

## Synthesis, structure and magnetic properties of the polyoxovanadate cluster $[\text{Zn}_2(\text{NH}_2(\text{CH}_2)_2\text{NH}_2)_5][\{\text{Zn}(\text{NH}_2(\text{CH}_2)_2\text{NH}_2)_2\}_2\{\text{V}_{18}\text{O}_{42}(\text{H}_2\text{O})\}]\cdot x\text{H}_2\text{O}$ ( $x \sim 12$ ), possessing a layered structure

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**Abstract.** A hydrothermal reaction of a mixture of  $\text{ZnCl}_2$ ,  $\text{V}_2\text{O}_5$ , ethylenediamine and water gave rise to a layered poly oxovanadate material  $[\text{Zn}_2(\text{NH}_2(\text{CH}_2)_2\text{NH}_2)_5][\{\text{Zn}(\text{NH}_2(\text{CH}_2)_2\text{NH}_2)_2\}_2\{\text{V}_{18}\text{O}_{42}(\text{H}_2\text{O})\}]\cdot x\text{H}_2\text{O}$  ( $x \sim 12$ ) (**I**) consisting of  $[\text{V}_{18}\text{O}_{42}]^{12-}$  clusters. These clusters, with all the vanadium ions in the +4 state, are connected together through  $\text{Zn}(\text{NH}_2(\text{CH}_2)_2\text{NH}_2)_2$  linkers forming a two-dimensional structure. The layers are also separated by distorted trigonal bipyramidal  $[\text{Zn}_2(\text{NH}_2(\text{CH}_2)_2\text{NH}_2)_5]$  complexes. The structure, thus, presents a dual role for the Zn-ethylenediamine complex. The magnetic susceptibility studies indicate that the interactions between the V centres in **I** are predominantly antiferromagnetic in nature and the compound shows highly frustrated behaviour. The magnetic properties are compared to the theoretical calculations based on the Heisenberg model, in addition to correlating to the structure. Crystal data for the complexes are presented.

**Keywords.** Polyoxovanadate clusters; layered structure; Zn-ethylenediamine complex; frustrated behaviour.

### 1. Introduction

Oxides, especially those of transition metals, are interesting owing to their many properties ranging from insulating to metallic and even superconducting.<sup>1,2</sup> In recent years, there has been an interest in the construction of oxidic solids with extended structures from molecular building blocks due to the advantages it offers for the design of materials. Employing discrete molecular building units for the assembly of extended networks requires stabilization of such building units in solution. Thus, great promise exists for the assembly of simple polygons (e.g. triangles and squares) into discrete and infinite structures based upon faceted polyhedra by using well-known geometric constraints and appropriate angular multifunctional ligands. The supramolecular organization through self-assembly of organic compounds from molecular building units has developed to maturity in the past few years.<sup>3</sup> Supramolecular inorganic chemistry, on

the other hand, is at a nascent stage. Pioneering research over the last decade or so by Muller and co-workers<sup>4-7</sup> has demonstrated that the principles of self-assembly can be invoked to design novel structures that are based upon closed surface polyhedra, more commonly known as Archimedean solids. Such structures are based upon edge-sharing of polygons and represent approaches to the design of both discrete (porous spheroidal structures) and infinite (nanoporous) structures.<sup>4-7</sup> Thus, polyoxomolybdates of varying compositions exhibiting a variety of structures have been isolated and characterized.<sup>5-7</sup> In recent years, polyoxovanadates of different compositions have been investigated in detail, resulting in many new compositions.<sup>8-15</sup> The polyoxovanadium compounds have been reviewed recently, especially with respect to the synthesis, structure and physicochemical properties.<sup>16</sup> Typical examples include  $\text{Cs}_{13}[\text{V}_{18}\text{O}_{42}\text{X}]^{13-}\cdot 12\text{H}_2\text{O}$ ,<sup>8,9</sup>  $[(\text{N}_2\text{H}_5)_2][\text{Zn}_3(\text{H}_2\text{O})_{12}\text{V}_{18}\text{O}_{42}(\text{SO}_4)]\cdot 24\text{H}_2\text{O}$ ,<sup>11</sup>  $[\text{Fe}_3(\text{H}_2\text{O})_{12}\text{V}_{18}\text{O}_{42}(\text{VO}_4)]\cdot 24\text{H}_2\text{O}$ ,<sup>12</sup>  $\text{K}\{[\text{V}_{18}\text{O}_{42}\text{Cl}][\text{Ni}(\text{en})_2]_3\}\cdot 8\text{H}_2\text{O}$ <sup>13</sup> and  $\text{M}_2(\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2)_5[\{\text{M}(\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2)_2\}_2\text{V}_{18}\text{O}_{42}(\text{X})]\cdot 9\text{H}_2\text{O}$  ( $\text{M} = \text{Zn}$  and  $\text{Cd}$ ;  $\text{X} = \text{Cl}$ ,  $\text{Br}$  or  $\text{H}_2\text{O}$ ).<sup>14</sup>

Dedicated to Prof J Gopalakrishnan on his 62nd birthday

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In a course of a programme aimed at producing new solids, we have been interested in organizing polyoxo-metal clusters into extended structures using covalent linkages. To this end, we have recently shown that *b*-octamolybdate clusters can be covalently linked to give rise to unusual solids with novel structures.<sup>17</sup> The continuing investigations on the polyoxovanadates have resulted in the assembly of  $[V_{18}O_{42}]^{12-}$  cluster anions, through zinc-ethylenediamine complex, into a two-dimensional solid,  $[Zn_2(NH_2(CH_2)_2NH_2)_5][\{Zn(NH_2(CH_2)_2NH_2)_2\}_2\{V_{18}O_{42}(H_2O)\}] \cdot xH_2O$  ( $x \sim 12$ ), **I**. In addition to being the first example of the assembly of  $[V_{18}O_{42}]^{12-}$  clusters with all the vanadium atoms in the +4 oxidation state, the dual role played by the zinc-ethylenediamine complex is also interesting and noteworthy. The structure of the present compound has close similarity to the  $[V_{18}O_{42}]$  cluster compound reported recently by Khan *et al*<sup>14</sup>. In this paper, we present the synthesis, structure, magnetic studies and theoretical study of the magnetic interactions between the  $V^{IV}$  ions in **I**.

