$[Mn(MAC)\{\mu_{1,5}\text{-}N(CN)_2\}](PF_6)$: a new one-dimensional coordination polymer with $\mu_{1,5}$-dicyanamido bridges (MAC = pentaaza macrocyclic ligand)—synthesis, crystal structure and magnetic properties

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Abstract

The dicyanamido-bridged manganese(II) compound, $[Mn(MAC)\{\mu_{1,5}\text{-}N(CN)_2\}](PF_6)$, (**1**), has been obtained by reacting $[Mn(MAC)(H_2O)_2]Cl_2 \cdot 4H_2O$ with $NaN(CN)_2$ and $NaPF_6$ in a 1:1:1 molar ratio (MAC = 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo-[12.3.1]octadeca-1(18),2,12,14,16-pentaene). The structure consists of $[Mn(MAC)\{\mu_{1,5}\text{-}N(CN)_2\}]_n^{n+}$ infinite chains and uncoordinated PF_6^- ions. The manganese ions display a pentagonal-bipyramidal geometry, with the macrocyclic ligand forming the equatorial plane. The {Mn(MAC)} units are connected through $\mu_{1,5}$-dicyanamido bridges (both nitrile nitrogens coordinated). The cryomagnetic investigation of **1** reveals a very weak exchange interaction between the manganese(II) ions within the chain ($J = -0.49$ cm^{-1}).
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Keywords: Crystal structures; Dicyanamido-bridged complexes; Manganese complexes; Macrocyclic ligands; Magnetic properties

1. Introduction

Although the dicyanamide ion, $N(CN)_2^-$, has been known for long time, its ability to act as a ligand has been only recently considered by inorganic chemists. The richness of its coordination chemistry is due to the various coordination modes it exhibits (Scheme 1). The interest in the chemistry generated by the dicyanamido ligand is mainly justified by the search for new magnetic materials [1]. The magnitude and nature of the exchange interaction (ferro- or antiferromagnetic) was found to be strongly dependent on the bridging mode.

The versatility of the dicyanamido ligand also prompted chemists to use it as a tecton in the crystal engineering of coordination polymers [2]. Interesting extended structures have been obtained by combining the bridging ability of the $N(CN)_2^-$ ligand with other bridging ligands, for example pyrazine [1d], bipyrimidine [2d], 4,4′-bipyridine [3], 1,2-bis(4-pyridyl)ethylene [2a,4]. Heteropolynuclear complexes with dicyanamido groups bridging different metal ions have been also characterized [5]. Moreover, the dicynamaide ion acts as a hydrogen bond acceptor and can sustain interesting solid-state supramolecular architectures [6].

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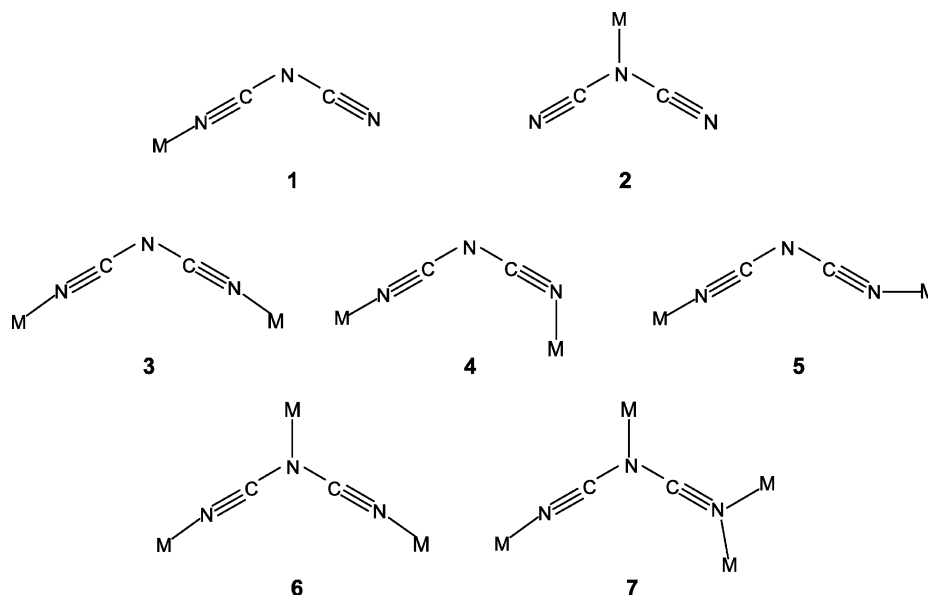
Scheme 1.

