Structural Characterization and Magnetic Behaviour of the Ferro-Antiferromagnetic Alternating Manganese–Azido Chain $[Mn(3\text{-Et,4-Mepy})_2(\mu\text{-}N_3)_2]_n$ (3-Et,4-Mepy = 3-Ethyl-4-methylpyridine)

Morsy A. M. Abu-Youssef,[a] Albert Escuer,*[b] Mohamed A. S. Goher,*[c] Franz A. Mautner,[a] and Ramon Vicente*[b]

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The ligands 3-ethyl-4-methylpyridine (3-Et,4-Mepy) and azide coordinate to Mn^{II} forming an alternating chain with the formula $[Mn(3\text{-Et,4-Mepy})_2(\mu\text{-}N_3)_2]_n$. This compound crystallizes in the space group $P-1$. The compound consists of chains of octahedrally coordinated manganese atoms alternately bridged by double end-to-end ($\mu_{1,3}$) and double end-on ($\mu_{1,1}$) azido bridges, which results in a structurally and magnetically alternating chain. The 3-ethyl-4-methylpyridine ligands are arranged *trans*, completing the six-fold coordination spheres of the manganese atoms. The Mn–Mn distances are distinctly different: Mn(1)–Mn(1A) = 5.149(3) Å (double end-to-end azido bridge) and Mn(1)–Mn(1B) = 3.402(2) Å (double end-on azido bridge). The magnetic properties of the compound, as studied in the temperature range 300–4 K, show bulk antiferromagnetic interaction. Fitting of the magnetic data by using an equation for alternating ferro-antiferromagnetic $S = 5/2$ 1-D systems gives the parameters $J_{AF} = -13.7(1)$ cm^{-1}, $J_F = 2.4(1)$ cm^{-1}, $g = 2.036(2)$.

The chemistry of the manganese(II)−(L)−azido-bridged system, L = N-aromatic ligand, affords habitually high-dimensional compounds: 3-D for L = pyridine (py)[1][2] and 2,2′-bipyrimidine (bipym),[3][4] 2-D for the substituted pyridines L = 3- and 4-acetylpyridine (3-Acpy[5] and 4-Acpy[6]), methyl- and ethyl isonicotinate (Meinc[7] and Etnic[2]), and 4-cyanopyridine (4-CNpy[5]), or 1-D for 2,2′-bipyridine,[8] 3-ethylpyridine, and 2-hydroxypyridine.[9] A 3-D network with a distorted perovskite structure has also been found for $[N(CH_3)_4][Mn(N_3)_3]$.[10] In contrast, only in the case of L = 2,2′:6′,2′′-terpyridine has a dinuclear compound been obtained.[11] The coordination mode of the azido bridge is commonly found to be $\mu_{1,3}$-N_3 (end-to-end, EE), although in some cases it is $\mu_{1,1}$-N_3 (end-on, EO), and even alternating 1-D or 2-D systems in which the two kinds of coordination mode coexist in the same compound have been found. No correlation has been identified between the properties of the ligand L and the coordination mode of the azido bridge, and from a synthetic point of view, the manganese(II)−azido system shows unpredictable behaviour, analogous to that observed for azido-bridged polynuclear copper(II) and nickel(II) systems. The magnetic behaviour of these compounds follows the same general trends as seen for copper and nickel(II) systems, i.e. end-to-end azido bridges lead to antiferromagnetic interaction, while end-on bridges give rise to ferromagnetic coupling. The main difference between these systems is the higher dimensionality shown by the manganese derivatives.

In continuation of our research on compounds of this kind, we report herein on a new system of the pyridine series, using L = 3-ethyl-4-methylpyridine to obtain the one-dimensional system $[Mn(3\text{-Et,4-Mepy})_2(\mu\text{-}N_3)_2]_n$ (**1**). This compound constitutes the second example of an alternating chain in which the manganese atoms are bridged alternately by two coplanar end-to-end and two end-on azido ligands, but is the first case with a *trans* arrangement of the EO and EE azido bridges. In the previously published alternating chain $[Mn(bipy)(\mu\text{-}N_3)_2]_n$, the EO and EE azido bridges have a *cis* arrangement.[8] The experimental magnetic susceptibility vs. T data for **1** have been fitted by using a recently published equation for $S = 5/2$ alternating F/AF-coupled 1-D systems.[8]

