

One-pot synthesis of an Mn(III)–Cu(II)–Mn(III) trinuclear heterometallic compound formed by Mn···S–Cu–S···Mn supramolecular interactions: Crystal structure of $[\{\text{Mn}^{\text{III}}(\text{salph})(\text{H}_2\text{O})\}_2\{\text{Cu}^{\text{II}}(\text{mnt})_2\}]\cdot 4\text{DMF}$

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Abstract. A one-pot synthesis, that includes $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$, Na_2mnt , H_2salph and $\text{Mn}(\text{CH}_3\text{COO})_3\cdot \text{H}_2\text{O}$, leads to the isolation of a trinuclear heterometallic compound $[\{\text{Mn}^{\text{III}}(\text{salph})(\text{H}_2\text{O})\}_2\{\text{Cu}^{\text{II}}(\text{mnt})_2\}]\cdot 4\text{DMF}$ (**1**) formed by Mn···S–Cu–S···Mn supramolecular interactions. Compound **1** crystallizes in the monoclinic space group $P21/c$ with $a = 13.433(4)$, $b = 16.283(5)$, $c = 15.072(4)$ Å, $\beta = 107.785(4)^\circ$, $Z = 2$. In the crystal structure, the complex anion $[\text{Cu}^{\text{II}}(\text{mnt})_2]^{2-}$ bridges two $[\text{Mn}^{\text{III}}(\text{salph})(\text{H}_2\text{O})]^{1+}$ cations through Mn···S contacts. The non-covalent hydrogen bonding and π – π interactions among the trinuclear $[\{\text{Mn}^{\text{III}}(\text{salph})(\text{H}_2\text{O})\}_2\{\text{Cu}^{\text{II}}(\text{mnt})_2\}]$ complexes lead to an extended chain-like arrangement of $[\text{Mn}^{\text{III}}(\text{salph})(\text{H}_2\text{O})]^{1+}$ cations with $[\text{Cu}^{\text{II}}(\text{mnt})_2]^{2-}$ anions embedded in between these chains.

Keywords. One-pot synthesis; trinuclear heterometallic compound; crystal structure; dithiolene; non-covalent supramolecular interactions.

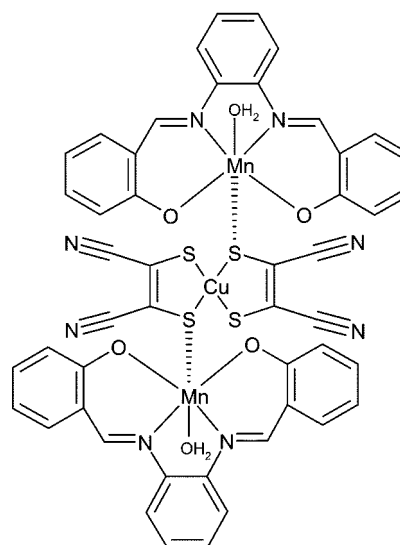
1. Introduction

Heterometallic transition metal compounds have attracted considerable interest in recent years because of their importance in the design and development of new magnetic systems.¹ Many of these multinuclear transition-metal complexes act as single molecule magnets (SMMs) that are mainly directed toward the development of new materials with novel electronic properties.² A common strategy to obtain such heterobimetallic systems is to use the metal precursors such as Cu(II)-oxamates, oximates, oxamides and hexacyanometalates; nevertheless, this kind of magnetically active heterometallic systems are still limited.³ We wish to introduce the classical inorganic coordination complex anion $[\text{Cu}(\text{mnt})_2]^{2-}$ as an active precursor to achieve a new multi-metallic heteronuclear system. In the present contribution, we describe synthesis and structural characterization of a Mn(III)–Cu(II)–Mn(III) heterometallic trinuclear compound $[\{\text{Mn}^{\text{III}}(\text{salph})(\text{H}_2\text{O})\}_2\{\text{Cu}^{\text{II}}(\text{mnt})_2\}]\cdot 4\text{DMF} \equiv$ (**1**) ($\text{H}_2\text{salph} = \text{N,N}'\text{-(o-phenylene)-bis(salicylideneimine)}$; $\text{mnt}^{2-} = 1,2\text{-dicyanoethylenedithiolate}$ ⁴). The molecular representation of **1** is outlined in scheme 1.

2. Experimental

2.1 Physical measurements

Microanalytical (C, H, N, S) data were obtained with a Flash EA 1112 Series CHNS analyser. IR spectra were recorded for KBr pellets with a JASCO



Scheme 1.

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FT/IR-5300 spectrometer in the region 400–4000 cm^{-1} . Electronic spectra were recorded with a UV-101PC/UV/Vis–NIR spectrophotometer (Shimadzu) equipped with a diffuse reflectance accessory. The ESR spectra were recorded on a (JEOL) JES-FA200 ESR spectrometer.

