Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polyhedron 24 (2005) 343–350

POLYHEDRON

www.elsevier.com/locate/poly

Synthesis, crystal structure, and magnetic properties of binuclear Mn^{III}-azido and 1D polymeric Mn^{II}-$\mu_{1,3}$-thiocyanato novel species based on a neutral hexadentate Schiff base

Soma Deoghoria [a], Sujit K. Bera [a], Brian Moulton [b], Michael J. Zaworotko [b], Jean-Pierre Tuchagues [c], Golam Mostafa [d], Tian-Huey Lu [d], Swapan K. Chandra [a,*]

[a] *Department of Chemistry, The University of Burdwan, Burdwan 713104, India*
[b] *Department of Chemistry, University of South Florida, 4202 E. Fowler Avenue, SCA 400, Tampa, FL 33620, USA*
[c] *Laboratoire de Chimie de Coordination du CNRS, UPR 8241, 205 route de Narbonne, 31077 Toulouse Cedex, France*
[d] *Physics Department, National Tsing Hua University, Hsinchu 300, Taiwan, ROC*

Received 18 October 2004; accepted 30 November 2004
Available online 29 December 2004

Abstract

A binuclear manganese(III) complex $[Mn_2(L^1)(N_3)_6]$ (**2**) and an unprecedented 1D chain of manganese(II) binuclear units bridged by two end-to-end thiocyanato anions $\{[Mn_2^{II}(L^1)(NCS)_4] \cdot 2CH_3CN\}_n$ (**3** · $2CH_3CN$) have been prepared from *N*-(1-pyridin-2-ylbenzylidene)-*N'*-[2-({2-[(1-pyridin-2-ylbenzylidene)amino]ethyl}amino)ethyl]ethane-1,2-diamine (L), manganese(II) salts and azide/thiocyanate anions in air. L^1, *N*-(1-pyridin-2-ylbenzylidene)-*N*-[2-(4-{2-[(1-pyridin-2-ylbenzylidene)amino]ethyl}piperazin-1-yl)ethyl]amine, results from an alkylating cyclization of the flexible hexadentate Schiff base L occurring along the course of the complexation reactions. Both complexes have been characterized by single crystal X-ray diffraction studies. The Mn centres of complexes **2** and **3** are in distorted octahedral (**2**: $Mn^{III}N_6$, **3**: $Mn^{II}N_5S$) coordination environments with intramolecular Mn···Mn distance (**2**: 6.473(2) Å, **3**: 6.437(1) Å) consistent with the absence of intramolecular magnetic interactions. Compound **3**, exhibits weak intermolecular antiferromagnetic interactions ($J = -1.5$ cm^{-1}) between pairs of Mn^{II} ions bridged via two $\mu_{1,3}$-NCS.
© 2004 Elsevier Ltd. All rights reserved.

Keywords: Schiff bases; Alkylating cyclization; Pseudo-halide bridges; Manganese polynuclear complexes; 1D Chains; Magnetic exchange interactions

---

1. Introduction

Coordination chemistry of manganese compounds is an area of considerable interest [1]. These complexes are significant not only for their redox active role in several biochemical processes, but also for the diversity of their magnetic properties [2–4]. Bridging ligands play an important role in the magnetic exchange pathways between paramagnetic centres: pseudo-halides (N_3^-, NCS^-, NCO^-) have been well documented for their numerous bonding abilities leading to various species [5]. End-on ($\mu_{1,1}$-N_3/NCS/NCO) [6] and end-to-end ($\mu_{1,3}$-N_3/NCS/NCO) [7] bridged complexes are known to mediate ferromagnetic [8] and antiferromagnetic [9] exchange interactions, respectively. The use of polydentate ligands, especially polynucleating ones, is an efficient way for assembling metal centres in close proximity, thus ensuring electronic communication. Coordination compounds including both polydentate ligands and suitable bridging anions such as

---

[*] Corresponding author. Tel.: +91 342 2557814; fax: +91 342 2557938.
E-mail address: dr_swapan@sify.com (S.K. Chandra).

0277-5387/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2004.11.014

pseudo-halide ions capable of propagating magnetic interactions between paramagnetic centres play an important role in the area of molecular magnetism [3–10].

We report here on the unusual behaviour of a flexible hexadentate ligand, *N*-(1-pyridin-2-ylbenzylidene)-*N*′-[2-({2-[(1-pyridin-2-ylbenzylidene)amino]ethyl}amino)ethyl] ethane-1,2-diamine, (L, Scheme 1) resulting from the bis-condensation reaction of 2-benzoylpyridine and triethylenetetramine. While $[Mn^{II}L](ClO_4)_2$ (**1**) resulted from the reaction of L with manganese(II) perchlorate, the binuclear complex $[Mn_2^{III}(L^1)(N_3)_6]$ (**2**) and the 1D polymer $\{[Mn_2^{II}(L^1)(NCS)_4]\cdot 2CH_3CN\}_n$ (**3** · 2CH$_3$CN) resulted from the reaction of L and manganese(II) salts, in the presence of sodium azide (**2**) or ammonium thiocyanate (**3**), respectively. L^1, *N*-(1-pyridin-2-ylbenzylidene)-*N*-[2-(4-{2-[(1-pyridin-2-ylbenzylidene)amino]-ethyl}piperazin-1-yl)ethyl]amine, results from an alkylating cyclization of L. The synthesis, characterization including X-ray structure, and magnetic properties of the novel compounds **2** and **3** are described in this report.

