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2D water layer enclathrated between Mn(II)–Ni(CN)$_4$ coordination frameworks

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ABSTRACT

A $[Ni(CN)_4]^{2-}$-based two-dimensional Mn(II) coordination polymer $\{Mn(H_2O)_2[NiCN]_4 \cdot 4H_2O\}$, in which the coordination layers are stacked on top of each other sandwiching 2D water layer of boat-shaped hexagonal water clusters has been synthesized. The complex exhibits high thermal decomposition temperature and reversible water absorption, which were clearly demonstrated by thermal and PXRD studies on the parent and rehydrated complex after dehydration.

1. Introduction

Water, undoubtedly, is the most important molecule for sustaining life and is also crucial in many technological and chemical processes [1]. To understand the structural and energetic aspects of various hydrogen bonded water networks of small water clusters, researchers have adopted mainly spectroscopic and theoretical means. On the other hand, for exploring the structural aspects of larger water clusters in higher-dimensional networks, both theoretical and spectroscopic techniques are, at present, inadequate and knowledge on them have been gathered mainly through the X-ray crystallographic studies of organic and metal-organic hydrated crystalline compounds. Larger discrete water clusters generally show 3D motif, whereas smaller ones $(H_2O)_n$ ($n = 2, 3, 4, 5$) adopt planar conformation [2,3]. The water hexamers, having planar as well as cage form act as the transition point from 2D planar geometries of smaller water clusters to 3D geometries of larger clusters. On the other hand, polymeric 1D zig-zag or helical [4], two-dimensional planar [5] and even three-dimensional [6] networks of water molecules have been found in crystalline materials. It has been found that higher-dimensional water structures result from different self-assembling modes of discrete low nuclearity water clusters, e.g. dimer, tetramer, hexamer, etc. Among these, water hexamer is particularly an interesting motif, as theoretical investigations have revealed the existence of six nearly isoenergic isomers—namely planar, chair, boat, cage, book and prism [7]. The boat-shaped water hexamer can join at the edges to produce one-dimensional tape [8] as well as two-dimensional water sheet [9], which are also the structural sub-units of hexagonal and cubic ice. It is interesting to note that many cyanometallate coordination polymers can host hexagonal water sheets which are found in $[M(H_2O)_2\{M'(CN)_4\}] \cdot 4H_2O$ where $M =$ Cd, Co, $M' =$ Pd or Ni) [9–12] The structural relationship between polymeric water structure and the metal ligand assembly is of particular importance to crystal engineers and this aspect is gradually being revealed through the analysis of more and more crystal structures and at present, it has opened up the possibility of engineering the water structures [13]. In the present article we report the results on structural, thermal and powder X-ray diffraction (PXRD) studies of the enclathrated water layer of boat-shaped fused hexamers in the tetracyanonickelate(II) bridged Mn(II) complex. The unusual stability of water of crystallization (561 K), as is evidenced from TGA study, may find applications in solid oxides fuel cells (SOFC) technology for the necessity of proton solid electrolytes operating at 433–773 K [14].

2. Experimental

2.1. Synthesis of $[Mn[Ni(CN)_4] \cdot 6H_2O$

To an anhydrous methanolic solution of $Mn(OAc)_2 \cdot 4H_2O$ (0.245 g,1.0 mmol) under nitrogen atmosphere, $Na_2[Ni(CN)_4]$

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(0.490 g, 2.0 mmol) dissolved in a minimum volume of water was added dropwise for 5 min with constant stirring. The pale-pinkish precipitate that appeared initially was dissolved in hot water and brown precipitate that left was filtered off. The light yellow filtrate was kept in a refrigerator at 4 °C for several weeks, during which time light yellow block-shaped crystals of **1** suitable for X-ray study were obtained. It was filtered and washed with cold water and dried in air at room temperature. Yield: 62% based on $Mn(OAc)_2 \cdot 4H_2O$. Anal. found (Calcd.) for $C_4H_{12}MnN_4NiO_6$: C, 16.01(15.50); H, 2.22(1.94); N, 18.06(18.08) %.. IR in cm^{-1} (KBr): 3617 (s), 3292 (w,br), 2152 (vs), 1632 (s), 788 (w,br). μ_{eff}: 5.96 μ_B at 27 °C.