Results and Discussion

Infrared Spectra

The IR spectrum of the title complex $[Mn(3\text{-Et,4-Mepy})_2(N_3)_2]_n$ shows bands attributable to the 3-Et,4-Mepy ligand at the normal frequencies. In the 2000−2100 cm^{-1} region, the complex shows a very intense split band that can be assigned to the asymmetric stretching vibrations of the azide group [$\nu_{as}(N_3)$], centred at 2056 and 2080 cm^{-1}. In the region 1280−1360 cm^{-1}, no band was observed that could be attributed to the $\nu_s(N_3)$ mode, while the two bands at 2056 and 2080 cm^{-1} indicate the presence of two different symmetric and asymmetric azido groups. This was tentatively rationalized in terms of the coexistence of both μ(1,1)-EO and μ(1,3)-EE bridging azido groups, which was supported by the X-ray structural data. In the far infrared

[a] Institut für Physikalische und Theoretische Chemie, Technische Universität Graz,
A-8010 Graz, Austria
E-mail: Mautner.PTC.NAWI.TU-Graz@ptc.tu-graz.ac.at
[b] Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, E-08028 Barcelona, Spain
E-mail: rvicente@kripto.qui.ub.es
[c] Chemistry Department, Faculty of Science, Kuwait University, P. O. Box 5969, Safat, 13060 Kuwait

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region, one band attributable to the $\nu(Mn-N_3)$ mode around 310 cm^{-1} and two bands due to the $\nu[Mn-N(L)]$ mode around 254 and 230 cm^{-1} were observed.

Crystal Structure of $[Mn(3\text{-Et},4\text{-Mepy})_2(\mu\text{-}N_3)_2]_n$ (1)

The labelled diagram for **1** is shown in Figure 1. The structure consists of octahedrally coordinated manganese atoms, about which the coordination sites are occupied by two 3-ethyl-4-methylpyridine ligands in a *trans* arrangement and four coplanar azido ligands. Two azido groups act as end-to-end bridging ligands with a neighbouring manganese atom, while the other two act as end-on bridging ligands with another neighbouring manganese atom, giving a one-dimensional system with alternating $\mu_{1,3}$ and $\mu_{1,1}$ bridges extending along the *a* axis of the unit cell. The bond parameters relating to the end-on bridges are Mn(1)−N(21) = 2.209(2) Å, Mn(1)−N(21B) = 2.240(2) Å, N(21)−N(22)−N(23) = 178.2(4)°, Mn(1)−N(21)−