2.2 Synthesis of compound $[\{\text{Mn}^{\text{III}}(\text{salph})(\text{H}_2\text{O})\}_2\{\text{Cu}^{\text{II}}(\text{mnt})_2\}]\cdot 4\text{DMF}$ (**1**)

$\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (0.043 g, 0.25 mmol) in 5 ml of MeOH was added with stirring to a solution of Na_2mnt (0.1 g, 0.537 mmol) in 5 ml of MeOH; stirring was continued for 30 min. The resulting mixture was added to a brown solution of MeOH (20 ml) containing H_2salph (0.157 g, 0.5 mmol), Mn(III) acetate hydrate (0.116 g, 0.5 mmol), NaClO_4 (0.070 g, 0.57 mmol). The reaction mixture was stirred for 4–5 min at room temperature and a brown colour precipitate appeared. The resulting compound was separated by filtration, and then dried in vacuum. The dried precipitate was dissolved in DMF and the filtrated DMF solution was diffused by ether. The diffusion process was kept for one week and the resulted dark brown crystals were separated by decantation of solvent and subsequently washed with Et_2O . These crystals were suitable for single crystal X-ray analysis. Yield: 0.15 g (42%).

Analysis: Calc. for $\text{C}_{60}\text{H}_{60}\text{CuMn}_2\text{N}_{12}\text{O}_{10}\text{S}_4$: C, 51.078; H, 4.3; N, 11.92; S, 9.10%. Found C, 53.037; H, 4.28; N, 10.46; S, 8.74%.

IR (KBr): 2189; 1601; 1576; 1534; 1460; 1433; 1377; 1308; 1236; 1194; 1150; 1127; 1028; 926; 855; 812; 745; 633; 563; 544; 509; 444 cm^{-1} .

2.3 X-ray crystallography

Data were measured at 298(2) K on a Bruker SMART APEX CCD area detector system [$\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$], graphite monochromator, 2400 frames were recorded with an ω scan width of 0.3° , each for 8 s, crystal-detector distance 60 mm, collimator 0.5 mm. Data reduction was done by SAINTPLUS,⁵ absorption correction using an empirical method (SADABS)⁶ structure solution using SHELXS-97⁷ and refinement using SHELXL-97.⁸ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on salph ligand and DMF solvents were introduced on calculated positions and included in the refinement riding on their respective parent atoms. Additional details of the data collection parameters and refinement are

collected in table 1. CCDC Reference Number CCDC-618962 contains the supplementary crystallographic data for compound **1**. This can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

3. Results and discussion

Compound **1** was prepared from $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$, Na_2mnt , $\text{Mn}(\text{CH}_3\text{COO})_3\cdot \text{H}_2\text{O}$ and H_2salph in MeOH solvent. In this synthesis, the complexes $[\text{Cu}^{\text{II}}(\text{mnt})_2]^{2-}$ and $[\text{Mn}^{\text{III}}(\text{salph})(\text{H}_2\text{O})]^{1+}$ are formed *in situ*. This leads to the formation of ion pair complex $[\text{Mn}^{\text{III}}(\text{salph})(\text{H}_2\text{O})]_2[\text{Cu}^{\text{II}}(\text{mnt})_2]$, which appears as a dark brown solid. This, on crystallization from DMF, forms crystals of $[\{\text{Mn}^{\text{III}}(\text{salph})(\text{H}_2\text{O})\}_2\{\text{Cu}^{\text{II}}(\text{mnt})_2\}]\cdot 4\text{DMF} \equiv (\mathbf{1})$. This compound was characterized by elemental analysis, ESR, IR and electronic spectral studies. Compound **1** was finally characterized unambiguously by single crystal X-ray structural analysis.

Table 1. Crystal data and structure refinement for (**1**).

Empirical formula	$\text{C}_{60}\text{H}_{60}\text{N}_{12}\text{O}_{10}\text{S}_4\text{CuMn}_2$
Formula weight	1410.86
T (K)	298(2)
λ (\AA)	0.71073
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimensions	
a (\AA)	13.433(4)
b (\AA)	16.283(5)
c (\AA)	15.072(4)
α (deg)	90
β (deg)	107.785(4)
γ (deg)	90
V (\AA^3)	3139.3(15)
Z	2
D_{calc} (Mg m^{-3})	1.493
μ (mm^{-1})	0.932
$F(000)$	1454
Crystal size (mm^3)	$0.24 \times 0.15 \times 0.15$
θ range for data collection (deg)	1.59 to 25
Reflections collected/unique	28873/5513 [$R(\text{int}) = 0.0637$]
Max. and min. transmission	0.8728 and 0.8072
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5513/0/412
Goodness-of-fit on F^2	1.143
Final R indices [$I > 2 \text{ sigma}(I)$]	$R1 = 0.0618$, $wR2 = 0.1173$
$R1/wR2$ (all data)	0.0831/0.1243
Largest diff. peak/hole ($\text{e}\text{\AA}^{-3}$)	0.481/−0.530