2.2. *Physical measurements*

Elemental analyses were carried out using a Perkin–Elmer 240 elemental analyzer. The infrared spectra (400–4000 cm^{-1}) were recorded from KBr pellets on a Nickolet Magna IR 750 series-II FTIR spectrophotometer. TGA/DTA thermograms were recorded on a Perkin–Elmer Pyris Diamond TGA/DTA thermal analyzer under a dynamic nitrogen environment. Powder X-ray diffraction data were collected on a Bruker D8 Advance powder diffractometer in the Bragg–Brentano geometry using monochromatic Cu$K_{\alpha 1}$ radiation ($k = 1.5406$ Å) selected with an incident beam germanium monochromator.

2.3. *X-ray data collection and analysis*

X-ray data were collected on a Siemens P4 diffractometer; MoK_α (radiation ((= 0.71073 Å) and the $\omega-2\theta$ scan mode in the range $2.44 \leq \theta \leq 26.47$. Crystal data: anhydrous, $M = 325.83$, $T = 293(2)$ K, orthorhombic, *Pnma* (No. 62) $a \sim 12.311(6)$, $b \sim 14.134(6)$, $c = 7.313(3)$; $V = 1272.5(10)$ Å^3, $Z = 4$, independent 1854 reflections (2431 measured), all data w$R_2 \sim 0.1724$, $R_1 \sim 0.0599$. The intensities were corrected for Lorentz and polarization effects and also for absorption effect. The structures were solved by direct methods. Data analysis was carried out with Crysalis Program [15]. All the non-hydrogen atoms were refined anisotropically by full-matrix least squares on F^2 using the PLUS-PC version of SHELXTL [16]. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. CCDC reference number 278583. See http://www.rsc.org/suppdata/ce/ for crystallographic data in CIF format.

3. Results and discussion

In the present complex the Mn(II) atoms occupy the inversion center and Ni atoms lie on a mirror plane. Mn(II) centers have octahedral coordination environment (Fig. 1) with four nitrogen atoms (N1, N2 and their symmetry related counterparts N1*, N2*, $^* = -x, 1-y, 1-z$) of four CN^- groups forming the equatorial plane and oxygen atoms of two water molecules (O1 and symmetry related O1*, $^* = -x, 1-y, 1-z$) occupy the two axial coordination sites. Mn2–N1 = 2.204(3) Å, Mn2–N2 = 2.205(3) Å and Mn–O1 = 2.239(2) Å. The Mn–Ni distance is 5.098 Å and Mn–Ni1 distance is 5.204 Å.

The crystal structure determination reveals that the $[Ni(CN)_4]^{2-}$ units act as a template for 2D coordination network having (4,4) net topology, which connects Mn(II) nodes extending the network in the (0 1 1) plane. Very recently, a 2D framework structure of $[MnNi(CN)_4(C_5H_5N)_2]$ has been reported [17], where a square mesh network was found to result from the 2D network of $Mn(C_5H_5N)_2)_2Ni(CN)_4$ through the linkage of cyanides between the equatorial coordination sites of octahedral Mn^{II} ions and square planar Ni^{II} ions.

Three lattice water molecules (Ow1, Ow2, Ow3) along with two coordinated water molecules (O1 and O1*) form 2D water layers (Fig. 1) sandwitched between successive coordination networks (Fig. 2). The water layers posses honeycomb-like

