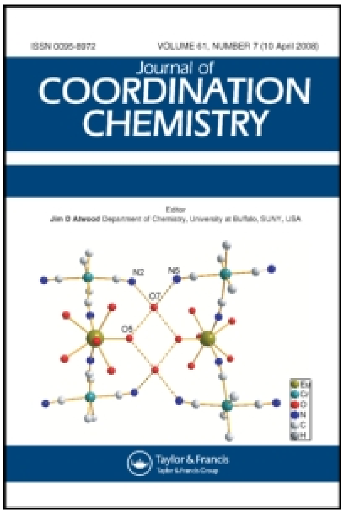

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Manganese(II)-phenanthroline-azide compounds: Versatile Precursors as Ligands in Designing Heteropolymetallic Systems

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MANGANESE(II)-PHENANTHROLINE-AZIDE COMPOUNDS: VERSATILE PRECURSORS AS LIGANDS IN DESIGNING HETEROPOLYMETALLIC SYSTEMS

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Two novel manganese(II) complexes, $[Mn(phen)_2N_3 \cdot H_2O]ClO_4 \cdot H_2O$ and $Mn(phen)_2(N_3)_2$ have been synthesized by the reaction of $Mn(ClO_4)_2 \cdot 6H_2O$ and $Mn(CH_3CO_2)_2 \cdot 4H_2O$ with NaN_3 and phen in $EtOH/H_2O$ solution, respectively (where phen = 1,10-phenanthroline). Their crystal structures have been determined by X-ray diffraction. Both complex molecules have distorted octahedral geometry and two 1,10-phenanthroline molecules chelate to a Mn(II) atom with a *cis*-configuration. To $[Mn(phen)_2N_3 \cdot H_2O]ClO_4 \cdot H_2O$, one nitrogen atom from an azide anion and one oxygen atom from a water molecule *cis*-coordinate to the Mn(II) atom while two nitrogen atoms occupy *cis* positions in $Mn(phen)_2(N_3)_2$. These complexes are versatile precursors for the design of heteropolymetallic systems.

Keywords: Manganese(II); Crystal structure; Molecular-based magnet; 1,10-Phenanthroline; Azido ligand

INTRODUCTION

Molecular-based magnets containing manganese(II) and azido ligand have attracted intensive interest in recent years [1–3]. Remarkable progress has been made with respect to their spontaneous magnetization and potential uses in high-density molecular-based memory devices [4–6]. A wide variety of structures, including dimers as well as polymers incorporating up to 3-D networks have been reported [7–10]. The most interesting characteristic of azido-bridged complexes is that the azido ligand determines the magnetic behavior of those systems where it serves as a linkage between paramagnetic metal ions. For instance, end-to-end (EE or 1,3) coordination of the azido group results in moderate to strong antiferromagnetic coupling whereas end-on (EO or 1,1) coordination gives rise to ferromagnetic coupling between paramagnetic centers. In a recent investigation on azido-bridged complexes, we succeeded in synthesizing

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one-dimensional complexes showing regular alternation of ferromagnetic and antiferromagnetic interactions [11,12]. However, one has to avoid the formation of a mixture of two homometallic $[M(N_3)M]^{3-}$ and $[M'(N_3)M']^{3-}$ species. To overcome this limitation, we have synthesized two stable mononuclear compounds $[Mn(phen)_2N_3 \cdot H_2O]ClO_4 \cdot H_2O$ (**1**) and $Mn(phen)_2(N_3)_2$ (**2**) (phen = 1,10-phenanthroline), to act as versatile precursors in designing heteropolymetallic systems. To our surprise, dimorphous compounds of **2** have been obtained in our experiments by using different synthetic methods.

EXPERIMENTAL

Synthesis

To synthesize **1**, 0.130 g (2.0 mmol) of sodium azide dissolved in a minimum of water was added to 5 cm^3 of deionized water containing 0.361 g (1.0 mmol) of $Mn(ClO_4)_2 \cdot 6H_2O$ with stirring at room temperature; 0.394 g (2.0 mmol) of 1,10-phenanthroline dissolved in 5 cm^3 of water–ethanol was added to the above mixture and yellow precipitates formed immediately. After stirring for half an hour, the reaction mixture was filtered. Yellow, single crystals were obtained by slow evaporation of the filtrate.

