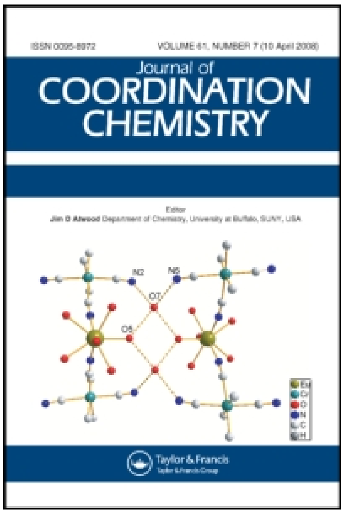

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, X-ray crystal structure and magnetic study of a μ $_{1,5}$-dca bridged ferromagnetic dimeric copper(II) complex

Dasarath Mal[a]; Rupam Sen[a]; Chandan Adhikary[a]; Yoshitaro Miyashita[b]; Ken-Ichi Okamoto[b]; Ashis Bhattacharjee[c]; Philipp Gütlich[c]; Subratanath Koner[a]
[a] Department of Chemistry, Jadavpur University, Kolkata 700 032, India [b] Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan [c] Institut für Anorganische Chemie und Analytische Chemie, Johannes-Gutenberg Universität, D-55099 Mainz, Germany

To cite this Article Mal, Dasarath , Sen, Rupam , Adhikary, Chandan , Miyashita, Yoshitaro , Okamoto, Ken-Ichi , Bhattacharjee, Ashis , Gütlich, Philipp and Koner, Subratanath(2008) 'Synthesis, X-ray crystal structure and magnetic study of a μ $_{1,5}$-dca bridged ferromagnetic dimeric copper(II) complex', Journal of Coordination Chemistry, 61: 21, 3486 — 3492

To link to this Article: DOI: 10.1080/00958970802072773

URL: http://dx.doi.org/10.1080/00958970802072773

Journal of Coordination Chemistry
Vol. 61, No. 21, 10 November 2008, 3486–3492

Synthesis, X-ray crystal structure and magnetic study of a $\mu_{1,5}$-dca bridged ferromagnetic dimeric copper(II) complex

DASARATH MAL†, RUPAM SEN†, CHANDAN ADHIKARY†,
YOSHITARO MIYASHITA‡, KEN-ICHI OKAMOTO‡,
ASHIS BHATTACHARJEE§, PHILIPP GÜTLICH§ and
SUBRATANATH KONER*†

†Department of Chemistry, Jadavpur University, Kolkata 700 032, India
‡Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan
§Institut für Anorganische Chemie und Analytische Chemie, Johannes-Gutenberg
Universität, D-55099 Mainz, Germany

(*Received 12 December 2007; in final form 18 January 2008*)

Reaction of $Cu(NO_3)_2 \cdot 3H_2O$, 1-(N-salicyalideneimine)-2-(N,N-dimethyl)-aminoethane (HL^1), $LiClO_4$, and sodium dicyanamide (Nadca) in aqueous medium affords a dimeric complex $[Cu_2(L^1)_2(\mu_{1,5}\text{-dca})](ClO_4)$ (**1**). Single crystal X-ray analysis reveals that **1** is dinuclear with copper(II) ions bridged by a single dicyanamide group in end-to-end fashion. The coordination environment around copper(II) is square planar. Two nitrogens and oxygen of the tridentate Schiff-base ligand (HL^1) occupy three coordination sites of the square plane while the remaining site is occupied by the nitrogen of a terminal nitrile of the bridging dca. The nitrogen of the other terminal nitrile group of the $\mu_{1,5}$-dca ligand connects a neighboring $[CuL^1]$ unit to yield $[Cu_2(L^1)_2(\mu_{1,5}\text{-dca})](ClO_4)$ (**1**). Variable temperature magnetic susceptibility measurements show that the magnetic interaction is ferromagnetic ($J = 1.93\,\text{cm}^{-1}$). The results of a magnetic model are in good agreement with the experimental data.

