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# Syntheses, structures and magnetic properties of 1-D complex $\{[Ni(\mu_{1,5}\text{-dca})(pn)_2](ClO_4)\}_n$, 2-D complex $[Mn(\mu_{1,5}\text{-dca})_2(phen)]_n$ and 3-D complex $[Mn(\mu_{1,5}\text{-dca})_2L]_n$ (dca = dicyanamide, $N(CN)_2^-$; pn = 1,3-propane diamine; phen = phenanthroline; L = 4,4′-ditriazole methane)

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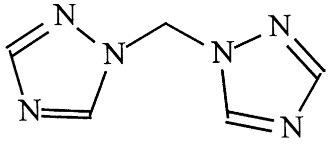
## Abstract

Three novel dicyanamide complexes $\{[Ni(\mu_{1,5}\text{-dca})(pn)](ClO_4)\}_n$ (**I**), $[Mn(\mu_{1,5}\text{-dca})_2(phen)]_n$ (**II**) and $[Mn(\mu_{1,5}\text{-dca})_2L]_n$ (**III**) have been synthesized and structurally characterized. Complex **I** forms 1-D chain and **II** forms 2-D layer structure, which are both bridged via $\mu_{1,5}$-dca ligands. Whereas complex **III** contains 3-D networks bridging via $\mu_{1,5}$-dca and 4,4′-ditriazole methane ligands. The magnetic measurements indicate that all these complexes exhibit weak antiferromagnetic interaction through the five-atom $[NCNCN]^-$ bridging ligands, with $J = -6.3$, $-1.3$ and $-1.1$ $cm^{-1}$ for complex **I**, **II** and **III**, respectively.

*Keywords:* Dicyanamide complexes; Crystal structures; Magnetic properties

## 1. Introduction

Recently, dicyanamide (dca) has been widely used as a building block in supramolecular chemistry and crystal engineering [1–12]. Dicyanamide ligand can act as in uni-, bi-, tridentate manner and both of its homo- and heteroleptic complexes have rich topologies and magnetic properties [1–8]. For example, most homoleptic complexes of $[M(dca)_2]$ class, with dca ligand only, have 3-D rutile-type architecture and exhibit ferromagnetism (Co, $T_c = 9$ K; Ni, $T_c = 20$ K; Fe, $T_c = 19$ K), antiferromagnetism (Cr, $T_N = 47$ K; Mn, $T_N = 16$ K; Fe, $T_N = 19$ K) and paramagnetism [9,10]. When co-ligands were introduced, a large number of networks of various topologies has been obtained and characterized [11,12]. To explore further in this area, it seemed interesting for us to design new dicyanamide coordination polymers with different topology structure, here we investigated three novel homoleptic compounds $\{[Ni(\mu_{1,5}\text{-dca})(pn)](ClO_4)\}_n$ (**I**), $[Mn(\mu_{1,5}\text{-dca})_2(phen)]_n$ (**II**) and $[Mn(\mu_{1,5}\text{-dca})_2L]_n$ (**III**). In which dca = dicyanamide, $N(CN)_2^-$; pn = 1,3-propane diamine; phen = phenanthroline; L = 4,4′-ditriazole methane (Scheme 1). The crystal structures and magnetic properties of **I**, **II** and **III** were also investigated.



Scheme 1. Structure of 4,4′-ditriazole methane.

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## 2. Experimental

### 2.1. Materials and methods

All reagents were of A.R. grade and used as received. The IR spectra were recorded as KBr discs on a Shimadzu IR-408 infrared spectrophotometer in the 4000–600 $cm^{-1}$ regions. C, H, N elemental analyses were carried out using a Perkin–Elmer analyzer model 240. Variable-temperature magnetic susceptibilities: LDJ 9600 Vibrating Sample Magnetometer; diamagnetic corrections were made with Pascal's constants for all the constituent atoms [13].

### 2.2. Synthesis of the compounds

#### 2.2.1. $\{[Ni(\mu_{1,5}\text{-}dca)(pn)](ClO_4)\}_n$ (**I**)

A methanol solution (10 ml) containing sodium dicyanamide (90 mg, 1 mmol) and pn (37.5 mg, 0.5 mmol) was added to an aqueous solution (10 ml) of $Ni(ClO_4)_2 \cdot 6H_2O$ (182.4 mg, 0.5 mmol). Slow evaporation of the resulted purple solution led to purple crystals of complex **I**. *Anal.* Calc. for $C_8H_{20}N_7O_4ClNi$: C, 25.8; H, 5.4; N, 26.3. Found: C, 25.4; H, 5.4; N, 26.6%.

