An unprecedented copper(I,II)–octacyanotungstate(V) 2-D network: crystal structure and magnetism of $[Cu^{II}(tren)]\{Cu^{I}[W^{V}(CN)_8]\}\cdot 1.5H_2O$†

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A novel two-dimensional cyanide-bridged polymer $[Cu^{II}(tren)]\{Cu^{I}[W^{V}(CN)_8]\}\cdot 1.5H_2O$ (tren = tris(2-aminoethyl)amine) formed *via* the simultaneous *in situ* metal–ligand redox reaction of $[Cu(tren)(OH_2)]^{2+}$ and self-assembly with $[W^{V}(CN)_8]^{3-}$ consists of a $\{Cu^{I}[W^{V}(CN)_8]\}$ square grid built of Cu^{I} centres of tetrahedral geometry coordinatively saturated by CN bridges and $[W^{V}(CN)_8]^{3-}$ capped by $[Cu^{II}(tren)]^{2+}$ moieties; it exhibits ferromagnetic coupling J_1 = +5.8(1) cm^{-1} within the Cu^{II}–W^{V} dinuclear subunits and weak antiferromagnetic coupling J_2 = −0.03(1) cm^{-1} between them through diamagnetic Cu^{I} spacers.

During the last few years, considerable research effort has been made on the design and construction of polynuclear networks based on octacyanometalate(IV,V) (M = Mo, W) and copper(II) building blocks in the context of molecule-based magnetic[1] and photomagnetic[2] materials. Discrete molecules, 1-D chains, 2-D layers and 3-D frameworks have already been generated due to the coordination versatility of Cu(II) complexes in self-assembly with $[M(CN)_8]^{n-}$ ions. The magnetic assemblies based on octacyanometalate(V) building blocks resulted exclusively in formation of 2- and 3-D networks. They include a series of ferromagnetic 2-D $\{(LH_n)Cu^{II}_n[M^{V}(CN)_8]_n\cdot xH_2O\}_\infty$ (L = tetraethylenepentaamine, tetren; diethylenetriamine, dien; M = Mo, W), characterised by T_C values within the range 28–37 K.[1a–c] The 2-D compounds $\{[Cu^{II}(3\text{-}CNpy)_2(H_2O)_2]_2[Cu^{II}(3\text{-}CNpy)_2(H_2O)_2][W^{V}(CN)_8]_2\}_n$ and $\{[Cu^{II}(4\text{-}CNpy)_2]_2[Cu^{II}(4\text{-}CNpy)_2(H_2O)_2][W^{V}(CN)_8]_2\cdot 6H_2O\}_n$, which reveal metamagnetic behaviour below a T_N of 8 and 4.4 K, respectively, have been reported.[1d] Analogous metamagnetic behaviour is featured in 2-D $[Cu^{II}(L)]_3[W^{V}(CN)_8]_2\cdot 3H_2O$ (L = 1,3 diaminopropane, tn; 1,2-diaminopropane, pn).[1e] 2-D $[Cu^{II}(\mu\text{-}4,4'\text{-}bpy)(DMF)_2][Cu^{II}(\mu\text{-}4,4'\text{-}bpy)(DMF)]_2[W^{V}(CN)_8]_2\cdot 2DMF\cdot 2H_2O$ built of $[Cu^{II}(\mu\text{-}4,4'\text{-}bpy)]^{2+}$ chains cross-linked by octacyanotungstate(V) ions shows the existence of ferromagnetic pentamers Cu_3W_2 coupled antiferromagnetically.[1f] The 3-D structures involve ferromagnetic $\{Cu^{II}_{1.5}[Mo^{V}(CN)_8]\cdot 3H_2O\}_n$ characterised by T_C = 35 K[1g] as well as $\{[Cu^{II}(en)_2]_3[W^{V}(CN)_8]\cdot H_2O\}_\infty$ (en = ethylenediamine) constructed of adjacent cube-like W_8Cu_{12} motifs with isolated $[W(CN)_8]^{3-}$ as a molecular template.[1h] The $[M^{IV}(CN)_8]^{4-}$ based assemblies provide the whole range of structural dimensionality. Among these, discrete $[Cu^{II}(bpy)_2]_2[Mo^{IV}(CN)_8]\cdot 5H_2O\cdot CH_3OH$[2a] and $\{Mo^{IV}(CN)_2[CNCu^{II}(tren)]_6\}(ClO_4)_8$[2b] photomagnetic molecules have been reported. 1-D chain topology is featured by $\{Cu^{II}_2(NH_3)_8[Mo^{IV}(CN)_8]\}_n$,[3a] whereas $\{[Cu(cyclam)]_2[Mo^{IV}(CN)_8]\cdot 10.5H_2O\}_n$[3b] exhibits a 2-D structure. 3-D architecture is realised in $\{[Cu(en)_2][Cu(en)][W^{IV}(CN)_8]\cdot H_2O\}_n$[3c] and $\{Cu^{II}_2[Mo^{IV}(CN)_8]\}\cdot xH_2O$[2c] has photomagnetic properties.