Keywords: Copper(II) Schiff base; Dicyanamide; Dimer; X-ray crystal structure; Ferromagnetic

1. Introduction

Inorganic coordination polymers and their use in solid-state architectures [1] has led to a number of compounds with interesting molecular magnetism, high porosity and catalytic activity. One strategy to improve the selectivity and reactivity of coordination polymers is to synthesize inorganic-organic hybrid frameworks with different metal coordination environments, as observed in some metalloenzymes [2]. Bridging organic or inorganic ligands play key roles in preparation of coordination polymers, pseudohalide, such as N_3^-, NCO^-, NCS^- and $N(CN)_2^-$ are important bridging ligands [3]. Especially $N(CN)_2^-$ (dca) is a ligand with capability to coordinate to metal ions monodentate, end-to-end bridging through the two nitrile nitrogens ($\mu_{1,5}$), tridentate bridging with the three metal

---

*Corresponding author. Email: snkoner@chemistry.jdvu.ac.in

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970802072773

atoms, unusual μ_4 coordination where one nitrile nitrogen binds to two metal atoms or μ_5 coordination, in which dca binds five metal centers [3–8]. Binary systems of dca exhibit either a 3D rutile-like structure or a 2D layer with a tetrahedral coordination environment. These systems show ferromagnetism, antiferromagnetism or paramagnetism depending on the metal [7, 9, 10]. For example, $Ni(dca)_2$ is ferromagnetic [7, 9], $Mn(dca)_2$ is antiferromagnetic [11a] below the corresponding transition temperature and $Cu(dca)_2$ is paramagnetic [10]. Additional organic ligands were also employed in the design of new structural types with various magnetic properties, and 1D, 2D and 3D polymers have been reported. Network topology can be varied through introduction of bridging or terminal coligands [11–13], or, in the case of anionic $M(dca)_3^-$ networks, variation in counterion [14]. Nevertheless, magnetic coupling through a dca bridge is generally weak; in some cases no measurable magnetic interaction was observed, especially for end-to-end dca bridged compounds [15–18a]. Chain compounds, $\{[Cu(L)(\mu_{1,5}\text{-dca})(dca)]\}_n$ with L=2,2′-bipyridine or 2,2′-bipyridylamine have been reported where copper(II) ions are bridged by a single $\mu_{1,5}$-dca [15–17]. While a weak antiferromagnetic coupling between copper(II) centers has been observed for the complexes with 2,2′-bipyridine, no significant magnetic coupling was observed in $\{[Cu(2,2'\text{-bipyridylamine})(\mu_{1,5}\text{-dca})(dca)]\}_n$; ferromagnetic $\mu_{1,5}$-dca bridged compounds are very rare [8, 18b].

To diversify the range of coligands, heterodonor, anionic tridentate Schiff-base (HL^1) ligands, which can bind metal centers via both amino, imino nitrogen atom and phenoxo oxygen, are used in our laboratory to synthesize new pseudohalide bridged transition metal complexes [19]. In the present article, we report the synthesis, X-ray crystal structure and magnetic properties of a new dinuclear copper(II) complex, $[Cu_2(L^1)_2(\mu_{1,5}\text{-dca})](ClO_4)$ (**1**).

2. Experimental

2.1. *General*

All chemicals and solvents used during the synthesis were of AR grade and used as received. Elemental analyses (CHN) were performed using a Perkin-Elmer 240 elemental analyzer. IR spectra were recorded on a Nicolate Magna IR 750 series II FT-IR spectrometer. Magnetic measurements were carried out with Quantum Design's SQUID MPMS XL magnetometer. The instruments used for other measurements were reported earlier [20].

2.2. *Synthesis of $[Cu_2(L^1)_2(\mu_{1,5}\text{-dca})](ClO_4)$*

The ligand HL^1 (chart 1) was synthesized by condensation of N,N-dimethylethylenediamine and salicyaldehyde in a 1:1 molar ratio in methanol. A 30 mL methanolic solution of the ligand (1 mmol, 0.190 g) was added to an aqueous solution of copper(II) nitrate trihydrate (1 mmol, 0.241 g) dissolved in 20 mL of H_2O. To the resulting solution, 0.89 g of sodium dicyanamide (1 mmol) dissolved in minimum water was added. Then, resulting mixture was stirred for 30 min. Finally, an aqueous solution of $LiClO_4$ (0.5 mmol, 0.53 g) was added. After brief stirring, the resulting solution was