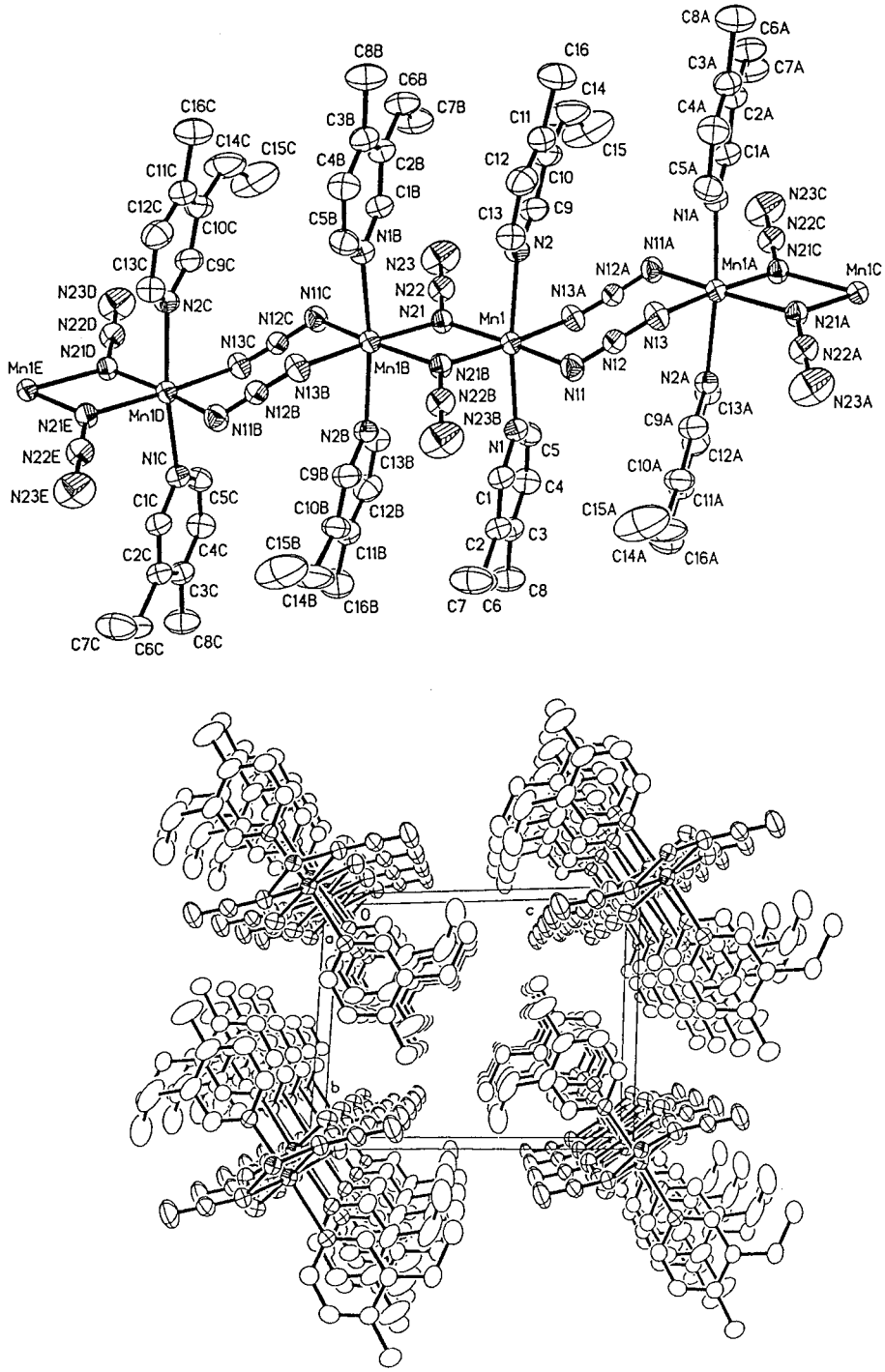
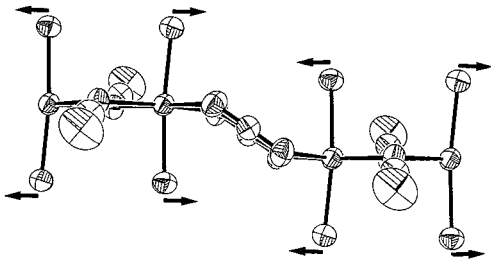


Figure 1. ORTEP drawing (thermal ellipsoids drawn at 40% probability) with atom labelling scheme and packing plot viewed along the *a* axis of the unit cell of $[Mn(3\text{-Et},4\text{-Mepy})_2(\mu\text{-}N_3)_2]_n$ (**1**)

Mn(1B) = 99.75(10)°, while those relating to the end-to-end bridges are Mn(1)−N(11) = 2.225(3) Å, Mn(1)−N(13A) = 2.256(3) Å, Mn(1)−N(11)−N(12) = 124.8(2) Å, Mn(1)−N(13A)−N(12A) = 123.2(2)°, N(11)−N(12)−N(13) = 177.9(3)°. The Mn(1)−Mn(1A) and Mn(1)−Mn(1B) distances amount to 5.149(3) Å and 3.402(2) Å, respectively. The degree of distortion of the $Mn_2(\mu_{1,3}\text{-}N_3)_2$ ring from planarity towards a chair form may be quantified by means of the acute angle δ between the normal to the planes defined by the six N atoms of the azido bridges and the corresponding N−Mn−N planes: δ in this case is 31.7(1)° [torsion Mn(1)−N(11)−N(12)−N(13)−Mn(1A) 51.2(2)°]. The neutral chains of **1** are well-isolated by the ligands, the minimum Mn−Mn interchain distance being 9.258(4) Å.