## 2. Experimental

Compound **I** was prepared in a single-step reaction of a mixture containing  $ZnCl_2$ , ethylenediamine, (*en*),  $V_2O_5$  in water at  $150^\circ C$ , and isolated as highly crystalline, dark-coloured thin plates and the structure was solved using single crystal X-ray diffraction. Typically, a mixture of  $ZnCl_2$  (0.136 g),  $V_2O_5$  (0.182 g), ethylenediamine (0.15 ml) and water (1 ml) was taken in a molar ratio of 1:1:2:55 and heated at  $150^\circ C$  for 96 h in a PTFE-lined 7 ml acid digestion bomb resulting in large quantities of dark bluish plate-like crystals. The product was filtered under vacuum, washed with plenty of deionized water and dried at ambient temperature. The initial pH of the reaction mixture was 9. The reaction mixture after heat treatment had a pH of  $\sim 8$ . The compound was obtained as a pure single-phase material (yield =  $\sim 80\%$  based on V). The compound was characterized using EDAX, IR, TGA, in addition to powder X-ray diffraction (XRD). The dark bluish colour of the product indicates that vanadium is in a reduced oxidation state and, since no external reducing agent is employed, the amine presumably serves in this capacity. Elemental analysis: obsd. C 8.89, N 9.51, H 3.49%; calcd. C 9.09, N 9.67, H 3.31%.

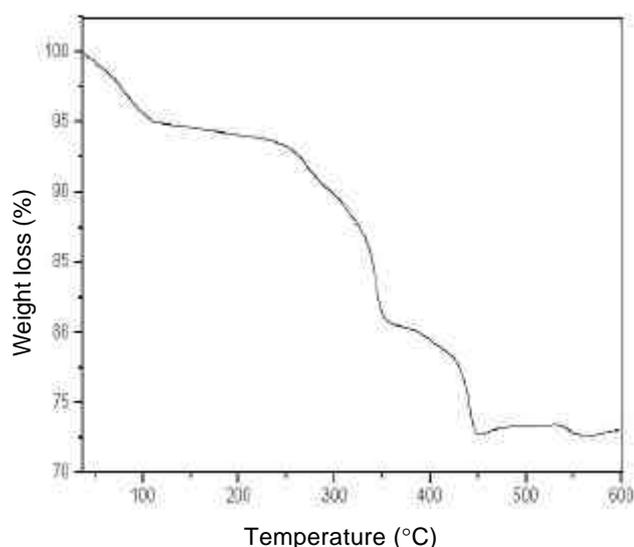
Thermogravimetric analysis (TGA) of **I** was carried out in flowing air (50 ml/min) in the range 25–

$600^\circ C$  (heating rate  $10^\circ C/min$ ). The results indicate that the weight loss occurs in four distinct steps (figure 1). The first weight loss of 5.5% occurring at  $\sim 100^\circ C$  corresponds to the loss of some of the extra-framework water molecules. The second and third weight losses occur continuously in the temperature range of  $200\text{--}350^\circ C$  with a total loss of 13.4% corresponding to the loss of the remaining water molecules along with the ethylenediamine molecules bonded to the extra-framework Zn atoms. The final loss around  $425^\circ C$  of 7.4% corresponds to the loss of the ethylenediamine molecules bound to the Zn centre of the layer structure. The total weight loss of 26.7% observed for all the above processes corresponds very well with the calculated value (16.7%). The final calcined sample is amorphous with very weakly diffracting lines by powder XRD that corresponds to  $V_2O_5$ .

Fourier transform infra-red (FT-IR) spectroscopic studies have been performed using the KBr pellet method in the region  $400\text{--}4000\text{ cm}^{-1}$ . The spectra show typical absorption bands: lattice water  $3581, 1610\text{ cm}^{-1}$ ,  $n(NH) = 1514\text{ cm}^{-1}$ ,  $n(CN) = 1096, 1051\text{ cm}^{-1}$ ,  $n(CH) = 3195, 3081\text{ cm}^{-1}$ ,  $n(V-O_{\text{terminal}}) = 1015, 960, 920\text{ cm}^{-1}$ ,  $n(V-O(m_b)) = 710, 625, 500\text{ cm}^{-1}$ .

## 3. X-ray crystallography

A suitable single crystal of compound **I** ( $0.20 \times 0.24 \times 0.32\text{ mm}$ ) was carefully selected under a polarizing microscope and glued to a thin glass fibre. Crystal



**Figure 1.** Thermogravimetric analysis (TGA) of **I**.

structure determination by X-ray diffraction was performed on a Siemen's Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å) operating at 40 kV and 40 mA. Pertinent details for the structure determinations are presented in table 1. An empirical absorption correction based on symmetry equivalent reflections was applied using the SADABS program.<sup>18</sup> The systematic absences in the reduced data ( $0k0$ ,  $k \neq 2n$ ) indicated space groups  $P2_1$  or  $P2_1/m$ , of which  $P2_1/m$  was chosen. The structure was solved and refined using the SHELXTL-PLUS suite of program.<sup>19</sup> The direct methods solution readily established all the heavy atom positions (Zn and V) and facilitated the identification of most of the other fragments (O, C, N and H) from the difference Fourier maps and the refinements to proceed to  $R < 10\%$ . All the hydrogen atoms were initially located in the difference Fourier maps and for the final refinement the hydrogen atoms were placed geometrically and held in the riding mode. Final  $R$  values of  $R_1 = 0.0457$  and  $wR_2 = 0.1504$  were obtained for refinements varying atomic positions for all the atoms, anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares refinement against  $|F^2|$  was carried out using the SHELXTL-PLUS<sup>19</sup> suite of programs. Details of the final refinements are given in table 1. The selected bond distances and angles for **I** are listed in tables 2 and 3 (CCDC Ref. No. 198457).

**Table 1.** Crystal data and structure refinement parameters for **I**  $[\text{Zn}_2(\text{en})_5][\{\text{Zn}(\text{en})_2\}_2\{\text{V}_{18}\text{O}_{42}(\text{H}_2\text{O})\}] \cdot x\text{H}_2\text{O}$  ( $x \sim 12$ ).