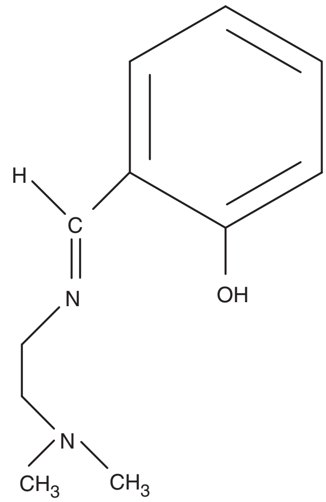

Chart 1. Structure of the ligand (HL^1).

filtered and the filtrate was left to stand at room temperature. Well-shaped brown crystals appeared in four weeks, were collected by filtration and dried in air (Yield 50%). Anal. Calcd for $C_{24}H_{30}ClCu_2N_7O_6$: C, 42.7; H, 4.4; N, 12.4. Found: C, 42.0; H, 4.3.; N, 11.9%. IR (KBr): $\nu_s(C\equiv N)$, 2140 cm^{-1} (vs); $\nu_{as}(C\equiv N)$, 2220 cm^{-1} (m); $\nu_s(C\equiv N) + \nu_{as}(C\equiv N)$ 2260 cm^{-1}; $\nu_{as}(C\equiv N)$ 1380 cm^{-1}.

2.3. *X-ray crystallography*

2.3.1. Crystal data. $C_{24}H_{30}ClCu_2N_7O_6$, $M = 675.09$, orthorhombic, space group *Pnma*, $a = 18.6435(8)$, $b = 6.8040(4)$, $c = 21.9813(10)$ Å, $V = 2788.3(2)$ Å^3, $Z = 4$, $D_{Calcd} = 1.608\ g\,cm^{-3}$, $F_{000} = 1384.00$, $\mu = 1.673\ mm^{-1}$, brown bar crystal, dimension $= 0.45 \times 0.20 \times 0.10$ mm, $T = 296$ K, $R_1 = 0.0922$, $wR_2 = 0.0954$, T_{max} and $T_{min} = 0.249$, 0.846.

2.3.2. X-ray single crystal structure determination of 1. Single crystals of **1** suitable for X-ray diffraction study were obtained by slow evaporation of its aqueous solution. All measurements were made on a Rigaku AFC7 diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å) equipped with a Rigaku Mercury CCD detector. The unit cell parameters and orientation matrix were determined by least squares refinements. Of the 4242 reflections collected, 499 were unique. Data were collected and processed using the crystal structure analysis package program of Rigaku, Crystal Clear [21]. The structures were solved by direct methods (SIR 97) [22] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogens were refined using the riding model. All calculations were carried out using the Crystal Structure 3.5.1 [23] and CRYSTALS [24] programs. Molecular graphics software used were ORTEP III [25] and MERCURY [26]. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.44 and $-0.96\ e^-$ Å^{-3}, respectively.

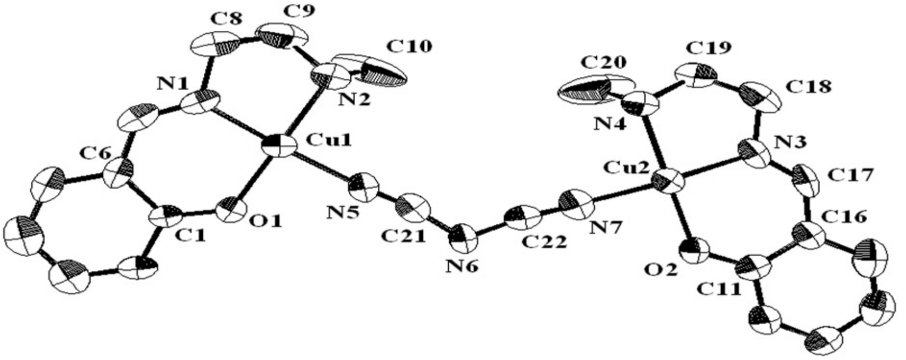

Figure 1. ORTEP diagram of **1** showing atom numbering scheme.