In this paper we report on a new 1D coordination polymer constructed from mononuclear Mn(II) nodes connected through $\mu_{1,5}$-bridging dicyanamido ligands.

2. Experimental

2.1. Synthesis

Chemicals were purchased from Aldrich and all manipulations were performed using materials as received. The manganese complex, [Mn(MAC)-(H$_2$O)$_2$]Cl$_2$·4H$_2$O, has been synthesized according to Ref. [7]. Aqueous solutions containing NaN(CN)$_2$ (10 ml, 1 mmol) and NaPF$_6$ (10 ml, 1 mmol) were added to an aqueous solution of *trans*-[MnL(H$_2$O)$_2$]Cl$_2$·4H$_2$O (15 ml, 1 mmol). Orange single crystals suitable for X-ray diffraction were obtained after 2 weeks from the resulting solution, which was left standing at room temperature. Yield: 85%. IR data (KBr, cm^{-1}): 3441m, 3305m, 2932m, 2878m, 2285s, 2221s, 2154vs, 1651m, 1593m, 1461m, 1428m, 1350m, 1258m, 1203m, 1107m, 1044m, 841vs, 815s, 737w, 653w, 557s.

2.2. Physical measurements

The IR spectra (KBr pellets) were recorded with a BIO-RAD FTS 135 spectrophotometer. The magnetic measurements were carried out with a Quantum Design MPMS-5S SQUID magnetometer. Diamagnetic corrections of the constituent atoms were estimated from Pascal constants.

2.3. Crystallography

The crystal was measured on a Bruker AXS SMART diffractometer (Mo Kα radiation monochromator). The structures were solved by direct methods and refined by full-matrix least-squares techniques based on F^2. The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-97 crystallographic software package [8]. The crystallographic data and other pertinent information are collected in Table 1.

Table 1
Crystallographic data for compound **1**

|	
Formula	C$_{17}$H$_{21}$F$_6$MnN$_8$P
M	537.33
Crystal system	Monoclinic
Space group	$P2_1/c$
Temperature (K)	188(2)
Unit cell dimensions	
a (Å)	11.4448(4)
b (Å)	13.6290(5)
c (Å)	14.8134(6)
α (°)	90
β (°)	101.4650(10)
γ (°)	90
V (Å^3)	2264.51(15)
Z	4
D_{calc} (Mg m^{-3})	1.576
Reflections collected	12966
Independent reflections	4884 [$R_{int} = 0.0183$]
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0396$, $wR_2 = 0.1055$
R indices (all data)	$R_1 = 0.0517$, $wR_2 = 0.1132$
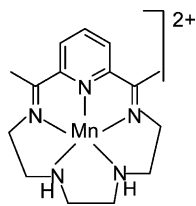
Scheme 2.

3. Results and discussion

The mononuclear manganese(II) complex, [Mn(MAC)(H$_2$O)$_2$]Cl$_2$·4H$_2$O (MAC = 2,13-dimethyl-3,6,9,12,18 - pentaazabicyclo - [12.3.1]octadeca - 1(18),2,-12,14,16-pentaene, Scheme 2) is a useful starting material for the synthesis of homo- and heteropolynuclear complexes with interesting architectures and magnetic properties [9]. In contrast with other manganese(II) complexes with aliphatic amines, it is very robust and can be handled in air without getting oxidized. In order to obtain a polynuclear manganese(II) complex with dicyanamido bridges, we have reacted [Mn(MAC)(H$_2$O)$_2$]Cl$_2$, NaN(CN)$_2$ and NaPF$_6$, in a molar ratio 1:1:1. The PF$_6^-$ anion has been chosen due to its poor coordination ability. The resulting compound has the formula [Mn(MAC){$\mu_{1,5}$-N(CN)$_2$}](PF$_6$) (1). The molar ratio Mn(II):dicyanamide was kept 1:1 in order to prevent the formation of the mononuclear bis(dicyanamido) complex.