2. Experimental

2.1. Materials

Triethylenetetramine, 2-benzoylpyridine, sodium azide and ammonium thiocyanate were purchased from Lancaster and used as received. All other solvents and chemicals were of analytical grade. The hexadentate ligand (L) was prepared as reported previously and gave satisfactory elemental analysis [11].

2.2. Synthesis of complexes

2.2.1. $[Mn^{II}L](ClO_4)_2$ (*1*)

A methanolic solution (4 cm^3) of the L ligand (0.239 g, 0.5 mmol) was added dropwise to a methanolic solution (4 cm^3) of $Mn(ClO_4)_2\cdot 6H_2O$ (0.181 g, 0.5 mmol) with constant stirring for 1 h at room temperature. The orange-red compound of composition $[MnL](ClO_4)_2$ (**1**) was filtered off, washed with methanol and dried under vacuum. Yield: 0.220 g, ~60%. *Anal.* Calc. for $C_{30}H_{32}N_6O_8Cl_2Mn$: C, 49.33; H, 4.42; N, 11.51, Mn, 7.52. Found : C, 49.28; H, 4.53; N, 11.39; Mn, 7.37%.

2.2.2. $[Mn_2^{III}(L^1)(N_3)_6]$ (*2*)

To a methanolic solution (5 cm^3) of $MnCl_2\cdot 4H_2O$ (0.396 g, 2.0 mmol) was added 0.477 g (1.0 mmol) of the L ligand in methanol (15 cm^3) over a period of 15 min. To the resulting deep orange solution, an aqueous solution of sodium azide (0.260 g, 6.0 mmol, 8 cm^3 H_2O) was added slowly. The solution was then filtered and the filtrate was left to stand. Within 2–3 days of slow evaporation a black compound was obtained. This resulting compound was dissolved in dichloromethane (~12 cm^3) and layered with hexane (~36 cm^3). After about 5 days black prismatic crystals suitable for X-ray analysis were obtained. Yield: 0.225 g, ~27%. *Anal.* Calc. for $C_{32}H_{34}N_{24}Mn_2$: C, 44.41; H, 3.96; N, 38.88, Mn, 12.70. Found: C, 44.48; H, 3.82; N, 38.76; Mn, 12.62%.

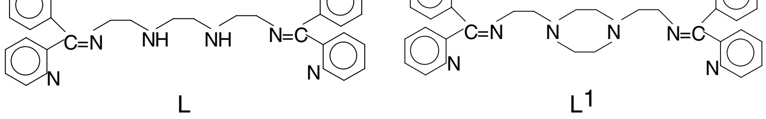
2.2.3. $\{[Mn_2^{II}(L^1)(NCS)_4]\cdot 2CH_3CN\}_n$ (*3* · 2CH$_3$CN)

Compound **3** was synthesized by slow addition of an acetonitrile solution (12 cm^3) containing the L ligand (0.239 g, 0.5 mmol) to an acetonitrile solution (16 cm^3) of $Mn(ClO_4)_2\cdot 6H_2O$ (0.362 g, 1.0 mmol) with constant stirring for 30 min. To the resulting solution, an aqueous solution of ammonium thiocyanate (0.152 g, 2.0 mmol, 12 cm^3 H_2O) was added slowly with constant stirring for 15 min. The resulting solution was left to stand at room temperature and after several days, orange, prismatic, X-ray quality single-crystal were obtained. Due to solvent loss when the crystals are taken out of the mother solution, the fully desolvated (under vacuum) sample subjected to elemental analyses had the formulation $[Mn_2^{II}(L^1)(NCS)_4]_n$ (**3**). Yield: 0.138 g, ~17%. *Anal.* Calc. for $C_{36}H_{34}N_{10}S_4Mn_2$: C, 51.18; H, 4.06; N, 16.58, Mn, 13.0. Found: C, 51.06; H, 3.92; N, 16.39; Mn, 12.74%.

CAUTION: *Perchlorate salts and azido compounds are potentially explosive especially in the presence of organic compounds. They must be prepared and handled in small amounts, and with special care.*

2.3. Physical measurements

Elemental analyses for C, H and N were performed using a Perkin Elmer 2400II elemental analyzer. Manganese contents were determined by titrimetric methods. IR spectra (4000–400 cm^{-1}) were recorded on KBr pellets at 298 K using a JASCO FT/IR-420 spectrometer. Magnetic data were obtained with a Quantum Design MPMS SQUID susceptometer. Magnetic susceptibility



Scheme 1. The hexadentate Schiff base ligands L and L^1.

measurements were performed in the 2–300 K temperature range in a 1 T applied magnetic field, and diamagnetic corrections were applied by using Pascal's constants [12]. The magnetic susceptibility has been computed by exact calculation of the energy levels associated to the spin Hamiltonian through diagonalization of the full matrix with a general program for axial symmetry [13]. Least-squares fittings were accomplished with an adapted version of the function-minimization program MINUIT [14].