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

Cu(1)–O(1)	1.879(6)	Cu(1)–N(2)	2.042(7)
Cu(1)–N(1)	1.918(7)	Cu(1)–N(5)	1.982(8)
Cu(2)–O(2)	1.889(6)	Cu(2)–N(3)	1.898(7)
Cu(2)–N(4)	2.071(8)	Cu(2)–N(7)	1.962(8)
O(1)–Cu(1)–N(1)	94.8(3)	O(1)–Cu(1)–N(2)	179.7(3)
O(1)–Cu(1)–N(5)	88.4(2)	N(1)–Cu(1)–N(2)	84.9(3)
N(1)–Cu(1)–N(5)	176.8(3)	N(2)–Cu(1)–N(5)	91.9(3)
O(2)–Cu(2)–N(3)	94.5(3)	O(2)–Cu(2)–N(4)	179.3(3)
O(2)–Cu(2)–N(7)	89.2(3)	N(3)–Cu(2)–N(4)	84.7(3)
N(3)–Cu(2)–N(7)	176.3(3)	N(4)–Cu(2)–N(7)	91.6(3)

3. Results and discussion

3.1. *Structure of* $[Cu_2(L^1)_2(\mu_{1,5}\text{-dca})](ClO_4)$

X-ray crystal structure analysis reveals that the asymmetric unit of **1** consists of a dimeric cationic $[Cu_2(L^1)_2(\mu_{1,5}\text{-dca})]^+$ along with a non-coordinated ClO_4^-. ORTEP diagram of the cationic part of the asymmetric unit of **1** with atom numbering scheme is shown in figure 1. Selected bond lengths and angles are collected in table 1. Both copper(II) ions possess square–planar coordination around copper. Three coordination sites around copper(II) ions are occupied by tridentate Schiff base through amino and imino nitrogens and the oxygen of deprotonated phenoxo. The fourth position of both copper sites is satisfied by nitrogen of the terminal nitrile groups of a $\mu_{1,5}$ dca. The $\{N(CN)_2\}^-$ ligand in **1** is bent around amide nitrogen through an angle of 117.7(8)°. The basal Cu–N distances were 1.918(7)–2.071(8) Å and Cu–O distances were 1.879(6) and 1.889(6) Å, consistent with reported values for the bond distances of similar complexes [19, 27].

3.2. *Magnetic properties of* $[Cu_2(L^1)_2(\mu_{1,5}\text{-dca})](ClO_4)$

The temperature dependence of the molar magnetic susceptibility, χ_M, for **1** was measured on a Quantum Design's SQUID MPMS XL magnetometer in 5–300 K temperature under magnetic field of 0.5 T. The $\chi_M T$ value of 0.67 $cm^3\,mol^{-1}\,K$ at 300 K for **1** is lower than the value expected for two isolated magnetically uncoupled copper(II)

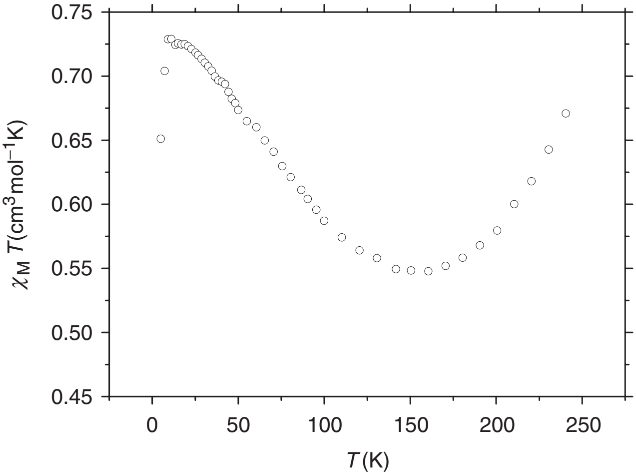

Figure 2. $\chi_M T$ *vs.* T plot for **1**.