Empirical formula	$\text{C}_{18}\text{H}_{94}\text{N}_{18}\text{O}_{54}\text{V}_{18}\text{Zn}_4$
Formula mass	2605.4
Crystal system	Monoclinic
Space group	$P2_1/m$ (no. 11)
$a$ (Å)	12.5537(1)
$b$ (Å)	21.1451(3)
$c$ (Å)	15.8920(2)
$b^\circ$	97.273(1)
$V$ (Å <sup>3</sup> )	4184.58(9)
$Z$	4
$T$ (K)	293(2)
$r_{\text{calc}}$ (gcm <sup>-3</sup> )	2.049
$m$ (mm <sup>-1</sup> )	3.126
Reflections total, observed	17190, 5280
$R$ indexes [ $I > 2\sigma(I)$ ]	$R_1 = 0.0457$ , $wR_2 = 0.1504$

<sup>a</sup> $R_1 = \sum |F_0| - |F_c| / \sum |F_0|$ ; <sup>b</sup> $wR_2 = \{ \sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2] \}^{1/2}$ .  $w = 1 / [s^2(F_0^2) + (aP)^2 + bP]$ ,  $P = [\max. (F_0^2, 0) + 2(F_c^2)^2] / 3$ , where  $a = 0.0883$  and  $b = 13.004$  for **I**

#### 4. Description of the structure

All the vanadium (IV) atoms are in square-pyramidal coordination with typical one short and four long bond lengths. The longer V–O distances are in the range 1.904(4)–1.967(4) Å (av. 1.944 Å) and the shorter V–O bonds have an average bond distance of 1.631 Å. Every vanadium atom has at least one neighbouring vanadium atom within 3.04 Å of itself, the shortest such distance being 2.86 Å. All the VO<sub>5</sub> square-pyramids are connected through their edges forming an octameric ring. The central octamer ring is then capped on either side by five VO<sub>5</sub> units, again connected through the edges, forming the  $[\text{V}_{18}\text{O}_{42}]^{12-}$  cyclic cluster with rhombicuboctahedron geometry (14th Archimedean body) (figure 2). One water molecule was encapsulated within the cluster. Bond valence sum calculations (BVS) clearly show that all the vanadium atoms are in 4<sup>+</sup> oxidation states with the BVS values in the range 4.02–4.273.<sup>20</sup> Isolated  $[\text{V}_{18}\text{O}_{42}]^{12-}$  clusters, containing all the V atoms in 4+ oxidation states, have been prepared and characterized earlier.<sup>8,9</sup> Presently we have been able to connect the clusters through a Zn-ethylenediamine complex, giving rise to a layer structure.

The extended and highly symmetrical structure of **I** consists of  $[\text{V}_{18}\text{O}_{42}]^{12-}$  cluster anions connected by  $[\text{Zn}(\text{NH}_2(\text{CH}_2)_2\text{NH}_2)_2]^{2+}$  units forming an infinite two-dimensional network as shown in figure 3. Zn atoms are covalently bonded directly to the  $[\text{V}_{18}\text{O}_{42}]^{12-}$  clusters through the shorter V–O bonds, [(V(6)–O(1)  $\times$  2, V(7)–O(14) and V(8)–O(12)], and are also coordinated with the ethylenediamine molecules, which are fully protonated. The macroanionic layers in **I**, are separated by  $[\text{Zn}_2(\text{en}_2)_5]^{6+}$ , in which the Zn atoms are in square-pyramidal coordination. This is indeed an unique structure.

Earlier existence of  $[\text{V}_{18}\text{O}_{42}]^{12-}$  clusters has been established earlier by Johnson and Schlemper<sup>8</sup> and later by Muller and coworkers,<sup>9</sup> but only few examples are known in the literature,<sup>11–15</sup> wherein these clusters have been linked to form an extended structure. These are samples in which the V atoms exist in mixed valence states (V<sup>V</sup> and V<sup>IV</sup>), and to our knowledge **I** is the first example wherein both the charge and structural integrity of the  $[\text{V}_{18}\text{O}_{42}]^{12-}$  clusters have been maintained.  $[\text{V}_{18}\text{O}_{42}]^{12-}$  clusters have been shown to exhibit two different symmetries,  $D_{4d}$  and  $T_d$ , based on the guest molecule contained within the cluster shell.<sup>9</sup> In the present case, the  $[\text{V}_{18}\text{O}_{42}]^{12-}$  cluster has a symmetry close to  $T_d$ .<sup>9</sup> The  $[\text{V}_{18}\text{O}_{42}]^{12-}$  cluster also encloses one molecule of water as a guest. In addition,

**Table 2.** Selected bond distances for **I** [Zn<sub>2</sub>(en)<sub>5</sub>][{Zn(en)<sub>2</sub>}<sub>2</sub>{V<sub>18</sub>O<sub>42</sub>(H<sub>2</sub>O)}]·xH<sub>2</sub>O (x ~ 12).

