

A One-Dimensional Manganese(II) Coordination Polymer Derived from Zerovalent Manganese and 1-Hydroxybenzotriazole – Synthesis, Characterization, Crystal Structure and Magnetic Properties

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Keywords: Coordination polymers / Nitrogen heterocycles / Magnetic properties / Manganese / X-ray crystal structure

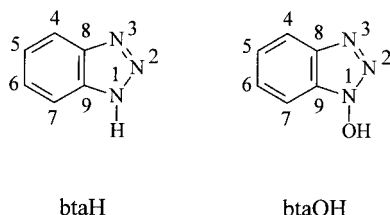
The reaction of zerovalent manganese with 1-hydroxybenzotriazole, btaOH, and NH_4SCN in DMF in the presence of dioxygen allows isolation of the one-dimensional coordination polymer $[\text{Mn}_3(\text{btaO})_2(\text{NCS})_4(\text{DMF})_8]_n$ (**3**). X-ray diffraction analysis reveals that the chain is best described as $[\text{Mn}_2(\text{btaO})_2(\text{NCS})_2(\text{DMF})_6]$ dimers linked by $\text{Mn}(\text{NCS})_2$ -

(DMF)₂ bridges. Molar magnetic susceptibility measurements of **3** in the 5–300 K range indicate weak antiferromagnetic coupling between the Mn^{II} atoms within the dinuclear subunits of the chain.

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Introduction

Over the last twenty years, we^[1] and others^[2] have been exploring the coordination chemistry of benzotriazole (btaH, Scheme 1) and its derivatives. The first reason for this is the anticorrosion properties of btaH and benzene ring-substituted benzotriazoles toward certain metals, particularly copper and its alloys.^[3] The second reason is the observation that reactions between metal β -diketonates or carboxylates and btaH or its ring-substituted (with non-donor groups) derivatives lead to incomplete replacement of β -diketonato or carboxylato ligands by the deprotonated benzotriazoles and the formation of large heteroleptic 3d-metal cages with unique structural motifs and exciting magnetic properties.^[1a,2b,2c] Thus, benzotriazolato ligands are amongst the most important in the field of high-nuclearity transition metal chemistry.



Scheme 1

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More recently,^[4,5] our efforts have turned towards the use of benzotriazoles, substituted on the azole ring with donor groups, to see how incorporation of this ligand type might affect the structures and physical properties of the products. The first ligand employed was 1-hydroxybenzotriazole (btaOH, Scheme 1). The synthetic investigation of the $[\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2]/\text{btaOH}$ reaction system in MeOH resulted in the isolation of the three-dimensional (3D), diamond-like polymeric complex $[\text{Cu}(\text{btaO})_2(\text{MeOH})]_n$ (**1**), which is a soft magnet exhibiting two critical temperatures at 6.4 and 4.4 K.^[4] Reaction of $[\text{Ni}(\text{NO}_3)_2] \cdot 6\text{H}_2\text{O}$ with btaOH in DMF/aqueous NH_3 has recently yielded the trinuclear complex $[\text{Ni}_3(\text{btaO})_6(\text{NH}_3)_6]$ (**2**).^[5]

In the present work, reactions of btaOH with zero-valent manganese were investigated. Zero-valent transition metals as starting materials are a good source for the construction of unusual polymeric and/or discrete metal complexes, which exhibit interesting magnetic properties and cannot be synthesised starting from conventional metal salts.^[6] The subject of the present paper is the 1D coordination polymer $[\text{Mn}_3(\text{btaO})_2(\text{NCS})_4(\text{DMF})_8]_n$ (**3**) which is the product of the reaction between Mn^0 , btaOH and NH_4SCN in DMF under aerobic conditions.

