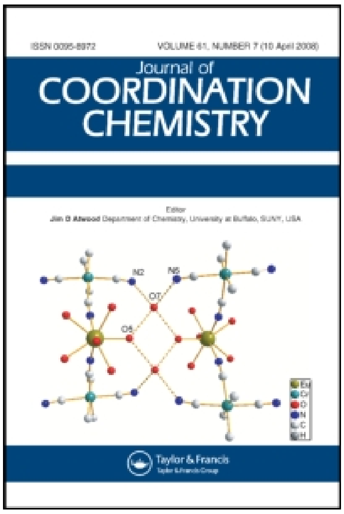

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Hydrothermal synthesis, crystal structure and magnetic properties of a new 2D layered vanadium oxide complex: $[Ni(phen)(H_2O)]_2V_4O_{12}$

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Hydrothermal synthesis, crystal structure and magnetic properties of a new 2D layered vanadium oxide complex: $[Ni(phen)(H_2O)]_2V_4O_{12}$

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A new organic–inorganic hybrid vanadium oxide complex, $[Ni(phen)(H_2O)]_2V_4O_{12}$, **1** (phen = 1,10-phenanthroline), has been synthesized using a hydrothermal method and structurally characterized. Complex **1** exhibits a layered structure in which vanadium oxide chains, $\{V_2O_6\}_n^{2n-}$, are linked to $[Ni(phen)(H_2O)]^{2+}$ subunits to form a two-dimensional (2D) topology. Crystals are triclinic, space group $P\bar{1}$, with $a = 7.869(2)$, $b = 9.437(2)$, $c = 20.992(4)$ Å, $\alpha = 89.95(3)$, $\beta = 89.84(3)$, $\gamma = 67.22(3)°$, $V = 1437.3(5)$ Å^3 and $Z = 2$. Magnetic measurements indicate that **1** exhibits a weak ferromagnetic exchange interaction.

Keywords: Hydrothermal synthesis; Nickel(II) complex; Vanadium oxide; 1,10-Phenanthroline; Crystal structure; Magnetic properties

1. Introduction

The synthesis of vanadium oxides linked by transition metal complexes has attracted much attention recently due to the rich variety of their structures and properties [1–10]. The complexes in such vanadium oxides not only act as charge-compensating constituents but also function as ligands, coordinating to the oxide scaffolding or to a secondary metal center. Many examples of vanadium oxides containing covalently linked complex fragments, including discrete clusters, one-dimensional (1D) chains, 2D layers and 3D networks, have been synthesized using hydrothermal techniques [1–10]. The vanadium oxide chain $\{V_2O_6\}_n^{2n-}$ is a common structural motif in hybrid organic–inorganic vanadium oxide chemistry, and the prototypical structure is generally observed in 1D chain complexes, for example in $Cu(NH_3)_2V_2O_6$ [2], $Cu(dien)V_2O_6 \cdot H_2O$ [3], $Cu(en)V_2O_6$ [4], $Cu(bipy)V_2O_6$ [4] and $Cu(bipy)_2V_2O_6$ [4]

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(dien = diethylenetriamine, bipy = 2,2′-bipyridyl). However, recent research indicates that the chain can also be bridged by $[M(bipy)(H_2O)]^{2+}$ (M = Co, Ni) subunits to generate 2D layer complexes such as $Ni(bipy)(H_2O)V_2O_6$ and $Co(bipy)(H_2O)V_2O_6$ [5a]. In this report, we present an analogous example in which the vanadium oxide chain $\{V_2O_6\}_n^{2n-}$ interacts with $[Ni(phen)(H_2O)]^{2+}$ ions to form a 2D hybrid vanadium oxide complex, $[Ni(phen)(H_2O)]_2V_4O_{12}$, **1** (phen = 1,10-phenanthroline). Complex **1** exhibits a weak ferromagnetic exchange interaction.