To elucidate the role of coordination and bridging geometry in Cu(II) complexes in tuning the topology and magnetic properties of the Cu(II)–octacyanometalate(V) networks, we employed Cu(II) complexes with an increasing number of N-donor atoms in the blocking aliphatic polyamine ligand. The copper(II) tectons with $[N_3]$ donor atoms sets lead to the construction of a family of related 1-D and 2-D coordination polymers.[3d] The release of the fully protonated polyamine ligands ($[N_3]$ and $[N_5]$) produced soft ferromagnetic 2-D polymers with Cu(II) centres coordinatively saturated solely by CN bridges supplied by $[W^{V}(CN)_8]^{3-}$ ions.[1a] A logical extension of the building block approach employed is to complete the missing member in the series with $[Cu(tren)(OH_2)]^{2+}$ (tren = tris(2-aminoethyl)amine) which has an $[N_4]$ donor atom set as a molecular building block. Herein, we report an entirely unexpected result of the self-assembly of $[Cu(tren)(OH_2)]^{2+}$ with octacyanotungstate(V): the formation of an unprecedented mixed-valence $[Cu^{II}(tren)]\{Cu^{I}[W^{V}(CN)_8]\}\cdot 1.5H_2O$ (**1**) 2-D cyanide bridged ferromagnetic framework.

Dark blue crystals were formed reproducibly by slow addition of $[Cu^{II}(tren)(OH)]ClO_4\cdot H_2O$ (0.5 mmol, 0.172 g, 50 ml) in an aqueous solution of pH = 6 adjusted by $HClO_4$ to a stirred aqueous solution of $K_3[W^{V}(CN)_8]\cdot 1.5H_2O$ (0.5 mmol, 0.268 g, 50 ml) and the reaction mixture was subjected to slow evaporation. After two months a small amount of dark blue crystals suitable for X-ray measurements was collected, washed with water and ethanol, and dried. Yield: 0.11 g, 32%. The elemental analysis is consistent with the formula obtained from the crystal structure determination. The XPS spectrum of the Cu 2p binding energy region‡ (Fig. S1†) shows three doublets of $2p_{1/2}$ and $2p_{3/2}$ peaks which are attributed to Cu^{I} (binding energies of 932.0 and 952.0 eV), Cu^{II} (935.4 and 955.4 eV) and its shake-up satellite (943.4 and 962.9 eV). The first doublet attributed to Cu^{I} and the second one attributed to Cu^{II} indicate that compound **1** contains Cu^{I} and Cu^{II} centres. Partial metal–ligand reduction of copper(II) *in situ* is a well known property of Cu(II) complexes with tertiary aliphatic amines or imine ligands.[4] The IR spectrum§ in the ν(CN) region exhibits sharp bands at 2200 m, 2171 sh, 2146 s, consistent

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† Electronic supplementary information (ESI) available: Fig. S1 (XPS spectrum of **1** in Cu 2p region) and Fig. S2 (H-bond network in crystal structure of **1**). See http://www.rsc.org/suppdata/cc/b5/b502308d/

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with maintaining the W(V) site and the presence of bridging cyano ligands.