The infrared spectrum of 1. The characteristic bands of the dicyanamido ligand are due to the following vibration modes: $\nu_s + \nu_{as}$(NC) and ν(C≡N) [10]. The $\nu_s + \nu_{as}$(NC) vibration is located at 2285 cm^{-1}. There are two ν(C≡N) bands at 2221 and 2154 cm^{-1}. The characteristic bands of PF$_6^-$ are located at 841 and 557 cm^{-1}.

The crystallographic investigation of compound 1 reveals one-dimensional infinite cationic chains, resulted by connecting the {Mn(MAC)}$^{2+}$ moieties through dicyanamido bridges, and uncoordinated PF$_6^-$ anions. A labeled diagram of the asymmetric unit of 1 is shown in Fig. 1. The manganese(II) ion displays a distorted pentagonal-bipyramidal geometry, with the macrocyclic ligand forming the equatorial plane. The Mn–N(MAC) distances fall in the range 2.261(2) and 2.322(2) Å. The axial positions are occupied by two nitrogen atoms arising from the cyanamido bridges [Mn(1)–N(7) = 2.297(2) Å; Mn(1)–N(8)#1 = 2.221(2) Å]. The {Mn(MAC)}$^{2+}$ moieties are connected through $\mu_{1,5}$-dicyanamido bridges resulting in infinite cationic chains running along the crystallographic c axis (Fig. 2). The distance between the manganese ions within a chain is 7.701 Å. At the bridge level, the Mn–N–C linkages are not linear: Mn(1)–N(7)–C(16) = 122.2(2)°; Mn(1)–N(8)#1–C(17) = 157.2(2)° (Table 2).

The magnetic properties of compound 1 are shown in the form of $\chi_M T$ versus T plot (Fig. 3). The value of the $\chi_M T$ product at room temperature (4.48 cm^3 mol^{-1} K) is as expected for an isolated spin $S = 5/2$ (4.37 cm^3 mol^{-1} K). By decreasing the temperature $\chi_M T$ remains constant down to 150 K, then decreases more and more, reaching a value of 0.84 cm^3 mol^{-1} K at $T = 2$ K. Moreover, the temperature dependence of χ_M passes through a maximum at 3 K (Insert Fig. 3). This indicates that an antiferromagnetic interaction occurs between the manganese(II) ions within the chain.

The magnetic data are analyzed by using the Hamiltonian: $H = -J\Sigma S_i S_{i+1}$. The temperature dependence of the magnetic susceptibility is given by the equation [11]:
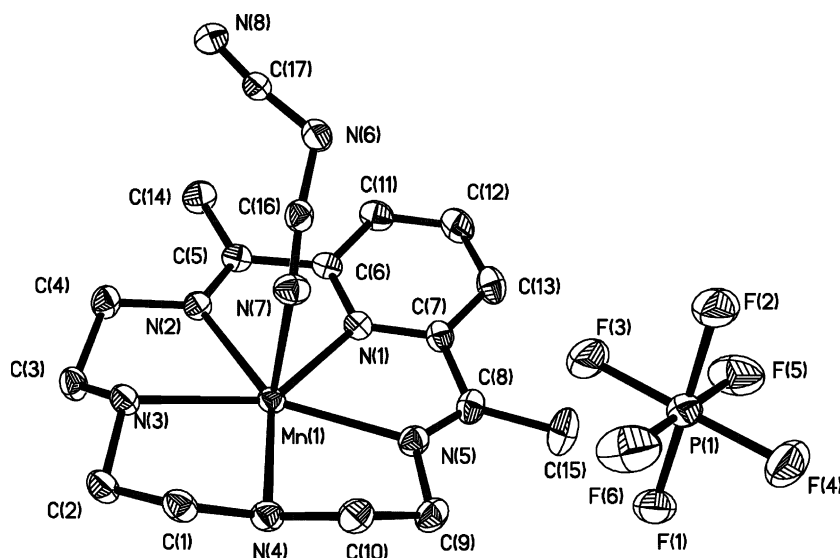
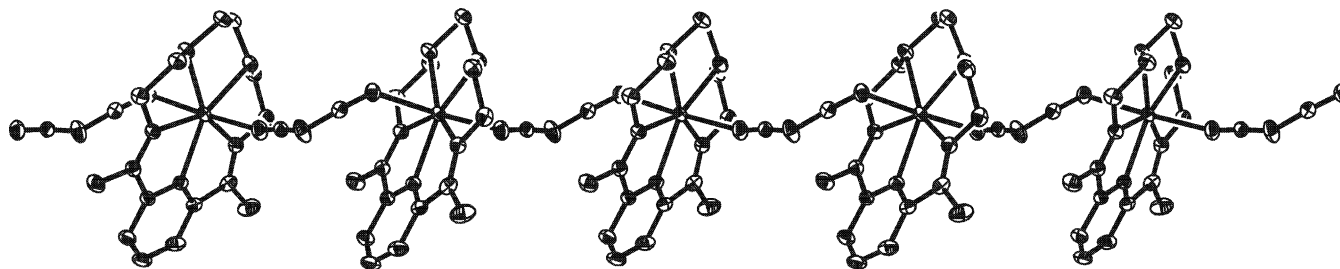Fig. 1. The asymmetric unit of 1, along with the atom numbering scheme.

