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Synthesis, X-ray crystal structure, and electrochemistry of polynuclear azido-bridged manganese(III) and copper(II) Schiff base complexes

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ABSTRACT

New azido-bridged $[\text{Mn}^{\text{III}}(\text{salabza})(\mu\text{-}1,3\text{-N}_3)]_n$ (**1**), and $[\text{Cu}^{\text{II}}_4(\text{salabza})_2(\mu\text{-}1,1\text{-N}_3)_2(\text{N}_3)_2(\text{HOCH}_3)_2]$ (**2**) complexes with an unsymmetrical Schiff base ligand, $\{\text{H}_2\text{salabza} = N,N'\text{-bis}(\text{salicylidene})\text{-}2\text{-aminobenzylamine}\}$, have been synthesized, characterized by spectroscopic and electrochemical methods, and their crystal structures have been determined by X-ray diffraction. In complex **1**, each manganese(III) atom is coordinated with N_2O_2 donor atoms from salabza and two adjacent Mn(III) centers are linked by an end-to-end (EE) azide bridge to form a helical polymeric chain with octahedral geometry around the Mn(III) centers. Complex **2** is a centrosymmetric tetranuclear compound containing two types of Cu(II) centers with square pyramidal geometry. Each terminal copper atom is surrounded by N_2O_2 atoms of a salabza ligand, and the oxygen atom of the methanol molecule. Each central copper(II) ion is coordinated with two phenoxo oxygen atoms from one salabza, one terminal azido, and two end-on (EO) bridging azido ligands. The central copper(II) ions are linked to each other by the two end-on (EO) azido groups.

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1. Introduction

The field of molecular magnetism has attracted considerable attention, and advances have been made in designing novel molecular-based magnets with potential usage in information storage, and investigating the relationship between their structure and magnetic behavior [1]. Recently, special attention has been paid to the study of azido-bridging complexes in the field of molecular magnets [2–26]. The azide ligand is an extremely versatile ligand and also an excellent magnetic coupler, which gives easily tunable magnetic interactions between paramagnetic metal ions. This is due to the fact that the azide ligand can act as a bridge between transition metal atoms with different bridging coordination modes: $\mu\text{-}1,1$ (end-on or EO) [2–7], $\mu\text{-}1,3$ (end-to-end or EE) [7–15], $\mu\text{-}1,1,3$ [16], $\mu\text{-}1,1,1$ [3], and monodentate $\mu\text{-}1$ [5,14], which typically

obtain different magnetic coupling, such as antiferromagnetism [8,12–15], ferromagnetism [2,5], alternating ferro- and antiferromagnetism [17], ferrimagnetism [18], metamagnetism [19–21], spin-canting [22], spin-flop [23], spin-glass [24], single-molecule magnetism [25] and single-chain magnetism [26]. The magnetic coupling mediated through azide bridges is normally ferromagnetic [2,5] for the $\mu\text{-}1,1$ (end-on) mode and antiferromagnetic for the $\mu\text{-}1,3$ mode (end-to-end) [8,12–15]. Moreover, the magnetic properties for the $\mu\text{-}1,1$ bridged metal complexes are dependent on the M–N–M angle, and for the $\mu\text{-}1,3$ bridged metal complexes, it is dependent on the M–N–N angle and the M–N₃–M dihedral angle [2,27].

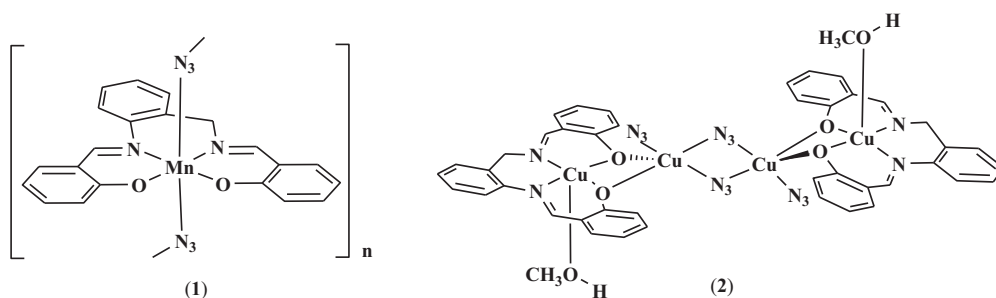
To date, numerous azido-bridging metal complexes have been reported, including distinct polynuclear (dinuclear, trinuclear, and tetranuclear) [3,8,28], one-dimensional (1D) chain [2,12,15], two-dimensional (2D) layered [7,23] and three-dimensional (3D) framework complexes [5].

