Spin Glass Behaviour in a 1D Mixed Molybdenum-Vanadium Heteropolyoxometalate-Bridged Coordination Polymer

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Keywords: Nickel / Hydrothermal synthesis / Polyoxometalate / Crystal structure / Magnetic properties

A 1D trimetallic coordination polymer containing mixed molybdenum-vanadium heteropolyoxometalate bridges, {[Ni(phen)$_2$(H$_2$O)]$_2$[Ni(phen)$_2$][V$^{IV}_8$Mo$^{VI}_6$Mo$^{V}_2$O$_{40}$(PO$_4$)]}{[Ni(phen)$_2$(H$_2$O)]$_2$[V$^{IV}_8$Mo$^{VI}_6$Mo$^{V}_2$O$_{40}$(PO$_4$)$_2$]}·5H$_2$O·2EtOH (**1**) (phen = 1,10-phenanthroline, EtOH = ethanol), has been synthesised hydrothermally. An X-ray crystallographic study revealed that **1** is composed of 1D zigzag chains of {[Ni(phen)$_2$(H$_2$O)]$_2$[Ni(phen)$_2$][V$^{IV}_8$Mo$^{VI}_6$Mo$^{V}_2$O$_{40}$(PO$_4$)]}$_n^{n+}$ cations, {[Ni(phen)$_2$(H$_2$O)]$_2$ [V$^{IV}_8$Mo$^{VI}_6$Mo$^{V}_2$O$_{40}$(PO$_4$)$_2$]}$^-$ anions and solvent molecules. Both the cation and the anion in **1** are mixed molybdenum-vanadium heteropolyoxometalates with covalently linked nickel complex fragments. Magnetic investigations of **1** indicate spin glass behaviour and several magnetic transitions occur at low temperatures (below 20 K).

Introduction

Heteropolyoxometalates with specific topological structural characteristics have a large range of potential applications in catalysis, nanotechnology, material science, medicine, biochemistry, magnetochemistry and other important areas.[1] One powerful strategy for the preparation of new heteropolyoxometalates with large clusters or high-dimensional extended solid frameworks has involved the hybrid reaction of a metal oxide and a traditional polymolybdate under hydrothermal conditions.[1a,2] On the other hand, use of the bridging capabilities of transitional metal complex fragments has recently been exploited to build more and more high-dimensional organic-inorganic hybrid oxide materials.[3−5] Therefore, connecting heteropolyoxometalate ions with transition metal complex fragments via covalent bonds forming heteropolyoxometalate coordination polymers is considerably appealing.[5] To date, many mixed molybdenum-vanadium polyoxometalate coordination polymers have been reported which include 1D chain-like complexes such as [Ni(en)$_2$]$_2$[Ni(en)$_2$Mo$^{VI}_6$V$^{VI}_{10}$O$_{40}$(V^{IV}O$_4$)]·4H$_2$O,[5f] 2D layer complexes such as [Co(en)$_2$][Co(bpy)$_2$]$_2$[PMo$^{VI}_5$Mo$^{V}_3$V$^{IV}_8$O$_{44}$]·4.5H$_2$O (en = ethylenediamine, bpy = 2,2′-bipyridine),[5a] [en]$_{0.5}$[Cu(en)$_2$]$_2$[Cu(en)$_2$Mo^{VI}Mo$^{V}_2$V$^{VI}_8$O$_{40}$(Mo^{IV}O$_4$)]·0.5H$_2$O[5f] and [Cu(en)$_2$(H$_2$O)]{PMo$^{VI}_8$V$^{IV}_6$O$_{42}$[Cu(en)$_2$][Cu$_{0.5}$(en)]$_3$}·5.5H$_2$O (en = ethylenediamine)[5e] and the 3D framework complex H$_3${V^{V}Mo$^{VI}_8$V$^{IV}_6$O$_{42}$[Cu(en)$_2$]$_4$}[MoO$_4$]$_2$·14H$_2$O (en = ethylenediamine).[5e] However, to the best of our knowledge, no heteropolyoxometalate coordination polymer exhibiting spin glass behaviour has been found although spin glass has become one of fundamental and general forms of magnetism[6] and many crystalline molecular materials have been reported to exhibit this important phenomenon.[7] In this paper, we report the hydrothermal synthesis, crystal structure and magnetic properties of a 1D coordination polymer with mixed molybdenum-vanadium heteropolyoxometalate bridges, namely {[Ni(phen)$_2$(H$_2$O)]$_2$[Ni(phen)$_2$][V$^{IV}_8$Mo$^{VI}_6$Mo$^{V}_2$O$_{40}$(PO$_4$)]}{[Ni(phen)$_2$(H$_2$O)]$_2$[V$^{IV}_8$Mo$^{VI}_6$Mo$^{V}_2$O$_{40}$(PO$_4$)$_2$]}·5H$_2$O·2EtOH (**1**) (phen = 1,10-phenanthroline, EtOH = ethanol). Both the cation and the anion are heteropolyoxometalates with covalently linked transitional metal complex fragments. Interestingly, this complex exhibits spin glass behaviour and several magnetic transitions at low temperature.

