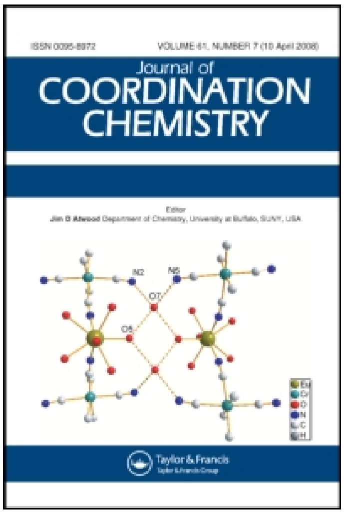

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

X-ray crystal structure, spectral and magnetic properties of end-to-end di-μ-thiocyanatobis(imidazole)M(II) polymeric complexes (M=Co, Mn): supramolecular network structure based on N-H ··· S hydrogen bonding and π ··· π stacking

Yi Jin[a]; Yun-xia Che[a]; Ji-min Zheng[a]
[a] Department of Chemistry, Nankai University, Tianjin 300071, People's Republic of China

To cite this Article Jin, Yi , Che, Yun-xia and Zheng, Ji-min(2007) 'X-ray crystal structure, spectral and magnetic properties of end-to-end di-μ-thiocyanatobis(imidazole)M(II) polymeric complexes (M=Co, Mn): supramolecular network structure based on N-H ··· S hydrogen bonding and π ··· π stacking', Journal of Coordination Chemistry, 60: 19, 2067 — 2074, First published on: 18 June 2007 (iFirst)

To link to this Article: DOI: 10.1080/00958970701236735

URL: http://dx.doi.org/10.1080/00958970701236735

Journal of Coordination Chemistry
Vol. 60, No. 19, 1 October 2007, 2067–2074

Taylor & Francis
Taylor & Francis Group

X-ray crystal structure, spectral and magnetic properties of end-to-end di-μ-thiocyanatobis(imidazole)M(II) polymeric complexes (M = Co, Mn): supramolecular network structure based on N–H $\cdots$ S hydrogen bonding and $\pi \cdots \pi$ stacking

YI JIN, YUN-XIA CHE and JI-MIN ZHENG*

Department of Chemistry, Nankai University, Tianjin 300071,
People's Republic of China

(*Received 25 October 2006; revised 15 November 2006; in final form 30 November 2006*)

Two isomorphous one-dimensional chain complexes $Co(NCS)_2(Him)_2$ (**1**) and $Mn(NCS)_2(Him)_2$ (**2**) (Him = imidazole) have been prepared and characterized structurally. Both **1** and **2** crystallize in the monoclinic system, space group $P2_1/n$, and the structures consist of one-dimensional polymeric chains in which metal ions are bridged by two thiocyanate groups bonding in end-to-end fashion. Both **1** and **2** exhibit two-dimensional sheet structures with N–H $\cdots$ S hydrogen bonds and three-dimensional supramolecular network structure with $\pi \cdots \pi$ stacking interactions. IR spectra indicate the presence of bridging thiocyanate groups in both **1** and **2**, confirmed by their structures. The variable temperature magnetic susceptibility, measured in the 2–300 K range, indicates weak antiferromagnetic exchange interactions in complex **2**.

Keywords: Thiocyanate; One-dimensional; Supramolecular network; $\pi \cdots \pi$ stacking; Antiferromagnet

1. Introduction

Structural and magnetic studies of binuclear and polynuclear complexes containing multidentate bridging ligands, in which metal–metal interactions such as magnetic coupling, energy or electron transfer, and intervalence transfer may occur, are of considerable interest in inorganic and bioinorganic chemistry [1–6]. The synthesis of pseudohalide bridged complexes continues to be of interest as a result of their diverse structures and potential applications in magnetic materials [7]. Coordination chemistry of pseudohalides of the type XCN (X = O, S, Se) [8], N_3^- [9] is interesting because of different modes of ligand coordination to metal ions. The chemistry and bonding of such complexes have been the subject of several reviews [10, 11].

End-to-end coordination of thiocyanate is usually found in dinuclear, one-dimensional or three-dimensional compounds. However, many doubly thiocyanato bridged Cu(II) complexes have been reported [12–16], and the crystal structure of the

---

*Corresponding author. Fax: +86 23508056. Email: jmzheng@public.tpt.tj.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970701236735

nickel(II) complex determined, but single crystal X-ray analysis of the cobalt(II) complex has not been determined [17].