Two synthetic methods were used for the synthesis of **2**. Method A has been used to synthesize **2A**. Some 0.130 g (2.0 mmol) of sodium azide dissolved in a minimum amount of water was added to 5 cm^3 of deionized water containing 0.245 g (1.0 mmol) of $Mn(CH_3CO_2)_2 \cdot 4H_2O$ with stirring at room temperature. Then, 0.394 g (2.0 mmol) of 1,10-phenanthroline dissolved in 5 cm^3 of water–ethanol was added to the mixture. Yellow precipitates formed immediately. After stirring for half an hour, the reaction mixture was filtered. Orange, single crystals were obtained by slow evaporation of the filtrate.

Method B, a hydrothermal method, has been used to synthesize **2B**. In a teflon tube, 0.130 g (2.0 mmol) of sodium azide dissolved in a minimum of water was added to 5 cm^3 of deionized water containing 0.245 g (1.0 mmol) of $Mn(CH_3CO_2)_2 \cdot 4H_2O$ and 0.394 g (2.0 mmol) of 1,10-phenanthroline dissolved in 5 cm^3 of water–ethanol. The teflon tube was sealed and heated to 140°C. After 7 days, the tube was cooled slowly to room temperature and orange crystals were recovered by filtration. *Anal.* Calc. for **1** (%): C 48.62, H 3.40, N 16.53. Found: C 48.20, H 3.33, N 16.51. Calc. for **2A** (%): C 57.72, H 3.23, N 28.03. Found: C 57.46, H 3.17, N 27.53. Infrared spectra of **1** and **2** were recorded with a Shimadzu IR-480 spectrophotometer (4000–600 cm^{-1}) using a powdered sample spread on a KBr plate.

Crystal Structure Determinations

X-ray data for a single-crystal of **1** having approximate dimensions 0.25 × 0.20 × 0.10 mm were collected on an Enraf-Nonius CAD 4 diffractometer equipped with graphite-monochromatized Mo$K\alpha$ ($\lambda = 0.71073$ Å) radiation at room temperature. An ω–2θ scan mode was employed for the collection of data in the range $2.39° \leq \theta \leq 24.97°$. A total of 4340 reflections was collected, and 4186 independent reflections ($R_{\text{int}} = 0.0677$) were considered for use in the succeeding refinement. The data were corrected for Lorentz-polarization and absorption effects (DIFABS [13]).

The structure was solved by direct methods and refined by full-matrix least-squares methods on *F* using the SHELXTL-PC computer program package [14]. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions. The final refinement including hydrogen atoms converged to $R = 0.0693$ and $R_w = 0.1728$. The number of refined parameters was 353 with no restraints. Maximum and minimum peaks in the final difference Fourier synthesis were 0.546 and $-0.413\,\mathrm{e\,Å^{-3}}$. Atomic coordinates and equivalent isotropic displacement parameters for nonhydrogen atoms of **1** are listed in Table I.

Single crystal X-ray diffraction data for **2A** were collected at room temperature on an Enraf-Nonius CAD 4 diffractometer equipped with graphite-monochromatized Mo*Kα* ($\lambda = 0.71073$ Å) radiation operating in ω–2θ scanning mode. Intensity data were collected in the θ range 2.42–24.97°. The final refinement including hydrogen atoms converged to

TABLE I Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathrm{Å}^2 \times 10^3$) for nonhydrogen atoms of **1**