Results and Discussion

A single-crystal X-ray structure analysis revealed that complex **1** consists of 1D zigzag cationic {[Ni(phen)$_2$(H$_2$O)]$_2$[Ni(phen)$_2$][V$^{IV}_8$Mo$^{VI}_6$Mo$^{V}_2$O$_{40}$(PO$_4$)]}$_n^{n+}$ chains and {[Ni(phen)$_2$(H$_2$O)]$_2$[V$^{IV}_8$Mo$^{VI}_6$Mo$^{V}_2$O$_{40}$(PO$_4$)$_2$]}$^-$ anions as well as solvent water molecules and solvent ethanol molecules (Figure 1 and 2). There are mixed molybdenum-vanadium polyoxoanion clusters [V$^{IV}_8$Mo$^{VI}_6$Mo$^{V}_2$O$_{40}$(PO$_4$)]$^{5-}$ in both the anion and the cation. This heteropolyanion shows a tetra-capping Keggin structural

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  DOI: 10.1002/ejic.200400593

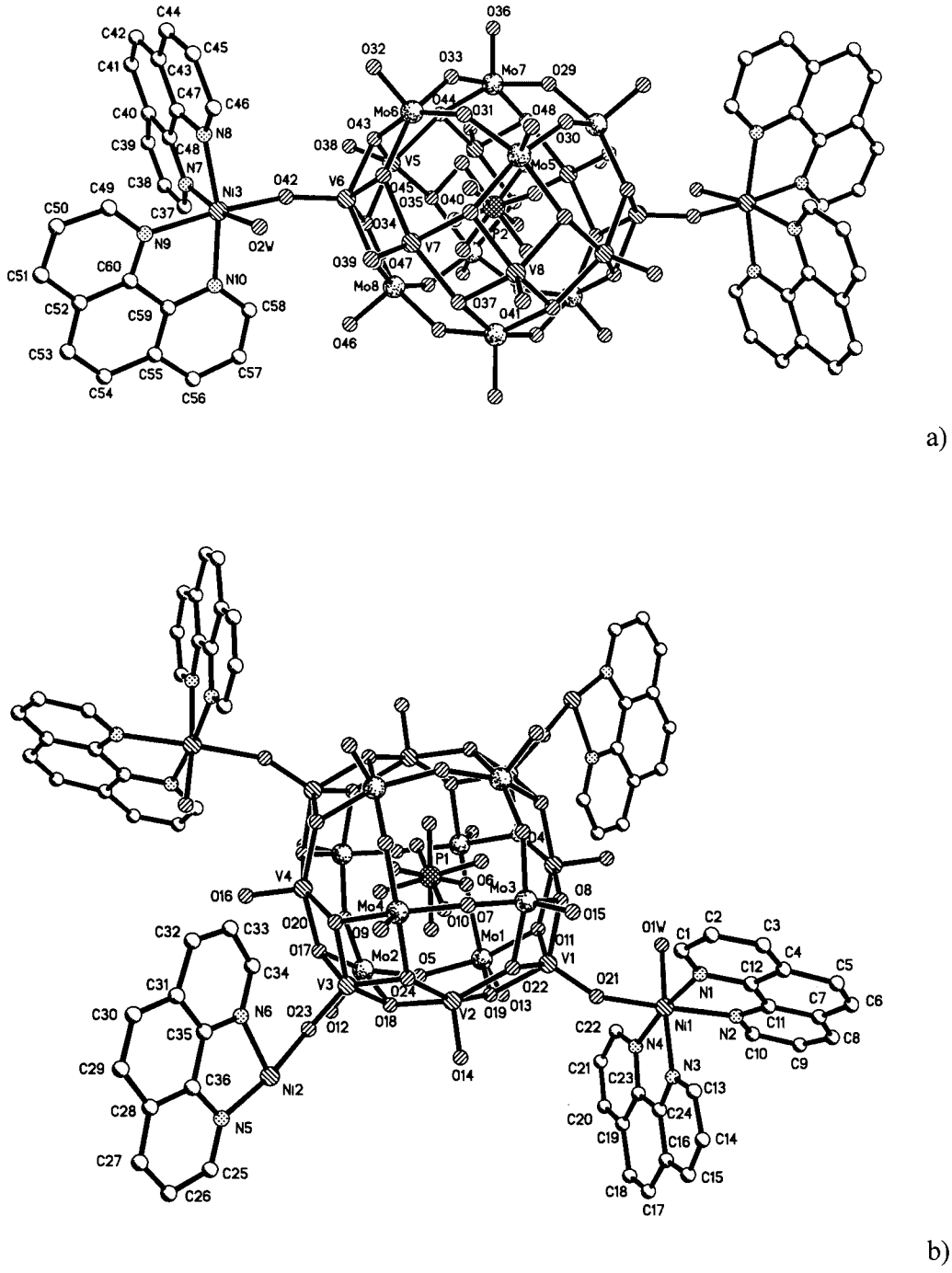

Figure 1. ORTEP view of the anion (a) and a unit of the cation (b) in **1** (50% probability displacement ellipsoids). The H atoms are omitted for clarity

feature and is very similar to that in $[Ni(tea)_2]_3[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]\cdot tea\cdot H_2O$ (tea = triethylenediamine),[2] $\{Co(tea)_2\}_2Na[PMo^{VI}_6Mo^{V}_2V^{IV}_8O_{44}]\cdot 