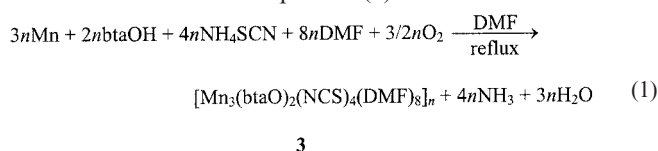
Transition metal coordination polymers are of considerable interest as magnetic, electronic and photooptical materials.^[7] Compounds with fascinating topologies and intricate interweaving of multiple networks have been discovered. Restricting further discussion to magnetic coordination polymers, we should mention that these molecular compounds may contain the same metal ion, two kinds of spin carriers (either two different metal ions or a metal ion and an organic radical) and, in a very limited number of cases,

three spin carriers. The attainment of magnetic ordering generally requires^[8] the organisation of transition metal centres into 3D networks. However, to better interpret magnetic properties of 3D coordination polymers, reduced dimensionalities (i.e. 1D and 2D) are preferred to develop the necessary theoretical models.^[9,10] In this context, 1D magnetic systems are being thoroughly investigated from both experimental and theoretical viewpoints.^[11]

Results and Discussion

Synthesis

The preparation of complex **3** can be achieved by the reaction of zero-valent manganese with btaOH and NH₄SCN in DMF under reflux in air for 2 h. This preparation is summarised in Equation (1).



In this reaction dioxygen is reduced to give H₂O and Mn is oxidized to Mn^{II}. The same product can be isolated from the 2:1:1, 1:1:1, 1:2:2, 1:2:3, 1:3:4, 1:4:4, 1:3:5, 1:4:5 and 1:5:5 Mn/btaOH/NH₄SCN reaction systems in DMF. When btaOH and/or SCN[−] are in excess the reaction proceeds faster (in less than 2 h) giving the same product in almost the same yield, while, when the quantities of btaOH and/or SCN[−] are less than the stoichiometric ones, the reaction proceeds more slowly and we do not observe complete dissolution of the Mn powder.

IR Spectra

The IR spectrum of **3** exhibits the ν(CN), ν(CS) and δ(NCS) modes at 2078, 787 and 478 cm^{−1}, respectively; these frequencies are typical of terminal isothiocyanato groups.^[12] The presence of coordinated DMF in **3** is manifested by a strong band at 1650 cm^{−1} and a medium intensity band at 1496 cm^{−1}, assigned to ν(C=O) and ν(C–N), respectively.^[13] The spectra of the sodium and potassium salts of 1-hydroxybenzotriazole (btaONa, btaOK) exhibit bands at 1178 and 1102 cm^{−1}, associated with the ν(N=N) and ν(N–N) vibrational modes, respectively.^[4] These bands are shifted to 1213 and 1128 cm^{−1}, respectively, in the spectrum of the complex; these shifts to higher frequencies are compatible with N(3) (Scheme 1) being the N-donor atom of btaO[−].^[1b] The band assignable to the N–O stretching vibration appears at 1224 cm^{−1} in the IR spectrum of btaOK.^[5] This band is shifted to 1155 cm^{−1} in the spectrum of **3** due to the coordination of the oxygen atom to the metal.^[4]

X-ray Crystal Structure

A labelled ORTEP^[14] drawing of the structure is shown in Figure 1. Selected distances and angles are listed in Table 1. The asymmetric unit of the one-dimensional (1D) polymer consists of three independent Mn^{II} atoms, Mn(2), Mn(1) and Mn(3). If we name the Mn(2), Mn(1) and Mn(3) ions as A, B and C, respectively, then a satisfactory way to describe this structure is to consider it as a chain of the alternating dimers CC and AA, which are connected via the Mn(1) ion (B) (Figure 2). Each dinuclear subunit (AA or CC) consists of two Mn^{II} atoms which are bridged by two μ₂-O atoms of two symmetry-related btaO[−] ligands, forming a planar four-membered ring (Mn₂O₂), in the centre