	x/a	*y/b*	*z/c*	*U*(eq)[a]
Mn(1)	2995(1)	4582(1)	2662(1)	50(1)
N(11)	1738(7)	2715(6)	2975(3)	63(2)
N(12)	2040(7)	1515(6)	3341(3)	61(1)
N(13)	2368(11)	276(7)	3713(4)	99(2)
N(1)	4562(6)	3735(6)	1536(3)	56(1)
N(2)	4543(7)	6331(6)	2114(3)	61(1)
C(1)	5647(8)	4573(8)	1120(3)	63(2)
C(2)	5665(8)	5953(8)	1429(4)	68(2)
C(11)	4463(11)	2517(9)	1249(4)	78(2)
C(12)	5505(15)	2009(11)	525(6)	107(3)
C(13)	6626(13)	2826(16)	134(6)	123(4)
C(14)	6738(10)	4163(11)	396(5)	94(3)
C(15)	7819(12)	5105(17)	0(6)	129(5)
C(16)	7887(13)	6408(17)	301(8)	143(6)
C(17)	6781(9)	6869(12)	1011(5)	91(3)
C(18)	6764(12)	8138(12)	1370(8)	119(4)
C(19)	5697(15)	8470(11)	2047(7)	116(4)
C(20)	4585(11)	7548(8)	2387(5)	81(2)
N(3)	4812(6)	3121(5)	3406(3)	47(1)
N(4)	2198(6)	5573(5)	3835(3)	55(1)
C(3)	4336(7)	3352(6)	4177(3)	45(1)
C(4)	2960(7)	4653(6)	4391(3)	49(2)
C(21)	6097(9)	2002(8)	3197(4)	64(2)
C(22)	6996(10)	985(8)	3726(4)	74(2)
C(23)	6475(10)	1200(8)	4506(4)	76(2)
C(24)	5159(9)	2391(7)	4752(4)	62(2)
C(25)	4606(11)	2728(10)	5556(4)	79(2)
C(26)	3316(11)	3928(10)	5735(4)	80(2)
C(27)	2474(9)	4977(8)	5182(4)	64(2)
C(28)	1133(10)	6292(10)	5335(5)	82(3)
C(29)	447(10)	7176(9)	4769(5)	73(2)
C(30)	975(9)	6801(8)	4025(4)	72(2)
C1(1)	446(3)	212(2)	1494(1)	73(1)
O(11)	305(11)	− 1070(10)	1222(6)	168(4)
O(12)	− 685(12)	1529(8)	1378(5)	169(4)
O(13)	270(2)	− 189(13)	2262(5)	299(10)
O(14)	2013(12)	293(12)	1123(7)	203(5)
O(1)	825(6)	6043(5)	2259(3)	81(1)
O(2)	8967(7)	4073(6)	2311(4)	106(2)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for nonhydrogen atoms of **2A**

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)[a]
Mn(1)	55(1)	−2138(1)	2366(1)	38(1)
N(1)	−479(3)	−2453(2)	731(2)	41(1)
N(2)	−1701(3)	−3483(2)	2594(2)	43(1)
N(3)	−595(3)	−1665(2)	4095(2)	39(1)
N(4)	−2322(3)	−418(2)	2442(2)	40(1)
C(1)	−1359(3)	−3304(2)	679(2)	40(1)
C(2)	−2024(3)	−3846(2)	1673(2)	43(1)
C(3)	−1843(3)	−594(2)	4290(2)	37(1)
C(4)	−2766(3)	75(2)	3409(2)	38(1)
N(11)	1690(3)	−971(2)	1753(2)	57(1)
N(12)	3117(4)	−1293(2)	1385(2)	59(1)
N(13)	4498(5)	−1580(4)	992(4)	126(2)
N(14)	2120(3)	−3780(2)	2699(2)	63(1)
N(15)	2166(3)	−4711(2)	3230(2)	51(1)
N(16)	2239(5)	−5653(3)	3739(3)	96(1)
C(11)	118(4)	−1929(3)	−178(2)	51(1)
C(12)	−127(4)	−2219(3)	−1173(2)	58(1)
C(13)	−977(4)	−3088(3)	−1239(2)	57(1)
C(14)	−1643(3)	−3661(2)	−295(2)	49(1)
C(15)	−2553(4)	−4593(3)	−287(3)	61(1)
C(16)	−3176(4)	−5090(3)	639(3)	65(1)
C(17)	−2942(3)	−4733(3)	1650(2)	51(1)
C(18)	−3571(4)	−5227(3)	2639(3)	66(1)
C(19)	−3237(4)	−4865(3)	3567(3)	65(1)
C(20)	−2284(4)	−3997(3)	3511(2)	53(1)
C(21)	221(3)	−2302(2)	4906(2)	45(1)
C(22)	−127(4)	−1908(3)	5932(2)	51(1)
C(23)	−1353(4)	−825(3)	6135(2)	51(1)
C(24)	−2279(3)	−124(2)	5304(2)	44(1)
C(25)	−3604(4)	1012(3)	5448(2)	54(1)
C(26)	−4469(4)	1634(3)	4631(2)	54(1)
C(27)	−4085(3)	1170(2)	3585(2)	44(1)
C(28)	−4999(3)	1767(3)	2716(2)	55(1)
C(29)	−4567(4)	1258(3)	1754(2)	58(1)
C(30)	−3221(4)	171(3)	1648(2)	50(1)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