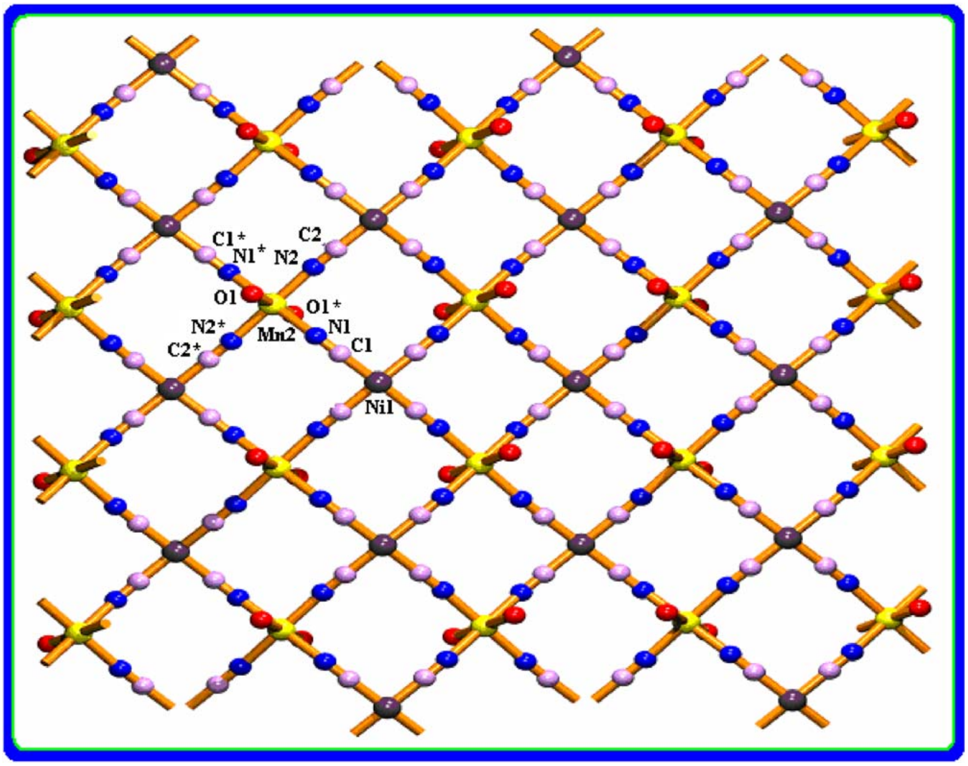

Fig. 1. The 2D polymeric sheet of $Ni(CN)_4$ and Mn(II) units ($^* = -x, 1-y, 1-z$).

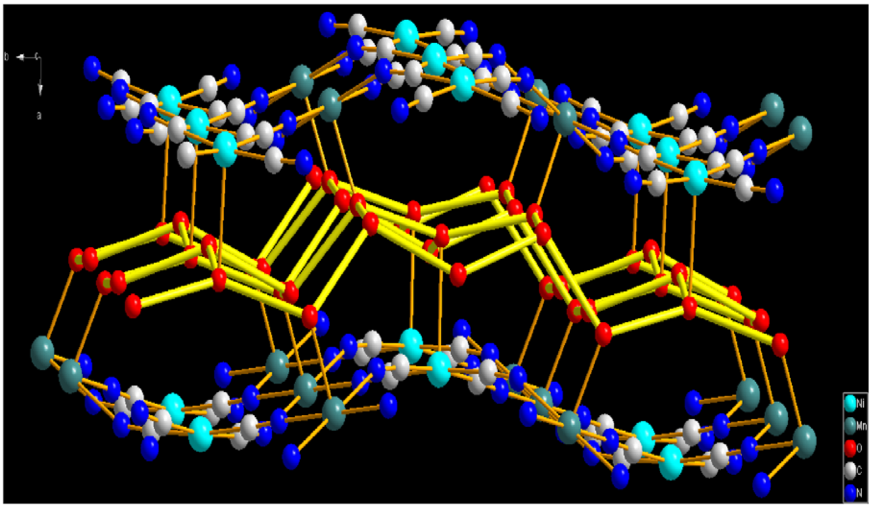

Fig. 2. The 2D supramolecular water sheet that is enclathrated between the tetracyano-nickelate bridged coordination polymeric sheets.

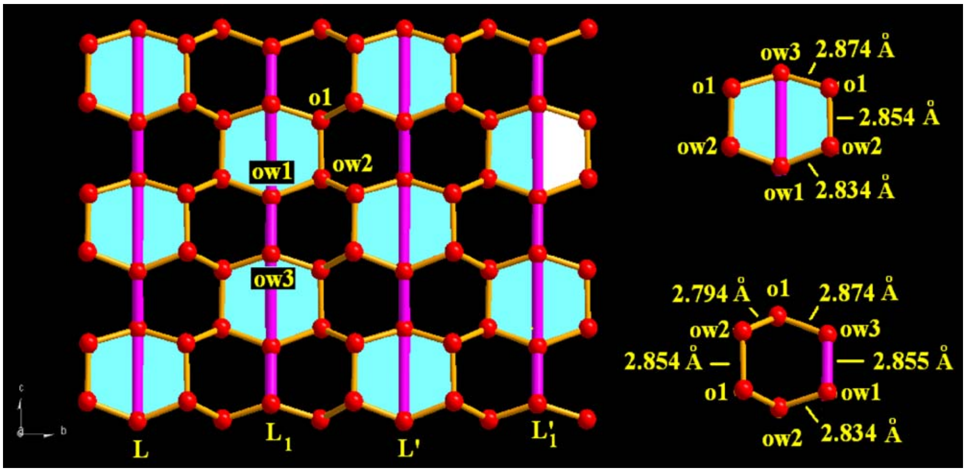

Fig. 3. The honeycomb water layer consisting of larger (shaded white) and smaller (shaded black) hexagonal boat-shaped water clusters. Larger hexagons are pierced through mirror lines (shown as thick pink lines) (for interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