In continuation of our work on the azido-bridged complexes [29,30], herein, we report on the synthesis, structure and electrochemical properties of a new helical one-dimensional coordination polymer, $[\text{Mn}(\text{salabza})$

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Scheme 1. The molecular structures of the compounds reported in this paper.

$(\mu\text{-}1,3\text{-N}_3)_n$, **1**, and a centrosymmetric tetranuclear copper(II) coordination complex $[\text{Cu}_4(\text{salabza})_2(\mu\text{-}1,1\text{-N}_3)_2(\text{N}_3)_2(\text{HOCH}_3)_2]$, **2** (Scheme 1). In complex **1**, the azide ligand acts in end-to-end mode, and in complex **2**, the azide ligand exhibits two types of coordination modes: end-on bridging fashion and terminal fashion.

2. Experimental

2.1. Materials and general methods

All the solvents and chemicals were of commercial reagent grade and used as received from Aldrich and Merck. Infrared spectra from KBr pellets were collected on a FT-IR JASCO 680 plus spectrometer in the range $4000\text{--}400\text{ cm}^{-1}$. UV-vis absorption spectra were recorded on a JASCO V-570 spectrophotometer. Elemental analyses were performed by using a PerkinElmer 2400 II CHNS-O elemental analyzer. Electrochemical properties of these complexes were studied by cyclic voltammetry. Cyclic voltammograms were recorded by using a SAMA 500 Research Analyzer using a three-electrode system, a glassy carbon working electrode (Metrohm 6.1204.110 with $2.0 \pm 0.1\text{ mm}$ diameter), a platinum disk auxiliary electrode and an Ag wire as reference electrode. CV measurements were performed in DMF with tetrabutylammonium hexafluoro phosphate (TBAH) as the supporting electrolyte. The solutions were deoxygenated by purging with Ar for 5 min. All electrochemical potentials were calibrated versus an internal $\text{Fc}^{+/0}$ ($E_0 = 0.46\text{ V}$ versus SCE) couple under the same conditions.

2.2. Synthesis of complexes

2.2.1. Synthesis of the $[\text{Mn}(\text{salabza})(\mu\text{-}1,3\text{-N}_3)]_n$ complex (**1**)

To 10 mL of a methanolic solution of $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.049 g, 0.2 mmol) were added 0.066 g (0.2 mmol) of $\text{H}_2\text{salabza}$ [31] dissolved in 10 mL of chloroform, and the resulting solution was stirred for 30 min. A solution of NaN_3 (0.052 g, 0.8 mmol) in methanol (15 mL) was then added slowly to the above mixture. The resulting brown solution was allowed to stand in the open air for about 3 hours to complete the air oxidation of Mn(II). The final solution was left undisturbed at room temperature, and dark brown crystals appeared after 6 days. The crystals were collected by filtration, washed with small amounts of methanol and dried in the air (Yield: 64%) Anal. calc. for $\text{C}_{21}\text{H}_{16}\text{MnN}_5\text{O}_2$: C, 59.30; H, 3.79; N, 16.47. Found: C, 59.12; H, 3.68; N, 16.30%. FT-IR (KBr, cm^{-1}) ν_{max} : 1617,

1603 (C=N), 2058 (bridging N_3). UV-vis: λ_{max} (nm) (ϵ , $\text{L mol}^{-1}\text{ cm}^{-1}$) (DMF): 322 (11942), 367 (9550), 620 (360).