$R = 0.0399$ and $R_w = 0.1107$. An orange cuboid crystal of **2B** was mounted on a computer-controlled BRUKER SMART 1000 CCD diffractometer with graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). Cell parameters were determined by least-squares calculations with θ ranging from 2.40 to 25.03° at room temperature. The final refinement including hydrogen atoms converged to $R = 0.0327$ and $R_w = 0.0846$. Atomic coordinates and equivalent isotropic displacement parameters for nonhydrogen atoms of **2A** and **2B** are listed in Tables II and III, respectively. Crystallographic data and structure refinement details for **1, 2A** and **2B** are given in Table IV.

RESULTS AND DISCUSSION

IR Spectra

Both the IR spectra of **1** and **2** exhibit intense absorption bonds at about 2050 and 1340 cm^{-1} associated with asymmetric and symmetric stretching modes of azide.

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for nonhydrogen atoms of **2B**

	x/a	y/b	z/c	U(eq)[a]
Mn(1)	5000	1963(1)	7500	43(1)
N(1)	3403(1)	1417(2)	7182(1)	46(1)
N(2)	5042(1)	200(2)	6560(1)	49(1)
N(3)	4605(2)	3404(3)	8405(2)	80(1)
N(4)	4013(2)	4029(2)	8719(1)	61(1)
N(5)	3398(3)	4624(4)	9042(2)	133(1)
C(1)	2600(2)	1976(3)	7508(2)	58(1)
C(2)	1639(2)	1580(3)	7309(2)	69(1)
C(3)	1507(2)	607(3)	6742(2)	71(1)
C(4)	2327(2)	− 8(3)	6374(2)	58(1)
C(5)	2249(2)	− 1042(3)	5776(2)	75(1)
C(6)	3057(3)	− 1635(3)	5458(2)	77(1)
C(7)	4031(2)	− 1250(3)	5712(2)	62(1)
C(8)	4895(2)	− 1861(3)	5415(2)	81(1)
C(9)	5798(2)	− 1441(3)	5683(2)	83(1)
C(10)	5841(2)	− 398(3)	6255(1)	63(1)
C(11)	4145(2)	− 222(2)	6289(1)	46(1)
C(12)	3276(2)	425(2)	6625(1)	46(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE IV Crystallographic data and structure refinement details for **1**, **2A** and **2B**

	1	**2A**	**2B**
Formula	$[\text{Mn(phen)}_2\text{N}_3 \cdot \text{H}_2\text{O}]$ $\text{ClO}_4 \cdot \text{H}_2\text{O}$	$\text{Mn(phen)}_2(\text{N}_3)_2$	$\text{Mn(phen)}_2(\text{N}_3)_2$
M	592.86	499.41	499.41
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	$Pbcn$
a(A)	8.624(2)	8.160(2)	13.4757(11)
b(A)	8.963(2)	11.095(2)	9.6051(8)
c(A)	17.782(4)	12.663(3)	16.9591(14)
α(°)	78.81(3)	83.78(3)	
β(°)	74.57(3)	82.57(3)	
γ(°)	73.61(3)	73.72(3)	
$V(\text{Å}^3)$	1260.5(5)	1088.1(4)	2195.1(3)
Z	2	2	4
D_{calc} (Mg m^{-3})	1.562	1.524	1.511
F(000)	606	510	1020
μ (Mo$K\alpha$) (mm^{-1})	0.685	0.644	0.638
hkl ranges	$-9\rightarrow10$, $-10\rightarrow12$, $0\rightarrow21$	$-9\rightarrow9$, $-13\rightarrow13$, $0\rightarrow15$	$-10\rightarrow16$, $-10\rightarrow11$, $-20\rightarrow20$
No. of collected reflections	4340	4001	8500
No. of independent reflections	4186	3812	1939
R_{int}	0.0677	0.0677	0.0336
Observed reflections ($I > 2\sigma(I)$)	1983	2874	1419
No. of refined parameters	353	316	159
Goodness-of-fit on F^2	1.436	1.021	1.012
R[a] [$I > 2\sigma(I)$]	0.0693	0.0399	0.0327
wR[a] [$I > 2\sigma(I)$]	0.1728	0.1107	0.0846
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.546, −0.413	0.310, −0.434	0.296, −0.250