2. Experimental

2.1. *Materials and methods*

All reagents were obtained from commercial sources and used without further purification. Elemental analyses were performed on a Heraeus CHN-Rapid instrument. IR spectra were recorded on a Perkin Elmer 2000 spectrophotometer with pressed KBr pellets. Magnetic susceptibility measurements were carried out on a polycrystalline sample (64 mg) of **1** using a MagLab System 2000 magnetometer at a field of 2 T. Diamagnetic corrections were estimated from Pascal's constants [11].

2.2. *$[Ni(phen)(H_2O)]_2V_4O_{12}$, 1*

A mixture of NH_4VO_3 (2 mmol), Na_2SO_3 (2 mmol), $Ni(NO_3)_2$ (1 mmol), 1,10-phenanthroline (1 mmol), $N_2H_4 \cdot 2HCl$ (1 mmol) and H_2O (14 cm^3) was stirred for 20 min and then transferred to a 25 cm^3 Teflon-lined steel autoclave. The mixture was heated at 170°C for 6 days, at which time black blocky crystals of **1** had separated from the blue mother liquor in *ca* 40% yield based on V. Anal. Calcd. for $C_{24}H_{20}N_4Ni_2O_{14}V_4$(%): C, 31.69; H, 2.22; N, 6.16. Found: C, 31.63; H, 2.30; N, 6.09. IR (cm^{-1}): 3328(bs), 3067(w), 1606(w), 1585(w), 1517(w), 1494(w), 1425(m), 1143(w), 1106(w), 1053(w), 968(s), 953(m), 904(s), 856(s), 840(s), 792(m), 726(m), 668(vs), 538(w).

2.3. *Single-crystal X-ray diffraction*

A black, single crystal of **1** with dimensions 0.37 × 0.27 × 0.17 mm was mounted on a Rigaku RAXIS-RAPID IP imaging plate system and intensity data were collected using Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K in the range $0.97° < \theta < 27.48°$. An empirical absorption correction from Ψ scans was applied. A total of 6075 reflections was collected with $-10 \le h \le 0$, $-12 \le k \le 10$, $-27 \le l \le 27$, of which 6075 were unique and 3547 had $I > 2\sigma(I)$. The structure was solved by the Patterson method and refined by full-matrix least-squares techniques based on F^2 using the SHELXL97 program [12]. All nonhydrogen atoms were refined anisotropically, and all hydrogen atoms except those in water molecules were included as riding atoms. Selected crystallographic data and structure determination parameters for **1** are given in table 1. Final atomic coordinates and equivalent isotropic displacement parameters, and selected bond lengths and angles are listed in tables 2 and 3, respectively.

Table 1. Crystal data and refinement details for **1**.

Chemical formula	$C_{24}H_{20}N_4Ni_2O_{14}V_4$
Formula weight	909.62
Space group	$P\bar{1}$
a/Å	7.869(2)
b/Å	9.437(2)
c/Å	20.992(4)
α/°	89.95(3)
β/°	89.84(3)
γ/°	67.22(3)
V/Å^3	1437.3(5)
Z	2
T/K	293(2)
λ(Mo Kα)/Å	0.71073
ρ_{calc}/g cm^{-3}	2.093
μ(Mo Kα)/mm^{-1}	2.610
R_1 [$I > 2\sigma(I)$]	0.0419
wR_2 [$I > 2\sigma(I)$]	0.0992
Goodness-of-fit on F^2	0.861

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

3. Results and discussion

3.1. *Crystal structure*

The crystal structure of **1** is composed of a 1D, zigzag, corner-sharing, tetrahedral $(VO_3)_n^{2n-}$ chain structural motif parallel to the *a* axis, bridged through [Ni(phen) $(H_2O)]^{2+}$ ions via oxygen atoms to form a 2D layer network (figures 1 and 2). A similar structure has been observed in the related vanadium oxide complexes Ni(bipy) $(H_2O)V_2O_6$ [5a], Co(bipy)$(H_2O)V_2O_6$ [5a] and Co(phen)$(H_2O)V_2O_6$ [10]. However, there are four crystallographically independent vanadium atoms and two crystallographically independent nickel atoms in **1**, representing a somewhat different arrangement to that found previously. Co(phen)$(H_2O)V_2O_6$ [10] shows only two crystallographically independent vanadium atoms and while **1** is triclinic, Ni(bipy) $(H_2O)V_2O_6$, Co(bipy) $(H_2O)V_2O_6$ and Co(phen)$(H_2O)V_2O_6$ are all monoclinic.