architecture due to fusion of hexagonal water clusters (Fig. 3). Each layer contains two kinds of hexamers: a relatively larger boat-shaped hexgonal water cluster and a comparatively smaller hexagonal water clusters having the same boat type topology. Each larger hexagonal cluster is encircled by six smaller clusters giving rise to L6(6) water layer in Infant's notation [18]. Lattice water molecules Ow1 and Ow3 lie on the mirror line and constitute two vertices of the larger hexagons. Two halves of this hexagon are mirror symmetric with O1…Ow3 constituting two arms of it. On the other hand, the smaller hexagons lie in between the mirror lines with only one edge on either side of the mirror line. As depicted in Fig. 3, the O…O distances lie in the range 2.794–2.874 Å. The O…O…O angles lie in the range 104.83–134.98°. The dihedral angles of the planes constituting the boat-shaped hexamer are 46.85° and 36.71° for the smaller hexagon and 51.39° and 68.15° for the larger hexagon. Successive two small and one large boats are arranged along the *b*-axis. That the formation of water layer and its topology are strongly influenced by the coordination framework is evident from the participation of the coordinated water molecule O1 in the network. Besides the lattice water molecule Ow3 interacts with the Ni atom on the framework through its lone pair. The Ni…OW3 distance is 2.788 Å. The (4,4) net topology of the coordination framework is transformed into the honeycomb netwrok in the water layer through these bondings.

Thermal decomposition of complex **1** (Fig. 4) starts at ~35 °C and continues up to ~100 °C and during this process it loses almost two (1.8) uncoordinated water molecules in the first step (found/calcd.: 9.16/9.95% with respect to loss of weight %) which is accompanied by a small endo-effect on the DTA curve at ca. 80 °C. After this initial loss the complex maintains its thermal stability up to ca. 288 °C, which on further heating loses three water molecules (found/calcd.: 28.18/27.64% with respect to loss of weight %) in the temperature range 288–332 °C and a small endo-peak appears at ca. 330 °C in the DTA curve. The remaining coordinated water molecule is eliminated at ca. 434 °C (found/calcd.: 31.20/31.88% with respect to the loss of weight %) and after this the complex decomposes completely. Thermal stability of the partly dehydrated complex in the temperature range 100–288 °C indicates that the initial two water molecules may be re-adsorbed. To verify this proposition, sample was heated up to 110 °C in the TGA run under N_2 atmosphere, where only two water molecules are eliminated. It was cooled to room temperature and then exposed to moisture in an open atmosphere for 3 days and the thermal decomposition study was again performed, which indeed corroborated the re-adsorption capability of the partially

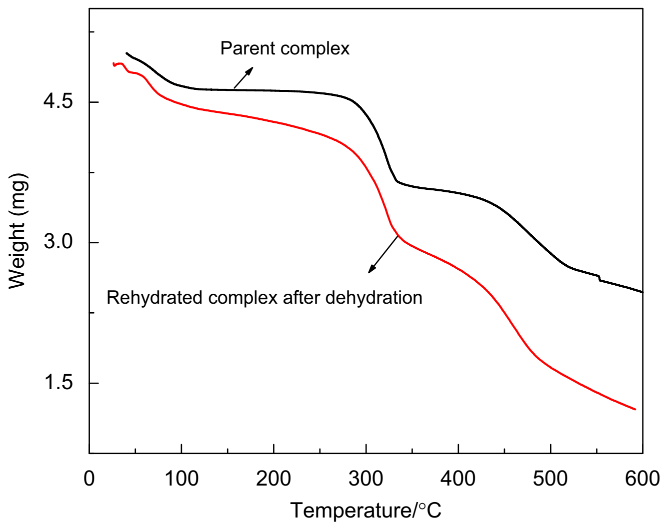

Fig. 4. Thermal stability study of the parent and rehydrated complexes.