In this work, we present synthesis and the crystal structure of $M(NCS)_2(Him)_2$ ($M = Co, Mn$), the magnetic properties of the Mn compound.

2. Experimental

2.1. *Materials and physical measurement*

The synthesis was conducted using reagent grade $CoCl_2 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, NH_4NCS and Him from commercial sources without further purification. Elemental analyses (C, H, N) were carried out on an Elementar Vario EL instrument. Infrared spectra (KBr pellets) were measured on a MAGNA–IR 560 FTIR spectrometer in the 400–4000 cm^{-1} region. Magnetic studies were performed in MPMS SQUID and Maglab 2000 magnetometers in the temperature range 2–300 K.

2.2. *Synthesis*

$Co(NCS)_2(Him)_2$ (1). Single crystals were grown in solution at room temperature. $CoCl_2 \cdot 6H_2O$ (0.24 g; 1 mmol), NH_4NCS (0.15 g, 2 mmol) and imidazole (0.13 g, 2 mmol) in the molar ratio of 1 : 2 : 2 were dissolved in distilled water (25 mL). The resulting solution was heated at 60°C for 2 h with stirring. The solvent was allowed to evaporate slowly at room temperature; small, light-red single crystals appeared in the bottom of the cup. IR (cm^{-1}): $\upsilon_{SCN} = 2112$, $\upsilon_{Him} = 3265$. Anal. Caldc for **1** $C_8H_8CoN_6S_2$ (%): C 30.87, H 2.59, N 27.00; found C 30.85, H 2.59, N 27.01.

$Mn(NCS)_2(Him)_2$ (2). This compound was prepared like **1**, $MnCl_2 \cdot 4H_2O$ (0.20 g. 1 mmol) substituted $CoCl_2 \cdot 6H_2O$, small light yellow single crystals appeared. IR(cm^{-1}): $\upsilon_{SCN} = 2098$, $\upsilon_{Him} = 3304$. Anal. Calcd for **2** $C_8H_8MnN_6S_2$ (%): C 31.27, H 2.62, N 27.35; found C 31.27, H 2.60, N 27.33.

2.3. *X-ray crystal structure determination*

Diffraction data for **1** and **2** were collected at 293 K, with a R-AXIS RAPID IP diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å) with the ω–2θ scan technique. A total of 5394 reflections were measured to give 1322 independent reflections ($R_{int} = 0.0401$) for **1**, 5762 reflections were measured to give 1400 independent reflections ($R_{int} = 0.0427$) for **2**, The structures were solved by direct methods and refined by full-matrix least-squares techniques based on F^2 with the SHELXTL program package [18]. Non-hydrogen atoms were subject to anisotropic refinement. The hydrogen atoms bound to the carbon atoms were calculated theoretically. The crystallographic data for **1** and **2** are summarized in table 1. Selected bond lengths and angles for **1** are given in table 2, selected bond lengths and angles for **2** are given in table 3.

Table 1. Crystal data and structure refinement for **1** and **2**.

Compound	**1**	**2**
Formula	$C_8H_8CoN_6S_2$	$C_8H_8MnN_6S_2$
Fw	311.25	307.26
Crystal system	Monolinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	7.6950(15)	7.7878(16)
b (Å)	5.6170(11)	5.6894(11)
c (Å)	13.772(3)	14.047(3)
β (°)	103.01(3)	102.44(3)
V (Å^3)	580.0(2)	607.8(2)
Z	2	2
D_{Calcd} (g cm^{-3})	1.782	1.679
μ(Mo-Kα (mm^{-1}))	1.824	1.415
$F(000)$	314	310
Crystal size (mm^3)	0.26 × 0.09 × 0.08	0.20 × 0.20 × 0.10
θ range (°)	3.04–27.48	3.33–27.48
Reflns. Collected/unique	5394/1322	5762/1400
Reflns. obsd. ($I > 2\sigma(I)$)	1167	1164
GOF on F^2	1.051	1.052
$R1$, $wR2$ (obsd.)	0.0280, 0.0660	0.0279, 0.0623
Max., min. peaks (e Å^{-3})	0.570, −0.458	0.310, −0.226