X-ray analysis¶ of **1** revealed that the compound consists of a 2-D square grid layer structure which is built of Cu^I centres of tetrahedral geometry coordinatively saturated by CN bridges and $[W^V(CN)_8]^{3-}$ capped by $[Cu^{II}(tren)]^{2+}$ moieties alternatively above and below the folded plane of the layer (Fig. 1a). Relevant bond lengths and angles are presented in Table 1. The octacyanotungstate(V) unit exhibits a distorted square antiprismatic (SAPR-8) geometry with metric parameters typical for a $[M^V(CN)_8]^{3-}$ building unit (Fig. 1b).[1] Four of the cyano groups of $[W^V(CN)_8]^{3-}$ are linked to Cu^I sites and one to the Cu^{II} centre. $[Cu^I(NC)_4]$ sites feature tetrahedral coordination geometry typical of Cu^I complexes and bond lengths within the range for structures containing $Cu^I[N_4]$ motifs.[5] $[Cu^{II}(tren)(NC)]$ fragments of trigonal bipyramidal (TBPY-5) geometry coordinate one bridging cyano ligand in the axial position. The W–C–N bridging unit appears to be almost linear, in opposition to the bent Cu–N–C units, which is typical for cyano-bridged octacyanometalates. The layers are connected through hydrogen bonds between amine N atoms, water molecules and terminal cyano ligands into a 3-D supermolecular architecture (Fig. S2†).

Table 1 Selected bond lengths (Å) and angles (°) in the crystal structure of **1**

$[W(CN)_8]^{3-}$	W1–C range/average	2.142(7)–2.210(7)/2.16(2)
	C–N range/average	1.126(8)–1.168(6)/1.14(1)
	W1–C–N range/average	174.1(5)–179.8(6)/178(2)
$Cu2(NC)_4$	Cu2–N11	1.963(4)
	Cu2–N11–C11	170.3(5)
	Cu2–N12	1.972(4)
	Cu2–N12–C12	158.5(5)
	Cu2–N15	1.974(4)
	Cu2–N15–C15	165.8(5)
	Cu2–N16	1.987(4)
	Cu2–N16–C16	173.2(5)
Cu3(NC)(tren)	Cu3–N18	1.958(6)
	Cu3–N18–C18	161.8(5)

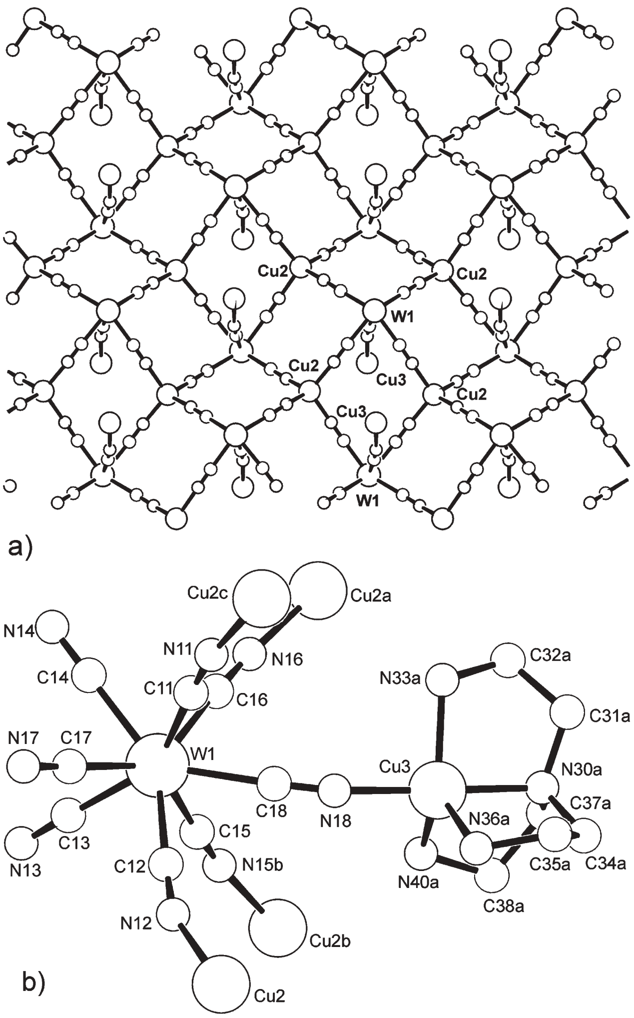

Fig. 1 (a) A view of the skeleton of the 2-D layered structure of **1**. Atoms not involved in bridging are removed for clarity. (b) Building structural fragment of **1** with labelling scheme. Symmetry operations: (a) $-x, y + 1/2, -z + 1/2$; (b) $x, -y + 1/2, z + 1/2$; (c) $-x, -y, -z$.