The complex **1** crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit of $[\text{Mn}(\text{salph})(\text{H}_2\text{O})]_2[\text{Cu}(\text{mnt})_2] \cdot 4\text{DMF}$ (**1**), consisting of a manganese complex cation $[\text{Mn}(\text{salph})(\text{H}_2\text{O})]^{1+}$, half of $[\text{Cu}(\text{mnt})_2]^{2-}$ complex anion and two DMF molecules, is presented in figure 1. The thermal ellipsoidal plot of the full molecular structure of **1** is depicted in figure 2. Bond angles and bond lengths are given in table 2.

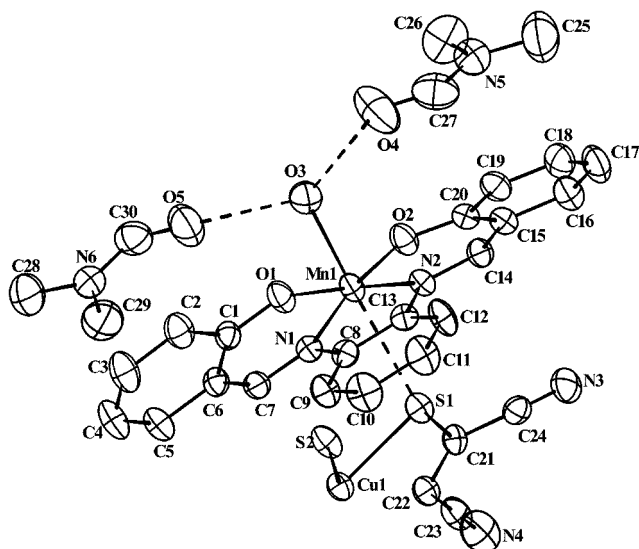


Figure 1. Thermal ellipsoidal plot (30% probability) of asymmetric unit, that contains one $[\text{Mn}(\text{salph})(\text{H}_2\text{O})]^{1+}$, half of $[\text{Cu}(\text{mnt})_2]^{2-}$ and two solvent DMF molecules. Hydrogen atoms are not shown for clarity.

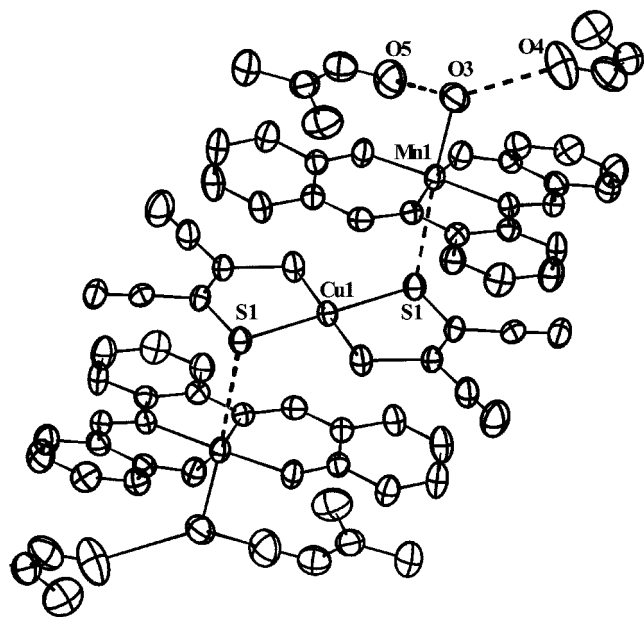


Figure 2. Thermal ellipsoidal plot (30% probability) of the full molecule. Hydrogens are not shown for clarity.