8H_2O$,[2] $[Co(en)_2][Co(bpy)_2]_2[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]\cdot 4.5H_2O$,[5a] $\{Mo^{VI}_6Mo^{V}_2V^{IV}_8O_{40}(PO_4)[Co(phen)_2(H_2O)]_2\}\text{-}[Co_2(phen)_2(OH)_2(H_2O)_4]_{1/2}$ [5b] and $\{Mo^{VI}_5Mo^{V}_3V^{IV}_8O_{40}(PO_4)[Co(phen)(en)(H_2O)]_2\}[Co(phen)_3]\cdot 1.5H_2O$ (en = ethylenediamine).[5b] The $[V^{IV}_8Mo^{VI}_6Mo^{V}_2O_{40}(PO_4)]^{5-}$ unit is constructed from eight VO_5 square pyramids by sharing square edges thus forming a central belt and two Mo_4 rings are bonded above and below this V_8 belt. A disordered PO_4^{3-} anion is located in the centre as a guest.

Two terminal nickel(II) complex fragments $[Ni(phen)_2(H_2O)]^{2+}$ link to two terminal V-O groups of the heteropolyoxoanion cluster $[V^{IV}_8Mo^{VI}_6Mo^{V}_2O_{40}(PO_4)]^{5-}$ from the opposite sides to generate the anion $\{[Ni(phen)_2(H_2O)]_2[V^{IV}_8Mo^{VI}_6Mo^{V}_2O_{40}(PO_4)_2]\}^{-}$ which is quite similar to the trimetallic nanocluster anion $\{Mo^{VI}_6Mo^{V}_2V^{IV}_8O_{40}(PO_4)[Co(phen)_2(H_2O)]_2\}^{-}$ in $\{Mo^{VI}_6Mo^{V}_2V^{IV}_8O_{40}(PO_4)[Co(phen)_2(H_2O)]_2\}[Co_2(phen)_2(OH)_2(H_2O)_4]_{1/2}$.[5b]