The nickel atom is coordinated by one 1,10-phenanthroline ligand, one water molecule and three oxygen atoms from three tetrahedral VO_4 units to give a slightly distorted octahedral geometry. Ni–N bond distances (average 2.069 Å) are comparable with those in Ni(bipy)$(H_2O)V_2O_6$ (average 2.064 Å) [5a]; the N1–Ni1–N2 bond angle [80.58(16)°] and the N3–Ni2–N4 bond angle [80.65(16)°] are slightly larger than that in Ni(bipy)$(H_2O)V_2O_6$ [79.56(9)°]. The Ni–Ow bond (2.141 Å) is a little longer than that in Ni(bipy)$(H_2O)V_2O_6$.

Neighboring $(VO_3)_n^{2n-}$ chains are covalently bridged with [Ni(phen)$(H_2O)]^{2+}$ fragments through O3, O5, O9 or their symmetry equivalents for Ni1 and O4, O10, O11 or their symmetry equivalents for Ni2, generating a layer parallel to the *ab* plane. The topology of metal–metal connections in the layer is shown in figure 3. Alternately arranged six-membered rings (defined by four VO_4 tetrahedra and two NiN_2O_3Ow octahedra) and four-membered rings (defined by three VO_4 tetrahedra and one NiN_2O_3Ow octahedron) exist within the layer. Each six-membered ring shares two edges with two adjacent six-membered rings and four edges with four neighboring

Table 2. Final atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **1**.

	x/a	y/b	z/c	U_{eq}
V1	0.33255(11)	0.38848(9)	0.26963(4)	0.0177(2)
V2	−0.42021(11)	1.02962(9)	0.33213(4)	0.0201(2)
V3	−0.66761(11)	0.88863(9)	0.23042(4)	0.0179(2)
V4	−1.42025(11)	1.52968(9)	0.16787(4)	0.0202(2)
Ni1	0.01973(9)	0.75380(7)	0.31695(3)	0.01984(17)
Ni2	−0.98036(9)	1.25384(7)	0.18305(3)	0.01990(17)
C1	−0.2505(7)	0.6010(6)	0.3556(3)	0.0302(13)
C2	−0.3567(8)	0.5600(6)	0.3986(3)	0.0404(15)
C3	−0.3406(8)	0.5836(6)	0.4617(3)	0.0391(15)
C4	−0.2165(7)	0.6494(6)	0.4827(3)	0.0290(13)
C5	−0.1895(8)	0.6765(6)	0.5472(3)	0.0360(15)
C6	−0.0648(9)	0.7365(6)	0.5649(3)	0.0386(15)
C7	0.0404(8)	0.7756(6)	0.5180(2)	0.0282(13)
C8	0.1725(8)	0.8369(6)	0.5325(3)	0.0332(14)
C9	0.2640(8)	0.8752(6)	0.4845(3)	0.0343(14)
C10	0.2250(7)	0.8526(6)	0.4216(3)	0.0289(12)
C11	0.0116(7)	0.7536(5)	0.4538(2)	0.0212(11)
C12	−0.1166(7)	0.6883(5)	0.4357(2)	0.0211(11)
C13	−0.7744(7)	1.3533(6)	0.0782(3)	0.0274(12)
C14	−0.7365(8)	1.3749(6)	0.0153(3)	0.0325(14)
C15	−0.8273(8)	1.3364(6)	−0.0324(3)	0.0332(14)
C16	−0.9595(7)	1.2757(6)	−0.0184(2)	0.0288(13)
C17	−1.0657(8)	1.2361(7)	−0.0652(3)	0.0376(15)
C18	−1.1902(8)	1.1767(6)	−0.0476(3)	0.0370(14)
C19	−1.2168(7)	1.1488(6)	0.0176(3)	0.0263(12)
C20	−1.3393(8)	1.0845(6)	0.0378(3)	0.0392(15)
C21	−1.3556(8)	1.0600(6)	0.1008(3)	0.0405(15)
C22	−1.2499(7)	1.1013(6)	0.1446(3)	0.0321(13)
C23	−1.1163(7)	1.1889(5)	0.0648(2)	0.0211(11)
C24	−0.9890(7)	1.2538(5)	0.0461(2)	0.0216(11)
N1	−0.1336(5)	0.6648(4)	0.37272(19)	0.0218(9)
N2	0.1020(5)	0.7935(4)	0.40596(19)	0.0214(9)
N4	−1.1335(5)	1.1652(4)	0.12762(19)	0.0213(9)
N3	−0.8971(5)	1.2936(4)	0.09372(19)	0.0223(10)
O1	0.4716(5)	0.2331(4)	0.31840(18)	0.0378(10)
O1W	−0.0921(5)	0.7108(4)	0.22944(17)	0.0363(10)
O2	0.4849(6)	0.4218(5)	0.2154(2)	0.0543(13)
O2W	−1.0918(5)	1.2109(4)	0.27044(16)	0.0357(10)
O3	0.2310(5)	0.5433(4)	0.31322(16)	0.0299(9)
O4	0.1765(5)	0.3488(4)	0.23045(18)	0.0371(10)
O5	−0.1963(5)	0.9672(4)	0.31450(17)	0.0302(9)
O6	−0.4452(5)	0.9938(4)	0.40573(17)	0.0380(10)
O7	−0.5137(6)	0.9216(5)	0.2841(2)	0.0546(13)
O8	−0.5289(5)	0.7339(4)	0.18113(18)	0.0372(10)
O9	−0.8233(5)	0.8490(4)	0.26975(18)	0.0376(10)
O10	−0.7693(5)	1.0434(4)	0.18678(16)	0.0296(8)
O11	−1.1957(5)	1.4673(4)	0.18542(17)	0.0302(9)
O12	−1.4450(5)	1.4931(4)	0.09447(17)	0.0392(10)