2.4. Crystal structures determination and refinement

Single-crystals suitable for X-ray crystallographic analysis were selected following examination under a microscope. X-ray data of **2** were collected at 293 K with a Siemens SMART CCD diffractometer. Crystals of $\{[\mathrm{Mn_2}^{\mathrm{II}}(\mathrm{L}^1)(\mathrm{NCS})_4]\cdot 2\mathrm{CH_3CN}\}_n$ ($\mathbf{3}\cdot 2\mathrm{CH_3CN}$) were quickly coated with an inert oil to prevent solvent loss and the X-ray data were collected at 200 K on a Bruker-AXS SMART APEX/CCD diffractometer. Both data collections were carried out using Mo Kα radiation ($\lambda = 0.71073$ Å) in an $\omega - 2\theta$ scan mode. 11942 reflections were collected for **2**, of which 4434 were independent ($R_{\mathrm{int}} = 0.056$) and 14195 reflections for **3**, of which 5227 were independent ($R_{\mathrm{int}} = 0.039$). In both cases, intensity data were corrected for Lorentz and polarization effects. Empirical absorption corrections were made based on ψ-scans for **2** [15] and using the SADABS program [16] for **3**. The structures were solved by direct methods and the structure solution and refinement was based on $|F|^2$. All non-hydrogen atoms were refined with anisotropic displacement parameters except those of the disordered acetonitrile which were refined isotropically. Even when located in the Fourier map, hydrogen atoms were placed in calculated positions and given isotropic U values 1.2 times that of the atom to which they are bonded. Acetonitrile hydrogen atoms were neither located nor placed in calculated positions. The atomic scattering factors and anomalous dispersion terms were taken from the standard compilation [17]. All crystallographic calculations were carried out using SHELX-97 [18] and ORTEP-3 [19] program packages. The crystal data and data collection details are gathered in Table 1.

Table 1
Crystallographic data for **2** and $\mathbf{3}\cdot 2\mathrm{CH_3CN}$

Compound	**2**	$\mathbf{3}\cdot 2\mathrm{CH_3CN}$
Formula	$\mathrm{C_{32}H_{34}N_{24}Mn_2}$	$\mathrm{C_{40}H_{40}N_{12}S_4Mn_2}$
Formula weight	864.71	926.96
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
Temperature (K)	293	200
a (Å)	8.8709(19)	7.8187(12)
b (Å)	9.770(2)	12.0249(18)
c (Å)	25.036(5)	12.1189(18)
α (°)	90	81.291(2)
β (°)	109.482(7)	87.416(2)
γ (°)	90	86.716(2)
V (Å^3)	2045.6(7)	1123.7(3)
Z	2	1
λ (Å)	0.71073	0.71073
$\rho_{\mathrm{calc.}}$ (g cm^{-3})	1.404	1.361
μ (Mo Kα) (mm^{-1})	0.675	0.791
R^{a}	0.0527	0.0413
wR^{b}	0.0798	0.1005

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$.

[b] $R_w = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o{}^2|^2]^{1/2}$.

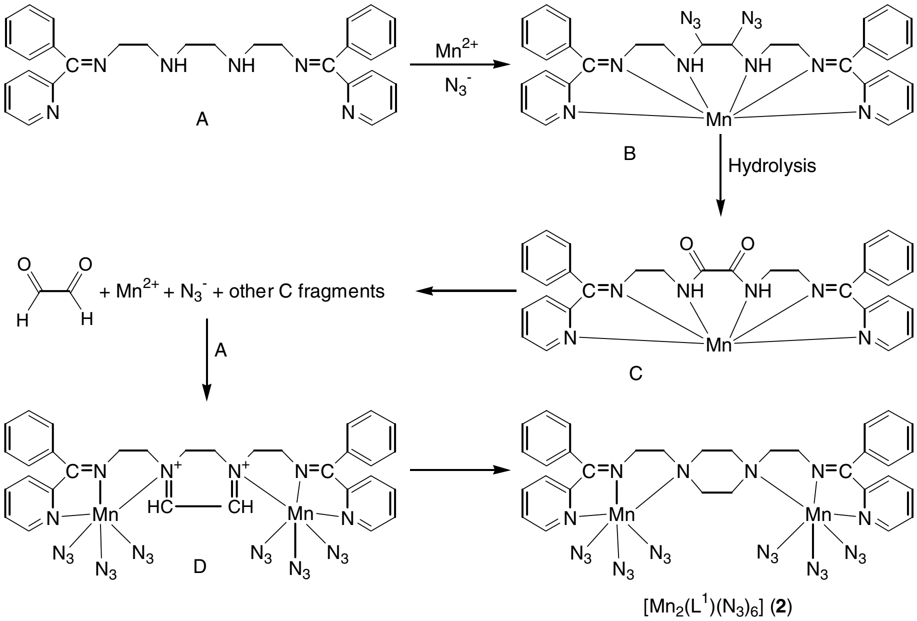
3. Results and discussion

3.1. Synthesis

The reaction of L with manganese(II) perchlorate hexahydrate using a 1:1 molar ratio in methanol/water or acetonitrile/water mixtures yielded an orange-red compound (**1**) formulated $[\mathrm{Mn^{II}L}](\mathrm{ClO_4})_2$ on the basis of elemental analyses and IR data. The crystal structure of the nickel analogue $[\mathrm{NiL}](\mathrm{ClO_4})_2$, prepared by a similar synthetic route evidenced a monomeric $\mathrm{Ni^{II}}$ compound where the hexadentate $\mathrm{N_6}$ ligand is L (no L to L^1 rearrangement) [20].

On the other hand, a manganese(III) binuclear crystalline complex, $[\mathrm{Mn_2}^{\mathrm{III}}(\mathrm{L}^1)(\mathrm{N_3})_6]$ (**2**) has been prepared in methanol/water from manganese(II) salts, L, and sodium azide (2:1:6 (or 2:1:4) molar ratio) in air. The same reactions carried out in acetonitrile/water instead of methanol/water yielded compound **1**, i.e., no L to L^1 rearrangement. Reaction of manganese(II) salts, L, and ammonium thiocyanate (2:1:4 (or 2:1:6) molar ratio) in acetonitrile/water yielded orange crystals of an unprecedented 1D chain of manganese(II) binuclear units bridged by $\mu_{1,3}$-NCS anions, $\{[\mathrm{Mn_2}^{\mathrm{II}}(\mathrm{L}^1)(\mathrm{NCS})_4]\cdot 2\mathrm{CH_3CN}\}_n$ ($\mathbf{3}\cdot 2\mathrm{CH_3CN}$). The same reactions carried out in methanol/water instead of acetonitrile/water yielded compound **1**, i.e., no L to L^1 rearrangement.