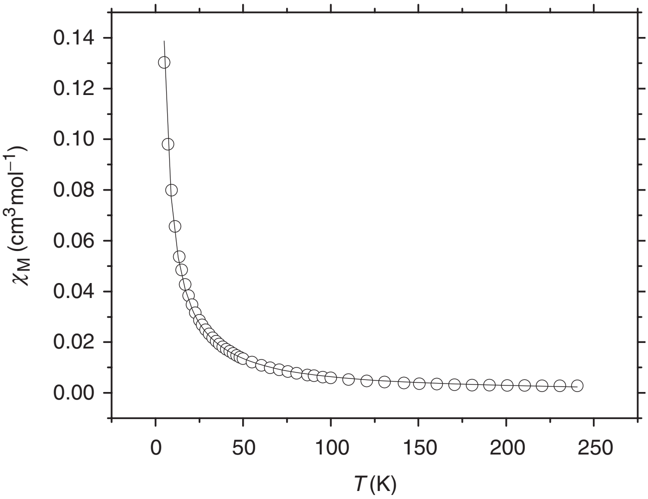

Figure 3. χ_M *vs.* T plot for **1**. Solid lines represent the best fit of the data with the model described in the text.

ions ($\chi_M T = 0.75\,\text{cm}^3\,\text{mol}^{-1}\,\text{K}$ for $g = 2.0$). Upon cooling, the $\chi_M T$ of **1** decreases until *ca.* 150 K and then increases gradually to reach a maximum of $0.73\,\text{cm}^3\,\text{mol}^{-1}\,\text{K}$ at 9 K indicating ferromagnetic interaction between copper(II) ions (figure 2).

To estimate the magnitude of ferromagnetic coupling, the magnetic susceptibility data (5–240 K) were fitted to the susceptibility equation for two interacting copper(II) ions ($S = 1/2$) with the Hamiltonian in the form $H = J\ \hat{S}_1 \cdot \hat{S}_2$ (figure 3). The susceptibility equation for such a dimeric system can be written [28]:

$$\chi = \frac{2\text{Ng}^2\beta^2}{\text{kT}}\left[3 + \exp\left(\frac{-\text{J}}{\text{kT}}\right)\right]^{-1}(1-\rho) + \frac{\text{Ng}^2\beta^2}{2\text{kT}}\rho \qquad (1)$$

where N, g, β and ρ parameters in the equation bear their usual meaning.

The best fit parameters were $J = 1.93\,\mathrm{cm}^{-1}$, $g = 2.03(1)$, $\rho = 0.0001$ and $R = 2.21 \times 10^{-6}$ ($R = \sum(\chi_{\mathrm{obsd}} - \chi_{\mathrm{calcd}})^2/(\chi_{\mathrm{obsd}})^2$). Though there are numerous examples of end-to-end dca-bridged transition metal complexes with antiferromagnetic interactions, the present study indicates that coupling between copper(II) ions is clearly ferromagnetic. A closer look into the structure of **1** indicates that the magnetic orbitals describing the single electron on Cu1 and Cu2 are mainly $x^2 - y^2$ type, extended along the basal plane of the copper ions. End-to-end azido groups connecting two copper centers through basal–basal linkage have shown ferromagnetic interaction in many cases [29, 30]. Theoretical results obtained from DFT calculations have been used to rationalize the magnetic behavior of such complexes [30]. Although no such theoretical studies or details of magnetostructural correlations exist for dca-bridged metal complexes, the $\mu_{1,5}$ dicyanamido connects two copper(II) ions through basal–basal linkage which may facilitate ferromagnetic interaction between coppers.

Supplementary data

CCDC 645212 contains supplementary crystallographic data for this article. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: (+44)-1223-336-033; or Email: deposit@ccdc.cam.ac.uk (CCDC 645212).

Acknowledgements

The work is financially supported by the University Grants Commission, New Delhi, by a grant (F. No. 32-235/2006 (SR)) to SK. Financial support from the CSIR, New Delhi, by a grant (01/(1972)/05/EMR II), the Deutsche Forschungsgemeinschaft (Priority Program 1137) and the Fonds der Chemischen Industrie is also gratefully acknowledged.

References

[1] (a) G.R. Desiraju. *The Crystal as a Supramolecular Entity*, Wiley, New York (1995); (b) G.R. Desiraju. *Angew. Chem. Int. Ed. Engl.*, **34**, 2311 (1995).