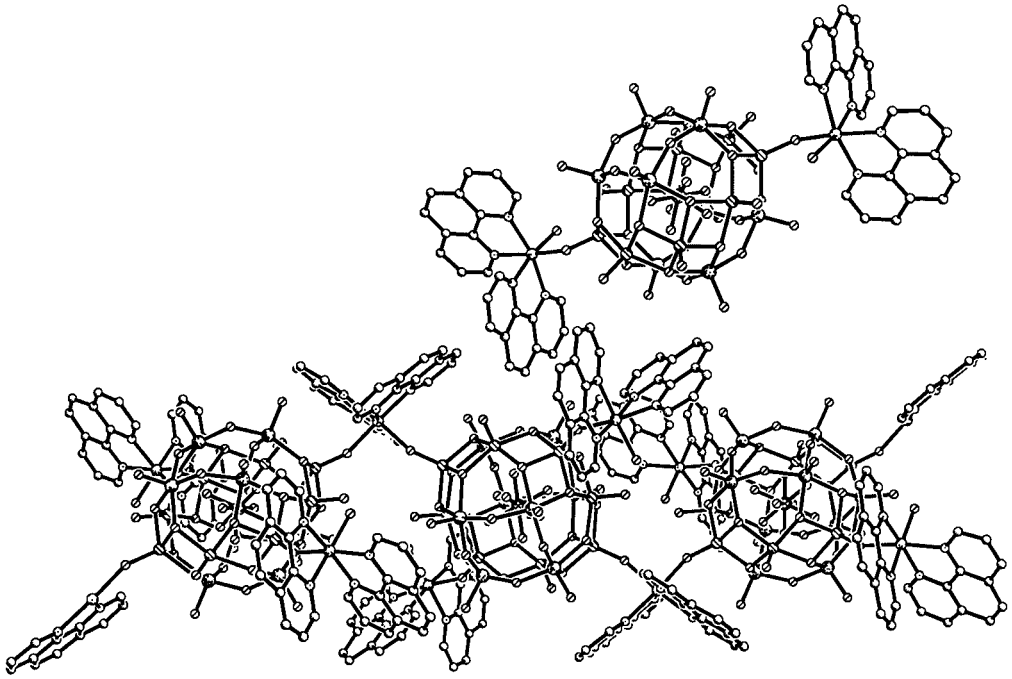

Figure 2. Molecular structure of complex **1** showing the zigzag cation chain (below) and an isolated anion (above); all solvent water molecules and ethanol molecules as well as H atoms are omitted for clarity

The Ni···Ni separation distance of 15.131Å is a little longer than the corresponding Co···Co separation distance of 14.843Å in $\{Mo^{VI}_6Mo^{V}_2V^{IV}_8O_{40}(PO_4)[Co(phen)_2(H_2O)]_2\}$-$[Co_2(phen)_2(OH)_2(H_2O)_4]_{1/2}$.[5b] The cation $\{Ni(phen)_2$-$(H_2O)\}_2[Ni(phen)_2][V^{IV}_8Mo^{VI}_6Mo^{V}_2O_{40}(PO_4)]\}^+$ also contains $\{[Ni(phen)_2(H_2O)]_2[V^{IV}_8Mo^{VI}_6Mo^{V}_2O_{40}(PO_4)_2]\}^-$ components but they are further connected to each other through *cis*-nickel complex fragments, $[Ni(phen)_2]^{2+}$, acting as bridges. Both $[Ni(phen)_2(H_2O)]^{2+}$ and $[Ni(phen)_2]^{2+}$ fragments connect the terminal V−O groups in the cation $\{Ni(phen)_2(H_2O)\}_2[Ni(phen)_2][V^{IV}_8Mo^{VI}_6Mo^{V}_2O_{40}(PO_4)]\}^+$. The Ni···Ni separation distance between two opposite $[Ni(phen)_2(H_2O)]^{2+}$ fragments (15.272 Å) is a little longer than that between two opposite $[Ni(phen)_2]^{2+}$ fragments (15.077 Å). These zigzag cationic chains are arranged parallel to the *c*-axis to form a layer along the *bc* plane with an interchain distance of about 15.7Å, whereas the isolated anions are located between cation layers to form the anion layer. It is noteworthy that although polyoxometalates with covalently linked transitional metal complex fragments have been extensively observed in many organic-inorganic hybrid oxide materials,[1e,3][5b][5c,8] cases of polyoxometalates with covalently linked transitional metal complex fragments acting as both the cations and the anions are quite rare. Complex **1** is the first coordination polymer of this type. The other reported complex with heteropolyoxocations and heteropolyoxoanions coexisting is $[PMo^{VI}_6Mo^{V}_2V^{IV}_8O_{44}$-$\{Co(2,2'\text{-bipy})_2(H_2O)\}_4][PMo^{VI}_4Mo^{V}_4V^{IV}_8O_{44}\{Co(2,2'$-$bipy)_2(H2O)\}_2]\cdot 4H_2O$ (2,2′-bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline)[5d] which is a zero-dimensional polyoxometalate.