The rearrangement from L to L^1 (Scheme 2), consisting in an alkylating cyclization centred on the two secondary amine functions of L, occurred exclusively along the course of complexation reactions where a pseudo-halide was involved in addition to L and a metal salt in the required solvent (methanol/water for **2**, and acetonitrile/water for **3**). L^1 could not be identified from reaction media devoid either of pseudo-halide or of metal salt, or carried out in different solvent mixtures. Similar rearrangement reactions also occurred with nickel(II) salts and pseudo-halides [11]. However, replacement of pseudo-halides by halides did not yield rearrangement of L to L^1. In addition, the poor yields of **2** and **3** suggest that the extra $-\mathrm{CH_2}$–$\mathrm{CH_2}-$ fragment present in L^1 compared to L most probably originates from the L ligand itself. A plausible mechanism for this



Scheme 2. A plausible mechanism for the alkylating cyclization of L to L^1 (case of complex **2**).

alkylating cyclization of L to L^1 may involve the following steps: (a) pseudo-halides in the presence of manganese ions may undergo a nucleophilic attack on the $–CH_2–CH_2–$ bridge located between the two secondary amine functions of L (A), producing a di-azido (-thiocyanato) (B) intermediate which on subsequent hydrolysis would generate an oxamido-like derivative (C) [21]; (b) this oxamido-like derivative would break down, producing glyoxal and C fragments; (c) glyoxal would then react, most possibly through a metal assisted concerted route, with the two secondary amine functions of another L ligand molecule, producing a di-imminium-like intermediate (D) [22], that would be subsequently reduced to L^1.

The role of the solvent with regard to the formation of compounds **2** or **3** is also remarkable. Indeed, while formation of **3** only requires the L to L^1 rearrangement, formation of **2** requires manganese oxidation from the +2 to the +3 state, in addition to the L to L^1 rearrangement. A possible explanation is that the stronger σ donor ability of the azido anion favours oxidation of the manganese centres in the presence of methanol, allowing formation of the $[Mn_2^{III}(L^1)(N_3)_6]$ (**2**) species. This oxidation may be further assisted by coordination of two extra azido ligands per binuclear unit, yielding the neutral hexacoordinated complex **2**. On the other hand, while the weaker σ donor ability of NCS does not favour oxidation of manganese centres, the presence of the very weakly coordinating acetonitrile solvent allows bridging of manganese(II) binuclear units into the 1D chain of **3** through $\mu_{1,3}$-NCS anions. Finally, formation of **1** in the reaction conditions of **2** or **3**, but in the absence of the required solvent (MeOH for **2** and CH_3CN for **3**), i.e. absence of L to L^1 rearrangement, indicates that at least one intermediate in this ligand rearrangement results from an equilibrium reaction: precipitation of the resulting complex (**2** or **3**) is most probably the driving force allowing the L to L^1 rearrangement.

3.2. IR spectroscopy

The IR spectrum of **2** exhibits a very strong absorption at 2040 cm^{-1} corresponding to the azido asymmetric stretching vibrations [6b,6c]. The IR spectrum of **3** exhibits strong absorptions at 2098 and 2053 cm^{-1} corresponding to the N,S-bonded thiocyanate ions [10a,10f]. The absorptions corresponding to the ν(C=N) stretches of L^1 are located at 1639 and 1590 cm^{-1} and 1633 and 1588 cm^{-1} for compounds **2** and **3**, respectively [10a,10f].

4. X-ray structures

4.1. $[Mn_2^{III}(L^1)(N_3)_6]$ (2)

The molecular structure of **2** consists of isolated binuclear molecules. The ORTEP drawing of the centrosymmetric binuclear unit with atom labeling scheme is shown in Fig. 1 and selected bond distances and angles are listed in Table 2.

Each manganese atom is located in a distorted octahedral N_6 coordination environment, with three nitrogen atoms from L^1 (N1, N2 and N3) and three nitrogen donors from terminal azido groups (N4, N7 and N10). The Mn–N(L^1) distances are in the