#### 2.2.2. $[Mn(\mu_{1,5}\text{-}dca)_2(phen)]_n$ (**II**)

Similar routes as that of preparing complex **I**, by using $Mn(ClO_4)_2 \cdot 6H_2O$ (181 mg, 0.5 mmol) instead of $Ni(ClO_4)_2 \cdot 6H_2O$, phen (99.1 mg, 0.5 mmol) instead of pn for **I**. Slow evaporation of the resulted purple solution led to light-yellow crystals of complex **II**. *Anal.* Calc. for $C_{16}H_8N_8Mn$: C, 52.3; H, 2.2; N, 30.5. Found: C, 52.3; H, 2.4; N, 30.2%.

#### 2.2.3. $[Mn(\mu_{1,5}\text{-}dca)_2L]_n$ (**III**)

Similar routes as that of preparing complex **I**, by using $Mn(ClO_4)_2 \cdot 6H_2O$ (181 mg, 0.5 mmol) instead of $Ni(ClO_4)_2 \cdot 6H_2O$, 4,4′-ditriazole methane (75 mg, 0.5 mol) instead of pn for **I**, giving colorless crystals of complex **III**. *Anal.* Calc. for $C_9H_6N_{12}Mn$: C, 32.0; H,1.8; N, 49.8. Found: C, 32.4; H, 1.8; N, 49.6%.

*Caution!* Perchlorate salts of metal complexes with organic ligand are potentially explosive and should be handed in small quantities with care.

### 2.3. X-ray crystallography

Determination of the unit cell and data collection was performed on a Bruker Smart 1000 area detector using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. Structures of complexes **I**, **II** and **III** were solved by direct methods and successive Fourier difference syntheses (SHELXS-97) and refined by full-matrix least-squares procedure on $F^2$ with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97) [14]. Crystal data and structure refinements are summarized in Table 1.

## 3. Results and discussion

### 3.1. Description of the structure

#### 3.1.1. Crystal structure of complex $\{[Ni(\mu_{1,5}\text{-}dca)(pn)](ClO_4)\}_n$ (**I**)

The labeled diagram for complex **I** is shown in Fig. 1 and selected bond lengths and angles are listed in

Table 1
Crystal data and structure refinement for complex **I**, **II** and **III**

| | **I** | **II** | **III** |
|---|---|---|---|
| Formula | $C_8H_{20}N_7O_4ClNi$ | $C_{16}H_8N_8Mn$ | $C_9H_6N_{12}Mn$ |
| $M_r$ | 372.47 | 367.24 | 337.20 |
| Crystal system | monoclinic | monoclinic | orthorhombic |
| Space group | $P2_1/n$ | $P2_1/c$ | *Fddd* |
| *a* (Å) | 8.860(4) | 10.161(4) | 19.117(10) |
| *b* (Å) | 14.827 | 10.957(4) | 19.799(10) |
| *c* (Å) | 12.435(5) | 14.433(6) | 28.946(15) |
| α (°) | 90 | 90 | 90 |
| β (°) | 104.075(6) | 100.532(6) | 90 |
| γ (°) | 90 | 90 | 90 |
| *V* (Å$^3$) | 1584.5(1) | 1579.9(10) | 10956(10) |
| *Z* | 4 | 4 | 32 |
| *T* (K) | 293(2) | 293(2) | 293(2) |
| Total reflections | 7321 | 7262 | 8847 |
| Independent reflections | 3221 | 3237 | 2324 |
| $R_{int}$ | 0.0342 | 0.0523 | 0.0868 |
| Data/restraints/parameters | 3221/21/191 | 3237/0/226 | 2324/0/245 |
| $R_1$, $wR_2[I > 2\sigma(I)]$ | 0.0417, 0.0934 | 0.0483, 0.0866 | 0.674, 0.1483 |
| $R_1$, $wR_2$ (all data) | 0.0707, 0.1046 | 0.1137, 0.1032 | 0.0940, 0.1616 |
| Goodness-of-fit on $F^2$ | 1.022 | 0.994 | 1.103 |
| Largest diffraction peak and hole (e Å$^{-3}$) | 0.479 and −0.269 | 0.275 and −0.326 | 0.454 and −0.492 |