Magnetic measurements were performed using a Quantum Design SQUID magnetometer. The cryomagnetic property of **1** in the form of $\chi_M T$ is shown in Fig. 2. The $\chi_M T$ value is 0.97 cm^3 K mol^{-1} at room temperature, which is very close to the value of 1.0 cm^3 K mol^{-1} characteristic for one Cu^{II} ($S_{Cu} = 1/2$) ion and one W^V ($S_W = 1/2$) ion ferromagnetically coupled. With decreasing temperature $\chi_M T$ increases gradually and then abruptly, reaching a maximum of 1.21 cm^3 K mol^{-1} at 4 K, indicating the presence of ferromagnetic interactions. Further decreasing of the temperature causes a sharp decrease of $\chi_M T$, suggesting the presence of antiferromagnetic interactions. The Curie–Weiss law appended with an additive constant χ_0 to account for both diamagnetism and temperature independent paramagnetism gave $\chi_0 = 0.00019(7)$ cm^3 K mol^{-1}, $C = 0.96(9)$ cm^3 K mol^{-1} and $\theta = 1.4(5)$ K. The positive Weiss constant θ indicates that the predominant interaction in the system is of ferromagnetic character. The field dependence of the magnetisation (Fig. 2, inset) measured at 2 K reaches a saturation value of 2 $N\beta$ per formula unit at 42 kOe. According to the X-ray structure of **1**, there is one type of W^V–CN–Cu^{II} linkage separated by four Cu^I diamagnetic spacers, so the system may be treated as $Cu^{II}W^V$ dinuclear subunits with identical ferromagnetic interactions defined by the

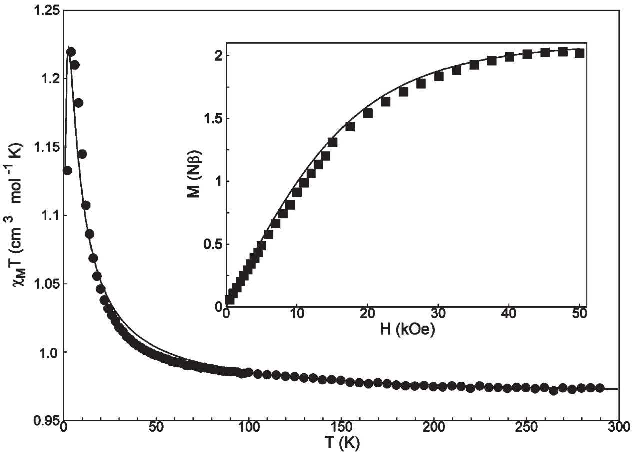

Fig. 2 Thermal dependence plot of $\chi_M T$ product of **1** in an external magnetic field of 1 kOe. Inset: field dependence of magnetisation for **1**. Fitted curves are represented by solid lines (see text).

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parameter J_1 (intraunit) and much weaker effective AF interactions through –CN–Cu^{I}–NC– linkages defined by the interunit parameter J_2. The Hamiltonian $\hat{H} = -J_1\hat{\boldsymbol{S}}_{\mathrm{Cu}}\cdot\hat{\boldsymbol{S}}_{\mathrm{W}} + g\beta \boldsymbol{S}_z\boldsymbol{H} - zJ_2 <S_z>\boldsymbol{S}_z$ represents the isotropic Heisenberg exchange interaction in a dinuclear subunit, and the interunit interaction in the molecular field approximation. The following expression for molar magnetic susceptibility was used: $\chi = (Ng^2\beta^2\cdot F(J_1,T))/(kT - zJ_2F(J_1,T))$, where $F(J_1,T) = 2/(3 + \exp(-J_1/kT))$.[6]

The fit performed for the experimental values of $\chi_{\mathrm{M}}T$ yields $J_1 = +5.8(1)\ \mathrm{cm}^{-1}$ and $J_2 = -0.03(1)\ \mathrm{cm}^{-1}$, $g = 2.2(7)$. This set of parameters satisfactorily reproduces the $\chi_{\mathrm{M}}T$ product throughout the entire temperature range as well as the isothermal magnetisation data (Fig. 2, inset).