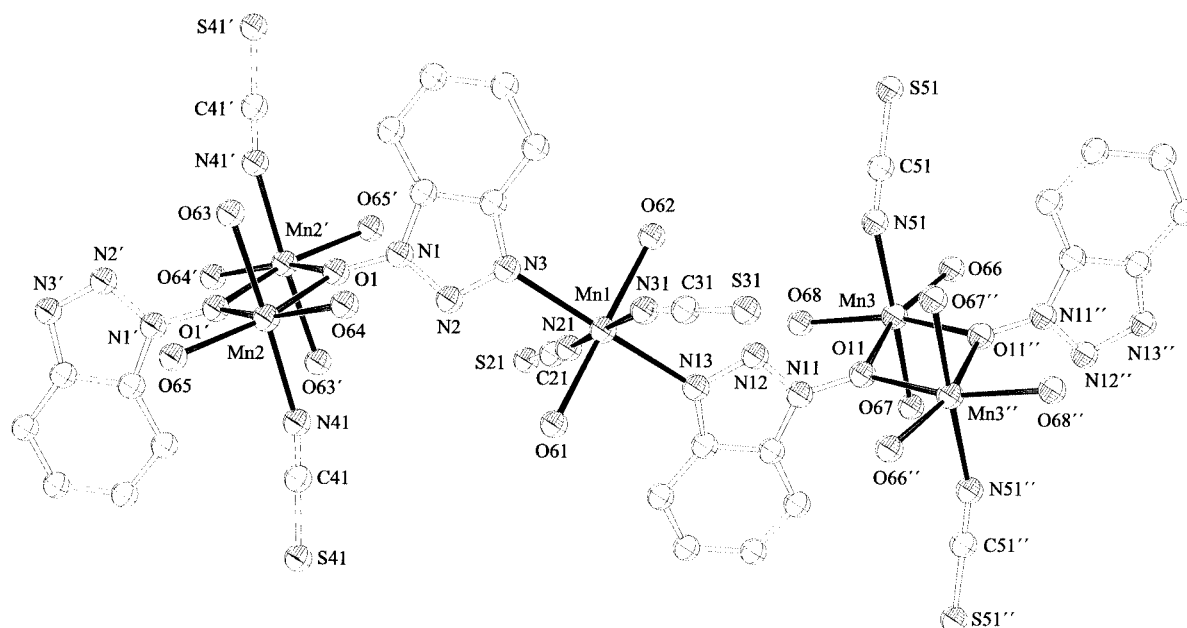


Figure 1. ORTEP plot of [Mn₃(btaO)₂(NCS)₄(DMF)₈]_n (**3**) at the 30% probability level; five Mn^{II} atoms are shown; all the carbon and nitrogen atoms of the DMF molecules, as well as all H atoms, have been omitted for clarity; the symbols ' and '' denote atoms related by symmetry (see Table 1)

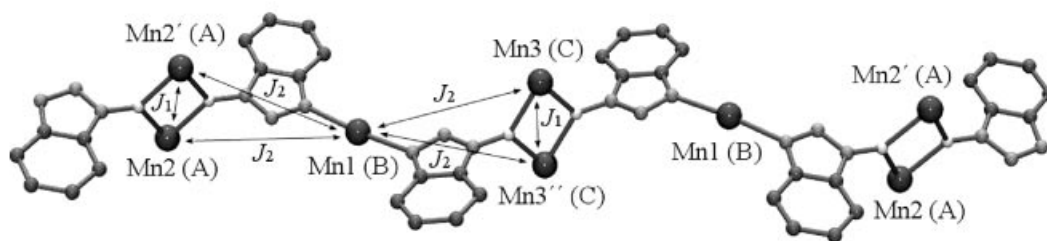


Figure 2. Ball and stick drawing of $[\text{Mn}_3(\text{btaO})_2(\text{NCS})_4(\text{DMF})_8]_n$ (**3**), where the ...AA-B-CC-B-AA... view of the chain is emphasized; only the Mn^{II} atoms and the bridging btaO^- ligands have been drawn; the magnetic exchange pathways between the metal ions are also shown

Table 1. Selected bond lengths (Å) and angles (°) for $[\text{Mn}_3(\text{btaO})_2(\text{NCS})_4(\text{DMF})_8]_n$ (**3**); symmetry transformations used to generate equivalent atoms: (') : $-x + 2, -y, -z + 1$; (')' : $-x + 1, -y + 1, -z$