Bond	Distance (Å)	Bond	Distance (Å)
Zn(1)–O(1)	2.352(4) × 2 [0.174]	V(8)–O(3)	1.945(4) × 2 [0.647]
Zn(1)–N(9)	2.093(6) × 2 [0.415]	V(8)–O(7)	1.937(4) × 2 [0.661]
Zn(1)–N(10)	2.143(6) × 2 [0.362]	V(8)–O(12)	1.660(6) [1.398]
<b>Σ(Zn–O/N)</b>	<b>1.901</b>	<b>Σ(V–O)</b>	<b>4.014</b>
Zn(5)–O(12)	2.221(6) [0.247]	V(9)–O(17)	1.921(4) [0.691]
Zn(5)–O(14)	2.402(6) [0.152]	V(9)–O(15)	1.960(5) [0.621]
Zn(5)–N(7)	2.117(6) × 2 [0.389]	V(9)–O(5)	1.920(5) [0.692]
Zn(5)–N(8)	2.127(6) × 2 [0.378]	V(9)–O(11)	1.912(4) [0.707]
<b>Σ(Zn–O/N)</b>	<b>1.83</b>	V(9)–O(16)	1.612(6) [1.562]
Zn(15)–N(5)	2.137(6) [0.368]	<b>Σ(V–O)</b>	<b>4.273</b>
Zn(15)–N(2)	2.107(6) [0.399]	V(10)–O(18)	1.612(6) [1.592]
Zn(15)–N(3)	2.160(7) [0.346]	V(10)–O(4)	1.963(4) × 2 [0.616]
Zn(15)–N(1)	2.199(6) [0.311]	V(10)–O(19)	1.919(4) × 2 [0.694]
Zn(15)–N(4)	2.101(5) [0.406]	<b>Σ(V–O)</b>	<b>4.212</b>
<b>Σ(Zn–N)</b>	<b>1.933</b>	V(11)–O(20)	1.628(5) [1.524]
V(2)–O(4)	1.966(4) × 2 [0.611]	V(11)–O(10)	1.947(2) [0.644]
V(2)–O(3)	1.959(4) × 2 [0.623]	V(11)–O(5)	1.952(4) [0.635]
V(2)–O(2)	1.621(6) [1.554]	V(11)–O(19)	1.965(4) [0.613]
<b>Σ(V–O)</b>	<b>4.022</b>	V(11)–O(21)	1.952(4) [0.635]
V(3)–O(6)	1.620(6) [1.558]	<b>Σ(V–O)</b>	<b>4.051</b>
V(3)–O(7)	1.948(4) × 2 [0.642]	V(12)–O(23)	1.928(4) [0.678]
V(3)–O(8)	1.950(4) × 2 [0.638]	V(12)–O(8)	1.935(4) [0.665]
<b>Σ(V–O)</b>	<b>4.118</b>	V(12)–O(15)	1.955(4) [0.630]
V(4)–O(5)	1.940(4) × 2 [0.656]	V(12)–O(17)	1.961(5) [0.620]
V(4)–O(11)	1.931(6) [0.672]	V(12)–O(22)	1.637(5) [1.488]
V(4)–O(9)	1.623(6) [1.545]	<b>Σ(V–O)</b>	<b>4.081</b>
V(4)–O(10)	1.935(6) [0.665]	V(13)–O(24)	1.632(4) [1.508]
<b>Σ(V–O)</b>	<b>4.194</b>	V(13)–O(4)	1.905(4) [0.721]
V(6)–O(7)	1.948(4) [0.642]	V(13)–O(19)	1.954(4) [0.632]
V(6)–O(1)	1.640(4) [1.476]	V(13)–O(21)	1.956(4) [0.628]
V(6)–O(23)	1.944(4) [0.649]	V(13)–O(13)	1.914(3) [0.704]
V(6)–O(3)	1.954(4) [0.632]	<b>Σ(V–O)</b>	<b>4.193</b>
V(6)–O(13)	1.960(3) [0.621]	V(14)–O(23)	1.953(5) [0.633]
<b>Σ(V–O)</b>	<b>4.02</b>	V(14)–O(25)	1.634(4) [1.500]
V(7)–O(15)	1.936(4) × 2 [0.663]	V(14)–O(17)	1.926(4) [0.681]
V(7)–O(8)	1.959(4) × 2 [0.623]	V(14)–O(21)	1.919(5) [0.676]
V(7)–O(14)	1.646(4) [1.452]	V(14)–O(13)	1.959(4) [0.623]
<b>Σ(V–O)</b>	<b>4.024</b>	<b>Σ(V–O)</b>	<b>4.113</b>

**I** also possesses a large number of extra-framework water molecules.

The remarkable ability of the [V<sub>18</sub>O<sub>42</sub>] cluster to have different charges is well illustrated by the synthesis of the present compound. [V<sub>18</sub>O<sub>42</sub>]<sup>n-</sup> clusters with a variety of charges (n = 6 to 12) have been prepared and characterized. Variation in the total cluster charge is generally balanced by some of the V atoms present in the V<sup>5+</sup> oxidation state. Thus, K<sub>2</sub>[{V<sub>18</sub>O<sub>42</sub>Cl}][Ni(en)<sub>2</sub>]<sub>3</sub>·8H<sub>2</sub>O<sup>13</sup> and M<sub>2</sub>(H<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>)<sub>5</sub>][{M(H<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>}<sub>2</sub>V<sub>18</sub>O<sub>42</sub>(X)]·9H<sub>2</sub>O, M = Zn, Cd and X = Cl, Br or H<sub>2</sub>O<sup>14</sup> possessing [V<sub>18</sub>O<sub>42</sub>] clusters have been synthesized. Of these, the structure of **I** is similar to that of the latter. Magnetometric titrations,

however, indicate that **I** contains all the V atoms in a +4 oxidation state compared to only 14 V atoms in M<sub>2</sub>(H<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>)<sub>5</sub>][{M(H<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>}<sub>2</sub>V<sub>18</sub>O<sub>42</sub>(X)]·9H<sub>2</sub>O, M = Zn, Cd and X = Cl, Br or H<sub>2</sub>O.<sup>14</sup> This is also confirmed by the detailed bond-valence sum calculations based on the method of Brown and Altermatt,<sup>20</sup> using r<sub>o</sub>(V–O) = 1.784 Å, r<sub>o</sub>(Zn–N) = 1.767 Å and r<sub>o</sub>(Zn–O) = 1.704 Å, which gave the valence sums for V atoms in the range 4.022–4.273. This clearly indicates that the valence state of V is +4. To further check the oxidation state of vanadium in **I**, we have performed X-ray photoelectron spectroscopy (XPS) studies, that clearly indicate the core level spectra of the vanadium 2p<sub>3/2</sub>, 2p<sub>1/2</sub> at 515 and