2.2.2. Synthesis of the $[\text{Cu}_4(\text{salabza})_2(\mu\text{-}1,1\text{-N}_3)_2(\text{N}_3)_2(\text{HOCH}_3)_2]$ complex (**2**)

The complex **2** was prepared by a procedure similar to that of **1** except that $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.04 g, 0.2 mmol) was used instead of $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$. Dark brown crystals were collected by filtration and washed with small amounts of methanol (Yield: 72%). Anal. calc. for $\text{C}_{44}\text{H}_{40}\text{Cu}_4\text{N}_{16}\text{O}_6$: C, 46.31; H, 3.36; N, 19.64. Found: C, 47.31; H, 3.18; N, 19.17%. FT-IR (KBr, cm^{-1}) ν_{max} : 1630, 1608 (C=N), 2035 (bridging N_3), 2072 (terminal N_3). UV-vis: λ_{max} (nm) (ϵ , $\text{L mol}^{-1}\text{ cm}^{-1}$) (DMF): 384 (32 036), 622 (860).

2.3. Crystal structure determination and refinement

2.3.1. X-ray crystallography for **1** and **2**

Single crystals of **1** and **2** were obtained by slow evaporation of methanol-chloroform (1:1 v/v) solutions of these complexes at room temperature.

X-ray data of these compounds were collected at $T = 100\text{ K}$ on a Bruker Kappa APEXII CCD diffractometer with graphite monochromated $\text{MoK}\alpha$ ($\lambda = 0.71073\text{ \AA}$) radiation. Cell refinement and data reduction were performed with program SAINT [32]. Correction for absorption was carried out by the multi-scan method and program SADABS [32]. The structure was solved using

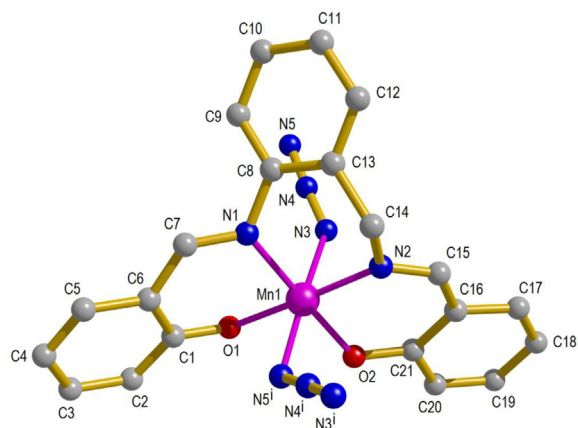


Fig. 1. The molecular structure of **1** with its atom labeling scheme. Symmetry code: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$. For interpretation of colors, see the online version of this article.

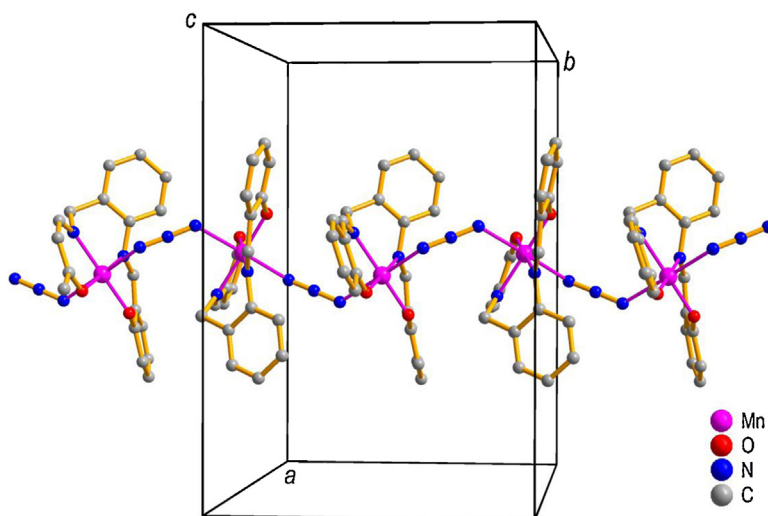


Fig. 2. The structure of **1**, showing the helical 1D-polymeric chain extending along the *b* axis. For interpretation of colors, see the online version of this article.

the program SHELXS97 and structure refinement on F^2 was carried out with the program SHELXL97 [33]. Structural diagrams were created with program DIAMOND [34].