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

C(1)–N(1)	1.326(3)	C(1)–N(2)	1.340(3)
C(2)–C(3)	1.361(3)	C(2)–N(1)	1.375(3)
C(3)–N(2)	1.361(3)	C(4)–N(3)	1.158(2)
C(4)–S(1)	1.6518(19)	Co(1)–N(3)	2.0858(16)
Co(1)–N(1)	2.1098(17)	Co(1)–S(1)#3	2.6613(8)
N(3)#1–Co(1)–N(3)	180.00(9)	N(3)#1–Co(1)–N(1)#1	90.08(6)
N(3)–Co(1)–N(1)#1	89.92(6)	N(1)#1–Co(1)–N(1)	180.0
N(3)–Co(1)–S(1)#2	87.90(5)	N(3)#1–Co(1)–S(1)#2	92.10(5)
N(1)#1–Co(1)–S(1)#2	89.81(5)	N(1)–Co(1)–S(1)#2	90.19(5)
N(3)#1–Co(1)–S(1)#3	87.90(5)	N(3)–Co(1)–S(1)#3	92.10(5)
S(1)#2–Co(1)–S(1)#3	180.0	C(1)–N(1)–Co(1)	125.44(14)
C(2)–N(1)–Co(1)	129.11(13)	C(4)–N(3)–Co(1)	156.73(15)
C(4)–S(1)–Co(1)#4	98.14(7)	N(3)–C(4)–S(1)	176.73(17)

Symmetry transformations used to generate equivalent atoms for **1**: #1 $-x+1$, $-y+2$, $-z+1$; #2 x, $y+1$, z; #3 $-x+1$, $-y+1$, $-z+1$; #4 x, $y-1$, z.

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

C(1)–N(1)	1.151(2)	C(1)–S(1)	1.6455(18)
C(2)–N(3)	1.317(3)	C(2)–N(2)	1.333(3)
C(3)–C(4)	1.339(3)	C(3)–N(3)	1.376(3)
Mn(1)–N(1)	2.1758(16)	Mn(1)–N(3)	2.2120(17)
Mn(1)–S(1)#2	2.7994(8)	S(1)–Mn(1)#4	2.7994(8)
N(1)–Mn(1)–N(1)#1	180.00(9)	N(1)–Mn(1)–N(3)	89.55(6)
N(1)#1–Mn(1)–N(3)	90.45(6)	N(1)–Mn(1)–S(1)#2	92.37(5)
N(1)#1–Mn(1)–S(1)#2	87.63(5)	N(3)–Mn(1)–S(1)#2	90.08(5)
N(3)#1–Mn(1)–S(1)#2	89.92(5)	N(1)#1–Mn(1)–S(1)#3	92.37(5)
S(1)#2–Mn(1)–S(1)#3	180.0	C(1)–N(1)–Mn(1)	154.37(16)
C(2)–N(2)–C(4)	108.19(19)	C(2)–N(3)–Mn(1)	126.32(14)
C(3)–N(3)–Mn(1)	129.02(14)	C(1)–S(1)–Mn(1)#4	96.11(7)

Symmetry transformations used to generate equivalent atoms for **2**: #1 $-x+1$, $-y+1$, $-z+1$; #2 $-x+1$, $-y$, $-z+1$ #3 x, $y+1$, z #4 x, $y-1$, z.

3. Results and discussion

3.1. *Crystal structures*

Complexes **1** and **2** are made up of 1D chains along the b-axis. Both coordination environments (around cobalt(II) for **1** and manganese(II) for **2**), are described as distorted octahedra with CoN_4S_2 for **1** (figure 1) and MnN_4S_2 for **2** (figure 2), the equatorial planes are occupied by two nitrogens from Him and two from thiocyanate anions; two sulfur atoms from bridging bidentate NCS groups are coordinated in the axial positions. The lengths of the Co–S bonds for **1**, 2.6613(8) Å, are greater than those of Co–N bonds, which are 2.0858(16) and 2.1098(17) Å; Mn–S bonds for **2**, at 2.7994(8) Å, are also greater than those of Mn–N bonds, which are 2.1758(16) and 2.2120(17) Å, causing significant distortion of the coordination polyhedron around Co(II) for **1** and Mn(II) for **2**. The end-to-end bidentate thiocyanate group is almost linear with an angle of 176.73° for **1**, which is smaller than the angle of 177.57° for **2**. Both complexes form extended one-dimensional chains, which are intertangled with each other. The eight-membered Co–(SCN)2–Co rings for **1** and Mn–(SCN)2–Mn rings for **2** adopt chair conformation. The distances between adjacent Co atoms in the same chain are 5.617 Å for **1**, and 5.689 Å for Mn in **2**, both Co···Co and Mn···Mn distances are longer than Ni···Ni distances [5.557(1) Å] [17], and shorter than Cu···Cu distances [5.722(2) Å] [16], and Cd···Cd distances [5.769 Å] [19].