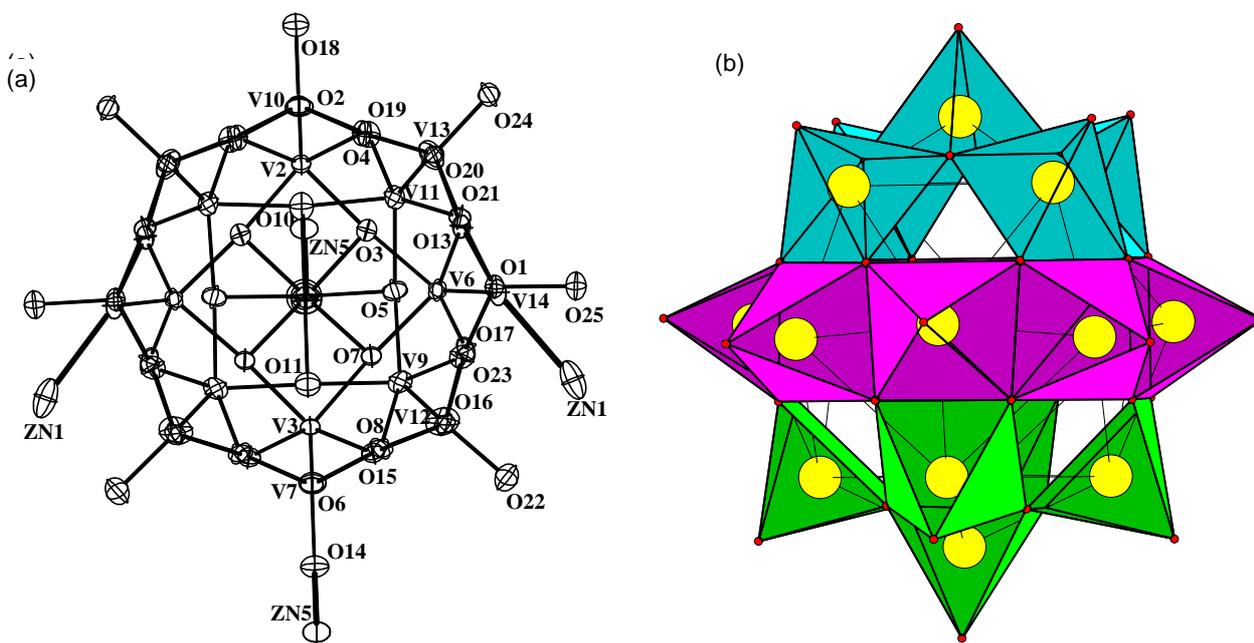
**Table 3.** Selected bond angles for **I** [Zn<sub>2</sub>(en)<sub>5</sub>][{Zn(en)<sub>2</sub>}<sub>2</sub>{V<sub>18</sub>O<sub>42</sub>(H<sub>2</sub>O)}].xH<sub>2</sub>O (x ~ 12).

Moiety	Angle (°)	Moiety	Angle (°)
O(1)–Zn(1)–N(9)	84.9(2) × 2	O(3)–V(8)–O(12)	112.5(2) × 2
O(1)–Zn(1)–N(10)	91.1(2) × 2	O(7)–V(8)–O(7)	82.1(2)
O(1)–Zn(1)–O(1)	180.0	O(3)–V(8)–O(3)	81.4(2)
O(1)–Zn(1)–N(9)	95.1 × 2	O(11)–V(9)–O(15)	87.7(2)
O(1)–Zn(1)–N(10)	88.9(2) × 2	O(11)–V(9)–O(16)	109.1(2)
N(9)–Zn(1)–N(10)	82.9(2) × 2	O(5)–V(9)–O(15)	147.08(17)
N(9)–Zn(1)–N(9)	180.0	O(15)–V(9)–O(16)	105.2(2)
N(10)–Zn(1)–N(10)	180.0	O(5)–V(9)–O(17)	89.05(19)
N(9)–Zn(1)–N(10)	97.1(2) × 2	O(11)–V(9)–O(17)	143.6(2)
O(12)–Zn(5)–O(14)	172.8(2)	O(16)–V(9)–O(17)	107.0(2)
O(12)–Zn(5)–N(7)	92.1(2) × 2	O(5)–V(9)–O(11)	84.2(2)
O(12)–Zn(5)–N(8)	92.2(2) × 2	O(5)–V(9)–O(16)	107.6(2)
O(14)–Zn(5)–N(7)	92.7(2) × 2	O(15)–V(9)–O(17)	78.84(18)
O(14)–Zn(5)–N(8)	83.2(2) × 2	O(4)–V(10)–O(19)	83.32(17) × 2
N(7)–Zn(5)–N(8)	81.9(2) × 2	O(19)–V(10)–O(19)	92.68(18)
N(7)–Zn(5)–N(7)	95.8(2)	O(4)–V(10)–O(18)	108.8(2) × 2
N(7)–Zn(5)–N(8)	175.1(3) × 2	O(4)–V(10)–O(4)	78.78(18)
N(8)–Zn(5)–N(8)	100.1(2)	O(18)–V(10)–O(19)	141.7(2) × 2
N(1)–Zn(15)–N(2)	80.3(2)	O(18)–V(10)–O(19)	108.7(2) × 2
N(1)–Zn(15)–N(3)	160.1(2)	O(5)–V(11)–O(19)	144.0(2)
N(1)–Zn(15)–N(4)	93.6(2)	O(5)–V(11)–O(10)	80.8(2)
N(1)–Zn(15)–N(5)	95.4(2)	O(5)–V(11)–O(21)	89.39(18)
N(2)–Zn(15)–N(3)	92.3(3)	O(10)–V(11)–O(19)	89.5(2)
N(2)–Zn(15)–N(4)	144.6(2)	O(5)–V(11)–O(20)	108.2(2)
N(2)–Zn(15)–N(5)	106.7(2)	O(19)–V(11)–O(21)	78.27(17)
N(3)–Zn(15)–N(4)	81.7(3)	O(20)–V(11)–O(21)	109.0(2)
N(3)–Zn(15)–N(5)	104.4(2)	O(10)–V(11)–O(21)	143.9(2)
N(4)–Zn(15)–N(5)	108.6(2)	O(19)–V(11)–O(20)	107.8(2)
O(2)–V(2)–O(4)	107.5(2) × 2	O(10)–V(11)–O(20)	107.1(2)
O(3)–V(2)–O(4)	90.1(2) × 2	O(15)–V(12)–O(22)	110.9(2)
O(2)–V(2)–O(3)	107.1(2) × 2	O(15)–V(12)–O(23)	139.10(19)
O(3)–V(2)–O(3)	80.8(2)	O(8)–V(12)–O(23)	92.89(18)
O(4)–V(2)–O(4)	78.6(2)	O(15)–V(12)–O(17)	78.03(18)
O(3)–V(2)–O(4)	145.3(2) × 2	O(8)–V(12)–O(17)	139.14(19)
O(7)–V(3)–O(8)	144.3(2) × 2	O(8)–V(12)–O(22)	110.1(2)
O(7)–V(3)–O(8)	88.96(17) × 2	O(17)–V(12)–O(22)	110.1(2)
O(6)–V(3)–O(7)	107.8(2) × 2	O(17)–V(12)–O(23)	80.38(18)
O(7)–V(3)–O(7)	81.5(2)	O(22)–V(12)–O(23)	109.0(2)
O(6)–V(3)–O(8)	107.9(2) × 2	O(8)–V(12)–O(15)	81.63(18)
O(8)–V(3)–O(8)	79.02(17)	O(4)–V(13)–O(13)	91.46(19)
O(5)–V(4)–O(10)	81.46(14) × 2	O(4)–V(13)–O(19)	82.91(18)
O(5)–V(4)–O(11)	83.19(16) × 2	O(4)–V(13)–O(21)	141.38(18)
O(10)–V(4)–O(11)	136.1(3)	O(19)–V(13)–O(21)	78.44(17)
O(5)–V(4)–O(9)	110.9(2) × 2	O(4)–V(13)–O(24)	108.09(19)
O(9)–V(4)–O(10)	111.5(3)	O(19)–V(13)–O(24)	109.8(2)
O(9)–V(4)–O(11)	112.4(3)	O(21)–V(13)–O(24)	109.98(19)
O(5)–V(4)–O(5)	138.11(2)	O(13)–V(13)–O(24)	109.7(2)
O(1)–V(6)–O(3)	110.13(18)	O(13)–V(13)–O(19)	139.85(18)
O(1)–V(6)–O(7)	107.4(2)	O(13)–V(13)–O(21)	81.85(18)
O(3)–V(6)–O(7)	81.26(16)	O(13)–V(14)–O(25)	111.3(2)
O(7)–V(6)–O(13)	143.42(18)	O(21)–V(14)–O(23)	141.17(18)
O(3)–V(6)–O(13)	89.74(15)	O(17)–V(14)–O(21)	93.82(19)
O(1)–V(6)–O(13)	108.9(2)	O(13)–V(14)–O(23)	78.51(15)
O(13)–V(6)–O(23)	78.7(2)	O(17)–V(14)–O(23)	80.61(18)
O(3)–V(6)–O(23)	144.93(17)	O(21)–V(14)–O(25)	109.2(2)
O(1)–V(6)–O(23)	104.94(19)	O(23)–V(14)–O(25)	109.0(2)