Fig. 2. Perspective view of a cationic chain in **1**.

$$\chi_M^{chain} = \{Ng^2\beta^2 S_{Mn}(S_{Mn}+1)/3kT\}\{(1+u)/(1-u)\}$$

(1)

(Fisher's infinite chain model) with:

$$u = \coth[JS_{Mn}(S_{Mn}+1)/kT] - [kT/JS_{Mn}(S_{Mn}+1)] \quad (2)$$

The least-squares fit to the data leads to $J = -0.49$ cm^{-1}, $g = 2.04$.

It is worthy to compare this value with those obtained for other Mn(II)-dicyanamido complexes (Table 3). With one exception ($J = +1.6$ cm^{-1}), in all other cases the exchange interaction is very weak antiferromagnetic. Further comparison with copper(II) dicyanamido com-plexes showed that the antiferromagnetic coupling is stronger for M = Cu [1d]. In the case of copper(II) the exchange interaction involves only one single occupied d-orbital, being dominated by the antiferromagnetic contribution to the J value. In the case of manganese(II) it occurs a more efficient compensation of the anti-ferromagntic contribution to the J value by a ferromag-netic one, arising from the other d-orbitals [1d].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 202617. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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

Bond lengths	
Mn(1)–N(1)	2.261(2)
Mn(1)–N(2)	2.321(2)
Mn(1)–N(3)	2.322(2)
Mn(1)–N(4)	2.320(2)
Mn(1)–N(5)	2.288(2)
Mn(1)–N(7)	2.297(2)
Mn(1)–N(8)#1	2.221(2)
Bond angles	
N(8)#1–Mn(1)–N(1)	95.63(8)
N(8)#1–Mn(1)–N(5)	94.06(8)
N(1)–Mn(1)–N(5)	69.99(7)
N(8)#1–Mn(1)–N(7)	176.95(8)
N(1)–Mn(1)–N(7)	87.36(7)
N(5)–Mn(1)–N(7)	87.55(7)
N(8)#1–Mn(1)–N(4)	85.98(8)
N(1)–Mn(1)–N(4)	143.28(7)
N(5)–Mn(1)–N(4)	73.30(7)
N(7)–Mn(1)–N(4)	92.00(7)
N(8)#1–Mn(1)–N(2)	90.85(8)
N(1)–Mn(1)–N(2)	69.30(7)
N(5)–Mn(1)–N(2)	139.28(7)
N(7)–Mn(1)–N(2)	89.62(7)
N(4)–Mn(1)–N(2)	147.42(7)
N(8)#1–Mn(1)–N(3)	93.37(8)
N(1)–Mn(1)–N(3)	140.07(7)
N(5)–Mn(1)–N(3)	147.84(7)
N(7)–Mn(1)–N(3)	83.91(8)
N(4)–Mn(1)–N(3)	76.08(7)
N(2)–Mn(1)–N(3)	71.74(7)