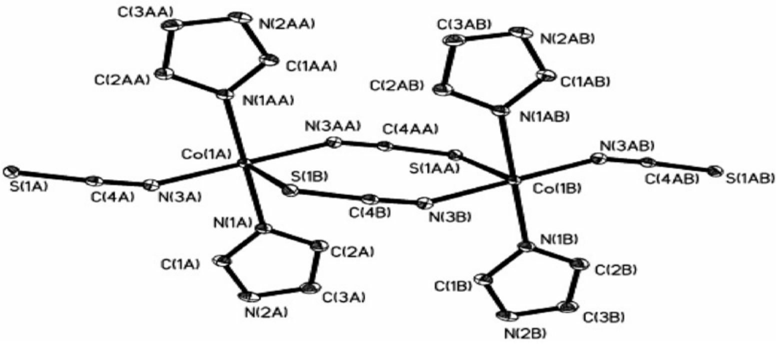

Figure 1. ORTEP diagram for **1** with atom numbering scheme.

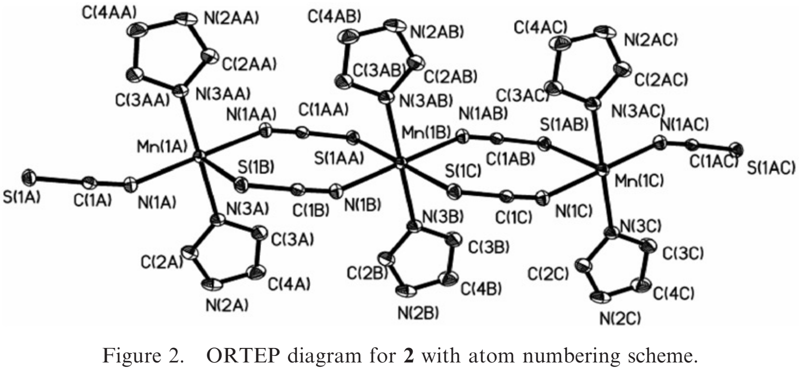

Figure 2. ORTEP diagram for **2** with atom numbering scheme.

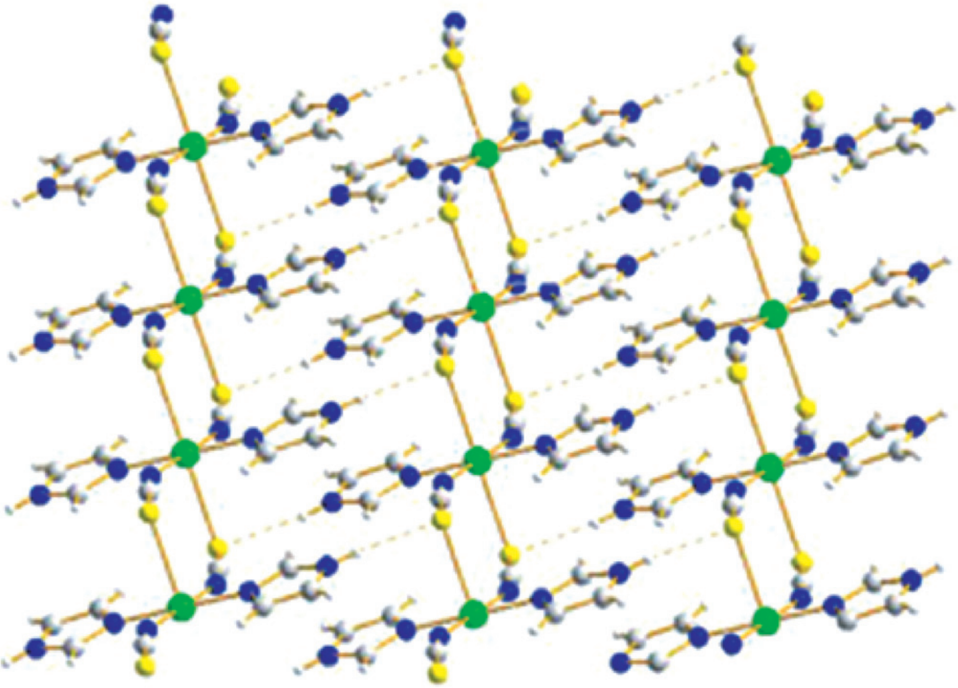

Figure 3. Packing view of the 2D supramolecular sheet formed by hydrogen bonding in **1**. (Carbon, gray; nitrogen, deep blue; sulfur, yellow; cobalt, green.)