(Cont...)

**Table 3.** (Cont...).

Moiety	Angle (°)	Moiety	Angle (°)
O(7)–V(6)–O(23)	88.56(17)	O(13)–V(14)–O(21)	81.39(15)
O(8)–V(7)–O(15)	81.50(17) × 2	O(13)–V(14)–O(17)	139.11(18)
O(8)–V(7)–O(15)	140.38(19) × 2	O(17)–V(14)–O(25)	108.6(2)
O(15)–V(7)–O(15)	92.87(19)	Zn(1)–O(1)–V(6)	127.9(2)
O(8)–V(7)–O(8)	78.61(17)	Zn(5)–O(12)–V(8)	137.2(4)
O(14)–V(7)–O(15)	107.67(19) × 2	Zn(5)–O(14)–V(7)	128.0(3)
O(14)–V(7)–O(8)	111.4(2) × 2	Zn(1)–N(9)–C(7)	107.8(5)
O(3)–V(8)–O(7)	81.76(17) × 2	Zn(1)–N(10)–C(8)	106.0(5)
O(7)–V(8)–O(12)	112.0(2) × 2	Zn(5)–N(7)–C(12)	108.1(5)
O(3)–V(8)–O(7)	135.49(19) × 2	Zn(5)–N(8)–C(11)	108.2(5)



**Figure 2.** (a) Single  $[V_{18}O_{42}]^{12-}$  cluster with the labeling. Thermal ellipsoids are given at 50% probability. (b) The polyhedral view of one single  $[V_{18}O_{42}]^{12-}$  cluster.

522 eV, corresponding to vanadium atoms in +4 oxidation state.

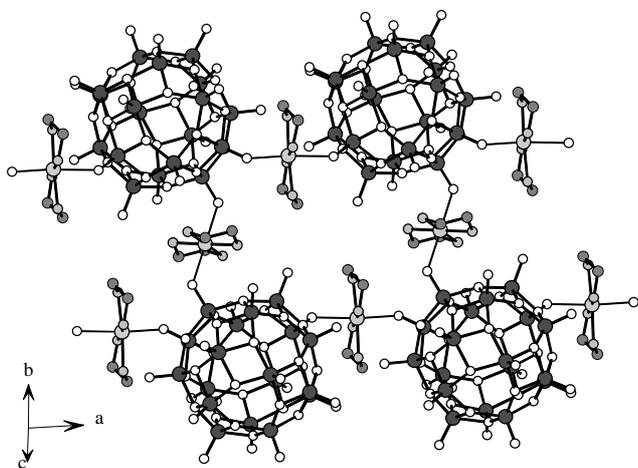
## 5. Magnetic susceptibility measurements

Magnetic susceptibility measurements were carried out using SQUID magnetometer (Quantum Design Inc, USA) in the temperature range 4.2 to 300 K. The temperature dependence of the magnetic susceptibility ( $\chi$ ) of **I** is shown in figure 4. The  $1/\chi$  vs  $T$  can be approximated to linear behaviour only at high  $T$ . A substantial deviation from the linear response is present throughout the temperature regime of measurement. The approximate linear fit at high tempera-

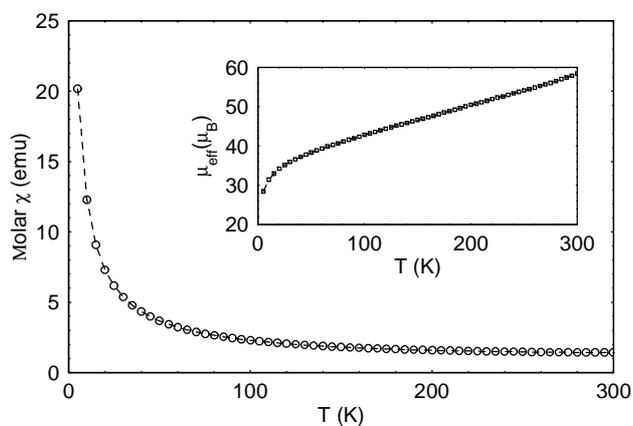
ture gives a value of  $\Theta_p \sim -65$  K, which gives an estimate of the strength of the exchange interactions present in the system. Since the inter-cluster interactions is negligible due to the large separation ( $\sim 7$  Å), the magnetic behaviour of **I** is similar to the individual  $[V_{18}O_{42}]^{12-}$  cluster.<sup>8,9</sup> The  $m_{\text{eff}}$  per V is  $3.25 m_B$  at  $RT$  and steadily decreases to  $1.58 m_B$  at 5 K, indicating anti-ferromagnetic nature of **I** (see inset of figure 4).