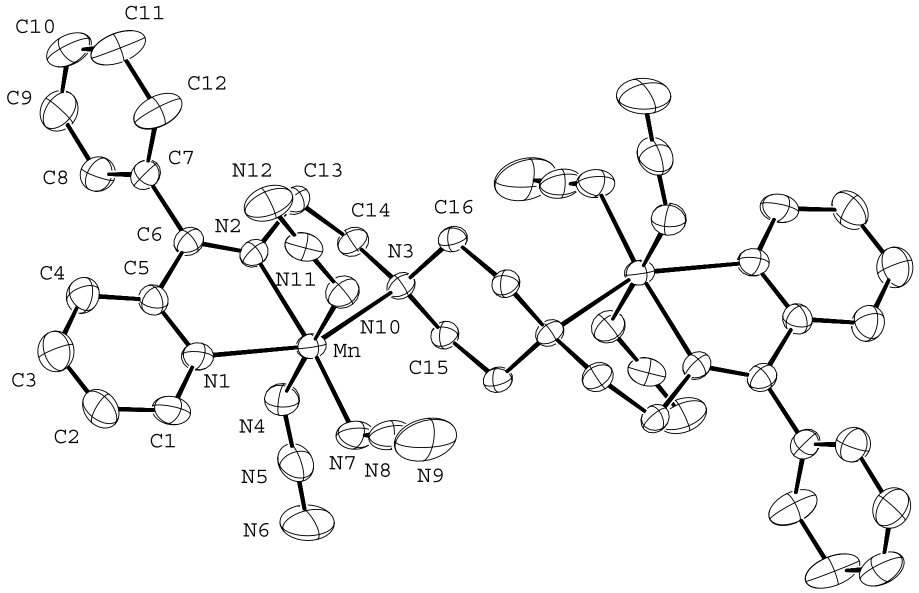


Fig. 1. ORTEP plot with atom labeling scheme for $[Mn_2(L^1)(N_3)_6]$ (**2**). For clarity the hydrogen atoms are omitted.

Table 2
Selected bond lengths (Å) and angles (°) for $[Mn_2(L^1)(N_3)_6]$ (**2**)

Bond lengths			
Mn–N1	2.249(3)	Mn–N2	2.094(3)
Mn–N3	2.395(3)	Mn–N4	1.949(3)
Mn–N7	1.955(4)	Mn–N10	1.962(3)
Bond angles			
N1–Mn–N2	73.76(10)	N1–Mn–N3	152.01(10)
N1–Mn–N4	90.74(12)	N1–Mn–N7	99.93(12)
N1–Mn–N10	90.41(13)	N2–Mn–N3	78.35(10)
N2–Mn–N4	91.24(12)	N2–Mn–N7	173.59(12)
N2–Mn–N10	89.01(12)	N3–Mn–N4	87.46(11)
N3–Mn–N7	108.00(11)	N3–Mn–N10	91.48(10)
N4–Mn–N7	89.94(13)	N4–Mn–N10	178.84(12)
N7–Mn–N10	89.94(13)	N4–N5–N6	177.8(5)
N7–N8–N9	174.8(5)	N10–N11–N12	177.9(4)

2.094(3)–2.395(3) Å range, while the Mn–N(azido) distances are almost equal (1.949(3)–1.962(3) Å range). It is worth noting that none of the azido anions behaves as a bridging ligand: this unusual azido coordination mode [6,7] may originate from the L to L^1 rearrangement. Due to the presence of the central $–N(–CH_2–CH_2–)_2N–$ cycle in L^1, the intramolecular Mn···Mn distance in complex **2** is quite large (6.473(2) Å).

4.2. $\{[Mn_2^{II}(L^1)(NCS)_4]\cdot 2CH_3CN\}_n$ (**3**)

The structure of $\mathbf{3}\cdot 2CH_3CN$ (Fig. 2) consists of centrosymmetric binuclear $[Mn_2^{II}(L^1)(NCS)_4]$ repeat units doubly $\mu_{1,3}$-NCS bridged into 1D chains extending along a. Selected bond distances and angles are listed in Table 3.

The octahedral coordination sphere around each manganese(II) consists of three nitrogen donors from L^1 (N3, N4 and N5, 2.183(2)–2.390(2) Å), two nitrogen donors from thiocyanate anions (N1 (2.090(2) Å) from an end-to-end NCS bridge and N2 (2.097(2) Å) from a terminal NCS), and one sulfur donor (S2) (3.084(1) Å) from another end-to-end NCS. This end-to-end thiocyanato bridging mode has already been observed, with corresponding M–S distances either in the 2.6–2.9 Å range [23], or in the longer 3.11–3.18 Å range [10f], the latter suggesting weak M···S interactions rather than the covalent bonding suggested by the former. The intermediate 3.084 Å value observed for 3 is close to the lower limit for weak M···S interactions preventing us to qualify this Mn···S interaction as a covalent bonding. The N_5S coordination sphere is severely distorted from octahedral symmetry, with quite large deviations from the regular *cis* and *trans* angles and large axial distortion evidenced by the quite long Mn–S distance. The intradimer $Mn^{II}\cdots Mn^{II}$ separation (6.437(1) Å), originating from the presence of the central $–N(–CH_2–CH_2–)_2N–$ cycle in L^1, is understandably quite similar to that in complex **2**, and slightly longer than the interdimer $Mn^{II}\cdots Mn^{II}$ distance (6.203(1) Å).

4.3. Magnetic properties

As expected from the large intramolecular $Mn^{III}\cdots Mn^{III}$ separation and nature of the polyatomic bridge, and absence of intermolecular contacts in compound **2**, there are no pathways for intra- and/or intermolecular magnetic interactions, as indicated by the paramagnetic behaviour of this binuclear compound. Its $\chi_M T$ product of 5.97 $cm^3\,K\,mol^{-1}$, close to the spin-only value for two non-interacting $S = 2$ ions, is constant over the whole 300–25 K temperature range and decreases from 5.78 (25 K) to 2.44 $cm^3\,K\,mol^{-1}$ (1.95 K) due to single-ion zero fields splitting (ZFS) of

