$ ($w = 1/[\sigma^2(F_o^2) + (0.0542P)^2 + 0.2190P]$, where $P = (F_o^2 + 2F_c^2)/3$), $(\Delta/\sigma) = 0.001$, $S = 1.038$, $(\Delta\rho)_{\mathrm{max}} = 0.589$ and $(\delta\rho)_{\mathrm{min}} = -0.504\,\mathrm{e/\mathring{A}^3}$. The crystallographic data are compiled in table 1 and selected bond lengths and angles are listed in table 2. CCDC reference number is 639943 for **1**.

3. Results and discussion

3.1. *Synthesis and infrared spectra*

Many variables can affect the result in hydrothermal synthesis. Malonic acid in the preparation of **1** provides a relatively lower pH (3.8) environment for the starting system and appeared to be needed, although it is not incorporated in the final product. The identical reaction with fumaric acid or 2-pyrazinecarboxylic acid instead of malonic acid proved fruitless.

Table 1. Crystal parameters and X-ray diffraction data of **1**.

Complex	**1**
Empirical formula	$C_4H_4N_2NiO_6V_2$
Formula weight	336.68
Crystal system	Orthorhombic
Space group	$P\ n\ n\ a$
a (Å)	10.1109(9)
b (Å)	11.3541(10)
c (Å)	7.3307(6)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3), Z	841.57(21)
ρ (mg cm^{-3})	2.657
μ (cm^{-1})	4.398

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

Ni(1)–O(1)	2.029(2)	V(1)–O(2)^b	1.621(2)
Ni(1)–O(1)^a	2.029(2)	V(1)–O(1)	1.625(2)
Ni(1)–O(2)	2.012(2)	V(1)–O(3)	1.766(2)
Ni(1)–O(2)^a	2.012(2)	V(1)–O(4)	1.769(2)
Ni(1)–N(1)	2.076(3)		
Ni(1)–N(1)^a	2.076(3)		
O(1)–Ni(1)–O(2)	88.4(1)	N(1)–Ni(1)–N(1)^a	166.2(2)
O(1)–Ni(1)–O(1)^a	94.6(1)	O(1)–V(1)–O(2)^b	108.6(1)
O(1) –Ni(1)–O(2)^a	175.6(1)	O(1)–V(1)–O(3)	107.4(1)
O(2)–Ni(1)–O(2)^a	88.9(2)	O(1)–V(1)–O(4)	107.8(1)
O(1)–Ni(1)–N(1)^a	85.2(1)	O(2)#2–V(1)–O(3)	108.5(1)
O(1)–Ni(1)–N(1)	85.4(1)	O(2)#2–V(1)–O(4)	111.9(2)
O(2)–Ni(1)–N(1)	98.3(1)	O(3)–V(1)–O(4)	112.5(1)
O(2)–Ni(1)–N(1)^a	91.6(1)		

Symmetry codes: (a) x, $-y+1/2$, $-z+1/2$; (b) $x-1/2$, y, $-z$.

The infrared spectrum of **1** exhibits strong intensity features in the range 1118 to 1630 cm^{-1} that are attributed to pyrazine rings. The bands at 941 and 914 cm^{-1} are assigned to symmetric and antisymmetric stretching vibration of V = O, while the features from 823 to 627 cm^{-1} are related to stretching of O–V–O in vanadium oxide chains $\{VO_3\}_n$. The positions of the bands and their assignments are consistent with literature reports [16, 17].

3.2. *Crystal structure*

The asymmetric unit of **1** with atom numbering scheme is depicted in figure 1. The Ni is coordinated by two N atoms from two equivalent pyrazines and four O atoms from three metavanadates. The bond lengths and the associated angles around Ni show that the Ni atom is in a distorted octahedral environment, in which four O atoms are located on a plane approximately (Ni–O 2.012(2) Å, 2.029(2) Å) where the sum of bond angles is 360.19° and N atoms occupied two axial positions (Ni–N, 2.076(3) Å). The coordination bond lengths associated with pyrazine are much shorter than that of the corresponding pyrazine ring observed in $[Ni(CN)(pz)]_n$ (Ni–N(pyrazine) 2.14 Å) [18]. Meanwhile, four O atoms are coordinated to V atom with a distorted tetrahedral geometry. As listed in table 2, the two O atoms linking two adjacent VO_4 tetrahedra have longer V–O bonds, 1.762(2) and 1.769(2) Å, and the other bridging VO_4 tetrahedron and one NiO_4N_2 octahedron have shorter V–O distances of 1.621(2) and 1.625(2) Å. Although this is consistent with those found in other coordination cation metavanadates [5, 19], the shorter V–O bond lengths are slightly shorter than those found in recently reported metavanadates with coordination cations covalently attached to the anion chains, such as $Ni(NH_3)_2(VO_3)_2$ (1.632(3) and 1.652(3) Å) [20], $[Co(bpy)V_2O_6]$ (1.660(2) and 1.664(2) Å) [21]. Figure 2 shows the crystal packing viewed from c and a directions, respectively, indicating that the structure of **1** is constructed by corner-sharing $\{VO_3\}_n$ chains running along [0 1 0] direction and $\{Ni(pz)\}_n$ chains. The polyhedral representations of $\{VO_3\}_n$ and $\{Ni(pz)\}_n$