As shown in Table 1, the Mo−O and V−O bond lengths are $Mo-O_t$ 1.654(6)−1.676(6)Å, $Mo-O_b$ 1.854(7)−2.004(7) Å, $V-O_t$ 1.600(6)−1.640(6) Å and $V-O_b$ 1.915(6)−2.019(7) Å for the anion $\{[Ni(phen)_2(H_2O)]_2$-$[V^{IV}_8Mo^{VI}_6Mo^{V}_2O_{40}(PO_4)_2]\}^-$ and $Mo-O_t$ 1.658(6)−1.672(6) Å, $Mo-O_b$ 1.859(7)−1.994(6) Å, $V-O_t$ 1.591(6)−1.643(5) Å and $V-O_b$ 1.923(6)−2.007(6) Å for the cation $\{Ni(phen)_2(H_2O)\}_2[Ni(phen)_2][V^{IV}_8Mo^{VI}_6Mo^{V}_2$-$O_{40}(PO_4)]\}^+$. The assignments of the oxidation states for the Mo atoms and the V atoms are consistent with the electric charge and can be confirmed by bond valence sum calculations[9] which give values of 5.840 for Mo1, 5.851 for Mo2, 5.673 for Mo3, 5.815 for Mo4, 4.040 for V1, 3.910 for V2, 4.098 for V3, 3.909 for V4 (the cation part), and 5.871 for Mo5, 5.723 for Mo6, 5.804 for Mo7, 5.780 for Mo8, 3.875 for V5, 4.063 for V6, 3.906 for V7 and 4.065 for V8 (the anion part), respectively. The average values calculated for the oxidation state of V are 3.988 for the cation $\{Ni(phen)_2(H_2O)\}_2[Ni(phen)_2][V^{IV}_8Mo^{VI}_6Mo^{V}_2O_{40}(PO_4)]\}^+$ and 3.977 for the anion $\{[Ni(phen)_2(H_2O)]_2[V^{IV}_8$-$Mo^{VI}_6Mo^{V}_2O_{40}(PO_4)_2]\}^-$ (expected value for V^{IV}_8 is 4.000). Both the average values calculated for the oxidation state of Mo in the cation $\{Ni(phen)_2(H_2O)\}_2[Ni(phen)_2][V^{IV}_8$-$Mo^{VI}_6Mo^{V}_2O_{40}(PO_4)]\}^+$ and in the anion $\{[Ni(phen)_2(H_2O)]_2[V^{IV}_8Mo^{VI}_6Mo^{V}_2O_{40}(PO_4)_2]\}^-$ are 5.795 (expected value for $Mo^{VI}_6Mo^{V}_2$ is 5.750) and the calculated result is in good agreement with the formula of **1**.

The 2−300 K magnetic susceptibility, χ, of a polycrystalline sample of **1** could be fitted to the Curie−Weiss law above 70 K with C = 9.77 $cm^{-3}\cdot mol^{-1}\cdot K$ and θ = −36.49 K, indicating antiferromagnetic interactions of

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

Cation part			
Ni1−N4	2.063(8)	Ni1−N1	2.084(8)
Ni1−N2	2.085(7)	Ni1−N3	2.103(8)
Ni1−O21	2.066(6)	Ni1−O1W	2.094(8)
Ni2−O23	2.068(5)	Ni2−N6	2.073(7)
Ni2−N5	2.088(7)	Mo1−O13	1.658(6)
Mo1−O5	1.874(7)	Mo1−O7	1.880(7)
Mo1−O11	1.975(6)	Mo1−O19	1.981(6)
Mo2−O12	1.667(6)	Mo2−O5	1.859(7)
Mo2−O18	1.989(6)	Mo3−O15	1.672(6)
Mo3−O10	1.864(7)	Mo3−O4	1.868(8)
Mo3−O8	1.964(6)	Mo3−O22	1.970(6)
Mo4−O9	1.668(6)	Mo4−O7	1.862(7)
Mo4−O10	1.871(6)	Mo4−O20	1.980(6)
Mo4−O24	1.982(6)	V1−O21	1.627(6)
V1−O8	1.926(6)	V1−O11	1.935(6)
V1−O22	1.943(6)	V1−O19	1.952(6)
V2−O14	1.591(6)	V2−O24	1.980(6)
V2−O18	1.987(6)	V2−O22	1.991(6)
V3−O23	1.643(5)	V3−O24	1.923(6)
V3−O20	1.932(6)	V3−O18	1.934(6)
V3−O17	1.946(7)	V4−O16	1.602(6)
V4−O20	1.977(6)	V4−O17	1.979(6)
N1−Ni1−N2	79.2(3)	N4−Ni1−N3	80.2(3)
O21−Ni1−N1	93.0(3)	O21−Ni1−N2	171.7(3)
O21−Ni1−N3	93.7(3)	N4−Ni1−O21	89.5(3)
N4−Ni1−O1W	93.4(4)	O21−Ni1−O1W	93.1(3)
O1W−Ni1−N3	170.6(3)	N6−Ni2−N5	79.8(3)
O23−Ni2−N6	94.3(3)	O23−Ni2−N5	172.8(3)
O23−Ni2−O23[a]	90.1(3)		
Anion part			
Ni3−O42	2.045(6)	Ni3−N10	2.084(7)
Ni3−O2W	2.085(7)	Ni3−N7	2.088(8)
Ni3−N9	2.110(7)	Ni3−N8	2.088(8)
Mo5−O48	1.676(6)	Mo5−O30	1.854(7)
Mo5−O31	1.868(7)	Mo5−O40	1.966(6)
Mo6−O32	1.656(7)	Mo6−O33	1.860(7)
Mo6−O31	1.866(6)	Mo6−O45	1.986(6)
Mo6−O43	1.988(5)	Mo7−O36	1.671(6)
Mo7−O29	1.854(7)	Mo7−O33	1.862(7)
Mo7−O44	1.992(6)	Mo8−O46	1.654(6)
Mo8−O39	1.973(6)	Mo8−O34	1.989(7)
V5−O38	1.602(6)	V5−O44	1.993(6)
V5−O43	2.000(6)	V5−O35	2.006(7)
V5−O34	2.019(7)	V6−O42	1.640(6)
V6−O45	1.915(6)	V6−O39	1.918(6)
V6−O34	1.936(6)	V6−O43	1.937(6)
V7−O47	1.600(6)	V7−O40	1.964(6)
V7−O37	1.981(7)	V7−O39	1.993(6)
V7−O45	1.995(7)	V8−O41	1.618(7)
V8−O37	1.935(6)	V8−O40	1.939(6)
O42−Ni3−N10	94.7(3)	O42−Ni3−O2W	89.6(3)
N7−Ni3−N8	79.5(4)	N10−Ni3−N9	79.1(3)
O42−Ni3−N7	85.2(3)	O42−Ni3−N8	95.3(3)
N10−Ni3−O2W	95.9(3)	N10−Ni3−N7	93.0(3)
O2W−Ni3−N7	170.1(3)	O2W−Ni3−N9	93.0(3)
O42−Ni3−N9	173.5(3)	O2W−Ni3−N8	92.6(4)