Mn(1)–N(31)	2.199(6)	Mn(3)–O(11'')	2.194(4)
Mn(1)–N(21)	2.218(6)	Mn(3)–O(67)	2.226(5)
Mn(1)–O(61)	2.219(4)	O(1)–N(1)	1.336(5)
Mn(1)–O(62)	2.221(4)	O(11)–N(11)	1.334(5)
Mn(1)–N(13)	2.262(4)	N(1)–N(2)	1.335(6)
Mn(1)–N(3)	2.277(4)	N(3)–N(2)	1.326(6)
Mn(2)–O(65)	2.155(5)	N(11)–N(12)	1.325(6)
Mn(2)–N(41)	2.162(6)	N(13)–N(12)	1.338(6)
Mn(2)–O(64)	2.176(4)	N(21)–C(21)	1.158(8)
Mn(2)–O(1)	2.186(4)	N(31)–C(31)	1.152(8)
Mn(2)–O(1')	2.206(4)	N(41)–C(41)	1.147(7)
Mn(2)–O(63)	2.217(4)	N(51)–C(51)	1.152(8)
Mn(3)–N(51)	2.155(6)	C(21)–S(21)	1.626(8)
Mn(3)–O(66)	2.169(5)	C(31)–S(31)	1.630(7)
Mn(3)–O(68)	2.176(5)	C(41)–S(41)	1.627(7)
Mn(3)–O(11)	2.184(4)	C(51)–S(51)	1.636(7)
N(21)–Mn(1)–O(61)	91.5(2)	O(64)–Mn(2)–O(1)	90.4(1)
N(31)–Mn(1)–O(62)	88.6(2)	O(65)–Mn(2)–O(1')	93.6(2)
N(21)–Mn(1)–O(62)	89.8(2)	N(41)–Mn(2)–O(1')	94.7(2)
O(61)–Mn(1)–O(62)	178.7(2)	O(64)–Mn(2)–O(1')	160.4(1)
N(31)–Mn(1)–N(13)	91.5(2)	Mn(2)–O(1)–Mn(2')	109.6(1)
N(21)–Mn(1)–N(13)	86.1(2)	N(51)–Mn(3)–O(67)	173.8(2)
O(61)–Mn(1)–N(13)	90.1(2)	O(66)–Mn(3)–O(67)	88.0(2)
N(31)–Mn(1)–N(21)	177.1(2)	O(68)–Mn(3)–O(67)	82.8(2)
N(31)–Mn(1)–O(61)	90.1(2)	O(11)–Mn(3)–O(67)	88.5(2)
O(62)–Mn(1)–N(13)	90.1(2)	O(11'')–Mn(3)–O(67)	90.7(2)
N(31)–Mn(1)–N(3)	93.9(2)	N(51)–Mn(3)–O(66)	88.1(2)
N(21)–Mn(1)–N(3)	88.4(2)	N(51)–Mn(3)–O(68)	93.4(2)
O(61)–Mn(1)–N(3)	92.4(2)	O(66)–Mn(3)–O(68)	102.8(2)
O(62)–Mn(1)–N(3)	87.6(2)	N(51)–Mn(3)–O(11)	96.6(2)
N(13)–Mn(1)–N(3)	174.0(2)	O(66)–Mn(3)–O(11)	163.7(2)
O(65)–Mn(2)–N(41)	87.8(2)	O(68)–Mn(3)–O(11)	92.5(2)
O(65)–Mn(2)–O(64)	105.1(2)	N(51)–Mn(3)–O(11'')	94.3(2)
N(41)–Mn(2)–O(64)	91.7(2)	O(66)–Mn(3)–O(11'')	93.4(2)
O(65)–Mn(2)–O(1)	163.5(2)	O(68)–Mn(3)–O(11'')	162.2(2)
N(41)–Mn(2)–O(1)	97.5(2)	O(11)–Mn(3)–O(11'')	70.7(1)
O(1)–Mn(2)–O(1')	70.4(1)	Mn(3)–O(11)–Mn(3'')	109.3(1)
O(65)–Mn(2)–O(63)	86.9(2)	N(21)–C(21)–S(21)	176.5(7)
N(41)–Mn(2)–O(63)	172.8(2)	N(31)–C(31)–S(31)	178.7(6)
O(64)–Mn(2)–O(63)	84.9(2)	N(41)–C(41)–S(41)	178.7(6)
O(1)–Mn(2)–O(63)	88.9(2)	N(51)–C(51)–S(51)	179.0(6)
O(1')–Mn(2)–O(63)	90.6(2)		