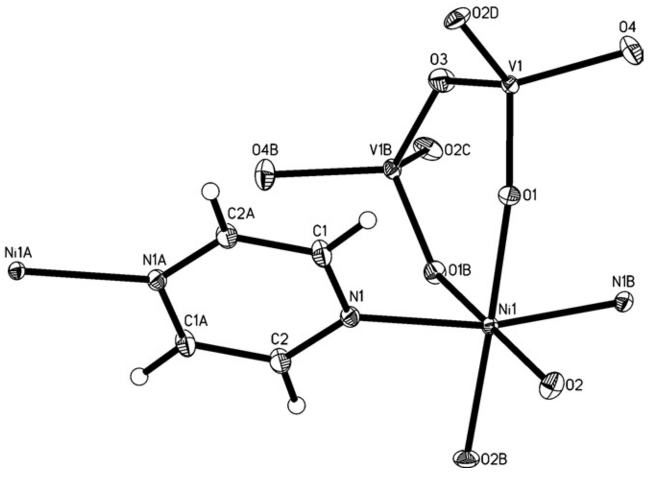


Figure 1. An ORTEP plot of **1** showing the coordination environment around Ni atom and V atom. The thermal ellipsoids are drawn at the 30% probability. [Symmetry codes: (A) $-x$, $1-y$, $-z$; (B) x, $1/2-y$, $1/2-z$; (C) $-1/2+x$, $1/2-y$, $1/2+z$; (D) $-1/2+x$, y, $-z$].

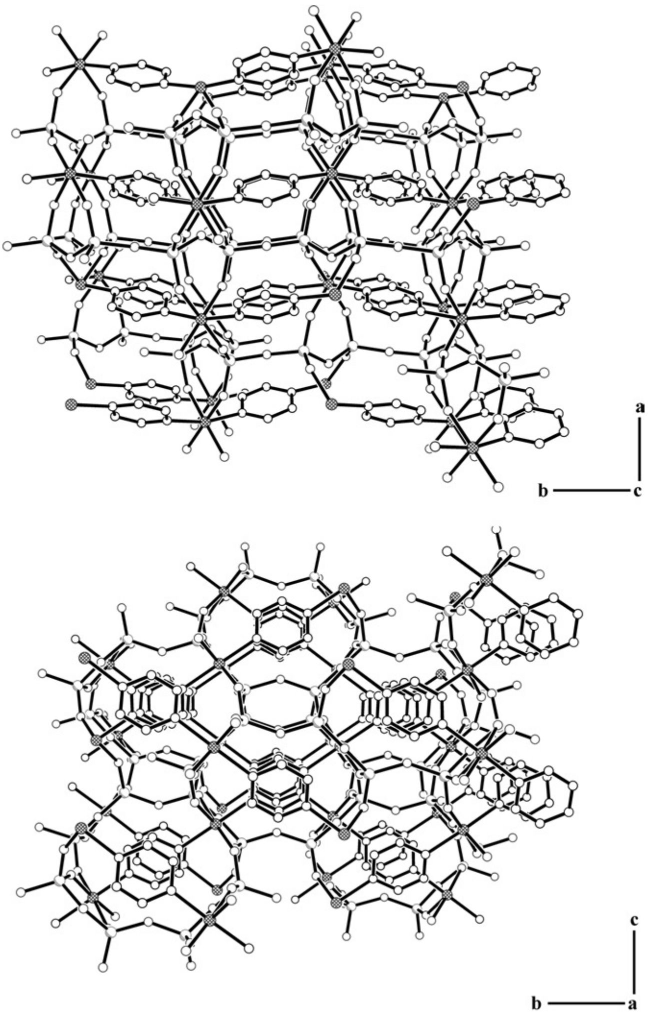
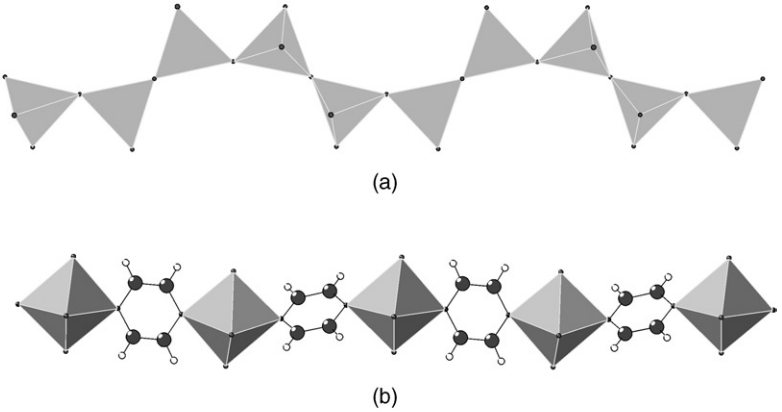