3. Results and discussion

3.1. Description of structures

3.1.1. Crystal structure of $[\text{Mn}(\text{salabza})(\mu\text{-}1,3\text{-N}_3)]_n$ (**1**)

The diagram of a single unit with its atomic labeling scheme and the one-dimensional polymeric structure of

$[\text{Mn}(\text{salabza})(\mu\text{-}1,3\text{-N}_3)]_n$ are shown in Figs. 1 and 2, respectively. The crystallographic and refinement data for **1** are summarized in Table 1, and selected bond distances and angles are listed in Table 2.

$[\text{Mn}(\text{salabza})(\mu\text{-}1,3\text{-N}_3)]_n$ crystallizes in the orthorhombic space group *Pbca*. In this complex, each Mn atom is in octahedral environment, consisting of N_2O_2 donor atoms (two phenoxo oxygen and two imine nitrogen atoms) from the salabza ligand in equatorial positions and two nitrogen atoms from two bridging azide groups in axial positions. The $\text{Mn}(\text{salabza})$ units are linked by the

Table 1
Crystal data and structure refinement for **1** and **2** complexes.

Compound	(1)	(2)
Empirical formula	$\text{C}_{21}\text{H}_{16}\text{MnN}_5\text{O}_2$	$\text{C}_{44}\text{H}_{40}\text{Cu}_4\text{N}_{16}\text{O}_6 \cdot 2(\text{CH}_4\text{O})$
Formula weight	425.33	1207.16
Temperature (K)	100 (2)	100 (2)
Crystal system	Orthorhombic	Triclinic
Space group	<i>Pbca</i>	<i>P1</i>
<i>a</i> (Å)	16.5827 (5)	9.8597 (4)
<i>b</i> (Å)	11.2289 (3)	11.0946 (5)
<i>c</i> (Å)	19.8004 (5)	13.3326 (9)
α (°)	90.00	99.216 (3)
β (°)	90.00	107.350 (3)
γ (°)	90.00	112.957 (2)
<i>V</i> (Å ³)	3686.94 (18)	1216.76 (11)
<i>Z</i>	8	1
D_{calc} (mg/m ³)	1.532	1.647
μ (mm ⁻¹)	0.75	1.80
Crystal size (mm)	0.52 × 0.18 × 0.16	0.48 × 0.32 × 0.28
<i>F</i> (000)	1744	616
θ Ranges (°)	2.1–30.1	2.1–30.0
Index ranges	$-2 \leq h \leq 23$ $-15 \leq k \leq 15$ $-27 \leq l \leq 27$	$-13 \leq h \leq 13$ $-15 \leq k \leq 15$ $-18 \leq l \leq 18$
Absorption correction	Multi-scan	Multi-scan
Reflections collected	77879	30846
R_{int}	0.034	0.025
Data/restraints/parameters	5415/0/262	7058/0/337
Goodness-of-fit on F^2	1.02	1.06
Final <i>R</i> indices [$I > 2\sigma(I)$] ^a	$R_1 = 0.027$, $wR_2 = 0.072$	$R_1 = 0.035$, $wR_2 = 0.088$
Largest diff. peak and hole (e·Å ⁻³)	–0.23 and 0.49	–0.80 and 1.56

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$.

Table 2

Selected bond lengths (Å) and angles (°) for (1).

Mn1–O1	1.9003 (8)	Mn1–N3	2.2155 (10)
Mn1–O2	1.8922 (8)	Mn1–N5 ⁱ	2.2453 (11)
Mn1–N1	2.0243 (10)	N3–N4	1.1730 (15)
Mn1–N2	2.0278 (9)	N4–N5	1.1734 (15)
O1–Mn1–O2	92.91 (3)	O2–Mn1–N5 ⁱ	90.60 (4)
O1–Mn1–N1	88.07 (4)	N1–Mn1–N2	88.55 (4)
O1–Mn1–N2	176.07 (4)	N1–Mn1–N3	91.06 (4)
O1–Mn1–N3	94.67 (4)	N1–Mn1–N5 ⁱ	90.56 (4)
O1–Mn1–N5 ⁱ	86.86 (4)	N2–Mn1–N3	87.40 (4)
O2–Mn1–N1	178.52 (4)	N2–Mn1–N5 ⁱ	91.16 (4)
O2–Mn1–N2	90.52 (4)	N3–Mn1–N5 ⁱ	177.81 (4)
O2–Mn1–N3	87.76 (4)	Mn1–N3–N4	140.98 (9)
		Mn1–N5 ⁱ –N4 ⁱ	127.40 (9)