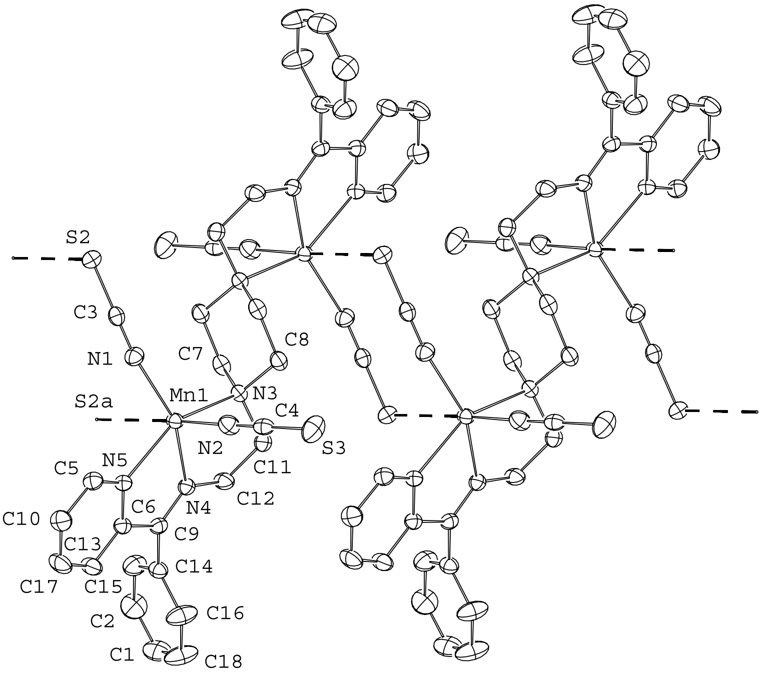


Fig. 2. ORTEP plot with atom labelling scheme of the $[Mn_2^{II}(L^1)(NCS)_4]_n$ 1D polymeric chain of ($\mathbf{3} \cdot 2CH_3CN$). For clarity the hydrogen atoms and solvent molecules are omitted.

Table 3
Selected bond lengths (Å) and angles (°) for $\mathbf{3} \cdot 2CH_3CN$

Bond lengths			
Mn–N1	2.0897(18)	Mn–N2	2.097(2)
Mn–N3	2.3897(18)	Mn–N4	2.1832(18)
Mn–N5	2.2436(17)	Mn···S2a	3.084(1)
Bond angles			
N1–Mn–N2	99.60(7)	N1–Mn–N3	108.00(7)
N1–Mn–N4	152.62(7)	N1–Mn–N5	100.46(7)
N2–Mn–N3	90.76(7)	N2–Mn–N4	107.50(7)
N2–Mn–N5	97.54(7)	N3–Mn–N4	76.02(6)
N3–Mn–N5	148.56(6)	N4–Mn–N5	72.55(6)
N1–Mn–S2a	82.90(6)	N2–Mn–S2a	177.41(7)
N3–Mn–S2a	89.08(5)	N4–Mn–S2a	69.96(5)
N5–Mn–S2a	81.30(4)	N1–C3–S2	179.2(2)
N2–C4–S3	179.3(2)		

Symmetry operation *a*: $1 - x$, $1 - y$, $-z$.

high-spin Mn^{III}. This result being perfectly consistent with the severe distortion of the MnN_6 octahedron evidenced by the crystal structure, we did not attempt to fit these data.

The experimental $\chi_M T$ product of **3** (desolvated crystals) smoothly decreases from 8.48 $cm^3\ K\ mol^{-1}$ at 300 K (slightly below the spin-only value for two non-interacting $S = 5/2$ ions) to 7.61 $cm^3\ K\ mol^{-1}$ at 80 K, and then sharply, down to 0.67 $cm^3\ K\ mol^{-1}$ at 1.96 K, clearly indicating operation of antiferromagnetic interactions in **3**. While no intramolecular magnetic interaction is expected between the Mn^{II} centres of **3** (same rationale as for **2**), weak intermolecular interactions are expected to be mediated by the double end-to-end thiocyanate bridges between binuclear $[Mn_2^{II}(L^1)\ (NCS)_4]$ repeat units along the 1D chains [9]. Taking into account the absence of intramolecular magnetic interaction between the Mn^{II} ions of binuclear constituting units, the overall magnetic behaviour of **3** can not result from extended magnetic interactions along 1D chains, but from pairwise interactions between Mn^{II} bridged by two NCS anions; in other words, the structural constituting units of complex **3** do not correspond to the magnetically interacting pairs.

The experimental magnetic susceptibility data (χ_M, lozenges in Fig. 3) were thus fitted by using the theoretical magnetic susceptibility calculated by exact diagonalization of the effective spin Hamiltonian for a pair of interacting $S_1 = S_2 = 5/2$ ions, taking into account single-ion ZFS: $\hat{H} = -2J\hat{S}_1\hat{S}_2 + D\hat{S}_Z^2$. The best fit (solid lines in

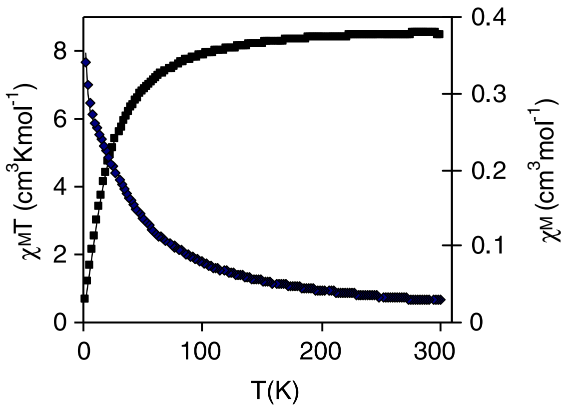


Fig. 3. χ_M and $\chi_M T$ vs. T data for complex **3**. Solid lines represent the best fit of the data with the model described in the text.