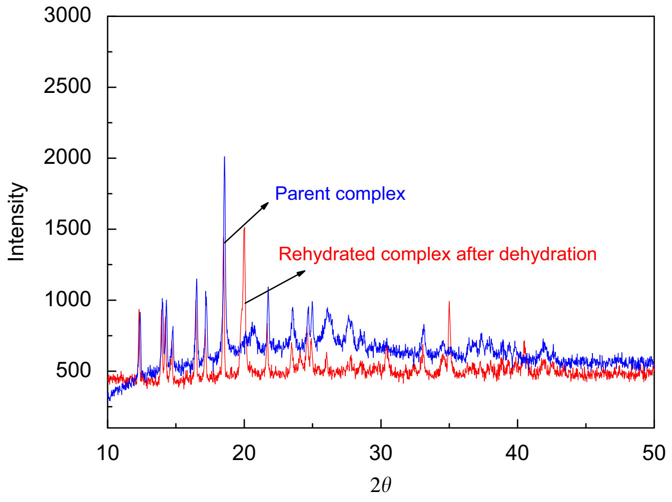

Fig. 5. PXRD patterns of parent and rehydrated complex after dehydration.

dehydrated compound (Fig. 4). This is further supported by the PXRD patterns of the parent and rehydrated complexes after dehydration, which are almost identical with minor changes in peak positions and intensity (Fig. 5). All these clearly indicate the single crystalline nature of the rehydrated complex. The thermal stability of the partly dehydrated complex in the temperature range 100–288 °C, above the boiling point of liquid water, is quite unusual. In order to ascertain that the observed significantly high stability of water of crystallization is not due to the instrumental artifacts we run the TGA experiment at a slower scan rate (2 °C per min). Interestingly, it was observed that the TGA curve remains invariant with the sacn rate. This high thermal stablity of the present complex is very interesting and is in contrast to the analogous compound $[Co(H_2O)_2\{Ni(CN)_4\} \cdot 4H_2O$ [11], which showed quite low thermal stability with respect to the loss of water of crystallization and needs further exploration.

Recently, numerous cyano-complexes have been shown to host water clusters of various morphologies [13,18,19]. The present crystal structure, in this respect, hints that cyano-bridged transition metal complexes having layered architecture may be more amenable to support 2D water layers. The present finding is not an isolation, as evidenced by a previous report on similar water morphology [7b] in an analogous compound. We assumed that the coordinated water molecules, which are the integral part of the planar water sheet, should be playing importanat role in its stabilization. This expectation has been corroborated by the thermal stability analysis which shows the water loss in two steps. Futhermore this study also shows that the compound retains water molecules up to an unsual very high temperature (603 K). It has been found that, two of the water molecules that are lost at ~100 °C are reversibly readsorbed.

4. Conclusion

In summary, we have prepared a $[Ni(CN)_4]^{2-}$-based Mn(II) coordination polymer in which successive coordination frameworks are stacked and in between them 2D water layers of boat-shaped hexagonal water clusters are sandwitched. Thermal studies establish the unusually high thermal stability of the coordinated water molecules strongly bound to the polymeric framework. Also the partially dehydrated compound shows reversible adsorption of the lost water molecules. This has been supported by the PXRD study on both the parent and rehydrated complex after dehydration.

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Appendix A. Supporting Information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2009.05.014.