Equivalent isotropic U is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

four-membered rings, while each four-membered ring shares all edges with four six-membered rings.

As with Co(phen)(H_2O)V_2O_6 [10], π–π stacking interactions between interlayer phen groups play an important role in the stabilization of the structure of **1**. Adjacent phen groups in **1** are parallel with a shortest C–C distance of 3.3–3.6 Å, in line with

Table 3. Selected bond distances (Å) and angles (°) for **1**.

Ni1–O3	2.039(3)	Ni1–N2	2.061(4)
Ni1–N1	2.075(4)	Ni1–O5	2.073(3)
Ni1–O1W	2.145(4)	Ni1–O9$^{\#1}$	2.041(4)
Ni2–O10	2.038(3)	Ni2–N3	2.066(4)
Ni2–O11	2.071(3)	Ni2–N4	2.073(4)
Ni2–O2W	2.136(3)	Ni2–O4$^{\#2}$	2.045(4)
V1–O1	1.777(4)	V1–O2	1.765(4)
V1–O3	1.645(3)	V1–O4	1.639(4)
V2–O5	1.668(3)	V2–O6	1.609(4)
V2–O7	1.784(4)	V2–O1$^{\#2}$	1.797(3)
V3–O9	1.634(4)	V3–O7	1.770(4)
V3–O8	1.777(3)	V3–O10	1.646(3)
V4–O11	1.674(3)	V4–O12	1.608(4)
N2–Ni1–N1	80.58(16)	O3–Ni1–N1	90.50(15)
O3–Ni1–N2	90.90(15)	O3–Ni1–O5	176.37(14)
N2–Ni1–O5	92.53(15)	O5–Ni1–N1	91.24(14)
O3–Ni1–O1W	91.35(15)	N2–Ni1–O1W	173.65(16)
O5–Ni1–O1W	85.37(15)	N1–Ni1–O1W	93.46(16)
O10–Ni2–N3	90.98(15)	O10–Ni2–O11	176.41(14)
N3–Ni2–O11	92.38(15)	O10–Ni2–N4	90.63(15)
N3–Ni2–N4	80.65(16)	O11–Ni2–N4	91.18(15)
O10–Ni2–O2W	91.17(15)	N3–Ni2–O2W	173.78(17)
O11–Ni2–O2W	85.62(15)	N4–Ni2–O2W	93.49(16)