The polymeric chains of [Co(Him)2(NCS)2]n for **1** (figure 3) and [Mn (Him)2(NCS)2]$_n$ for **2** (figure 4) pack alongside each other to give a 2D sheet-like structure in the *bc*-plane. Closest 1D chains are arranged side by side to facilitate a weak N–H $\cdots$ S hydrogen bond arising from the interaction of imidazole NH and the S atom from a NCS group, N(2)–H(2A) $\cdots$ S(1) $[-x+2, -y+1, -z+1]$ 3.382 Å for **1**, N(2)–H(2) $\cdots$ S(1) $[-x+2, -y, -z+1]$ 3.444 Å for 2, comparable with N–H $\cdots$ S hydrogen bonding of 3.381 Å for the Ni compound [17] and 3.417 Å for the Cd compound [19], but weaker than N–H $\cdots$ S hydrogen bond distance of 2.585 Å for the Cu compound [16].

The self-assembled structures of the two-dimensional layers are further stabilized by face-to-face $\pi \cdots \pi$ interactions from two terminal Him rings of two closest chains to extend to a three-dimensional supramolecular network. The centroid separation of two rings for **1** is 4.060 Å, which is longer than 3.783 Å for a Cu compound [16]; $\pi \cdots \pi$ interaction distance for **2** is 4.206 Å, which is similar to 4.324 Å in the Cd compound [19].

3.2. *IR spectra*

Diagnostic IR spectral data come mainly from bands of thiocyanate. The position of bands corresponding to the stretching frequency (CN) can be used for characterization of mode of coordination to the metal. The ν(CN) of a bridging thiocyanate is usually

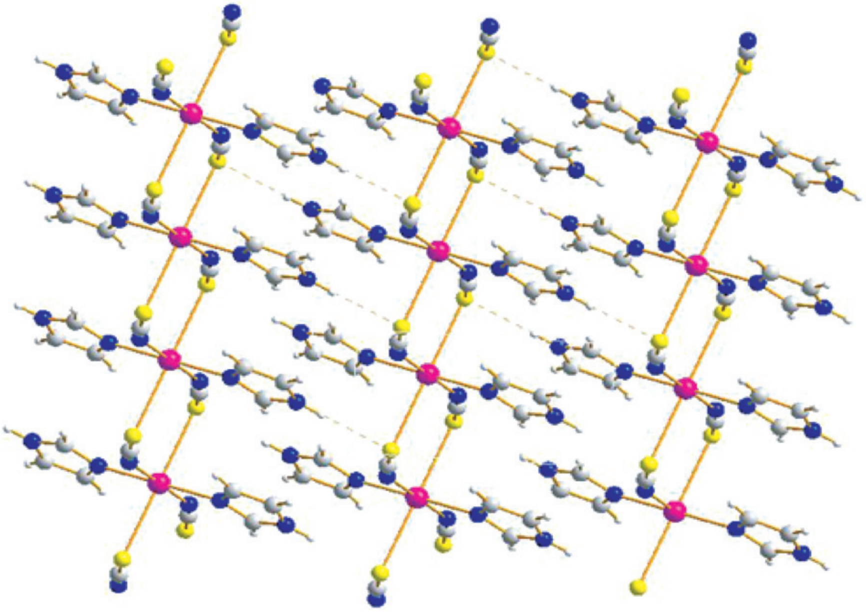

Figure 4. Packing view of the 2D supramolecular sheet formed by hydrogen bonding in **2**. (Carbon, gray; nitrogen, deep blue; sulfur, yellow; manganese, purple.)

found to be above 2100 cm^{-1} [20]; in **1**, the stretching frequency ν(CN) occurs at 2112 cm^{-1}; and in **2**, the stretching frequency ν(CN) occurs at 2098. Such high frequencies of these vibrations suggest the presence of end-to-end NCS bridges, and they are almost in the range observed for polymeric pseudoctahedral $ML_2(NCS)_2$ complexes [20]. The bands corresponding to the stretching frequency ν(CS) appear at 767 cm^{-1} for **1**, 766 cm^{-1} for **2**. Bands belonging to the deformation frequency δ(NCS) were found at 464 cm^{-1} for **1** and at 468 cm^{-1} for **2**. The above bands are consistent with a bridging thiocyanate anion. In addition several absorption bands observed at higher frequencies 3265.28 cm^{-1} for **1**, 3131.55 cm^{-1} and 3303.84 cm^{-1} for **2**, characteristic of the Im groups.