In summary, a 2-D [Cu^{II}(tren)]{Cu^{I}[W^{V}(CN)$_8$]}·1.5H$_2$O complex revealing the unique simultaneous presence of Cu^{I} and Cu^{II} centres in a [W^{V}(CN)$_8$]$^{3-}$ based polymeric network was synthesised and characterised by means of X-ray crystallography, XPS and magnetometry. It displays strong ferromagnetic behaviour within dinuclear Cu^{II}–NC–W^{V} subunits and weak antiferromagnetic coupling resulting from interactions between the subunits through the diamagnetic Cu^{I} centres .

Compound **1** is important in the context of the reversible photomagnetic properties of {[Cu^{II}(tren)]$_6$[Mo^{IV}(CN)$_8$]}$^{8+}$, where MMCT excitation produces Cu^{I}Mo^{V}Cu$^{II}{}_5$ species characterised by a ferromagnetic interaction.[2b] This compares favourably with the dominant ferromagnetic interaction characterised by the exchange coupling constant $J_1 = +5.8(1)\ \mathrm{cm}^{-1}$ of the tungsten analogue Cu^{I}W^{V}Cu^{II} framework, **1**.

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Notes and references

‡ XPS measurements details: VSW (Vacuum Systems Workshop Ltd. England) spectrometer with Al Kα 1,2 non-monochromatised radiation (1486.6 eV). The C–C and C–H binding energy of 284.6 eV was used as a reference. We note also that the XPS spectrum evolves under the X-ray beam with time, resulting in an increase of the intensity of Cu^{I} peaks.

§ IR spectrum of **1**: ν(O–H) 3624 sh, 3536 s, 3447 s; ν(N–H) 3312 s, 3258 s, 3240 s; ν(C–H) 3067 m, 2959 m, 2922 m, 2857 m; ν(CN) 2200 m, 2171 sh, 2146 s; δ(N–H)1613 s; δ(CH$_2$) in-plane 1524 m, 1506 w, 1471 m; ν(C–N), ν(C–C), δ(C–H) 1358 w, 1120 m, 1054 m, 973 m; γ(N–H) out-of-plane 891 w, 764 w, 668 w; ν(W–C, Cu–N) 473 w, 455 w, 441 w.

¶ Crystal data for **1**: $C_{28}H_{42}Cu_4N_{24}O_3W_2$, $M = 1384.72$, orthorhombic, $a = 25.6673(2)$, $b = 13.4786(3)$, $c = 13.5486(6)$ Å, $U = 4687.3(2)$ Å^3, $T = 293(2)$ K, space group *Pccn* (no. 56), $Z = 4$, μ(Mo-Kα) = 6.728 mm^{-1}, 12131 reflections measured, 6621 unique ($R_{\mathrm{int}} = 0.0416$), 4413 unique with $I > 2\sigma(I)$. Final $R1 = 0.0400$, w$R2 = 0.0827$, $S = 0.957$. Positions of hydrogen atoms in water molecules were not found. CCDC 264537. See http://www.rsc.org/suppdata/cc/b5/b502308d/ for crystallographic data in CIF or other electronic format.