The basic structure of **1** is a Mn(III)–Cu(II)–Mn(III) trinuclear heterometallic entity, which is formed by two penta-coordinated Mn(III) monocationic $[\text{Mn}(\text{salph})(\text{H}_2\text{O})]^{1+}$ complexes and tetra-coordinated Cu(II) complex anion $[\text{Cu}(\text{mnt})_2]^{2-}$. The geometry around the Mn centre in the complex $[\text{Mn}(\text{salph})(\text{H}_2\text{O})]^{1+}$ is distorted square pyramidal, in which the equatorial positions are occupied by two nitrogen and two oxygen atoms of Schiff base ligand salph (see figures 1 and 2) and a water molecule is coordinated to the manganese centre from the apical position. The five-coordinated Mn(III) ion is situated 0.059 Å above the N_2O_2 plane of the Schiff base. Out-of-plane displacements (0.19 and 0.305 Å) are also found in the structures of similar compounds $[\text{Mn}(\text{salen})\text{Cl}]^9$ and $[\text{Mn}(\text{salen})\text{-S-P-C}_6\text{H}_4\text{NO}_2]^{10}$ respectively. The anion $[\text{Cu}(\text{mnt})_2]^{2-}$ has a planar structure, in good agreement with other relevant literature data.¹¹ Two $[\text{Mn}(\text{salph})(\text{H}_2\text{O})]^{1+}$ cations and one $[\text{Cu}(\text{mnt})_2]^{2-}$ anion interact through a strong $\text{Mn}\cdots\text{S}$ interaction (scheme 1, figures 1 and 2) and form the compound $\{[\text{Mn}^{\text{III}}(\text{salph})(\text{H}_2\text{O})]_2[\text{Cu}^{\text{II}}(\text{mnt})_2]\}$ in (**1**). The formation of **1** can be explained by the $\text{Mn}\cdots\text{S}$ contact that communicates between the vacant coordination site of manganese (an apical position opposite to the water apical position) and one of the dithiolate sulphur of complex $[\text{Cu}(\text{mnt})_2]^{2-}$ anion. One complex anion brings two $[\text{Mn}(\text{salph})(\text{H}_2\text{O})]^{1+}$ cations together from opposite directions and forms the trinuclear hetero-trimetallic compound **1**. In compound **1**, the sixth coordination about Mn1 is completed by the above-mentioned weak bond to S1 (the average Mn–S distance is 2.923 Å) from $[\text{Cu}(\text{mnt})_2]^{2-}$ anion. Thus, in the crystal structure of compound **1**, the geometry around the manganese ion is distorted octahedral. The Mn–S distance in **1** is unusually longer. This is probably due to its axial position in this Jahn–Teller distorted d^4 system.

The copper ion is located in a square-planar environment, formed from two dithiolene ligands. The copper ion is deviated by 0.0237 Å from the S_4 -plane of two mnt^{2-} ligands. The average $\text{Cu}\cdots\text{S}_\text{C}$ (S_C = sulphur involving interaction with Mn(III) cation) distance is 2.270 Å, which is shorter by 0.019 Å than the Cu–SN bond distance (2.289 Å), in which SN is sulphur atom, which is not involved in interactions with Mn(III) cation. The separations of $\text{Mn}\cdots\text{Cu}$ and $\text{Mn}\cdots\text{Mn}$ within **1** are 4.220 Å and 8.439 Å respectively. This $\text{Mn}\cdots\text{Mn}$ separation is slightly shorter than this (8.451 Å) in the crystal structure of the

Table 2. Bond lengths [Å] and angles [°] for **1**.