References

[1] (a) P.A. Thiel, T.E. Madey, Surf. Sci. Rep. 7 (1987) 211;
(b) M.A. Henderson, Surf. Sci. Rep. 46 (2002) 1;
(c) D.G. Blackmond, A. Armstrong, V. Coombe, A. Wells, Angew. Chem. Int. Ed. 46 (2007) 3798;
(d) N. Zotova, A. Franzke, A. Armstrong, D.G. Blackmond, J. Am. Chem. Soc. 129 (2007) 15100;
(e) S. Wang, H. Yao, S. Sato, K. Kimura, J. Am. Chem. Soc. 126 (2004) 3428.
[2] (a) R. Ludwig, Angew. Chem. Int. Ed. 40 (2001) 1808;
(b) P. Ball, H_2O: A Biography of Water, Weidenfeld and Nicolson, 1999.
[3] R. Ludwig, Chem. Phys. Chem. 1 (2000) 53.
[4] (a) H. Cui, B. Zhou, L.-S. Long, Y. Okano, H. Kobayashi, A. Kobayashi, Angew. Chem. Int. Ed. 47 (2008) 3376;
(b) L.E. Cheruzel, M.S. Pometun, M.R. Cecil, M.S. Mashuta, R.J. Wittebort, R.M. Buchanan, Angew. Chem. Int. Ed. 42 (2003) 5452;
(c) S. Ray Choudhury, A.D. Jana, E. Colacio, H.M. Lee, G. Mostafa, S. Mukhopadhyay, Cryst. Growth Des. 7 (2007) 212;
(d) S. Pal, N.B. Sankaran, A. Samanta, Angew. Chem. Int. Ed. 42 (2003) 1741;
(e) S.J. Langford, C.P. Woodward, Cryst. Eng. Comm 1 (2007) 218;
(f) B. Sreenivasulu, J.J. Vittal, Angew. Chem. Int. Ed. 43 (2004) 5769;
(g) J. Kim, K.S. Kim, J. Chem. Phys. 109 (1998) 5886;
(h) K. Liu, M.G. Brown, C. Carter, R.J. Saykally, J.K. Gregory, D.C. Clary, Nature 381 (1996) 501;
(i) K. Kim, K.D. Jordan, T.S. Zwier, J. Am. Chem. Soc. 116 (1994) 11568.
[5] (a) S. Upreti, A. Datta, A. Ramanan, Cryst. Growth Des. 7 (2007) 966;
(b) X.-J. Kong, Y.-P. Ren, P.-Q. Zheng, Y.-X. Long, L.-S. Long, R.-B. Huang, L.-S. Zheng, Inorg. Chem. 45 (2006) 10702;
(c) B.-Q. Ma, H.-L. Sun, S. Gao, Angew. Chem. Int. Ed. 43 (2004) 1374.
[6] Rosa Carballo, Berta Covelo, Carlos Lodeirob, Ezequiel M. Vázquez-Lópeza, Cryst. Eng. Comm. 7 (2005) 294.
[7] (a) S.O. Kang, D. Powell, V.W. Day, K. Bowman-James, Cryst. Growth Des. 7 (2007) 606;

(b) T. K Prasad, M.V. Rajasekharan, Cryst. Growth Des. 6 (2006) 488;
(c) J. Wang, L.-L. Zheng, C.-J. Li, Y.-Z. Zheng, M.-L. Tong, Cryst. Growth Des. 6 (2006) 357;
(d) M. Febles, N. Pérez-Hernández, C. Pérez, M.L. Rodríguez, C. Foces-Foces, M.V. Roux, E.Q. Morales, G. Buntkowsky, H.-H. Limbach, J.D. Martín, J. Am. Chem. Soc. 128 (2006) 10008.
[8] B.K. Saha, A. Nangia, Chem. Commun. (2006) 1825.
[9] (a) M. Tadokoro, S. Fukui, T. Kitajima, Y. Nagao, S. Ishimaru, H. Kitagawa, K. Isobe, K. Nakasuji, Chem. Commun. (2006) 1274;
(b) K.-M. Park, R. Kuroda, T. Iwamoto, Angew. Chem. Int. Ed. 32 (1993) 884.
[10] J.Z. Gu, L. Jiang, X.L. Feng, M.Y. Tan, T.B. Lu, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry 38 (2008) 28.
[11] T. Niu, G. Crisci, J. Lu, A.J. Jacobson, Acta Crystallogr. C 54 (1998) 565–567.
[12] N.J. Robertson, Z. Qin, G.C. Dallinger, E.B. Lobkovsky, S. Lee, G.W. Coates, Dalton Trans. (2006) 5390.
[13] R. Luna-García, B.M. Damián-Murillo, V. Barba, H. Höpfl, H.I. Beltrán, L.S. Zamudio-Rivera, Chem. Commun. (2005) 5527.
[14] T. Norby, Nature 410 (2001) 877.
[15] Crysalis VI, Oxford Diffraction Ltd., Oxford, UK, 2005.
[16] G. M. Sheldrick, SHELXL-93, University of Göttingen, Göttingen ,Germany, 1993.
[17] K. Hosoya, R. Sekiya, S. Nishikiori, Acta Cryst. E 62 (2006) m1627.
[18] L. Infantes, S. Motherwell, Cryst. Eng. Comm. 4 (2002) 454.
[19] (a) U. Mukhopadhyay, I. Barnal, Cryst. Growth Des. 5 (2005) 1687;
(b) U. Mukhopadhyay, I. Bernal, Crystal Growth Design 6 (2006) 363;
(c) M. Estrader, J. Ribas, V. Tangoulis, X. Solans, M. Font-Bardía, M. Maestro, C. Diaz, Inorg. Chem. 35 (2000) 3523, (45 (2006) 8239).