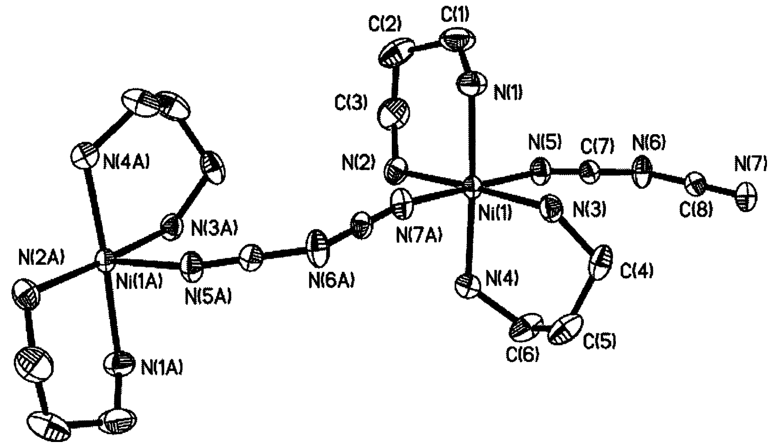

Fig. 1. The atom numbering scheme and 1-D chain structure of complex **I**.

Table 2. Ni(II) is six-coordinated, with four nitrogen atoms from two pn ligands and two nitrogen atoms from two dca bridges, forming a distorted octahedron geometry. Four nitrogen atoms from two pn ligands are nearly planar; the deviations of these four donor atoms and the central Ni(II) atom from this equatorial plane are ±0.024–0.024 and 0.052 Å, respectively. Dicyanamide ligand acts as $\mu_{1,5}$-bridging ligand and links two neighboring Ni(II) atoms, giving a uniform zig-zag one-dimensional system. The bond parameters related to the bridge are: Ni(1)–N(5) = 2.093(3) Å, Ni(1)–N(7A) = 2.119(3) Å, Ni(1)–N(5)–C(7) = 154.7(3)°, C(8)–N(6)–C(7) = 119.2(3)°.

### 3.1.2. *Crystal structure of complex [Mn($\mu_{1,5}$-dca)2(phen)]$_n$* (**II**)

The labeled diagram for complex **II** is depicted in Fig. 2 and selected bond lengths and angles are listed in Table 3. Mn(II) atom is six-coordinated, with two nitrogen atoms of phen ligand and four nitrogen atoms of four $\mu_{1,5}$-dca bridging ligands. Each Mn atom is linked to three Mn atoms by four $\mu_{1,5}$-dca bridges. Thus, two Mn atoms and two $\mu_{1,5}$-dca bridges form a [Mn(NCNCN)$_2$Mn] unit; such units are further linked together through more four $\mu_{1,5}$-dca ligands, which extends to *bc* plane to form a 2-D layer topology structure. Different layers are connected through π–π interaction

Table 2
Selected bond lengths (Å) and angles (°) for complex **I**

| | | | |
|---|---|---|---|
| Ni(1)–N(1) | 2.123(3) | Ni(1)–N(7A) | 2.119(3) |
| Ni(1)–N(5) | 2.093(3) | Ni(1)–N(3) | 2.122(3) |
| N(5)–Ni(1)–N(7A) | 177.37(11) | N(5)–Ni(1)–N(4) | 90.70(11) |
| N(5)–Ni(1)–N(2) | 93.55(12) | N(1)–Ni(1)–N(3) | 175.77(11) |
| C(8)–N(6)–C(7) | 119.2(3) | C(7)–N(6)–Ni(1) | 154.7(3) |