Figure 2. A packing diagram of **1**. (a) Viewed along the *c* axis. (b) along the *a* axis. H atoms are omitted for clarity.

chains are displayed in figure 3. Within the inorganic chains, $(V_2O_6)^{2-}$ formed by sharing O(3) is associated each other by corner sharing through O(4). The dimer further shares O(1) and O(2) atoms with three NiO_4N_2 octahedra. There are two types of metal-organic chains $\{Ni(pz)\}_n$, paralleling [0 1 1] and [0 1 −1] directions, respectively. The flexible $\{VO_3\}_n$ chains link these $\{Ni(pz)\}_n$ chains to give a three-dimensional framework structure. The shortest Ni···Ni distance over pyrazine and VO_4 bridge are 6.89 and 6.24 Å, respectively.

3.3. *Thermal analysis*

Thermal analysis has been performed under nitrogen for **1** between room temperature and 600°C. Similar to $[Co(pz)(VO_3)_2]$ [8], the thermal behavior shows a one-step, sharp


(a)

(b)

Figure 3. Polyhedral representation of the chains in **1**. (a) $\{VO_3\}_n$ chain. (b) $\{Ni(pz)\}_n$ chain.

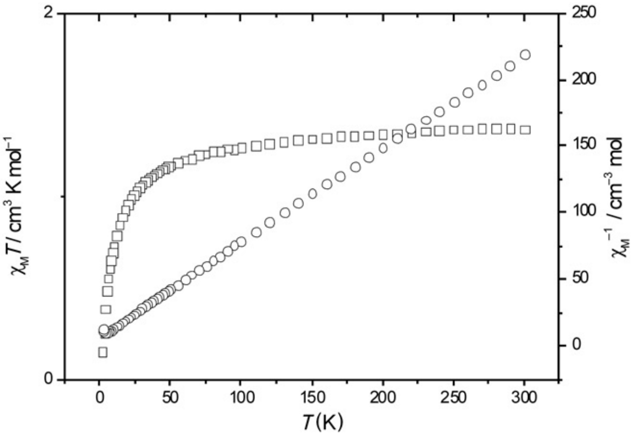


Figure 4. Temperature dependence of $\chi_m T$ and χ_m^{-1} for **1**.

decomposition process. Complex **1** begins to lose weight at ca. 390°C and reaches the maximum losing rate at ca. 430°C. The weight loss of 24.79% agrees well with the removal of pyrazine ligand (Calcd 23.72%). Compared with other metal pyrazine coordination polymers without polyoxovanadates, the thermal stability of **1** is significantly higher [22, 23].

3.4. *Magnetic property*

The temperature dependences of $\chi_m T$ (χ_m being the molar magnetic susceptibilities for Ni(II) ion) and inverse susceptibilities χ_m^{-1} of **1** are shown in figure 4. The effective magnetic moment μ_{eff} at 280 K is 3.3 μ_B, determined from $\mu_{eff} = 2.828\ (\chi_m T)^{1/2}$, higher than expected for spin-only for $S = 1$ ($\mu_{eff} = 2.8\ \mu_B$). Above 50 K, the χ_m^{-1} *versus* T curve is almost linear and can be fit to the Curie–Weiss expression giving $g = 2.39$, $\theta = -11.2\,\mathrm{K}$, suggesting a weak antiferromagnetic interaction. In **1**, the pyrazine-bridged $\{\mathrm{Ni(pz)}\}_n$ chain is isolated by diamagnetic metavanadate chains with the shortest $\mathrm{Ni}\cdots\mathrm{Ni}$ distance across VO_4 bridge being 6.24 Å. Therefore, the magnetic exchange coupling would most likely occur through pyrazine bridges.

Aknowledgement

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