Symmetry codes: (i) 1 – x, y – ½, ½ – z

azide bridging groups, in μ -end-to-end (EE) mode, to form a one-dimensional coordination polymer. The unique feature of the resulting chain is that each monomeric unit is related to its neighboring ones by a 2-fold screw axis, leading to a helix propagating along the crystallographic *b* axis. The equatorial donor atoms N1, N2, O1, and O2 are nearly co-planar, with slight deviation from the mean plane: 0.026, –0.026, –0.027, and 0.027 Å, respectively, and the Mn atom deviates by only 0.007 Å from this plane. As expected for the Mn(III) ion, the axial Mn–N3 and Mn–N5 distances (2.2155 (10) and 2.2453 (11) Å, respectively) are longer than the two Mn–N distances in equatorial sites (Mn–N1 = 2.0243 (10) Å and Mn–N2 = 2.0278 (9) Å), due to the Jahn–Teller distortion of Mn(III) ions. In this complex, the bond angles about Mn are slightly distorted from the ideal values for a regular octahedral structure. The N–Mn–N *cis* angles are in the range 87.40 (4)–91.16 (4)° and the N–Mn–O *trans* angles are 176.07 (4) and 178.52 (4)°. All distances and angles of this complex are consistent with the corresponding distances in related manganese(III) complexes [15,22,35].

Table 3

Selected bond lengths (Å) and angles (°) for (2).

Cu1–O1	1.9100 (13)	Cu2–O1	2.2728 (13)
Cu1–O2	1.9393 (13)	Cu2–O2	1.9795 (13)
Cu1–O3	2.4569 (17)	Cu2–N3	1.9865 (16)
Cu1–N1	1.9692 (16)	Cu2–N3 ⁱ	2.0062 (16)
Cu1–N2	1.9399 (16)	Cu2–N6	1.9637 (17)
O1–Cu1–O2	81.86 (6)	O1–Cu2–O2	72.38 (5)
O1–Cu1–O3	84.69 (6)	O1–Cu2–N3	111.54 (6)
O1–Cu1–N1	94.41 (6)	O1–Cu2–N3 ⁱ	104.79 (6)
O1–Cu1–N2	168.55 (7)	O1–Cu2–N6	94.37 (6)
O2–Cu1–O3	100.81 (6)	O2–Cu2–N3	168.29 (6)
O2–Cu1–N1	159.23 (7)	O2–Cu2–N3 ⁱ	91.17 (6)
O2–Cu1–N2	92.31 (6)	O2–Cu2–N6	96.74 (7)
O3–Cu1–N1	99.16 (7)	N3–Cu2–N3 ⁱ	77.20 (7)
O3–Cu1–N2	86.76 (6)	N3–Cu2–N6	93.97 (7)
N1–Cu1–N2	94.46 (7)	N3 ⁱ –Cu2–N6	160.72 (7)
Cu1–O1–Cu2	97.99 (5)	N4–N3–Cu2	128.50 (14)
Cu1–O2–Cu2	107.75 (6)	N4–N3–Cu2 ⁱ	127.66 (14)
Cu2–N3–Cu2 ⁱ	102.81 (7)	N7–N6–Cu2	118.04 (15)

Symmetry codes: (i) 1 – x, 1 – y, 1 – z.

3.1.2. Crystal structure of $[Cu_4(\text{salabza})_2(\mu\text{-}1,1\text{-}N_3)_2(N_3)_2(\text{HOCH}_2)_2]$ (2)

The molecular structure of complex **2** is shown in Fig. 3. The crystallographic and refinement data for **2** are summarized in Table 1, and selected bond distances and angles are listed in Table 3.