of which there is an inversion centre. The $\text{Mn}\cdots\text{Mn}$ distances are 3.588(1) and 3.570(1) Å for the AA [$\text{Mn}(2)\cdots\text{Mn}(2')$] and CC [$\text{Mn}(3)\cdots\text{Mn}(3')$] subunits, respectively. The octahedral coordination at each Mn^{II} atom, which is part of a dinuclear subunit, is completed by three

oxygen atoms of three DMF molecules at *fac* positions and one nitrogen atom of a linear, terminal SCN^- anion. Thus, the empirical formula of each dinuclear subunit is $\text{Mn}_2(\text{btaO})_2(\text{NCS})_2(\text{DMF})_6$. The two dinuclear subunits AA and CC are connected via a mononuclear subunit containing the $\text{Mn}(1)$ (B) ion, through the nitrogen atom at the 3-position of the 1-hydroxybenzotriazolato(–1) ligands. The octahedral coordination at $\text{Mn}(1)$ is completed by the oxygen atoms [O(61), O(62)] of two *trans* DMF molecules and the nitrogen atoms [N(21), N(31)] of two *trans* isothiocyanato ligands. The $\text{Mn}\cdots\text{Mn}$ distances between the isolated $\text{Mn}(1)$ ion (B) and the Mn^{II} atoms of the dinuclear subunits (AA and CC) are 6.687(1) and 6.875(1) Å for the $\text{Mn}(1)\cdots\text{Mn}(2)$ and $\text{Mn}(1)\cdots\text{Mn}(2')$ pairs, and 6.601(1) and 6.965(1) Å for the $\text{Mn}(1)\cdots\text{Mn}(3)$ and $\text{Mn}(1)\cdots\text{Mn}(3')$ pairs, respectively.

The $\text{Mn}-\text{N}_{\text{isothiocyanato}}$ bond lengths are in the range 2.155(6)–2.218(6) Å; this range is typical for octahedral manganese(II) complexes containing terminal isothiocyanato ligands.^[15a] The SCN^- ions are not perfectly linear, the $\text{N}-\text{C}-\text{S}$ bond angles being in the range 176.5(7)–179.0(6)°. The terminal isothiocyanate anions involving N(31), N(41) and N(51) as donor atoms are coordinated in a slightly bent fashion, as indicated by the $\text{Mn}-\text{N}\equiv\text{C}$ angles [157.7(5)–164.6(5)°]; the fourth SCN^- ion is coordinated in an almost linear fashion [$\text{Mn}(1)-\text{N}(21)-\text{C}(21) = 176.8(6)^\circ$]. The average $\text{Mn}(1,2,3)-\text{O}_{\text{DMF}}$ bond length is 2.194(5) Å, as in other high-spin octahedral manganese(II) complexes with O-donors.^[15b] The $\text{Mn}(2)-\text{O}(1)-\text{Mn}(2')$ and $\text{Mn}(3)-\text{O}(11)-\text{Mn}(3'')$ angles are 109.6(1) and 109.3(1)°, respectively. The angles around the Mn^{II} atoms show that the $\text{Mn}(1)\text{N}_4\text{O}_2$, $\text{Mn}(2)\text{NO}_5$ and $\text{Mn}(3)\text{NO}_5$ coordination octahedra are distorted, with the $\text{Mn}(1)$ polyhedron being less distorted.

Complex **3** joins a small family of structurally characterised, neutral, 1D coordination polymers containing six-coordinate Mn^{II} sites; representative examples have been described previously.^[16–18] This compound also extends to three the number of structurally characterised coordination complexes of any metal with btaO^- ion as ligand; the other two examples are complexes **1** and **2**.

Magnetic Properties

Complex **3** shows a $\chi_{\text{M}}T$ value of 12.98 $\text{cm}^3\cdot\text{K}\cdot\text{mol}^{-1}$ at room temperature for each Mn_3 unit, which is slightly lower than the expected value for three isolated Mn^{II} centres.

Upon cooling, $\chi_M T$ decreases continuously down to $6.07 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 5 K, indicating an overall antiferromagnetic coupling. The molar susceptibility χ_M increases continuously upon decreasing the temperature. The EPR spectrum at room temperature (Figure 3) consists of an isotropic signal ($\Delta H_{\text{pp}} = 210 \text{ G}$) centred at $g = 2.01$, and one weak half-field signal centred at $g = 3.97$ ($\Delta H_{\text{pp}} = 180 \text{ G}$), which arises from the dipolar interaction in the Mn_2O_2 rings, in which the average $\text{Mn} \cdots \text{Mn}$ distance is only $3.579(1) \text{ \AA}$.