The dependence of magnetization ( $M$ ) as a function of magnetic field ( $H$ ) at 5 K is shown in figure 3. At low  $H$ ,  $M(H)$  increases rapidly indicating that the excited spin states are significantly populated. To confirm this, two Brillouin functions, one with 18 independent  $S = 1/2$  spins, and another with 1 in-

dependent  $S = 9$  spin are plotted (figure 5). As seen from the figure depicting  $M(H)$ , the response closely follows the Brillouin functions for a unit spin with  $S = 9$  (a large spin consisting of 18 spin  $1/2$ ). Such magnetization behaviour can be understood from the nature of spin excitations present in this system. The lowest energy excitation at low magnetic fields is a triplet state. Theoretical calculations based on Heisenberg model with 18  $S = 1/2$  vanadium ions (within the cluster) gives a magnetic gap of about 1 K to this state. This magnetic gap will be marginally reduced due to small inter-cluster anti-ferromagnetic interactions. This explains the sharp initial rise in the magnetization (see inset, figure 5). As  $H$  increases, the



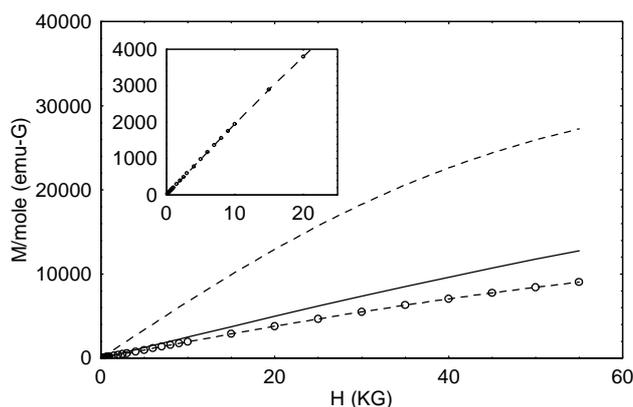
**Figure 3.**  $[\text{Zn}_2(\text{en})_5][\{\text{Zn}(\text{en})_2\}_2\{\text{V}_{18}\text{O}_{42}(\text{H}_2\text{O})\}] \cdot x\text{H}_2\text{O}$  ( $x \sim 12$ ), **I**, showing the connectivity between the  $\text{V}_{18}\text{O}_{42}$  clusters. Hydrogen atoms of the amine molecule are not shown for clarity. The layers are separated by another Zn-ethylenediamine complex (not shown).



**Figure 4.**  $\chi$  (emu/mole) vs  $T$  plot at 100 G. Dashed line is a guide to the eye. Inset shows the effective magnetic moment ( $\mu_{\text{eff}}$ ) as a function of  $T$ .

magnetic gap to the spin states with much higher spin values decreases, as the Zeeman coupling to these states is stronger than to the states with smaller spin values. The ground state at very high field strengths should be ferromagnetic. The magnetization is 9034.7 emuG per mole for the highest measured field (55 KG). As  $T \rightarrow 0$  K, for a fixed value of  $H$ , the  $M$  would be proportional to the highest spin value possible for the system. However, such an alignment (saturation) is only possible if temperature is very small compared to the field. Since temperature of 1 K  $\equiv 10^4$  G ( $g\mu_{\text{B}}H/k_{\text{B}}$  for  $H = 10^4$  G), at  $T = 5$  K, we expect complete saturation only at  $\sim 10^6$  G, and partial saturation (alignment of spins within the octameric ring) at  $10^5$  G.

Frustration effect has been shown to be one of the strong interesting phenomena in many of the magnetic systems.<sup>21,22</sup> The topological arrangements of the transition metal ions in many poly-nuclear complexes, with anti-ferromagnetic exchanges, can give rise to interesting phenomena due to variations between the ground and excited spin states.<sup>23</sup> In the present case, the system is highly frustrated owing to the competing nature of the triangular exchange interactions. However, all the three exchanges in such a triangle are similar in magnitude accompanied by a common V–O–V exchange between two adjacent triangles. Due to these factors, the pairing of all the nearest neighbour vanadium ions ( $S = 1/2$ ) are equal, leaving no room for magnetic ground state. Interestingly, the variations in the coordination



**Figure 5.** Magnetization ( $M$ ) as a function of field ( $H$ ) at 5.5 K (circles). Theoretically calculated  $M(H)$  for a unit spin of  $S = 9$  (solid line) and for 18 independent  $S = 1/2$  spins (dashed line) are also shown. Note that the experimental  $M(H)$  is close to that for a unit spin of  $S = 9$ . Inset shows the initial rapid rise of the  $M$  (see text).

**Table 4.** Important hydrogen bond interactions in **I**  $[\text{Zn}_2(\text{en})_5][\{\text{Zn}(\text{en})_2\}_2\{\text{V}_{18}\text{O}_{42}(\text{H}_2\text{O})\}] \cdot x\text{H}_2\text{O}$  ( $x \sim 12$ ).