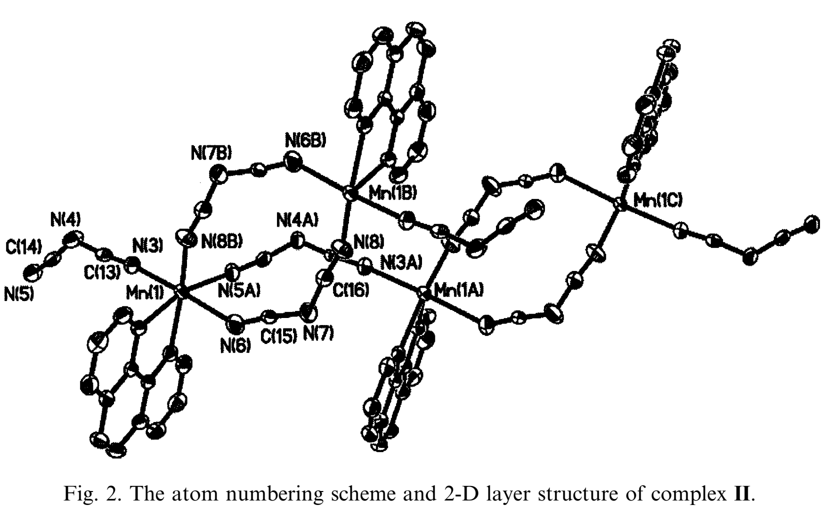

Fig. 2. The atom numbering scheme and 2-D layer structure of complex **II**.

Table 3
Selected bond lengths (Å) and angles (°) for complex **II**

| | | | |
|---|---|---|---|
| Mn(1)–N(1) | 2.264(3) | Mn(1)–N(2) | 2.247(3) |
| Mn(1)–N(5A) | 2.197(3) | Mn(1)–N(3) | 2.188(3) |
| Mn(1)–N(8A) | 2.156(3) | Mn(1)–N(6) | 2.339(3) |
| N(8A)–Mn(1)–N(5A) | 94.02(12) | N(8A)–Mn(1)–N(3) | 93.14(12) |
| N(1)–Mn(1)–N(1) | 89.4(2) | N(8A)–Mn(1)–N(2) | 166.61(12) |
| N(3)–Mn(1)–N(2) | 91.35(10) | N(5)–Mn(1)–N(1) | 164.13(11) |
| N(1)–Mn(1)–N(3) | 96.184(10) | N(8A)–Mn(1)–N(1) | 93.64(12) |
| N(3)–Mn(1)–N(6) | 177.48(11) | | |

between aryl rings of phen ligands, which are parallel to each other and the distance between carbon atoms is about 3.47–3.49 Å, furthermore giving a 3-D network. The bond parameters related to $MnN_6$ octahedral environment are: Mn(1)–N(3) = 2.188 Å, Mn(1)–N(1) = 2.264(3) Å, Mn(1)–N(6) = 2.339(3) Å, Mn(1)–N(8) = 2.156(3) Å, N(8)–Mn(1)–N(3) = 93.14(12)°, N(3)–Mn(1)–N(6) = 177.48(11)°, N(8)–Mn(1)–N(2) = 166.61(12)°, N(5)–Mn(1)–N(1) = 164.13(11)°.

### 3.1.3. Crystal structure of complex $[Mn(\mu_{1,5}\text{-}dca)_2L]_n$ (**III**)

The labeled diagram for complex **III** is shown in Fig. 3 and selected bond lengths and angles are listed in Table 4. The structure consists of octahedrally coordinated Mn(II) atoms in which the coordination sites are occupied by four nitrile nitrogen atoms of bridging $\mu_{1,5}$-dca ligands and two nitrogen atoms of two 4,4′-ditriazole methane ligands in *cis*-arrangement. Two dicyanamide ligands act as end-to-end bridging ligands with two neighboring Mn(II) atom to form a 1-D $[Mn(NCNCN)_2Mn]_n$ zig-zag chain; such chains are further linked together through two *cis*-bridging 4,4′-ditriazole methane ligands, resulting in a unique 3-D network. The bond parameters related to $MnN_6$ octahedral environment are: Mn(1)–N(3) = 2.219(5) Å, Mn(1)–N(1) = 2.200(5) Å, Mn(1)–N(6) = 2.208(6) Å, Mn(1)–N(4) = 2.240(5) Å, Mn(1)–N(7) = 2.247(4) Å, Mn(1)–N(10) = 2.31(2) Å, N(1)–Mn(1)–N(6) = 93.7(2)°, N(1)–Mn(1)–N(7) = 173.58(19)°, N(3)–Mn(1)–N(4) = 175.49(19)°.