Symmetry transformations used to generate equivalent atoms: (#1) $x, -y+1/2, z+1/2$ (#2) $x, -y+1/2, z-1/2$.
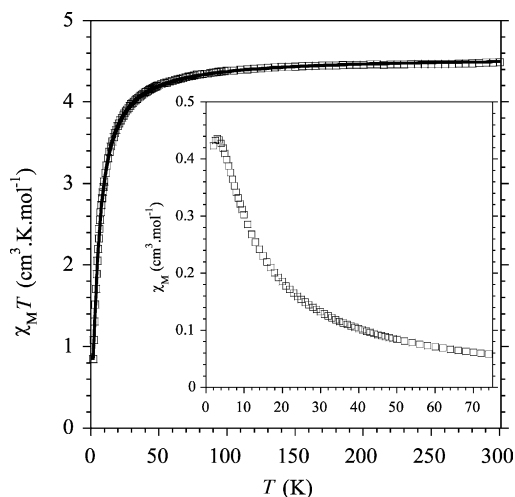

Fig. 3. Temperature dependence of the $\chi_M T$ product. The solid line represents the best fit curve (*Insert:* detail of the χ_M vs. T behavior showing the maximum exhibited by the curve).

Table 3
Exchange parameters in dicyanamido-bridged manganese(II) complexes

No	Compound	J (cm^{-1})	Ref.
1	[Mn(dca)$_2$bypm]·H$_2$O [a]	−0.105	[12]
2	*trans*-[Mn(4-bzpy)$_2$(dca)$_2$]$_n$ [b]	−0.3	[13]
3	*cis*-[Mn(2,2′-bipy)$_2$(dca)$_2$]$_n$ [c]	−0.4	[13]
4	Mn(pyr)$_2$(dca)$_2$ [d]	+1.6	[14]
5	Mn(dca)$_2$(H$_2$O)	−0.19	[15]
6	[Mn(dca)(NO$_3$)(terpy)]$_n$ [e]	−0.12	[16]
7	[Mn(dca)(H$_2$O)(terpy)]$_n$[dca]$_n$ [e]	−0.20	[16]
8	Mn(dca)$_2$(4,4′-bipy)(H$_2$O)·0.5MeOH [f]	−0.104	[17]
9	Mn(dca)$_2$(4,4′-bipy)(H$_2$O)·0.5H$_2$O [f]	−0.16	[18]
10	Mn(dca)$_2$(py)$_2$ [g]	−0.14	[19]
11	Mn(dca)$_2$(2,2′-bipy) [c]	−0.238	[19]
12	Mn(dca)$_2$(4,4′-bipy)·3/2H$_2$O [f]	−0.336	[19]
13	Mn(dca)$_2$(CH$_3$OH)$_2$	−0.24	[20]
14	Mn(dca)$_2$(DMF)$_2$ [h]	−0.24	[20]
15	[Mn(dca)$_2$(H$_2$O)$_2$]·H$_2$O	−0.34	[20]
16	Mn(dca)$_2$(py)$_2$ [g]	−0.24	[20]
17	Mn(dca)$_2$bypm [a]	−0.18	[2d]
18	Mn$_2$(dca)$_4$bypm [a]	−0.86	[2d]
19	[Mn(dca)$_2$(4CN-py)$_2$]$_n$ [i]	−0.154	[21]
20	[Mn(dca)$_2$(bpe)]$_n$ [j]	−1.25	[21]
21	Mn(dca)$_2$(pyz) [k]	−0.25	[22]
22	[Mn(MAC)(dca)](PF$_6$)	−0.49	this work

[a] bpym = 2,2′-bipyrimidine.
[b] 4-bzpy = 4-benzoylpyridine.
[c] 2,2′-bipy = 2,2′-bipyridine.
[d] pyr = 2-pyrrolidone.
[e] terpy = 2,2′:6′,2″-terpyridine.
[f] 4,4′-bipy = 4,4′-bipyridine.
[g] py = 2-pyridine.
[h] DMF = dimethylformamide.
[i] 4CN-py = 4-cyanopyridine.
[j] bpe = 1,2-bis(4-pyridyl)ethane.
[k] pyz = pyrazine.

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