Fig. 3) was obtained for the following set of parameters: $J = -1.5\ \mathrm{cm}^{-1}$, $D = -2 \times 10^{-4}\ \mathrm{cm}^{-1}$, $g = 1.996$, and 1.4% of paramagnetic impurity. This result is in good agreement with the presence of a weak antiferromagnetic interaction between the binuclear $[\mathrm{Mn_2}^{\mathrm{II}}(\mathrm{L}^1)(\mathrm{NCS})_4]$ repeat units along the 1D chains of **3**. The negligible single $\mathrm{Mn^{II}}$ ion ZFS value, *D*, is in agreement with the expectation for a d^5 shell. The fit evidenced as well a low contribution from temperature independent paramagnetism (TIP = 1.2×10^{-4}). Finally, attempts made to take into account additional inter-pair interactions (molecular field approximation according to Ginsberg and Lines' approach [24]) also yielded a negligible value of the intermolecular interaction parameter zj', thus confirming that the magnetic behaviour of **3** does not result from extended magnetic interactions along 1D chains, but from pairwise interactions between $\mathrm{Mn^{II}}$ ions.

5. Concluding remarks

Upon reaction with metal salts the Schiff base L, resulting from the bis-condensation of triethylenetetramine and 2-benzoylpyridine, behaves as a straightforward hexadentate ligand, yielding mononuclear complexes where the metal centre is coordinated to the six nitrogen donors of L. On the other hand, when such reactions are conducted in suitable solvents and in the presence of pseudo-halides ($\mathrm{N_3}^-$, NCS^-) a rearrangement from L to L^1, consisting in an alkylating cyclization centred on the two secondary amine functions of L, systematically occurs. In the case of manganese(II), the reaction between the product L^1 and the metal assisting this rearrangement depends on the pseudo-halide and solvents used: while a binuclear manganese(III) complex, $[\mathrm{Mn_2(L^1)(N_3)_6}]$ (**2**) is obtained in the case of azido anions in methanol/water mixtures, a polymeric manganese(II) compound, $\{[\mathrm{Mn_2}^{\mathrm{II}}(\mathrm{L}^1)(\mathrm{NCS})_4] \cdot 2\mathrm{CH_3CN}\}_n$ (3.2CH$_3$CN), is obtained with thiocyanato anions in acetonitrile/water mixtures.

The Mn centres of complexes **2** and **3** are in distorted octahedral coordination environments (**2**: $\mathrm{Mn^{III}N_6}$, **3**: $\mathrm{Mn^{II}N_5S}$) with intramolecular Mn···Mn distance (**2**: 6.473(2) Å, **3**: 6.437(1) Å) consistent with the absence of intramolecular magnetic interactions. Compound **3**, the first example of manganese(II) 1D chain where binuclear units are bridged via two $\mu_{1,3}$-NCS anions, exhibits weak intermolecular antiferromagnetic interactions ($J = -1.5\ \mathrm{cm}^{-1}$) between pairs of $\mathrm{Mn^{II}}$ ions.

Acknowledgements

The authors thank the Council of Scientific and Industrial Research, New Delhi (S.K.C.: Grant No. 01(1836)/03/EMR-II) and University Grants Commission (under DSA program), New Delhi, for financial support. S.D. thanks The University of Burdwan for a fellowship.

Appendix A. Supplementary data

X-ray crystallographic files in CIF format for complexes **2** and **3**, CCDC Reference Nos. 172397 and 187481, respectively. This material is available free of charge via 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 deposit@ccdc.ca.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2004.11.014.

References

[1] (a) V.L. Pecoraro, W.-Y. Hsieh, in: A. Sigel, H. Sigel (Eds.), Metal Ions in Biological Systems: Manganese and its Role in Biological Processes, vol. 37, Marcel Dekker, New York, 2000, pp. 431–444;
(b) V.L. Pecoraro, Manganese Redox Enzymes, VCH, New York, 1992.

[2] (a) K. Weighardt, Angew. Chem., Int. Ed. Engl. 28 (1989) 1153;
(b) G.C. Dismukes, Chem. Rev. 96 (1996) 2909;
(c) W. Ruttinger, G.C. Dismukes, Chem. Rev. 97 (1997) 1.

[3] (a) O. Kahn, Molecular Magnetism, VCH, New York, 1993;
(b) D. Gatteschi, O. Kahn, J.S. Miller, F. Palacio, Magnetic Molecular Materials, NATO ASI, Kluwer, Dordrecht, 1991.

[4] (a) M.A.M. Abu-Youssef, M. Drillon, A. Escuer, M.A.S. Goher, F.A. Mautner, R. Vicente, Inorg. Chem. 39 (2000) 5022;
(b) J.-P. Costes, F. Dahan, B. Donnadieu, M.-J. Rodriguez Douton, A. Bousseksou, J.-P. Tuchagues, Inorg. Chem. 43 (2004) 2736;
(c) N. Matsumoto, Y. Sunatsuki, H. Miyasaka, Y. Hashimoto, D. Luneau, J.-P. Tuchagues, Angew. Chem., Int. Ed. Eng. 38 (1999) 171;
(d) K.R. Reddy, M.V. Rajasekharan, J.-P. Tuchagues, Inorg. Chem. 37 (1998) 5978;
(e) R. Sessoli, H.-L. Tsai, A.R. Schake, S. Wang, J.B. Vincent, K. Folting, D. Gatteschi, G. Christou, D.N. Hendrickson, J. Am. Chem. Soc. 115 (1993) 1804;
(f) R. Sessoli, D. Gatteschi, A. Caneschi, M. Novak, Nature 365 (1993) 141;
(g) C. Palopoli, B. Chansou, J.-P. Tuchagues, S. Signorella, Inorg. Chem. 39 (2000) 1458.