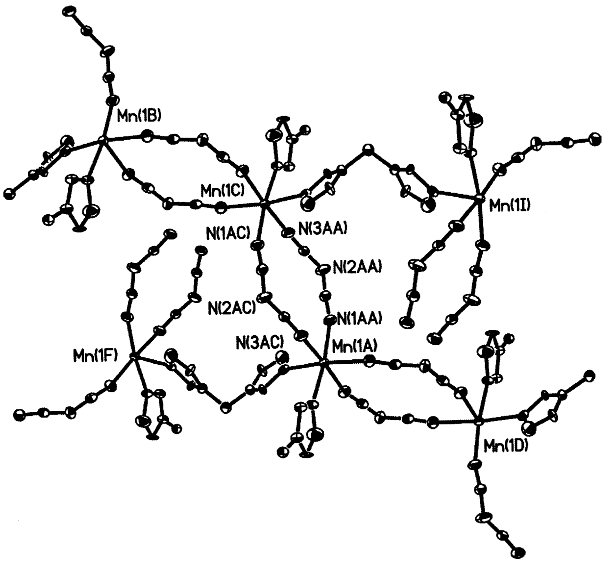

Fig. 3. The structure and atom numbering scheme of complex **III**.

### 3.2. IR spectra

The solid-state infrared spectra of complexes depict several $\nu_{CN}$ bands at 2275s, 2249s, 2161s $cm^{-1}$ in complex **I**, 2301s, 2252s, 2175s $cm^{-1}$ in complex **II** and 2304s, 2252m, 2100s $cm^{-1}$ in complex **III**, which are attributed to $\nu_{sym} + \nu_{asym}(CN)$, $\nu_{asym}(CN)$ and $\nu_{sym}(CN)$ modes. All the data are in good agreement with those reported in the literature [1–8] and differ significantly from those of $Na[N(CN)_2]$, which are at 2129, 2232 and 2286 $cm^{-1}$, respectively [15].

### 3.3. Magnetic properties

The magnetic susceptibility of complexes **I**–**III** was measured on the LDJ-9600 VSM in the temperature ranges 77–300 K with an applied magnetic field of

Table 4
Selected bond lengths (Å) and angles (°) for complex **III**

| | | | |
|---|---|---|---|
| Mn(1)–N(3) | 2.219(5) | Mn(1)–N(1) | 2.200(5) |
| Mn(1)–N(6) | 2.208(6) | Mn(1)–N(4) | 2.240(5) |
| Mn(1)–N(7) | 2.247(4) | Mn(1)–N(10) | 2.31(2) |
| N(1)–Mn(1)–N(6) | 93.7(2) | N(1)–Mn(1)–N(7) | 173.58(19) |
| N(3)–Mn(1)–N(4) | 175.49(19) | N(1)–Mn(1)–N(3) | 88.1(2) |
| N(6)–Mn(1)–N(3) | 94.5(2) | N(1)–Mn(1)–N(4) | 96.01(19) |
| N(6)–Mn(1)–N(4) | 87.0(2) | N(7)–Mn(1)–N(4) | 88.73(17) |

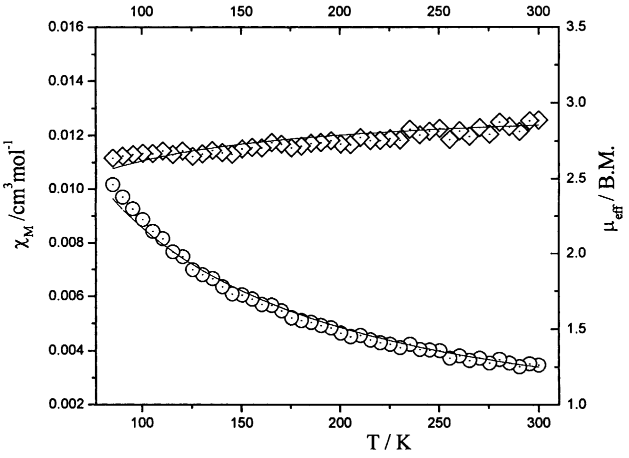

Fig. 4. Thermal variation of $\chi_m$ (○) and $\mu_{eff}$ (◇) for complex **I**. The continuous lines represent the best fit to the theoretical models.