O(5)–C(30)	1.229(6)	C(25)–N(5)	1.443(6)
C(28)–N(6)	1.460(6)	C(30)–N(6)	1.298(6)
O(1)–C(1)	1.310(5)	O(1)–Mn(1)	1.864(3)
Mn(1)–O(2)	1.873(3)	Mn(1)–N(2)	1.982(3)
Mn(1)–N(1)	1.988(3)	Mn(1)–O(3)	2.184(4)
Mn(1)–S(1)	2.9226(14)	N(2)–C(14)	1.302(5)
N(2)–C(13)	1.431(5)	O(2)–C(20)	1.316(5)
N(1)–C(7)	1.295(5)	N(1)–C(8)	1.422(5)
C(13)–C(8)	1.387(5)	C(13)–C(12)	1.399(5)
C(15)–C(16)	1.409(6)	C(15)–C(20)	1.410(6)
C(15)–C(14)	1.424(5)	C(1)–C(2)	1.407(6)
C(1)–C(6)	1.417(5)	C(7)–C(6)	1.426(5)
C(20)–C(19)	1.406(5)	C(9)–C(10)	1.369(6)
C(9)–C(8)	1.381(5)	C(2)–C(3)	1.366(6)
C(6)–C(5)	1.416(6)	C(18)–C(19)	1.370(6)
C(18)–C(17)	1.379(6)	C(16)–C(17)	1.360(6)
C(4)–C(5)	1.357(6)	C(4)–C(3)	1.391(6)
C(12)–C(11)	1.370(6)	C(10)–C(11)	1.378(6)
Cu(1)–S(1) ^{#1}	2.2698(11)	Cu(1)–S(1)	2.2698(11)
Cu(1)–S(2)	2.2886(12)	Cu(1)–S(2) ^{#1}	2.2886(12)
S(2)–C(22) ^{#1}	1.734(4)	C(21)–C(22)	1.359(5)
C(21)–C(24)	1.437(5)	C(21)–S(1)	1.743(4)
C(22)–C(23)	1.427(6)	C(22)–S(2) ^{#1}	1.734(4)
C(24)–N(3)	1.139(5)	C(23)–N(4)	1.147(5)
N(5)–C(27)	1.307(7)	N(5)–C(26)	1.444(7)
N(6)–C(29)	1.439(6)	O(4)–C(27)	1.236(7)
O(5)–C(30)–N(6)	124.7(5)	C(1)–O(1)–Mn(1)	129.7(3)
O(1)–Mn(1)–O(2)	92.75(12)	O(1)–Mn(1)–N(2)	174.72(13)
O(2)–Mn(1)–N(2)	92.53(13)	O(1)–Mn(1)–N(1)	92.37(13)
O(2)–Mn(1)–N(1)	170.66(13)	N(2)–Mn(1)–N(1)	82.38(13)
O(1)–Mn(1)–O(3)	90.57(15)	O(2)–Mn(1)–O(3)	93.83(14)
N(2)–Mn(1)–O(3)	89.25(15)	N(1)–Mn(1)–O(3)	93.93(14)
O(1)–Mn(1)–S(1)	93.02(10)	O(2)–Mn(1)–S(1)	87.07(9)
N(2)–Mn(1)–S(1)	87.08(10)	N(1)–Mn(1)–S(1)	84.86(9)
O(3)–Mn(1)–S(1)	176.26(12)	C(14)–N(2)–C(13)	121.9(3)
C(14)–N(2)–Mn(1)	125.1(3)	C(13)–N(2)–Mn(1)	113.0(2)
C(20)–O(2)–Mn(1)	129.6(3)	C(7)–N(1)–C(8)	121.9(3)
C(7)–N(1)–Mn(1)	124.5(3)	C(8)–N(1)–Mn(1)	113.3(2)
C(8)–C(13)–C(12)	120.0(4)	C(8)–C(13)–N(2)	115.6(3)
C(12)–C(13)–N(2)	124.4(4)	C(16)–C(15)–C(20)	118.8(4)
C(16)–C(15)–C(14)	117.5(4)	C(20)–C(15)–C(14)	123.7(4)
O(1)–C(1)–C(2)	118.7(4)	O(1)–C(1)–C(6)	123.8(4)
C(2)–C(1)–C(6)	117.5(4)	N(1)–C(7)–C(6)	125.9(4)
O(2)–C(20)–C(19)	118.3(4)	O(2)–C(20)–C(15)	123.4(4)
C(19)–C(20)–C(15)	118.2(4)	C(10)–C(9)–C(8)	120.0(4)
N(2)–C(14)–C(15)	125.4(4)	C(3)–C(2)–C(1)	120.5(4)
C(5)–C(6)–C(1)	119.6(4)	C(5)–C(6)–C(7)	117.7(4)
C(1)–C(6)–C(7)	122.6(4)	C(19)–C(18)–C(17)	121.0(4)
C(17)–C(16)–C(15)	121.6(4)	C(5)–C(4)–C(3)	118.3(4)
C(16)–C(17)–C(18)	119.5(4)	C(9)–C(8)–C(13)	119.6(4)
C(9)–C(8)–N(1)	125.0(4)	C(13)–C(8)–N(1)	115.4(3)
C(11)–C(12)–C(13)	119.3(4)	C(18)–C(19)–C(20)	120.9(4)
C(2)–C(3)–C(4)	122.4(4)	C(9)–C(10)–C(11)	120.7(4)
C(4)–C(5)–C(6)	121.6(4)	C(12)–C(11)–C(10)	120.3(4)
S(1) ^{#1} –Cu(1)–S(1)	180.00(5)	S(1) ^{#1} –Cu(1)–S(2)	90.82(4)
S(1)–Cu(1)–S(2)	89.18(4)	S(1) ^{#1} –Cu(1)–S(2) ^{#1}	89.18(4)
S(1)–Cu(1)–S(2) ^{#1}	90.82(4)	S(2)–Cu(1)–S(2) ^{#1}	180.00(3)

(Contd...)

Table 2. (Contd...)