[a] **1** : $w = 1/[\sigma^2(F_o^2) + (0.0800P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$; **2A** : $w = 1/[\sigma^2(F_o^2) + (0.0880P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$; **2B** : $w = 1/[\sigma^2(F_o^2) + (0.0487P)^2 + 0.7269P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Both of **1** and **2** have absorption bands at about 3050 cm^{-1} ($\nu_{C\text{–}H}$) and 1620, 1588, 1561 cm^{-1} ($\nu_{C=C}$, $\nu_{C=N}$), characteristic of phen. Water in **1** was evident in the IR spectrum. A broad band centered at 1100 cm^{-1} in **1** is signed to the ClO_4^- ($\nu_{Cl\text{–}O}$) stretch [15].

Crystal Structures

The molecular structure of **1** is illustrated in Fig. 1 with the atom-labeling scheme. Two 1,10-phenanthroline molecules chelate to a Mn(II) atom with *cis*-configuration. One nitrogen atom from an azide anion and one oxygen atom from a water molecule *cis*-coordinate to the Mn(II) atom to complete a distorted octahedral geometry. The main distortion arises from the bond angles [100.21(2)°, 94.43(19)°, 94.71(17)° for O(1)–Mn(1)–N(1), N(11)–Mn(1)–N(1), N(1)–Mn(1)–N(3), respectively]. Mn–N(phen) bond lengths range from 2.232(5) to 2.286(5) Å and are longer than Mn–N(azide) bond lengths (2.151(5) Å). The average N–N bond length (1.161 Å) for the azide ligand is slightly shorter than 1.181, 1.184 and 1.178 Å for terminal azide ligands [16–18].

The molecular structures of **2A** and **2B** are shown in Fig. 2. **2A** and **2B** are dimorphous compounds obtained by different synthetic procedures. The molecular structure of **2A** is quite similar to that of **1** with the main difference being that the water molecule is replaced by an azide ligand. The main distortion of the octahedron arises from the bond angles [93.47(9)°, 101.85(10)°, 89.83(8)° for N(11)–Mn(1)–N(1), N(14)–Mn(1)–N(1), N(1)–Mn(1)–N(4), respectively]. Mn–N(phen) bond lengths range from 2.252(2) to 2.315(2) Å, again being longer than Mn–N(azide) bond lengths (2.131(3) and 2.153(3) Å). The average N–N bond length (1.158 Å) is almost equal to that of **1**.

As can be seen from **2B** in Fig. 2, the coordination polyhedron around Mn(II) ion is a distorted octahedron with four nitrogen atoms of phen and two of N_3^-, where the latter two nitrogen atoms occupy two *cis*-positions. The molecular structure exhibits significant asymmetry. Two nitrogen atoms belonging to different phen molecules and two coordinating azide nitrogen atoms form a basal plane around Mn(II), the other two nitrogen atoms of phen occupy adjacent apical positions of a distorted

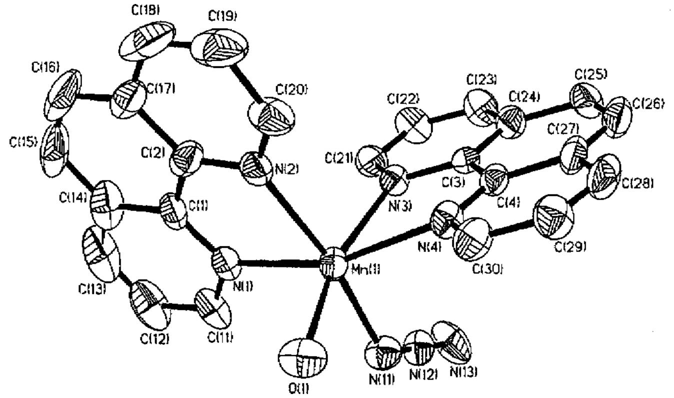

FIGURE 1 The molecular structure and atom-labeling scheme for **1**. H atoms have been omitted for clarity.