3.3. *Magnetic properties*

Magnetic measurements of **2** were carried out in a magnetic field of 500 Oe in the temperature range of 2–300 K, and the results were given as $\chi_M T$ *versus* T and $\chi_M{}^{-1}$ *versus* T plot (figure 5), in which χ_M is the corrected magnetic susceptibility per asymmetric [Mn $(Him)_2(NCS)_2$] unit. The inverse susceptibility plot as a function of temperature is linear above 20 K fitted the Curie–Weiss law $\chi_M = C/(T-\theta)$, giving a Curie constant $C = 4.27\ cm^3 mol^{-1} K$, the Weiss constant $\theta = -25.89$ K, the negative Weiss constant indicates antiferromagnetic interactions between Mn(II) ions through the bis-bridged end-to-end thiocyanato ligands. The $\chi_M T$ value at room temperature is 3.85 $cm^3 mol^{-1}$ K, which is smaller than the spin-only value of 4.375 $cm^3 mol^{-1}$ K for Mn(II) ($S = 5/2$, $g = 2.0$), and decreases with decreasing temperature to a minimum value of 0.197 $cm^3 mol^{-1}$ K at 2 K. This behavior is characteristic of an antiferromagnet;

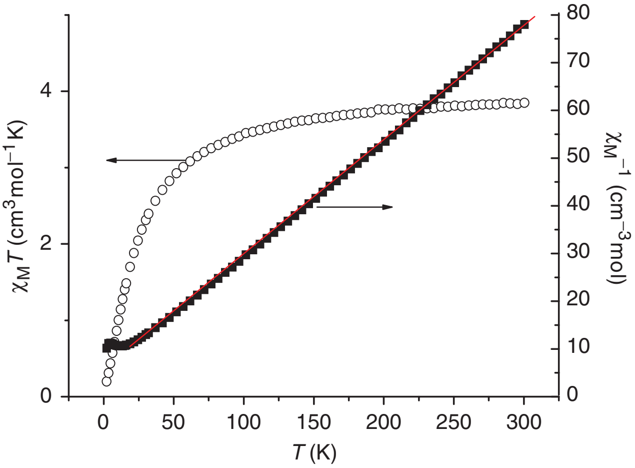

Figure 5. Plot of $\chi_M T$ *vs.* T and χ_M^{-1} *vs.* T for 2.

taking the structure into account, this behavior could be justified on pure ground-state basis of the sum of configuration of Mn(II) ions and the longer distance of Mn–SCN–Mn though end-to-end thiocyanato bridges.

Supplementary data

Crystallographic data for the structural analysis of the two compounds have been deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK, and are available free of charge from the Director on request quoting the deposition numbers CCDC 621091 and 621092 (Fax: C44 1223 336033, Email: deposit@ccdc.cam.ac.uk).

Acknowledgement

This work was supported by the National Natural Science Foundation of China (No. 50572040).

References

[1] J.D. Peterson, W.R. Murphy, R. Sahai, K.J. Brewer, R.R. Ruminski. *Coord. Chem. Rev.*, **64**, 261 (1985).
[2] P.J. Steel. *Coord. Chem. Rev.*, **106**, 227 (1990).
[3] C.T. Chen, K.S. Suslick. *Coord. Chem. Rev.*, **128**, 293 (1993).
[4] O. Kahn. *Angew. Chem., Int. Ed. Engl.*, **24**, 834 (1985).
[5] O. Kahn. *Struct. Bonding (Berlin)*, **68**, 89 (1987).
[6] D. Gatteschi, O. Kahn, J.S. Miller, F. Palacio (Eds). *Magnetic Molecular Materials*; NATO ASI Series E198, Kluwer, Dordrecht (1991).
[7] P. Talukder, A. Datta, S. Mitra, G. Rosair, M. Salah, J. Ribas. *Dalton Trans.*, 4161 (2004).