This complex crystallizes in triclinic space group $P\bar{1}$, and the structure consists of a centrosymmetric tetranuclear molecule with two types of Cu(II) centers. The coordination geometry around all copper atoms is distorted square pyramidal. The terminal copper(II) ions, Cu1, are coordinated with N_2O_2 donor atoms from the salabza ligand in basal positions and one oxygen atom from CH_3OH in apical position. The central copper(II) ions, Cu2, are coordinated with one of the two phenoxo oxygen atoms from one salabza ligand, one terminal azido ligand, and two end-on (EO) bridging azido groups in the basal

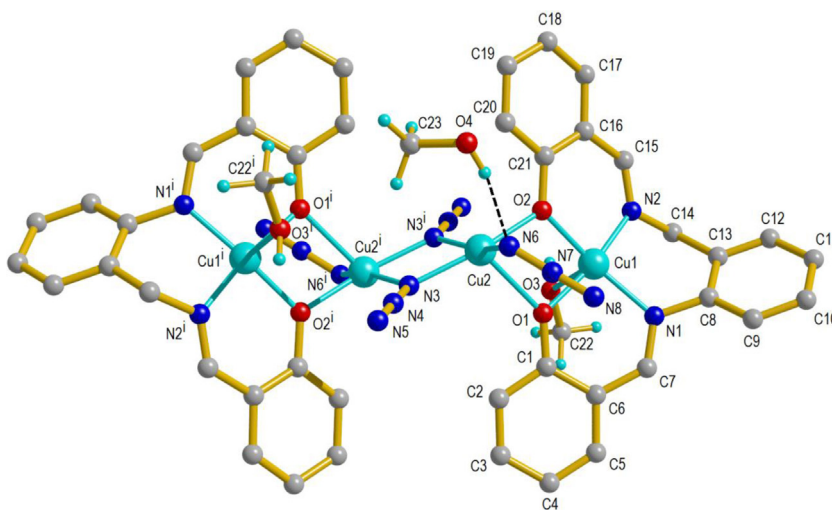


Fig. 3. The molecular structure of **2** with its atom labeling scheme. Symmetry code: (i) 1 – x, 1 – y, 1 – z. For interpretation of colors, see the online version of this article.

Table 4
Hydrogen bonds for **2** (Å and°).

D–H...A	D–H	H...A	D...A	D–H...A
O3–H3O...N5 ⁱⁱ	0.84	2.14	2.930 (3)	156
O4–H4O...N6	0.84	2.16	2.972 (3)	162

Symmetry codes: (ii) $x + 1, y, z$.

plane. The axial position is occupied by the second phenoxo oxygen atom from the same salabza ligand. The central copper(II) ions are linked to each other via two end-on (EO) azido groups.

In Cu1 centers, the bond lengths in the basal plane are Cu1–N1 = 1.9692 (16), Cu1–N2 = 1.9399 (16), Cu1–O1 = 1.9100(13), Cu1–O2 = 1.9393 (13) Å, and the axial Cu1–O3_{methanol} distance (2.4569 (17) Å) is markedly longer than the basal Cu1–O_{phenoxo} distance. This axial elongation could be attributed to the Jahn–Teller distortion of copper(II) ions. The deviations of the four basal donor atoms from the mean basal plane N1, N2, O1, and O2 are –0.223, 0.227, 0.256, and –0.261 Å, respectively, and the Cu1 atom is 0.098 Å out of the plane towards the apex. The two *trans* angles around the Cu1 centers, O1–Cu1–N2 = 168.55 (7)° and O2–Cu1–N1 = 159.23 (7)°, deviate significantly from the ideal value of 180° for a regular square pyramidal structure. The trigonality index (Addison parameter) $\tau = 0.155$ [$\tau = (\beta - \alpha)/60^\circ$, where α, β are the two largest L–M–L angles of the coordination sphere, with $\tau = 0$ and 1 for perfect square pyramidal and trigonal bipyramidal geometries, respectively [36]] confirms the distorted square pyramidal environment for Cu1.