The alternation of $\mu_{1,3}$ and $\mu_{1,1}$ bridges along the *a* axis of the unit cell may be due to the effects of steric hindrances: In the $[Mn_2(\mu_{1,1}\text{-}N_3)_2(L_4)]$ unit the L rings are not oriented exactly perpendicular to the $[Mn_2(\mu_{1,1}\text{-}N_3)_2]$ mean plane, but are inclined out of this plane along the chain direction, resulting in an N(1)−Mn(1)−N(2) angle of 172.61(8)°.



For this reason, it is not possible to repeat the $[Mn_2(\mu_{1,1}\text{-}N_3)_2(L_4)]$ unit, which would necessitate short Mn−Mn distances. The structural solution to have a one-dimensional system is to add the $[Mn_2(\mu_{1,3}\text{-}N_3)_2(L_4)]$ unit, with longer Mn−Mn distances.

Magnetic Properties

The $\chi_M{\cdot}T$ product and the molar magnetic susceptibilities of $[Mn(3\text{-Et},4\text{-Mepy})_2(\mu\text{-}N_3)_2]_n$ (**1**) vs. *T* in the range 300−4 K are plotted in Figure 2. The overall behaviour of **1** corresponds to a bulk antiferromagnetically coupled system. The $\chi_M{\cdot}T$ value, which amounts to 3.75 $cm^3{\cdot}K{\cdot}mol^{-1}$ at 290 K, decreases on cooling and tends to zero at low temperatures. The χ_M vs. *T* plot shows an increase in χ_M from 1.29×10^{-2} $cm^3{\cdot}mol^{-1}$ at 290 K to a broad maximum between 60 and 20 K. On further cooling, this plot quickly tends to zero. The magnetic data were analysed by means of the expression recently published[8] by Cortés et al. for alternating ferro-antiferro one-dimensional *S* = 5/2 compounds, which was derived from the spin Hamiltonian:

$$H = -J_1\Sigma S_{2i}S_{2i+1} - J_2\Sigma S_{2i+1}S_{2i+2}$$

The best fit parameters obtained were $J_1 = -13.7(1)$ cm^{-1}, $J_2 = 2.4(1)$ cm^{-1} and $g = 2.036(2)$. No other local minima in the fitting process were found. J_1 and J_2 correspond to the double EE and the double EO superexchange pathways, respectively.

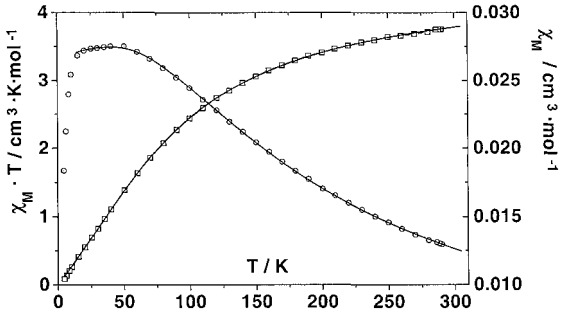


Figure 2. χ_M vs. *T* (○) and $\chi_M{\cdot}T$ vs *T* (□) plots for $[Mn(3\text{-Et},4\text{-Mepy})_2(\mu\text{-}N_3)_2]_n$ (**1**); the solid line shows the best fit theoretical curve

EPR spectra recorded on powdered samples at room temperature show an isotropic signal centred at $g = 2.020$ with a linewidth of 320 G. This signal is temperature-dependent; the spectrum at 4 K shows a signal centred at $g = 2.038$ with linewidth 541 G, as well as a weak signal at half-field. This linewidth is much larger than that of the sharp signals (linewidth 35 G at room temperature) recently reported for the related compounds $[Mn(pyOH)_2(\mu\text{-}N_3)_2]_n$ and $[Mn(3\text{-Etpy})_2(\mu\text{-}N_3)_2]_n$, where pyOH and 3-Etpy denote 2-hydroxypyridine and 3-ethylpyridine, respectively.[9]