5000 G. The overall behavior of three compounds corresponds to weak antiferromagnetically coupled systems and a representative figure of the effective magnetic moment ($\mu_{eff}$) and the molar magnetic susceptibility ($\chi_M$) vs. $T$ for complex **I** is plotted in Fig. 4. At room temperature, the $\mu_{eff}$ values are 2.85 BM for complex **I**, 5.71 BM for **II** and 5.81 BM for **III**, all close to the spin-only value of M(II) ions (2.83 BM for complex **I**, 5.92 BM for **II** or **III**). Upon cooling to 77 K, the $\mu_{eff}$ value for these complexes steadily decreases, suggesting that an antiferromagnetic interaction is operating between adjacent M(II) ions through the $\mu_{1,5}$-bridges. According to homogeneous chain structure, the magnetic data was analyzed by means of the analytical expression

$$\chi_{chi} = (Ng^2\beta^2/KT)[A + BX^2][1 + CX + DX^3]^{-1},$$

where $X = |J|/KT$. For Ni(II) ($S = 1$), $A = 0.6667$, $B = 2.5823$, $C = 3.6035$, $D = 39.558$. For Mn(II) ($S = 5/2$), $A = 2.9167$, $B = 208.04$, $C = 15,543$, $D = 2707.2$.The best fitting parameters were: $J = -6.3$ cm$^{-1}$, $g = 2.12$ and $R = 1.19 \times 10^{-3}$ for complex **I**; $J = -1.3$ cm$^{-1}$, $g = 2.00$ and $R = 2.84 \times 10^{-4}$ for **II** and $J = -1.1$ cm$^{-1}$, $g = 2.00$ and $R = 1.22 \times 10^{-3}$ for **III**, where $R$ is the agreement factor: $R = \sum(\chi_{obsd} - \chi_{calcd})^2/\sum\chi^2_{obsd}$. The small $J$ values indicate that the $\mu_{1,5}$-dicyanamide bridge should be assumed to be a very poor superexchange mediator, which are in agreement with those reported in the literature [1–10].

## 4. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. 197786 for complex **I**, 197787 for **II** and 207637 for **III**, respectively. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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## References

[1] S.R. Batten, P. Jensen, B. Moubaraki, K.S. Murray, R. Robson, J. Chem. Soc., Chem. Commun. (1998) 439.
[2] M. Kurmoo, C.J. Kepert, New J. Chem. 22 (1998) 1515.
[3] P. Jensen, S.R. Batten, G.D. Fallon, B. Moubaraki, K.S. Murray, D.J. Price, J. Chem. Soc., Chem. Commun. (1999) 177.
[4] J.L. Manson, C.R. Kmety, A.J. Epstein, J.S. Miller, Inorg. Chem. 38 (1999) 2552.
[5] A. Escuer, F.A. Mautner, N. Saz, R. Vicente, Inorg. Chem. 39 (2000) 1668.
[6] P.M. van der Werff, S.R. Batten, P. Jensen, B. Moubaraki, K.S. Murray, Inorg. Chem. 40 (2001) 1718.
[7] S. Martin, M.G. Barandika, J.I.R. Larramendi, R. Cortes, M. Font-bardia, L. Lezama, Z.E. Serna, X. Solans, T. Rojo, Inorg. Chem. 40 (2001) 3687.
[8] Z.M. Wang, B.W. Sun, J. Luo, S. Gao, C.S. Liao, C.H. Yan, Y. Li, Inorg. Chim. Acta 332 (2002) 127.
[9] J.L. Manson, C.R. Kmety, Q. Huang, J.W. Lynn, G.M. Bendele, S. Pagola, P.W. Stephens, L.M. Liable-Sands, A.L. Rheingold, A.J. Epstein, J.S. Miller, Chem. Mater. 10 (1998) 2552.
[10] H. Hoshino, K. Lida, T. Kawamoto, T. Mori, Inorg. Chem. 38 (1999) 4229.
[11] L. Dasna, S. Golhen, L. Ouahab, O.P. Guillevic, M. Fettouhi, J. Chem. Soc., Dalton Trans. (2000) 129.
[12] G.A. Van Albada, M.E. Quiroz-Castro, I. Mutikainen, U. Turpeinen, J. Reedijk, Inorg. Chem. Acta 298 (2000) 221.
[13] P.W. Selwood, Magnetochemistry, Interscience, New York, 1956, p. 78.
[14] G.M. Sheldrick, SHELXS-97 and SHELXL-97: Software for Crystal Structure Analysis, Siemens Analyical X-ray Instruments Inc., Madison, WI, 1997.
[15] S.R. Batten, P. Jenson, S.R. Batten, B. Moubaraki, K.S. Murray, Chem. Commun. (2000) 2331.