In Cu2 centers, the basal plane around the Cu is defined by N3, N3ⁱ, N6 and O2, with bond lengths of Cu2–N3 = 1.9865 (16), Cu2–N3ⁱ = 2.0062 (16), Cu2–N6 = 1.9637 (17), and Cu2–O2 = 1.9795 (13) Å. The apical position of Cu2 is occupied by O1 with the Cu2–O1 bond length 2.2728 (13) Å, which is different from the Cu2–O2 bond length in basal position. This axial elongation is due to the Jahn–Teller effect reflecting the unique character of the copper(II) ion. The deviations of the four basal donor atoms from the mean basal plane N3, N3ⁱ, N6, and O2 are 0.132, –0.134, –0.111, and 0.113 Å, respectively, and the Cu2 atom is 0.176 Å out of

the plane towards the apex. The two *trans* angles, O2–Cu2–N3 = 168.29 (6)° and N6–Cu2–N3ⁱ = 160.72 (7)°, deviate significantly from the ideal value. The trigonality index of Cu2 is $\tau = 0.126$, while the corresponding value for the terminal copper(II) atoms is 0.155, indicating that the geometry of the terminal copper(II) atoms is more distorted than that of the central one. All distances and angles of this complex are consistent with the corresponding distances in related copper(II) azide complexes [28,37–39].

The intramolecular Cu...Cu distances between the adjacent copper atoms in **2** are 3.166 Å for Cu1...Cu2 and 3.121 Å for Cu2...Cu2ⁱ. Intermolecular hydrogen bond interactions occur between the hydroxyl H atoms of the methanol molecules (coordinated as well as uncoordinated) and the terminal N atoms of the azide groups (Table 4). The hydrogen bonds of the Cu1-bonded methanol, O3–H3O...N5, link the molecules in infinite chains parallel to [100] (Fig. 4). The uncoordinated methanol molecules establish branches.

3.2. Spectral characterization

The FT-IR spectral data of the two complexes are listed in Section 2. The vibrations appearing at 1617 and 1603 cm^{–1} for **1** and at 1630 and 1608 cm^{–1} for **2** are characteristic of two different imine (C=N) groups, as expected for the unsymmetrical Schiff base ligands. The strong absorption band at 2058 cm^{–1} in **1** is assigned to the bridging azido ligand, and the two strong absorption bands at 2035 and 2072 cm^{–1} in **2** clearly indicate the presence of both bridging and terminal azide ligands.

The UV–visible spectra of these compounds were recorded in DMF solution in the 200–800 nm region and the data are presented in Section 2. The absorption spectrum of Mn(III) complex consisted of a weak band at 620 nm attributed to the metal-centered ⁵E_g → ⁵T_{2g} transition, and two relatively intense bands at 367 and 322 nm corresponding to intraligand and charge-transfer transitions. The copper(II) complex shows a weak band at 622 nm, assigned to the d–d transition, ²B₁ → ²A₁, and an intense band at 384 nm, corresponding to the charge-transfer transition. The intraligand transition is observed as a shoulder close to the charge-transfer band.

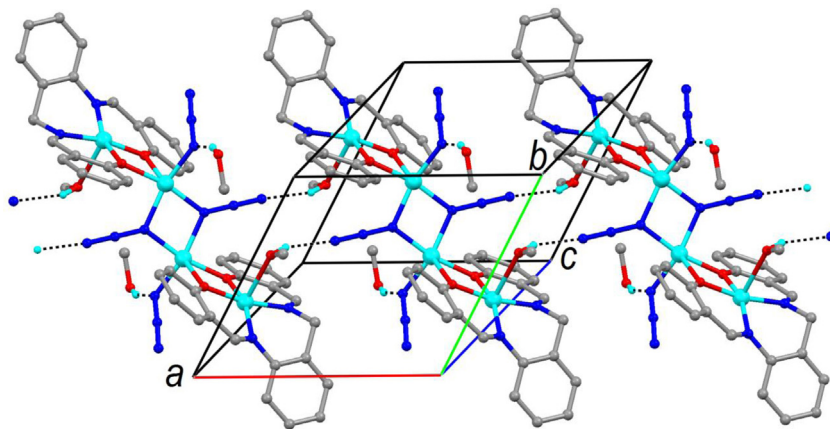


Fig. 4. Packing and hydrogen bonds (dashed lines) of 2. C-bonded H atoms were omitted for clarity. For interpretation of colors, see the online version of this article.