This behaviour may be explained by considering the main factors[12] that influence the linewidth for an isotropic Heisenberg one-dimensional system, i.e. exchange narrowing, due to the superexchange interactions along the chain, and dipolar interactions, which induce broadening of the signal. Adequate characterization of these effects requires well-isolated chains in order to reduce the interchain interactions. This condition reduces the number of suitable systems and the well-known compound $[(CH_3)_4][MnCl_3]$, abbreviated as TMMC,[13] remains the standard reference compound 25 years after the first studies in this field. In the three $[Mn(R)_2(\mu\text{-}N_3)_2]_n$ complexes (R = 3-Et,4-Mepy; pyOH, and 3-Etpy), the chains are neutral and are well-isolated by the large pyridyl ligands (see Figure 1). Moreover, the interchain distances are slightly shorter than the 9.15 Å found in TMMC and compare well with the 7.60 Å reported for $Cs[MnBr_3]$[14] or the 7.5 Å reported for $[Mn(py)_2Cl_2]_n$.[15] The sharp signals reported for the pyOH and 3-ethyl derivatives may be attributed to exchange narrowing, taking into account the $-J$ values larger than 10 cm^{-1} and the negligible dipolar contribution (Mn···Mn distances larger than 5.4 Å in the EE bridges). In contrast, although $[Mn(3\text{-Et},4\text{-Mepy})_2(\mu\text{-}N_3)_2]_n$ has comparable superexchange interactions, it shows alternating Mn···Mn distances of 5.149 and 3.402 Å and thus the dipolar broadening mechanism becomes active in the Mn_2N_2 rings with double EO azide bridges. The same explanation may account for the large linewidth (close to 500 G) observed for the EPR signal of the alternating system $[Mn(bipy)(\mu\text{-}N_3)_2]_n$, which shows comparable superexchange parameters

J, interchain packing, and alternating Mn···Mn intrachain distances.[8]

Experimental Section

General: Infrared spectra (4000−400 cm^{-1}) were recorded using KBr pellets with a Nicolet 520 FT-IR spectrophotometer. Magnetic measurements were carried out with a DSM8 pendulum susceptometer, operating in the temperature range 300−4 K. The applied external magnetic field was 1.5 T. Diamagnetic corrections were estimated from Pascal tables. EPR spectra were recorded at X-band frequency with a Bruker ES200 spectrometer equipped with an Oxford liquid helium cryostat for variable-temperature work.

Synthesis of the Compound: The title complex $[Mn(3\text{-Et},4\text{-Mepy})_2(N_3)_2]_n$ was synthesized by mixing ca. 50 mL of a pure methanolic solution of manganese perchlorate hexahydrate (1.00 g, 2.7 mmol) and a solution of 0.61 g (ca. 5 mmol) of 3-ethyl-4-methylpyridine in 20 mL of methanol, with subsequent dropwise addition of a concentrated aqueous solution of sodium azide (0.65 g, 10 mmol). The solution became turbid and a gelatinous precipitate was produced, which was filtered off. By slow evaporation of the solvent from the clear filtrate, colourless transparent plates of the title complex, suitable for X-ray analysis, were formed within 6 d; yield: 0.60 g (ca. 65%). − $C_{16}H_{22}MnN_8$ (381.36): calcd. C 50.4, H 5.8, Mn 14.4, N 29.4; found C 50.6, H 5.9, Mn 14.3, N 29.2.

Table 1. Crystal data and structure refinement for $[Mn(3\text{-Et},4\text{-Mepy})_2(N_3)_2]_n$ (**1**)

Empirical formula	$C_{16}H_{22}MnN_8$
Formula mass	381.36
Crystal system	triclinic
Space group	$P-1$ (no. 2)
a [Å]	8.455(4)
b [Å]	9.778(3)
c [Å]	12.065(5)
α (°)	89.86(3)
β (°)	78.25(3)
γ (°)	75.08(3)
V [$Å^3$]	942.3(7)
Z	2
T [°C]	22(2)
λ(Mo-K_α) [Å]	0.71069
$d_{calcd.}$ [$g \cdot cm^{-3}$]	1.344
μ(Mo-K_α) [mm^{-1}]	0.716
max. transmission	1.000
min. transmission	0.395
max. peak in final diff. synthesis [$eÅ^{-3}$]	0.464
min. peak in final diff. synthesis [$eÅ^{-3}$]	−0.637
parameters refined	230
R[a]	0.0501
R^2w[b]	0.1243

[a] $R(F_o) = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. − [b] $R_\omega(F_o)^2 = \{\Sigma[\omega[(F_o)^2 - (F_c)^2]^2]/\Sigma[\omega[(F_o)^2]^2]\}^{1/2}$.