[2] (a) D.E. Vos, F.-T. Starzyk, P.A. Jacobs. *Angew. Chem. Int. Ed. Engl.*, **33**, 431 (1994); (b) A.L. Balch, M. Mazzanti, M.M. Olmstead. *J. Chem. Soc., Chem. Commun.*, 269 (1994).

[3] (a) I. Potocnak, M. Dunaj-Jurco, D. Miklos, M. Kabesova, L. Jager. *Acta Crystallogr. Sect.*, **51**, 600 (1995); (b) I. Dansa, L. Golhen, O. Pena, N. Daro, J.-P. Sutter. *C. R. Acad. Sci. Ser. IIc: Chim.*, **4**, 125 (2001).

[4] (a) B.-W. Sun, S. Gao, B.Q. Ma, D.Z. Niu, Z.M. Wang. *J. Chem. Soc., Dalton Trans.*, 4187 (2000); (b) Z.M. Wang, B.-W. Sun, J. Luo, S. Gao, C.S. Liao, C.H. Yan, Y. Li. *Polyhedron*, **22**, 433 (2003); (c) B.-W. Sun, S. Gao, B.-Q. Ma, Z.-M. Wang. *Inorg. Chem. Commun.*, **4**, 72 (2001); (d) J.L. Manson, Q.-Z. Huang, J.W. Lynn, H.-J. Koo, M.-H. Whangbo, R. Bateman, T. Otsuka, N. Wada, D.N. Argyriou, J.S. Miller. *J. Am. Chem. Soc.*, **123**, 162 (2001).

[5] S.R. Batten, P. Jensen, B. Moubaraki, K.S. Murray, R. Robson. *Chem. Commun.*, 439 (1998).

[6] Y.M. Chow, D. Britton. *Acta Crystallogr. Sect. B*, **31**, 1934 (1975).

[7] J.L. Manson, C.R. Kmety, Q.-Z. 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**, 2552 (1998).

[8] S.R. Batten, K.S. Murray. *Coord. Chem. Rev.*, **246**, 103 (2003).

[9] M. Kurmoo, C.J. Kepert. *New J. Chem.*, **22**, 1515 (1998).

[10] M. Kurmoo, C.J. Kepert. *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A*, **334**, 693 (1999).

[11] (a) S.R. Batten, P. Jensen, C.J. Kepert, M. Kurmoo, B. Moubaraki, K.S. Murray, D.J. Price. *J. Chem. Soc., Dalton Trans.*, 2987 (1999); (b) A.M. Kutasi, S.R. Batten, B. Moubaraki, K.S. Murray. *J. Chem. Soc., Dalton Trans.*, 819 (2002); (c) S.R. Batten, K.S. Murray. *Aust. J. Chem.*, **54**, 605 (2001); (d) G.A. van Albada, M.G. van der Horst, I. Mutikainen, U. Turpeinen, J. Reedijk. *Inorg. Chem. Commun.*, **10**, 1014 (2007) and references therein.

[12] (a) J.L. Manson, C.D. Incarvito, A.L. Rheingold, J.S. Miller. *J. Chem. Soc., Dalton Trans.*, 3705 (1998); (b) J.L. Manson, A.M. Arif, C.D. Incarvito, L.M. Liable-Sands, A.L. Rheingold, J.S. Miller. *J. Solid State Chem.*, **145**, 369 (1999); (c) B.-W. Sun, S. Gao, B.-Q. Ma, Z.-M. Wang. *New J. Chem.*, **24**, 953 (2000); (d) J.L. Manson, J.A. Schlueter, U. Geiser, M.B. Stone, D.H. Reich. *Polyhedron*, **20**, 1423 (2001); (e) S.R. Marshall, C.D. Incarvito, J.L. Manson, A.L. Rheingold, J.S. Miller. *Inorg. Chem.*, **39**, 1969 (2000); (f) S. Martin, M.G. Barandika, J.I.R. de Larramendi, R. Cortes, M. Font-Bardia, L. Lezama, Z.E. Serna, X. Solans, T. Rojo. *Inorg. Chem.*, **40**, 3687 (2001).

[13] P. Jensen, S.R. Batten, B. Moubaraki, K.S. Murray. *J. Solid State Chem.*, **159**, 352 (2001).