1 (*a*) R. Podgajny, T. Korzeniak, M. Bałanda, T. Wasiutyński, W. Errington, T. J. Kemp, N. W. Alcock and B. Sieklucka, *Chem. Commun.*, 2002, 1138; (*b*) T. Korzeniak, R. Podgajny, N. W. Alcock, K. Lewiński, M. Bałanda, T. Wasiutyński and B. Sieklucka, *Polyhedron*, 2003, **22**, 2183; (*c*) B. Sieklucka, T. Korzeniak, R. Podgajny, M. Bałanda, Y. Nakazawa, Y. Miyazaki, M. Sorai and T. Wasiutyński, *J. Magn. Magn. Mater.*, 2004, **272–276**, 1058; (*d*) Sh. Ohkoshi, Y. Arimoto, T. Hozumi, H. Seino, Y. Mizobe and K. Hashimoto, *Chem. Commun.*, 2003, 2772; (*e*) D. Li, L. Zheng, X. Wang, J. Huang, S. Gao and W. Tang, *Chem. Mater.*, 2003, **15**, 2094; (*f*) T. Korzeniak, K. Stadnicka, M. Rams and B. Sieklucka, *Inorg. Chem.*, 2004, **43**, 4811; (*g*) S. Ohkoshi and K. Hashimoto, *J. Photochem. Photobiol., C: Photochem. Rev.*, 2001, **2**, 71; (*h*) D. Li, S. Gao, L. Zheng, W. Sun, T. Okamura, N. Ueyama and W. Tang, *New J. Chem.*, 2002, **26**, 485.
2 (*a*) G. Rombaut, M. Verelst, S. Golhen, L. Ouahab, C. Mathonière and O. Kahn, *Inorg. Chem.*, 2001, **40**, 1151; (*b*) J. M. Herrera, V. Marvaud, M. Verdaguer, J. Marrot, M. Kalisz and C. Mathonière, *Angew. Chem., Int. Ed.*, 2004, **43**, 5468; (*c*) G. Rombaut, C. Mathonière, Ph. Guionneau, St. Golhen, L. Ouahab, M. Verelst and P. Lecante, *Inorg. Chim. Acta*, 2001, **326**, 27.
3 (*a*) W. Meske and D. Babel, *Z. Naturforsch.*, 1999, **54b**, 117; (*b*) J. Larionova, R. Clérac, B. Donnadieu, St. Willemin and Ch. Guérin, *Cryst. Growth Des.*, 2003, **3**, 267; (*c*) D. Li, T. Okamura, W. Sun, N. Ueyama and W. Tang, *Acta Crystallogr., Sect. C*, 2002, **C58**, m280; (*d*) R. Podgajny, T. Korzeniak, K. Stadnicka, Y. Dromzee, N. W. Alcock, W. Errington, K. Kruczała, M. Bałanda, T. J. Kemp, M. Verdaguer and B. Sieklucka, *Dalton Trans.*, 2003, 3458.
4 A. W. Addison, *Inorg. Chim. Acta*, 1989, **162**, 217; D. Hargman, R. P. Hammond, R. Haushalter and J. Zubieta, *Chem. Mater.*, 1998, **10**, 2091; E. A. Ambundo, M. V. Deydier, A. J. Grall, N. Aguera-Vega, L. T. Dressel, T. H. Cooper, M. J. Heeg, L. A. Ochrymowycz and D. B. Rorabacher, *Inorg. Chem.*, 1999, **38**, 4233; P. Weinberger, O. Costisor, R. Tudose, O. Baumgartner and W. Linet, *J. Mol. Struct.*, 2000, **519**, 21; S. M.-F. Lo, S. S.-Y. Chui, L.-Y. Shek, Z. Lin, X. X. Zhang, G. Wen and I. D. Williams, *J. Am. Chem. Soc.*, 2000, **122**, 6293; M. Becker, F. W. Heinemann, F. Koch, W. Donaubaure, G. Liehr, S. Schindler, G. Golub, H. Cohen and D. Meyerstein, *Eur. J. Inorg. Chem.*, 2000, 719; E. Colacio, R. Kivekäs, F. Lloret, M. Sunberg, J. Suarez-Varela, M. Bardaji and A. Laguna, *Inorg. Chem.*, 2002, **41**, 5141; J. Tao, Y. Zhang, M.-L. Tong, X.-M. Chen, T. Yuen, C. L. Lin, X. Huang and J. Li, *Chem. Commun.*, 2002, 1342; J. C. Liu, G. C. Guo, J. S. Huang and X. Z. You, *Inorg. Chem.*, 2003, **42**, 235; M.-L. Tong, L.-J. Li, K. Mochizuki, H.-Ch. Chang, X.-M. Chen, Y. Li and S. Kitagawa, *Chem. Commun.*, 2003, 428; N. Lah, I. Kralj Cigić and I. Leban, *Inorg. Chem. Commun.*, 2003, **6**, 1441; Y.-Z. Zheng, M.-L. Tong and X.-M. Chen, *New. J. Chem.*, 2004, **28**, 1412; X.-Ch. Huang, J.-P. Zhang, Y.-Y. Lin, X.-L. Yu and X.-M. Chen, *Chem. Commun.*, 2004, 1100; A. G. Blackman, *Polyhedron*, 2005, **24**, 1.
5 L. A. Kovbasyuk, O. A. Babich and V. N. Kokozay, *Polyhedron*, 1997, **16**, 161; V. Vrabel, J. Garaj, J. Sivy and D. Oktavec, *Acta Crystallogr., Sect. C*, 1999, **C55**, 1381; X. J. Zhao, S. R. Batten and M. Du, *Acta Crystallogr., Sect. E*, 2004, **E60**, m1237.
6 O. Kahn, *Molecular Magnetism*, VCH, New York, 1993, ch. 6.