Equivalent atoms at: $^{\#1}\,1+x, y, z$; $^{\#2}\,x-1, y+1, z$.

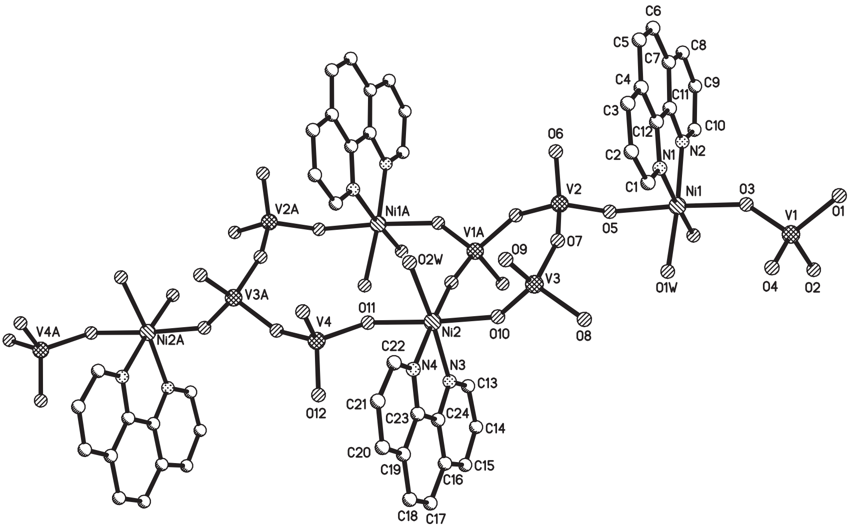

Figure 1. An ORTEP diagram of $[Ni(phen)(H_2O)]_2V_4O_{12}$, **1**, showing the atom labeling scheme.

the suggested existence of π–π stacking [5d]. The bimetallic layers of **1** are therefore extended into 3D supramolecular arrays.

3.2. *Magnetic properties*

Variation in the molar magnetic susceptibilities of complex **1** was investigated in the temperature range 2–299 K in a 20 kG applied field and is shown as χT and

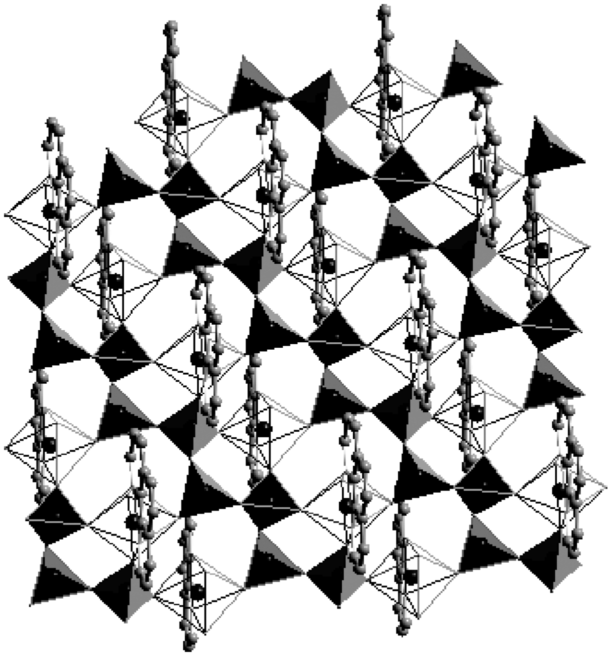

Figure 2. A polyhedral view of the 2D layer structure of **1**.