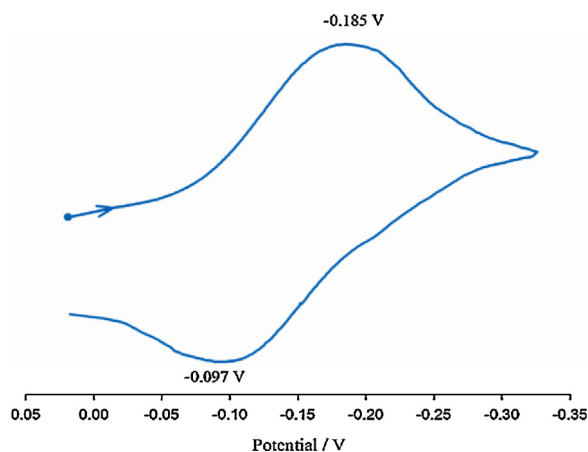


Fig. 5. Cyclic voltammogram of the **1** in DMF at 298 K, $c \approx 1 \times 10^{-3}$ M, scan rate = 100 mV/s.

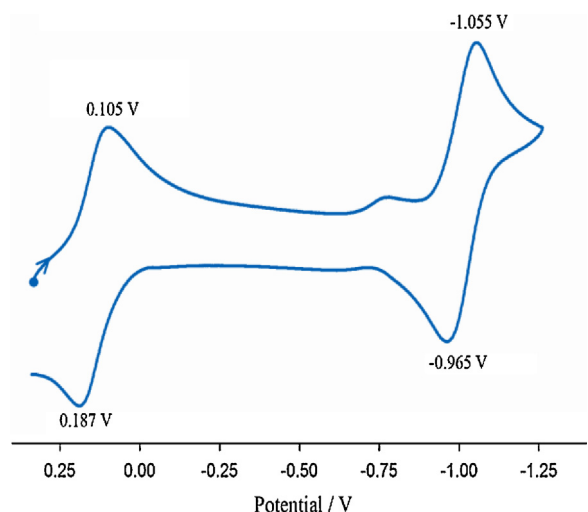


Fig. 6. Cyclic voltammogram of the **2** in DMF at 298 K, $c \approx 1 \times 10^{-3}$ M, scan rate = 100 mV/s.

3.3. Electrochemical studies

The cyclic voltammogram of $[\text{Mn}(\text{salabza})(\mu\text{-}1,3\text{-N}_3)]_n$ in DMF solution (Fig. 5) shows a quasi-reversible reduction process at -0.185 V, which is attributed to the reduction of $\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}$. A possible explanation of this feature is that in DMF solution compound **1** transforms into a mononuclear complex $[\text{Mn}(\text{salabza})(\kappa_1\text{-N}_3)(\kappa_1\text{O-DMF})]$ [40].

The cyclic voltammogram of the $[\text{Cu}_4(\text{salabza})_2(\mu\text{-}1,1\text{-N}_3)_2(\text{N}_3)_2(\text{HOCH}_3)_2]$ complex in DMF is shown in Fig. 6. Two successive quasi-reversible two-electron reductions were observed at 0.105 V for two Cu2 centers and at -1.055 V for two Cu1 centers. These $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ reductions reflect the existence of two types of Cu(II) centers with different coordination environments. The redox process for Cu2 centers appear at more positive potential as compared to that for the corresponding Cu1 centers, due to the electron-withdrawing nature of the azido ligands.

4. Conclusions

In summary, a new one-dimensional azido-bridged manganese(III) polymer, $[\text{Mn}(\text{salabza})(\mu\text{-}1,3\text{-N}_3)]_n$, and a centrosymmetric tetranuclear azido-bridged copper(II) complex $[\text{Cu}_4(\text{salabza})_2(\mu\text{-}1,1\text{-N}_3)_2(\text{N}_3)_2(\text{HOCH}_3)_2]$ have been synthesized, and fully characterized. The single crystal X-ray structure analysis of these complexes shows that, in complex **1**, the azide ligand acts in end-to-end ($\mu\text{-}1,3$) mode, and in complex **2**, the azide ligand exhibit two types of coordination modes: end-on bridging ($\mu\text{-}1,1$) mode and terminal mode.

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Appendix A. Supplementary data

Crystallographic data for **1** and **2** have been deposited within the Cambridge Crystallographic Data Centre. CCDC 919821 and 919822 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.crci.2013.03.010>.

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