[14] (a) P.M. van der Werff, S.R. Batten, P. Jensen, B. Moubaraki, K.S. Murray, E.H.-K. Tan. *Polyhedron*, **20**, 1129 (2001); (b) P.M. van der Werff, S.R. Batten, P. Jensen, B. Moubaraki, K.S. Murray. *Inorg. Chem.*, **40**, 1718 (2001); (c) S.R. Batten, P. Jensen, B. Moubaraki, K.S. Murray. *Chem. Commun.*, 2331 (2000); (d) L. Jager, C. Wagner, M. Korabik, A. Zygmunt, J. Mrozinski. *J. Mol. Struct.*, **570**, 159 (2001); (e) J.W. Raebiger, J.L. Manson, R.D. Sommer, U. Geiser, A.L. Rheingold, J.S. Miller. *Inorg. Chem.*, **40**, 2578 (2001).

[15] B. Vangdal, J. Carranza, F. Lloret, M. Julve, J. Sletten. *J. Chem. Soc., Dalton Trans.*, 566 (2002).

[16] I. Potocnak, M. Burcak, C. Wagner, L. Jagar. *Acta Cryst. C*, **58**, m327 (2002).

[17] J. Carranza, C. Brennan, J. Sletten, F. Lloret, M. Julve. *J. Chem. Soc., Dalton Trans.*, 3164 (2002).

[18] (a) D. Mal, S. Koner, J.-P. Tuchagues, G.M. Rosair. *Inorg. Chim. Acta*, **360**, 3575 (2007); (b) P. Jenson, S.R. Batten, B. Moubaraki, K.S. Murray. *Chem. Commun.*, 793 (2000).

[19] (a) C. Adhikary, D. Mal, K.-I. Okamoto, S. Chaudhuri, S. Koner. *Polyhedron*, **25**, 2191 (2006); (b) M. Zibiri, S. Saha, C. Adhikary, S. Chaudhuri, C. Daul, S. Koner. *Inorg. Chim. Acta*, **359**, 1193 (2006); (c) S. Koner, S. Saha, T. Mallah, K. Okamoto. *Inorg. Chem.*, **43**, 840 (2004).

[20] S. Koner, S. Saha, K. Okamoto, J.-P. Tuchagues. *Inorg. Chem.*, **42**, 4668 (2003).

[21] (a) *Crystal Clear: Crystal Clear Software User's Guide*, Molecular Structure Corporation, Rigaku Corporation, 1999; (b) J.W. Plugrath. *Acta Cryst. D*, **55**, 1718 (1999).

[22] SIR97: A. Altomare, M. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. Moliterni, G. Polidori, R. Spagna. *J. Appl. Cryst.*, **32**, 115 (1999).

[23] *Crystal Structure 3.5.1: Crystal Structure Analysis Package*, Rigaku and Rigaku/MSC (2000–2003).9009 New Trails Dr., The Woodlands, TX 77381 USA.

[24] CRYSTALS issue 10: D.J. Watkin, C.K. Prout, J.R. Carruthers, P.W. Betteridge, Chemical Crystallography Laboratory, Oxford, UK (1996).

[25] M.N. Burnett, C.K. Jonnson. *ORTEP III, Report ORNL-6895*, Oak Ridge National Laboratory, Tennessee, USA (1996).

[26] I.J. Bruno, J.C. Cole, P.R. Edgington, N.K. Kessler, C.F. Macrwe, P. Maccabe, J. Pearson, R. Taylor. *Acta Crystallogr. B*, **58**, 389 (2002).

[27] D. Mal, C. Adhikary, E. Rentschler, Y. Miyashita, K. Okamoto, S. Koner. *Polyhedron*, **26**, 736 (2007).

[28] (a) L.K. Thompson, S.S. Tandon. *Comments Inorg. Chem.*, **18**, 125 (1996); (b) O. Kahn, *Molecular Magnetism*, VCH, New York (1993).

[29] A. Escuer, M. Font-Bardia, S.S. Massoud, F.A. Mautner, E. Penãlba, X. Solans, R. Vicente. *New J. Chem.*, **28**, 681 (2004).

[30] S. Triki, C.J. Gómez-García, E. Ruiz, J. Sala-Pala. *Inorg. Chem.*, **44**, 5501 (2005).