[a] Symmetry transformations used to generate equivalent atoms: $-x, y, -z + 3/2$.

nearest-neighbour spin units. As shown in Figure 3, χT has a value of 8.90 emu·K·mol^{-1} at room temperature which is smaller than that expected for the total value of 16 uncoupled $S = 1/2$ spins of the V^{4+} atoms, 4 uncoupled $S = 1/2$ spins from the Mo^{5+} atoms and 5 uncoupled $S = 1$ spins from the Ni^{2+} atoms (≈ 13.83 emu·K·mol^{-1} assuming $g = 2.0$ for V^{4+} and Mo^{5+} and $g = 2.25$ for Ni^{2+}). This is due to spin pairing[5,10] which is favoured by electron delocalisation in the cluster $[V^{IV}{}_8Mo^{VI}{}_6Mo^{V}{}_2O_{40}(PO_4)]^{5-}$. The value of χT decreases upon cooling but a sharp increase in $\chi T(T)$ occurs near 50 K and a maximum of 27.02 emu K·mol^{-1} is reached at 16 K. Below 16 K, $\chi T(T)$ decreases abruptly down to 2 K because of saturation effects and/or increasing antiferromagnetic interactions.

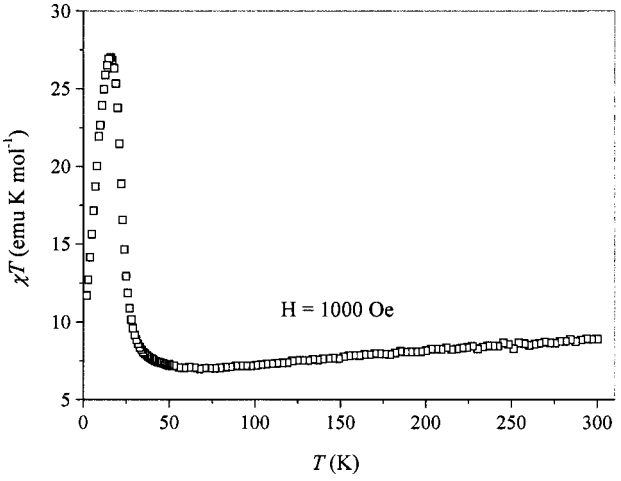

Figure 3. χT vs. T plot of **1** at 1000 Oe

The ac susceptibility measurements indicated that both real χ' and imaginary χ'' components of the susceptibility show rather complicated behaviour (Figure 4). Firstly, there are two peaks in the $\chi'(T)$ and $\chi''(T)$ curves: both the cusped one and the rounded one are frequency dependent while the latter is more sensitive to frequency, suggesting unusual spin glass behaviour. Secondly, below 8 K, $\chi'(T)$ increases gradually, possibly indicating the existence of another phase transition. This peculiar ac susceptibility behaviour may occur for a *ferroglass* system (also called a re-