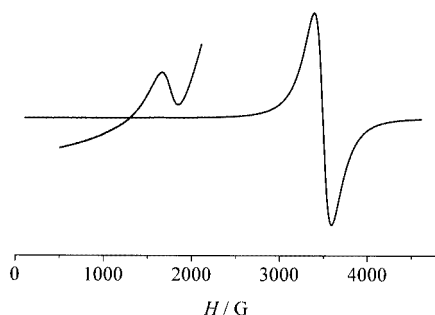


Figure 3. Room-temperature X-band EPR spectrum of a powdered sample of complex $[\text{Mn}_3(\text{btaO})_2(\text{NCS})_4(\text{DMF})_8]_n$ (**3**), showing an isotropic signal centred at $g = 2.01$ and a weak half-field signal centred at $g = 3.97$.

From the structural data we can assume that the magnetic interactions between the isolated Mn(1) ion (B) and the four surrounding Mn(2) (A), Mn(2') (A), Mn(3) (C) and Mn(3') (C) ions are the same, and that the magnetic interactions within the Mn(2) , Mn(2') [AA] and Mn(3) , Mn(3') [CC] dinuclear subunits are also equal because the $\text{Mn}-\text{O}-\text{Mn}$ bond angles differ by only 0.3° . Thus we can describe the chain as an alternating system with a J_1 – $(J_2)_2$ – $(J_2)_2$ – J_1 interaction sequence, where J_1 describes the magnetic interaction between the Mn^{II} atoms within each dinuclear subunit and J_2 describes the magnetic interaction between the central Mn(1) ion and each one of the Mn^{II} atoms of the neighbouring dinuclear subunits (Figure 2).

Analytical expressions to calculate the interaction parameters for systems of this kind are not available, but a simplified analysis of this system can be done assuming that the value of the J_2 coupling parameter is close to zero. This assumption is fully justified on the basis of the large distances (6.601 – $6.965 \text{ \AA}$) between Mn(1) and Mn(2,2',3,3') ions bridged by a four-atom ligand, and the reported magnetic properties of complex **1**,^[20] which shows a very weak coupling for a similar bridge. Additionally, in **3**, the quasi-orthogonal arrangement of the Mn_2O_2 plane with respect to the btaO^- plane reduces the possibility of any coupling between the isolated Mn(1) atom and each of the Mn^{II} atoms of the dinuclear subunits. Assuming that $J_2 = 0$, compound **3**, which is a one-dimensional system from the structural viewpoint, may be adequately described from the magnetic viewpoint as an ordered sequence of dinuclear units and isolated Mn^{II} paramagnetic centres.

The molar susceptibility for this system can be treated as the sum of two contributions: a contribution from one dimeric entity for which the Hamiltonian $H = -J_1 S_1 \cdot S_2$ can be applied,^[19] and a second Curie-law contribution corre-

sponding to one isolated isotropic Mn^{II} atom. The analytical expression used to fit the experimental data was therefore the conventional equation for a pair of interacting $S = 5/2$ centres plus a constant $S = 5/2$ Curie contribution with $g = 2.00$. The best-fit parameters for the dimeric unit were $J_1 = -2.45(4) \text{ cm}^{-1}$ and $g = 2.024(4)$, with $R = 2.2 \times 10^{-4}$ [agreement factor $R = \Sigma(\chi_M^{\text{calc}} - \chi_M^{\text{obs}})^2 / (\chi_M^{\text{obs}})^2$]. The fit is in very good agreement with the experimental data, confirming the validity of the $J_2 = 0$ approach. Figure 4 shows the best-fit plot, together with the isolated contributions of the single Mn(1) atoms (a typical exponential Curie–Weiss plot) and the dimeric Mn(2) , Mn(2') and Mn(3) , Mn(3') subunits, for which the plot exhibits a susceptibility maximum at 10 K. It has recently been pointed out that a weak antiferromagnetic coupling should be expected between O-bridged Mn^{II} atoms when the $\text{Mn}-\text{O}-\text{Mn}$ bond angles are large.^[20] The low J value in **3** is in good agreement with the low J values (-1 to -5 cm^{-1}) found for other RO^- bridges between Mn^{II} atoms with $\text{Mn}-\text{O}-\text{Mn}$ bond angles larger than 105° .^[21]