Crystal Structure Determination and Refinement of the Structure: Single-crystal X-ray data for $[Mn(3\text{-Et},4\text{-Mepy})_2(N_3)_2]_n$ were collected with a modified STOE four-circle diffractometer. Crystal size: 0.60 × 0.50 × 0.24 mm. The crystallographic data, conditions maintained for the intensity data collection, and some features of the structure refinement are listed in Table 1. Graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å) was used to collect the data set, employing the ω-scan technique. The accurate unit cell parameters were determined from automatic centering of 40 reflections (9.2° < θ < 14.9°) and refined by least-squares methods. 5167 reflections (4539 independent reflections, R_{int} = 0.0275) were collected in the range 2.76° < θ < 27.99°. An intensity decay of 12% for control reflections, measured after every set of 100 reflections, was observed during the data collection. Corrections were applied for Lorentz and polarization effects, for intensity decay, as well as for absorption, using the DIFABS[16] computer program. The structure was solved by direct methods using the SHELXS-86[17] program, and refined by full-matrix least-squares methods on F^2 using the SHELXL-93[18] program, as incorporated in the SHELXTL/PC V 5.03[19] program library, and the graphics program PLUTON.[20] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were geometrically fixed with the HFIX utility[19] (i.e.: hydrogen atoms riding with idealized geometrical values on their parent carbon atoms with fixed distances: CH = 0.93 Å, CH_2 = 0.97 Å and CH_3 = 0.96 Å; for each methyl group the torsion angle was set which maximizes the sum of the electron density at the three calculated hydrogen positions). Selected bond parameters are given in Table 2.

Atomic positional and thermal parameters, lists of bond lengths and angles, and F_o/F_c values are available as supplementary material from one of the authors (F. A. M.). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-103250. Copies of the data can be obtained free of charge on application to CCDC,

Table 2. Selected bond lengths [Å] and angles [°]; symmetry codes: (a) $-x, -y, -z$; (b) $-x+1, -y, -z$

Mn(1)···Mn(1B)	3.402(2)	Mn(1)···Mn(1A)	5.149(3)
Mn(1)−N(21)	2.209(2)	Mn(1)−N(11)	2.225(3)
Mn(1)−N(21B)	2.240(2)	Mn(1)−N(13A)	2.256(3)
Mn(1)−N(1)	2.278(2)	Mn(1)−N(2)	2.305(2)
N(11)−N(12)	1.170(3)	N(12)−N(13)	1.166(3)
N(21)−N(22)	1.185(3)	N(22)−N(23)	1.152(4)
N(21)−Mn(1)−N(11)	168.61(9)	N(21)−Mn(1)−N(21B)	80.25(10)
N(11)−Mn(1)−N(21B)	88.77(9)	N(21)−Mn(1)−N(13A)	95.42(10)
N(11)−Mn(1)−N(13A)	95.47(10)	N(21b)−Mn(1)−N(13A)	175.42(9)
N(21)−Mn(1)−N(1)	92.60(9)	N(11)−Mn(1)−N(1)	91.37(10)
N(21B)−Mn(1)−N(1)	95.09(9)	N(13a)−Mn(1)−N(1)	86.58(9)
N(21)−Mn(1)−N(2)	90.59(9)	N(11)−Mn(1)−N(2)	86.75(10)
N(21B)−Mn(1)−N(2)	92.02(9)	N(13A)−Mn(1)−N(2)	86.49(9)
N(1)−Mn(1)−N(2)	172.61(8)	N(12)−N(11)−Mn(1)	124.8(2)
N(13)−N(12)−N(11)	177.9(3)	N(12)−N(13)−Mn(1A)	123.2(2)
N(22)−N(21)−Mn(1)	128.0(2)	N(22)−N(21)−Mn(1B)	125.8(2)
Mn(1)−N(21)−Mn(1B)	99.75(10)	N(23)−N(22)−N(21)	178.2(4)

12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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