[8] (a) M. Julve, M. Verdaguer, G. De Munno, J.A. Real, G. Bruno. *Inorg. Chem.*, **32**, 795 (1993); (b) M. Montfort, J. Ribas, X. Solans. *Inorg. Chem.* **33**, 4271 (1994); (c) T. Rojo, R. Cortés, L. Lezama, M.I. Arriortua, K. Urtiaga, G. Villeneuve. *J. Chem. Soc., Dalton Trans.*, 1779 (1991); (d) R. Vicente, A. Escuer, J. Ribas, X. Solans. *J. Chem. Soc., Dalton Trans.*, 259 (1994); (e) R. Vicente, A. Escuer, J. Ribas, X. Solans, M. Font-Bardıá. *Inorg. Chem.*, **32**, 6117 (1993).

[9] (a) G. De Munno, M. Julve, G. Viau, F. Lloret, J. Faus, D. Viterbo. *Angew. Chem., Int. Ed. Engl.*, **35**, 1807 (1996); (b) R. Cortés, L. Lezama, J.L. Pizarro, M.I. Arriortua, T. Rojo, *Angew. Chem., Int. Ed. Engl.* **35**, 1810 (1996); (c) J. Ribas, M. Monfort, I. Resino, X. Solans, P. Rabu, F. Maingot, M. Drillon. *Angew. Chem., Int. Ed. Engl.*, **35**, 2520 (1996); (d) J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortés, L. Lezama, T. Rojo. *Coord. Chem. Rev.*, **193–195**, 1027 (1999); (e) T. Sato, W. Mori, Y. Xie, N. Kanehisa, Y. Kai, M. Fujii, S. Goto, E. Nagai, Y. Nakao. *Inorg. Chim. Acta.*, **359**, 2271 (2006); (f) M.A.S. Goher, A.A. Youssef, F.A. Mautner. *Polyhedron*, **25**, 1531 (2006); (g) Z.L. Lu, M. Yuan, F. Pan, S. Gao, D.Q. Zhang, D. B. Zhu. *Inorg. Chem.*, **45**, 3538 (2006); (h) W. Ouellette, J.R. Galán-Mascarós, K.R. Dunbar, J. Zubieta. *Inorg. Chem.*, **45**, 1909 (2006).

[10] J.L. Burmeister. *Coord. Chem. Rev.*, **3**, 225 (1968).

[11] A. H.Norbury, A.J.P.Q. Sinha. *Rev., Chem. Soc.*, **24**, 69 (1970).

[12] R. Vicente, A. Escuer, E. Peñalba, X. Solans, M. Font-Bardía. *Inorg. Chim. Acta*, **255**, 7 (1997).

[13] R.K. Bhubon Singh, K.M. Abdul Malik, S.O.G. Mahalli, M.S. El Fallah, N.K. Karan, S. Mitra. *Inorg. Chem. Commun.*, **4**, 315 (2001).

[14] (a) K. Kozísek, M. Kabesová. *Polyhedron*, **9**, 1029 (1990); (b) J.Soldánová, M. Kabesová, J. Gajo. *Inorg. Chim. Acta*, **76**, 203 (1983); (c) R.E. Marsh. *Acta Crystallogr., Sect. B*, **55**, 931 (1999).

[15] C. Diaz, J. Ribas, N. Sanz, X. Solans, M. Font-Bardia. *Inorg. Chim. Acta*, **286**, 169 (1999).

[16] H.Y. Bie, J.H. Yu, J.Q. Xu, J. Lu, Y. Li, X.B. Cui, X. Zhang, Y.H. Sun, L.Y. Pan. *J. Mol. Struc.*, **660**, 107 (2003).

[17] B. Żurowska, J. Mrozinski, M. Julve, F. Lloret, A. Maslejova, W. Sawka-Dobrowolska. *Inorg. Chem.*, **41**, 1771 (2002).

[18] G.M. Sheldrick. *SHELXTL: Structure Determination Software Programs*, *Bruker Analytical X-ray System*, Inc., Madison, WI, USA (1997).

[19] D. Bose, J. Banerjee, S.H. Rahaman, G. Mostafa, H.K. Fun, R.D.B. Walsh, M.J. Zaworotko, B.K. Ghosh. *Polyhedron*, **23**, 2045 (2004).

[20] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York (1978).