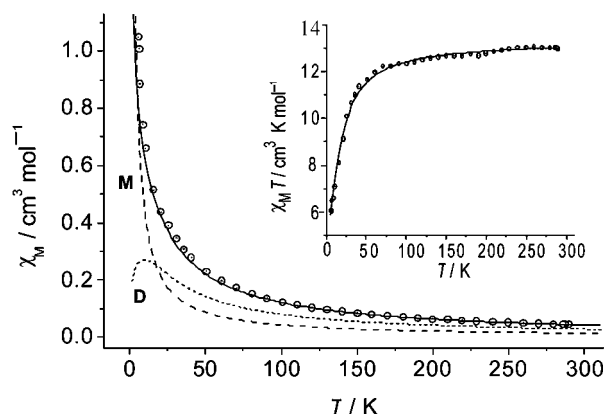
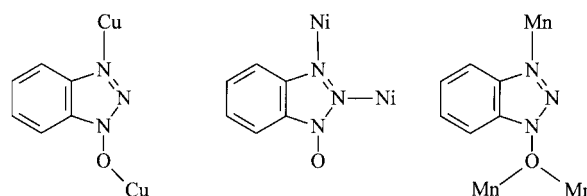


Figure 4. Susceptibility plot versus temperature for $[\text{Mn}_3(\text{btaO})_2(\text{NCS})_4(\text{DMF})_8]_n$ (**3**); dot-centred circles correspond to the experimental data and the solid line is the best fit, the solid line can be considered the addition of an antiferromagnetically coupled dinuclear subunit (plot D) and one isolated Mn^{II} atom (plot M); inset: the $\chi_M T$ versus T plot is presented showing the best overall fit

Conclusions

The initial use of btaOH in manganese chemistry has provided access to an 1D manganese(II) complex with interesting structural and magnetic characteristics. The use of zero-valent Mn has also fulfilled its promise as a source of unusual products. Compound **3** is the third structurally characterised coordination complex of any metal containing btaO^- ions as ligands, the other two complexes being **1** and **2**. The ligand adopts completely different coordination modes in the three complexes (Scheme 2). Al-



Scheme 2

though the outcome of the reaction system described by Equation (1) was unpredictable, the btaO^- ion in **3** exhibits a novel μ_3 -coordination mode binding through N(3) to an Mn^{II} atom and bridging two other Mn^{II} atoms through the deprotonated oxygen. The 1-hydroxybenzotriazolate ligand is also present^[22] in the organometallic compounds $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\text{btaO})]$, $[\text{Os}_3(\text{CO})_{10}(\text{btaO})(\text{C}=\text{NH}n\text{Pr})]$ and $[\text{Os}_3(\text{CO})_{10}(\text{btaO})(\text{C}=\text{NHCH}_2\text{Ph})]$, where it adopts the μ_2 -coordination mode observed in the Ni^{II} complex **2**. The flexibility of btaO^- observed in the structures of **1**, **2**, **3** and some new complexes (recently isolated by us) makes this ion a versatile new ligand for a variety of objectives, including variable denticity levels, high-nuclearity cluster formation, linking of clusters into 1D, 2D and 3D polymeric arrays, 3d-4f mixed-metal chemistry and ferromagnetic exchange interactions.

As far as the magnetic properties of **3** are concerned, the system can be described as a summation of antiferromagnetically coupled dinuclear subunits and isolated mononuclear subunits.

Experimental Section

Physical Methods: Elemental analyses (C, H N) were performed by the University of Ioannina (Greece) Microanalytical Laboratory using an EA 1108 Carlo Erba analyzer. Magnetic susceptibility measurements were carried out on a polycrystalline sample of **3** with a DSM8 pendulum-type susceptometer working in the range 5–300 K at magnetic fields of approximately 1 T. Diamagnetic corrections were estimated from Pascal tables. EPR spectra were recorded on a Bruker ES200 spectrometer at X-band frequency. Infrared spectra ($4400\text{--}450\text{ cm}^{-1}$) were recorded from KBr pellets on a Perkin–Elmer PC 16 FTIR spectrometer.