C(22) ^{#1} –S(2)–Cu(1)	100.35(14)	C(22)–C(21)–C(24)	120.9(4)
C(22)–C(21)–S(1)	122.3(3)	C(24)–C(21)–S(1)	116.8(3)
C(21)–C(22)–C(23)	119.8(4)	C(21)–C(22)–S(2) ^{#1}	123.5(3)
C(23)–C(22)–S(2) ^{#1}	116.8(3)	N(3)–C(24)–C(21)	178.3(5)
C(21)–S(1)–Cu(1)	100.96(13)	C(21)–S(1)–Mn(1)	101.80(13)
Cu(1)–S(1)–Mn(1)	108.05(4)	N(4)–C(23)–C(22)	179.2(6)
C(27)–N(5)–C(25)	123.3(5)	C(27)–N(5)–C(26)	119.4(5)
C(25)–N(5)–C(26)	117.2(5)	C(30)–N(6)–C(29)	118.9(4)
C(30)–N(6)–C(28)	122.7(5)	C(29)–N(6)–C(28)	118.4(4)
O(4)–C(27)–N(5)	125.5(6)		

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

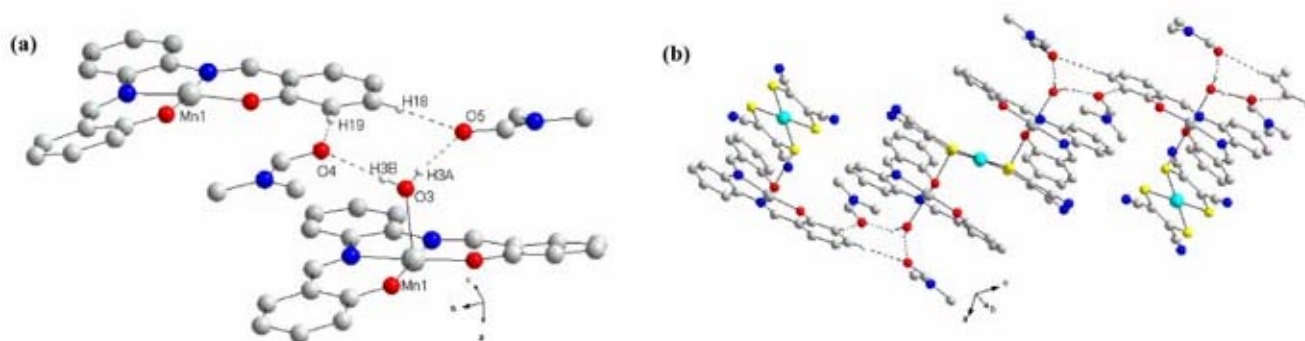


Figure 3. (a) Hydrogen bonding interactions that involve two $[\text{Mn}(\text{saloph})(\text{H}_2\text{O})]^{1+}$ complex cations and two DMF molecules. (b) The chainlike arrangement formed by hydrogen bonding interactions. Colour code: C, black; O, red; N, blue; S, yellow; Mn, gray; Cu, cyan.

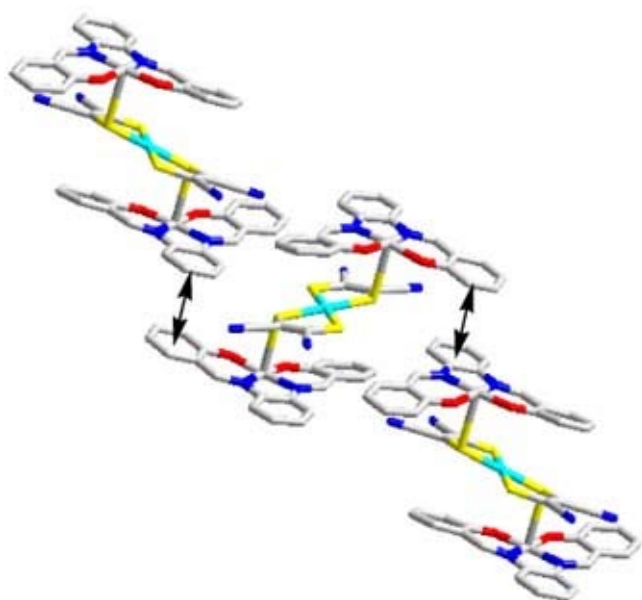


Figure 4. The π - π interactions among the trinuclear compounds. Colour code: as in figure 3.

previously reported Mn(III)–Cu(II)–Mn(III) trinuclear heterometallic system, in which the three complexes are linked by Mn–O contact.¹² In the crystal structure of **1**, the Mn(III)–S–Cu(II) angle is 108° .