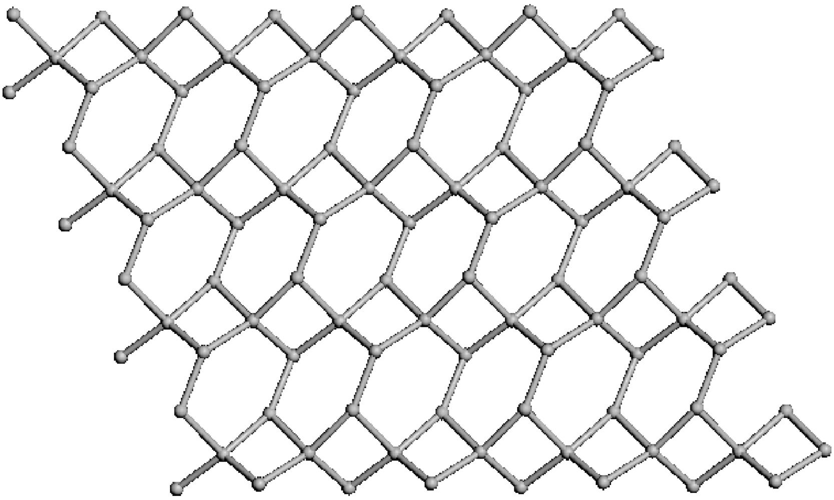

Figure 3. Projection of **1** along the *c* axis direction showing the topology of the layer based on metal–metal connections. The link represents the oxo-bridge and the 1,10-phenanthroline ligand is omitted for clarity.

χ *versus* T plots in figure 4. Upon cooling, the χT value continuously increases from 299 to 6 K, then falls to 2 K, indicating the presence of a ferromagnetic exchange interaction. The room temperature χT value of 2.49 emu K mol^{-1} is in good agreement with the spin-only value of 2.53 emu K mol^{-1} expected for two isolated nickel(II) ions ($S = 1$) assuming $g = 2.25$. The magnetic susceptibility plot obeys the Curie–Weiss law in the

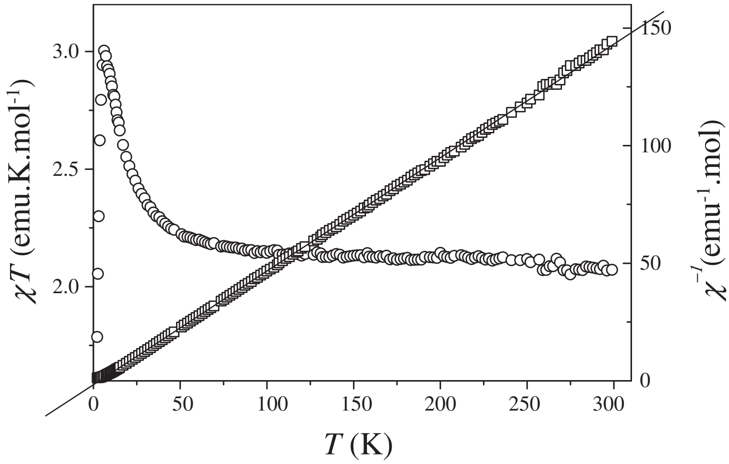

Figure 4. Plots of the dependence of χT (○) and χ^{-1} (□) on temperature for **1**.

range 2–299 K with Weiss constants $\theta = 3.42$ K and $C = 2.49\,\text{cm}^3\,\text{K}\,\text{mol}^{-1}$. The small θ value suggests that the ferromagnetic coupling between Ni^{2+} ions separated by diamagnetic V^{5+} ions is weak. Upon cooling, the decrease and increase in χT at high temperature and below 6 K, respectively, might be ascribed to the competition between zero-field splitting of Ni^{2+} in an axially distorted octahedral environment and weak ferromagnetic coupling between separated Ni^{2+} ions. Because no suitable theoretical model is available in the literature [11] for such a system, further magnetic analyses were not performed for the present complex.

Acknowledgements

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Supplementary material

Full lists of crystallographic data are available from the authors upon request.

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