[5] K. Vrieze, G. van Koten, in: G. Wilkinson, R.D. Gillard, J.A. McLeverty (Eds.), Comprehensive Coordination Chemistry, vol. 2, Oxford, England, 1987, p. 225.

[6] (a) A. Escuer, R. Vicente, J. Ribas, X. Solans, Inorg. Chem. 34 (1995) 1793;
(b) R. Cortes, J.I. Ruiz de Larramendi, L. Lezama, T. Rojo, K. Urtiaga, M.I. Arriortua, J. Chem. Soc., Dalton Trans. (1992) 2723;
(c) M.G. Barandika, R. Cortes, L. Lezama, M.K. Urtiaga, M.I. Arriortua, T. Rojo, J. Chem. Soc., Dalton Trans. (1999) 2971;
(d) J. Cano, G.D. Munno, F. Lloret, M. Julve, Inorg. Chem. 39 (2000) 1611;
(e) M.I. Arriortua, R. Cortes, J.L. Mesa, L. Lezama, T. Rojo, G. Villeneuve, Trans. Met. Chem. 13 (1988) 371.

[7] (a) A. Escuer, I. Castro, F. Mautner, M.S. El Fallah, R. Vicente, Inorg. Chem. 36 (1997) 4633;
(b) A. Escuer, R. Vicente, M.S. El Fallah, X. Solans, M. Font-Bardia, Inorg. Chim. Acta 278 (1998) 43;
(c) A. Escuer, R. Vicente, M.S. El Fallah, X. Solans, M. Font-Bardia, J. Chem. Soc., Dalton Trans. (1996) 1013.

[8] E. Ruiz, J. Cano, S. Alvarej, P. Alemany, J. Am. Chem. Soc. 120 (1998) 11122.

[9] F.F. de Biani, E. Ruiz, J. Cano, J.J. Novoa, S. Alvarej, Inorg. Chem. 39 (2000) 3221.

[10] (a) M.G. Borandika, M.L. Hernandez-Pino, M.K. Urtiaga, R. Cortes, L. Lezama, M.I. Arriortua, T. Rojo, J. Chem. Soc., Dalton Trans. (2000) 1469;
(b) M.J. Plater, M.R.J. Foreman, R.A. Howie, J.M.S. Skakle, Inorg. Chim. Acta 318 (2001) 175;
(c) T.K. Maji, P.S. Mukherjee, S. Koner, G. Mostafa, J.-P. Tuchagues, N.R. Chaudhuri, Inorg. Chim. Acta 314 (2001) 111;
(d) J.M. Clemente-Juan, C. Mackiewicz, M. Verelst, F. Dahan, A. Bousseksou, Y. Sanakis, J.-P. Tuchagues, Inorg. Chem. 41 (2002) 1478;
(e) S. Koner, S. Saha, K.-I. Okamoto, J.-P. Tuchagues, Inorg. Chem. 42 (2003) 4668;
(f) A.K. Boudalis, J.M. Clemente-Juan, F. Dahan, J.-P. Tuchagues, Inorg. Chem. 43 (2004) 1574;
(g) A.K. Boudalis, B. Donnadieu, V. Nastopoulos, J.M. Clemente-Juan, A. Mari, Y. Sanakis, J.-P. Tuchagues, S.P. Perlepes, Angew. Chem., Int. Ed. Eng. 43 (2004) 2266.

[11] S. Deoghoria, S. Sain, M. Soler, W.T. Wong, G. Christou, S.K. Bera, S.K. Chandra, Polyhedron 22 (2003) 257.

[12] P. Pascal, Ann. Chim. Phys. 19 (1910) 5.

[13] B. Mabad, P. Cassoux, J.-P. Tuchagues, D.N. Hendrickson, Inorg. Chem. 25 (1986) 1420.

[14] F. James, M. Roos, Comput. Phys. Commun. 10 (1975) 345.

[15] A.C.T. North, D.C. Phillips, F.S. Mathews, Acta Crystallogr. A 24 (1968) 351.

[16] SAINT+ v6.02. Bruker AXS, Madison, WI, USA, 1999.

[17] International Tables for Crystallography, vol. C, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992.

[18] G.M. Sheldrick, SHELX-97, Program for Solution of Crystal Structure, University of Göttingen, Germany, 1997.

[19] ORTEP-3 for Windows: L.J. Farrugia, J . Appl. Crystallogr. 30 (1997) 565.

[20] S. Deoghoria, S.K. Chandra, Unpublished results.

[21] P.A. Manis, M.W. Rathke, J. Org. Chem. 45 (1980) 4952.

[22] S.J. Benkovic, P.A. Benkovic, D.R. Comfort, J. Am. Chem. Soc. 91 (1969) 1860.

[23] (a) R. Vicente, A. Escuer, E. Peñalba, X. Solans, M. Font-Bardia, Inorg. Chim. Acta 255 (1997) 7;
(b) P. Gómez-Saiz, J. García-Tojal, F.J. Arnáiz, M.J. Maestro, L. Lezama, T. Rojo, Inorg. Chem. Commun. 6 (2003) 558;
(c) T.K. Maji, G. Mostafa, J.M. Clemente-Juan, J. Ribas, F. Lloret, K. Okamoto, N.R. Chaudhuri, Eur. J. Inorg. Chem. (2003) 1005.

[24] A.P. Ginsberg, M.E. Lines, Inorg. Chem. 11 (1972) 2289.