Interestingly, the non-covalent intermolecular interactions (such as hydrogen bonding and π - π interactions) among trinuclear complexes play an important role in constructing a new type of supramolecular assembly. The oxygens of two solvated DMF molecules undergo bifurcated hydrogen-bonding interactions, that involve coordinated water hydrogens (H3A and H3B, see figure 3a) from a trinuclear complex and two aromatic hydrogen atoms (H18 and H19, see figure 3a) of an adjacent trinuclear complex, leading to a chainlike arrangement (figure 3b). The linking region is a nine-membered ring, formed by two DMF molecules and two manganese complexes as shown in figure 3a. The relevant hydrogen bonding parameters are given in table 3. The π - π interaction between trinuclear complexes, in which the mean plane separation (MPS) is 3.908 \AA , is shown

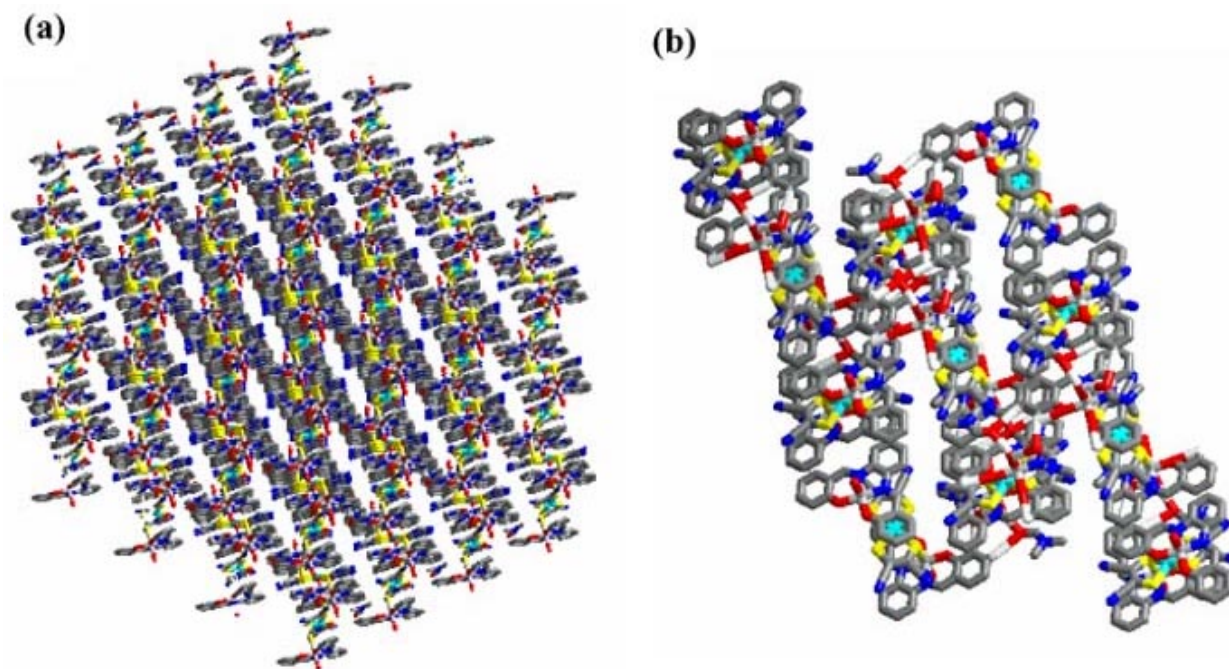


Figure 5. (a) Molecular packing in the crystal structure of **1** showing a porous type of supramolecular framework. (b) A close view of the packing diagram. Colour code: as in figure 3.

Table 3. Hydrogen bonding parameters in the crystal structure of **1**.

D–H···A	$d(\text{D}\cdots\text{H})$	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle(\text{DHA})$
O3–H3A···O5 ^{#1}	0.82	1.86	2.664(5)	165.4
O3–H3B···O4 ^{#2}	0.73(4)	1.98(5)	2.712(5)	174(6)
C19–H19···O4 ^{#3}	0.93	2.50	3.425(6)	173.8
C18–H18···O5 ^{#4}	0.93	2.65	3.561(6)	165.1

Atoms with additional labels #1, #2, #3, and #4 are related to each other by symmetry operations: #1 $x, y - 1, z$, #2 $x, -y + 1/2, z - 1/2$, #3 $x, y, z - 1$, #4 $x, -y + 3/2, z - 1/2$

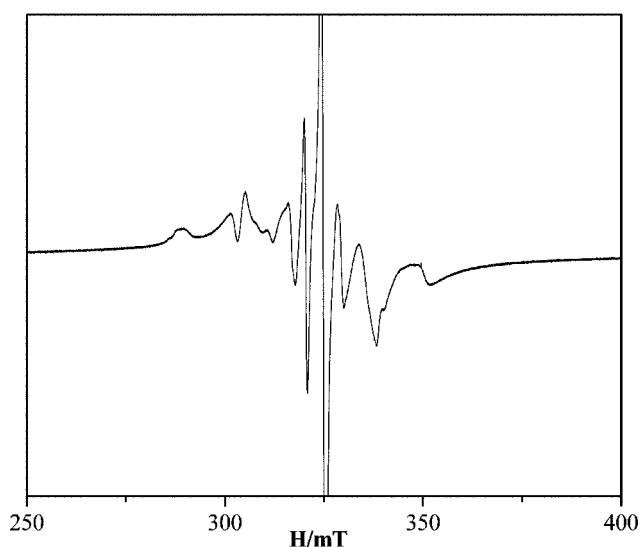


Figure 6. ESR spectrum of **1** at liquid N₂ temperature in DMF solvent.

in figure 4. The combination of the above described hydrogen bonding and π – π interactions results in the formation of porous type of supramolecular framework as shown in figure 5a. In this framework, the chainlike arrangements (formed by H-bonding interactions) are brought together by π – π interaction, which is more clearly shown in figure 5b.