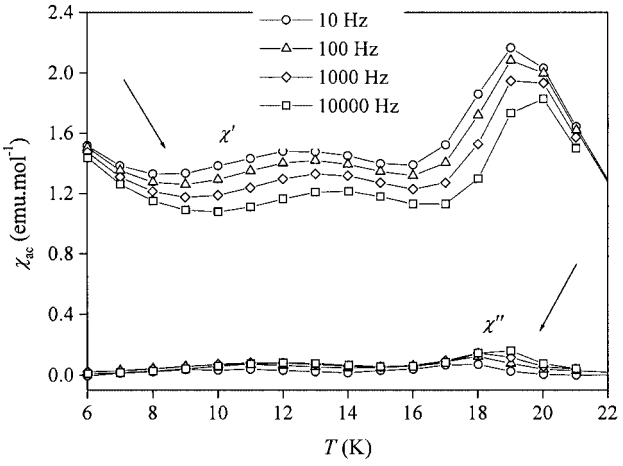

Figure 4. Real(χ') and imaginary(χ'') parts of the *ac* susceptibility at a bias DC field of 10 Oe for **1**

entrant spin glass system) because it generally undergoes multiple magnetic phase transitions.[11] Therefore, the cusped peak could be assigned to a spin glass transition while the rounded one probably corresponds to a ferroglass transition.[11b] The spin-freezing temperature T_f (= 19 K) may be defined approximately by the sharp cusp in χ' at 10 Hz and the spin-freezing at a lower temperature T_{fg} may be estimated by the rounded peak in χ' at 10 Hz (T_{fg} = 12 K). The spin-glass state was also confirmed by the divergence of the zero-field-cooled (ZFC) and field-cooled (FC) $\chi(T)$ data of **1** below 20 K, indicating the occurrence of irreversibility of magnetisation. Furthermore, hysteresis can be observed with coercive fields (*Hc*) of 191 Oe at 20 K (Figure 5), 386 Oe at 12.5 K and 660 Oe at 5 K, respectively. However, the field dependent magnetisation of **1** measured at 5 K shows that at the highest field measured (50 kOe), a low magnetisation value of 7.4 $N\beta$ is achieved and saturation does not occur, this being consistent with weak ferromagnetism owing to spin glass.

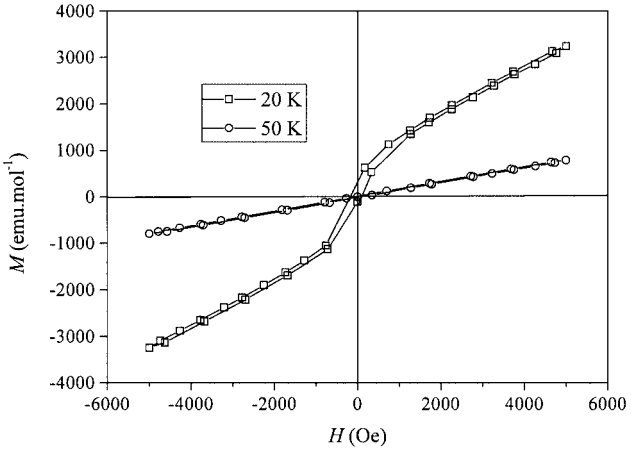

Figure 5. Hysteresis loops at 20 K and 50 K

In summary, the successful synthesis of $Ni_5[V^{IV}{}_8Mo^{VI}{}_6Mo^{V}{}_2O_{40}(PO_4)]_2(phen)_{10}(H_2O)_9(EtOH)_2$ **1** indicates that a new type of organic-inorganic hybrid oxide material in which polyoxometalate clusters act as both the cation and the anion can be prepared hydrothermally. The anion in **1** is a trimetallic nanocluster $\{Mo^{VI}{}_6Mo^{V}{}_2V^{IV}{}_8O_{40}(PO_4)[Ni(phen)_2(H_2O)]_2\}^-$ and the cation $\{Ni(phen)_2(H_2O)\}_2[Ni(phen)_2][V^{IV}{}_8Mo^{VI}{}_6Mo^{V}{}_2O_{40}(PO_4)]\}^+$ also contains trimetallic units $\{Mo^{VI}{}_6Mo^{V}{}_2V^{IV}{}_8O_{40}(PO_4)[Ni(phen)_2(H_2O)]_2\}^-$ which are further connected to each other through *cis*-nickel complex fragments, $Ni(phen)_2{}^{2+}$, to form a zigzag chain. Both the cation and the anion in **1** are high-spin systems which would generate randomness either in the positions of the spins or the signs of the neighbouring couplings in a field and spin glass behaviour is then expected.