Preparation of $[\text{Mn}_3(\text{btaO})_2(\text{NCS})_4(\text{DMF})_8]_n$ (3**):** Solid btaOH (0.08 g, 0.6 mmol) and NH_4SCN (0.09 g, 1.2 mmol) were dissolved with stirring in DMF (25 cm^3). Manganese powder (0.05 g, 0.9 mmol) was then added and the mixture was refluxed for approximately 2 h until all the powder had disappeared and the solution had turned yellow. The yellow solution was cooled and layered with Et_2O (50 cm^3). Yellow, X-ray quality crystals of the product formed over a period of three weeks. The needles were collected by filtration, washed with Et_2O and dried in air. Yield 0.28 g, 74%. $\text{C}_{40}\text{H}_{64}\text{Mn}_3\text{N}_{18}\text{O}_{10}\text{S}_4$ (1250.2): calcd. C 38.43, H 5.16, N 20.16; found C 38.40, H 5.10, N 20.18.

Crystal Structure Determination and Refinement of the Structure: A crystal of **3** with approximate dimensions of $0.10 \times 0.10 \times 0.50\text{ mm}$ was mounted in a capillary filled with drops of mother liquor. Diffraction measurements were made on a Crystal Logic Dual Goniometer diffractometer using graphite monochromated $\text{Mo-K}\alpha$ radiation. Complete crystal data and parameters for data collection and refinement are listed in Table 2. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centred reflections in the range $11 < 2\theta < 23^\circ$. Intensity data were recorded using a θ - 2θ scan with a scan speed of 2°min^{-1} and a scan range of 2° plus a_1a_2 separation. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz polarisation corrections were applied using the Crystal Logic software package.

Table 2. Crystal data and structure refinement for $[\text{Mn}_3(\text{btaO})_2(\text{NCS})_4(\text{DMF})_8]_n$ (**3**)

Empirical formula	$\text{C}_{40}\text{H}_{64}\text{Mn}_3\text{N}_{18}\text{O}_{10}\text{S}_4$
Mol. wt.	1250.15
Colour and habit	Yellow prisms
Crystal size [mm]	$0.10 \times 0.10 \times 0.50$
Crystal system	Triclinic
Space group	$P\bar{1}$
a [Å]	13.582(7)
b [Å]	11.313(5)
c [Å]	20.474(9)
α [°]	89.67(2)
β [°]	86.65(2)
γ [°]	73.98(2)
V [Å ³]	3019(1)
Z	2
ρ [$\text{Mg}\cdot\text{m}^{-3}$]	1.375
T [°C]	25
λ (Mo- $K\alpha$) [Å]	0.71073
μ [mm^{-1}]	0.819
$F(000)$	1298
$2\theta_{\text{max}}$ [°]	48
Index ranges [°]	$-15 \leq h \leq 15$ $-12 \leq k \leq 12$ $0 \leq l \leq 23$
No. of reflections collected	9778
No. of indep. refls./ R_{int}	9468/0.0377
Data with $I > 2\sigma(I)$	6209
Parameters refined	864
$[\Delta/\sigma]_{\text{max}}$	0.146
GOF (on F^2)	1.118
$R1$ ^[a]	0.0615
$wR2$ ^[b]	0.1333
Residuals [$\text{e}\cdot\text{\AA}^{-3}$]	0.909/−0.606

^[a] $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^[b] $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$.

The structure was solved by direct methods using SHELXS-86^[23a] and refined by full-matrix least-squares techniques on F^2 with SHELXL-93.^[23b] All hydrogen atoms [except those on C(66), C(69), C(77) and C(78), which were introduced at calculated positions as riding on their parent atoms] were located by difference maps and refined isotropically. All non-hydrogen atoms were refined anisotropically.

CCDC-179198 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the Greek General Secretariat of Research and Technology (Grant 99ED139 to S.P.P.) and the CICYT (Grant BQU2000/0791 to A.E. and R.V.).

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Received February 26, 2002

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