The ESR spectrum of compound **1** was recorded at liquid nitrogen temperature in DMF solution (figure 6). The ESR spectrum, originated from $[\text{Cu}(\text{mnt})_2]^{2-}$, gets resolved due to ^{63}Cu nucleus and is considerably perturbed by the presence of paramagnetic manganese complexes interacting with copper complex (see also figures 1 and 2).

The electronic absorption spectrum of **1** in DMF solution is shown in figure 7. This is characterized by absorptions with λ_{max} at 286 nm and 324 nm and a shoulder at ~ 430 nm (figure 7a). A weak feature is observed at 1200 nm (figure 7b). The absorption band

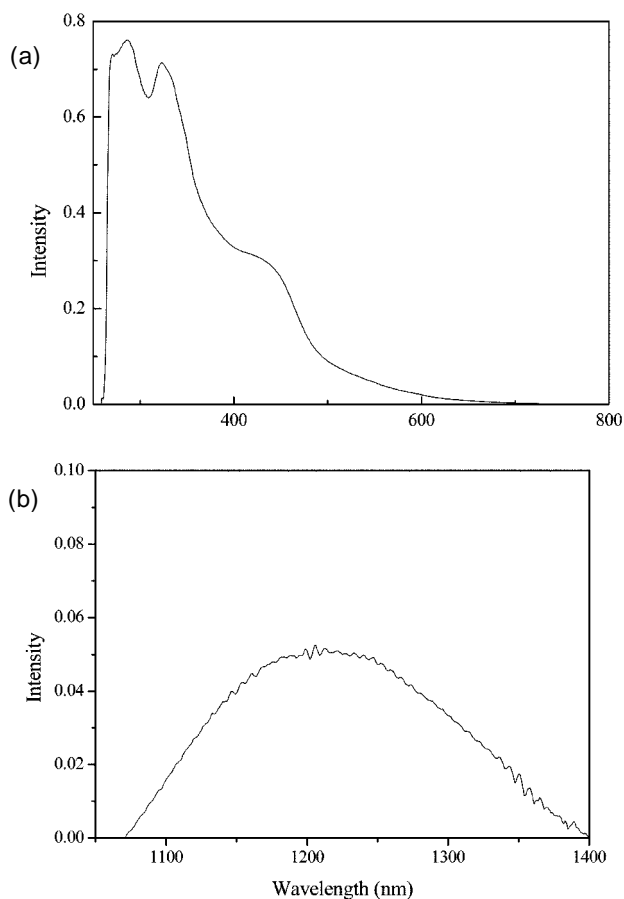


Figure 7. Electronic absorption spectra **1**: (a) 1×10^{-5} M and (b) 1×10^{-3} M in DMF at room temperature.

in the near-IR region is assigned to $d-d$ transition for a Cu^{2+} ion present in $[\text{Cu}(\text{mnt})_2]^{2-}$ complex anion.

4. Conclusion

We succeeded in demonstrating that two $[\text{Mn}(\text{salph})(\text{H}_2\text{O})]^{1+}$ Schiff base cationic complexes recognize a $[\text{Cu}(\text{mnt})_2]^{2-}$ dianion mediated by $\text{Mn}\cdots\text{S}-\text{Cu}-\text{S}\cdots\text{Mn}$ strong supramolecular interaction. In other words, the anionic $[\text{Cu}(\text{mnt})_2]^{2-}$ complex precursor is capable of functioning as a bridging ligand to give rise to a Mn(III)–Cu(II)–Mn(III) heterometallic trinuclear system induced by $\text{Mn}\cdots\text{S}$ interaction. In the near future, we intend to explore the chemistry of other similar heterometallic systems with magnetic properties by choosing different $[\text{M}(\text{Schiff base})]^{n+}$ complex cations ($\text{M} = \text{Mn}^{3+}$, Fe^{3+} and Cr^{3+}) and $[\text{M}(\text{dithiolate})_2]^{n-}$ anions ($\text{M} = \text{Ni}^{2+}$, Pd^{2+} , Pt^{2+}). Taking advantage of this synthetic strategy, we hope to generate a series of SMM (single molecular magnet) and SCM (single chain magnet) materials.

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