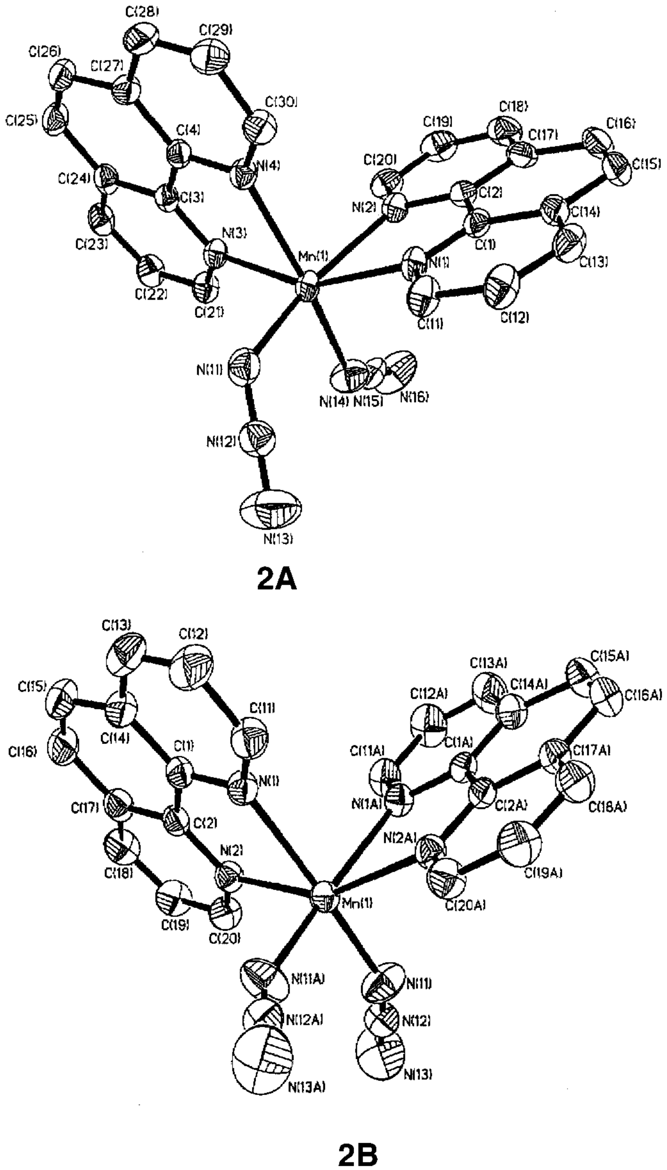

FIGURE 2 The molecular structures and atom-labeling schemes for **2A** and **2B**. H atoms have been omitted for clarity.

octahedron. It is noteworthy that the molecular structure of **2B** has C_2 symmetry, while **2A** does not. N(3)–Mn(1)–N(1), N(3A)–Mn(1)–N(1), N(1)–Mn(1)–N(2A) bond angles are 94.80(8), 102.40(9), 88.38(6)°, respectively, illustrating the main distortion. Mn–N(phen) bond lengths are 2.2793(17) and 2.3266(19) Å, respectively, while Mn–N(azide) bond lengths are 2.134(2) Å. The average N–N bond length is 1.138 Å, slightly shorter than in **1** and **2A**.

In summary, the syntheses and crystal structures of two stable mononuclear compounds $[Mn(phen)_2N_3 \cdot H_2O]ClO_4 \cdot H_2O$ and $Mn(phen)_2(N_3)_2$ have been reported.

These may be versatile precursors for the design of the heteropolymetallic systems. Further investigations of the synthesis and properties of homo- and hetero-nuclear compounds are in progress.

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Supplementary Material

Full lists of crystallographic data are available from the authors upon request.

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