Experimental Section

Materials and Methods: All reagents were obtained from commercial sources and used without further purification. The elemental analyses were performed with a Heraeus Chn-Rapid elemental analyser. The inductively coupled plasma (ICP) analysis was conducted with a Perkin−Elmer Optima 3300DV spectrometer. The infrared spectra were recorded with a Pekin-Elmer 2000 spectrophotometer with pressed KBr pellets. X-ray photoelectron spectroscopy data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300-W Al-K_α radiation. The base pressure was around 3×10^{-9} mbar. The binding energies were referenced to the C 1s line at 284.6 eV from adventitious carbon. The magnetic susceptibility measurements for **1** were carried out on a polycrystalline sample (202.84 mg) using a MagLab System 2000 magnetometer in a field up to 5 T. Diamagnetic corrections were estimated from Pascal's constants.[12]

Synthesis of 1: A mixture of NH_4VO_3 (3 mmol), $H_3[P(Mo_3O_{10})_4]\cdot xH_2O$ (0.5 mmol), $Ni(NO_3)_2$ (1 mmol), 1,10-phenanthroline (1 mmol), *N*,*N*′-diethylethylenediamine (3 mmol), ethanol (0.2 mL) and H_2O (18 mL) was stirred for 20 min and then transferred into a 30 mL Teflon-lined steel autoclave. The mixture was heated at 170 °C for 6 days and black block crystals of **1** were separated from the blue supernatant solution in ca. 40% yield (463 mg) based on V. $C_{124}H_{110}Mo_{16}N_{20}Ni_5O_{99}P_2V_{16}$ (6169.89): calcd. C 24.14, H 4.54, N 1.80, Mo 24.9, Ni 4.8, V 13.2; found C 24.06, H 4.60, N 1.75, Mo 24.8, Ni 4.7, V 13.2. IR (KBr): $\tilde{\nu}$ = 1055(w) [$\nu_{(P-O)}$], 951(vs) [$\nu_{(M=O)}$], 792(s) cm^{-1} [$\nu_{(M-O-M)}$] (M = V or Mo). XPS: calcd. C 1s 284.75, O 1s 530.10, P 2p 132.90, Ni $2p_3$ 855.90, V $2p_3$ 516.10, Mo 3d 231.80 eV.

X-ray Crystal Structure Determination: A black single crystal of **1** with dimensions 0.37 × 0.27 × 0.17 mm was selected and mounted on a Rigaku RAXIS RAPID IP imaging plate system with Mo-K_α radiation (λ = 0.71073Å) at 300(2) K in the range $1.38° < \theta < 27.48°$. An empirical absorption correction from Ψ scans was applied. A total of 28115 reflections were collected ($-64 \le h \le 64$, $-20 \le k \le 20$, $-33 \le l \le 33$) of which 18729 were unique (R_{int} = 0.0441) and 15227 with $I > 2\sigma(I)$. The structure was solved by the Patterson method and refined using full-matrix least-squares techniques based on F^2 using the SHELXL 97 program. All nonhydrogen atoms were refined anisotropically and all hydrogen atoms but those in water molecules were placed as riding atoms.

Crystal Data For 1: $C_{124}H_{110}Mo_{16}N_{20}Ni_5O_{99}P_2V_{16}$, monoclinic, space group *C*l*2c*, *Mr* = 6169.89, *a* = 49.658(10), *b* = 15.675(3), *c* = 25.916(5) Å, β = 115.39(3)°, *V* = 18225(6) Å^3, *Z* = 4, $D_{calcd.}$ = 2.242 g·cm^{-3}, *T* = 293(2) K, μ = 2.457 mm^{-1}, R_1 = 0.0694, wR_2 = 0.1855 for 15227 observed reflections [$I > 2\sigma(I)$], GOF = 1.087.

CCDC-213185 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 20201012, 90101025), the Major State Basic Research Development Program of the People's Republic of China (G2000077500 and 2001CB610507) and the Chinese Academy of Sciences. The authors also thank the anonymous reviewers for their excellent suggestions for improving the manuscript.

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Received July 9, 2003