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
N(1)–H(1)...O(24)	0.90	2.23	3.091(8)	161
N(1)–H(2)...O(20)	0.90	2.20	3.040(8)	155
N(2)–H(7)...O(16)	0.90	2.15	2.931(8)	144
N(2)–H(8)...O(4)	0.90	2.56	3.380(7)	152
N(2)–H(9)...O(4)	0.90	2.55	3.391(8)	156
N(3)–H(10)...O(9)	0.90	2.45	3.170(8)	137
N(4)–H(15)...O(25)	0.90	2.26	2.990(7)	139
N(4)–H(16)...O(24)	0.90	2.28	3.082(7)	149
N(8)–H(21)...O(800)	0.90	2.43	3.25(2)	152
N(7)–H(27)...O(2)	0.90	2.54	3.312(8)	144
N(7)–H(28)...O(15)	0.90	2.26	3.132(7)	162
N(9)–H(31)...O(23)	0.90	2.32	3.084(8)	142
N(9)–H(31)...O(25)	0.90	2.45	3.207(8)	142
N(10)–H(37)...O(7)	0.90	2.40	3.231(8)	154
N(10)–H(38)...O(400)	0.90	2.48	3.324(1)	157
C(2)–H(5)...O(1)	0.97	2.49	3.443(1)	166

geometry of the V atoms coupled with differences in V–O–V angles can alter the exchange interactions resulting in a high-spin system. The approach, then, would be to couple spin frustrated vanadium clusters and scale it to an extended structure for engineering new ferromagnetic materials. The differences in the V–O–V angles can also give rise to partially open polyhedra or faceted polyhedra that are distinctly different from closed surface polyhedra as they are linked through the vertices of their building blocks rather than by their edges. Besides, the resulting structures from such linkages would be porous. Additionally, they could be prototypes for a much wider range of structures based upon faceted polyhedra formed from other molecular triangles and squares. For example, such structures can be prepared from a wide range of metals, including catalytically and magnetically active ones.

Hydrothermal synthesis is used for the preparation of metastable phases. In many of the preparations we can, in fact, exploit the principle of self-assembly. In the present study, the formation of  $[\text{V}_{18}\text{O}_{42}]^{12-}$  clusters is achieved by utilizing the reducing ability of the organic amine molecule (*en*). We have been able to isolate the fully reduced  $\text{V}^{\text{IV}}$  species. In many of the earlier compounds, both fully reduced as well as mixed-valent polyoxovanadates have been obtained.<sup>13,14,24</sup> The formation of spherical clusters and their assembly through octahedral amine complexes, as in the present case, is dependent on the pH of the reaction medium. The amine template-controlled linking of the simplest inorganic units leading to a

completely different structure has been shown recently in a layered vanadate  $[\text{N}(\text{CH}_3)_4]_5[\text{V}_{18}\text{O}_{46}]$ . Muller and coworkers, on the other hand, have isolated a large number of oxo-clusters in the family of polyoxomolybdates, by careful adjustment of pH and other reaction parameters.<sup>5</sup> These compounds, in principle, can be considered as materials based on metal oxides with different geometries as many of these clusters contain a large number of metal atoms connected through oxygen atoms.<sup>5</sup> This type of compounds formed from clusters (Archimedean solids) has specific influence on the bulk properties, especially so when cluster dimensions are in the nanoregime. This approach of forming materials would provide newer opportunities for studying structure–property correlations. As mentioned earlier, structures based upon faceted polyhedra formed from molecular triangles and squares would be of interest for many property related studies, especially for magnetism.

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### References

1. Rao C N R and Gopalakrishnan J 1996 *New directions in solid state chemistry* (Cambridge: University Press)

2. Rao C N R and Raveau B (eds) 1998 *Transition Metal Oxides* (Singapore: World Scientific)
3. Lehn J M (ed.) 1995 *Supramolecular chemistry, concepts and perspectives* (Weinheim: VCH)
4. Muller A, Reuter K and Dillinger S 1995 *Angew. Chem. Int. Ed.* **34** 2328, and references therein
5. Muller A, Kogerler K and Dress A M W 2001 *Coord. Chem. Rev.* **222** 193, and references therein
6. Muller A, Krickemeyer E, Das S K, Kogerler P, Sarkar S, Bogge H, Schmidtman M and Sarkar Sh 2000 *Angew. Chem. Int. Ed.* **39** 1612
7. Muller A, Luban M, Schroder C, Modler R, Kogerler P, Axenovich M, Schnak J, Canfield P, Bud'ko S and Harrison N 2001 *Chemphyschem* **2** 517
8. Johnson G K and Schlemper E O 1979 *J. Am. Chem. Soc.* **100** 3645
9. Muller A, Penk M, Rohlfing R, Krickemeyer E and Doring J 1990 *Angew. Chem., Int. Ed. Engl.* **26** 1045
10. Rijssenbeek T R, Rose D J, Haushalter R C and Zubieta J 1997 *Angew. Chem., Int. Ed.* **36** 1008, and references therein
11. Khan M I, Yohannes E and Powell D 1999 *Chem. Commun.* 23
12. Khan M I, Yohannes E and Doedens R J 1999 *Angew. Chem., Int. Ed.* **38** 1292
13. Pan C-L, Xu J-Q, Li G-H, Cui X-B, Ye L and Yang G D 2003 *Dalton Trans.* 517
14. Khan M I, Yohannes E and Doedens R J 2003 *Inorg. Chem.* **42** 3125, and references therein
15. Way V W, Klemperer W G and Yaghi O M 1989 *J. Am. Chem. Soc.* **111** 4518
16. Khan M I 2000 *J. Solid State Chem.* **151** 105, and references therein
17. Chakrabarti S and Natarajan S 2002 *Crystal growth and design* **2** 333
18. Sheldrick G M 1994 *SADABS Siemens area detector absorption correction program*, University of Göttingen, Göttingen, Germany
19. Sheldrick G M 1997 *SHELXTL-PLUS Program for crystal structure solution and refinement*, University of Göttingen, Göttingen, Germany
20. Brown I D and Altermatt D 1985 *Acta Crystallogr.* **B41** 244
21. Tanaka M, Iwasaki H, Siratori K and Shindo I 1989 *J. Phys. Soc. Jpn.* **58** 1433
22. Pati S K, Ramasesha S and Sen D 2000 In *Magnetism: Molecular to materials* (eds) M Drillon and J Miller (VCH: J Wiley)
23. McCusker J K, Schmitt E A and Hendrickson D N 1991 In *Magnetic molecular materials* (eds) D Gatteschi, O Kahn, J S Miller and F Palacio (F. NATO ASI Series) E198 (Dordrecht: Kluwer Acad. Publ.)
24. Khan M I, Chen Q and Zubieta J 1993 *Inorg. Chim. Acta* **212** 199