

Synthesis, Crystal Structure, and Magnetic Properties of $\{[\text{Cu}(\text{oxbe})]\text{Mn}(\text{H}_2\text{O})[\text{Cu}(\text{oxbe})(\text{DMF})]\}_n \cdot n\text{DMF} \cdot n\text{H}_2\text{O}$: From Dissymmetrical Mononuclear Entities to a 3D Heterometallic Supramolecular Coordination Polymer

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Self-assembly of the building block $[\text{Cu}(\text{oxbe})]^-$ with $\text{Mn}(\text{II})$ led to a novel coordination polymer $\{[\text{Cu}(\text{oxbe})]\text{Mn}(\text{H}_2\text{O})[\text{Cu}(\text{oxbe})(\text{DMF})]\}_n \cdot n\text{DMF} \cdot n\text{H}_2\text{O}$, where H_3oxbe is a new dissymmetrical ligand *N*-benzoato-*N'*-(2-aminoethyl)-oxamido and DMF = dimethylformamide. The crystal forms in the triclinic system, space group $P\bar{1}$, with $a = 9.260(4)$ Å, $b = 12.833(5)$ Å, $c = 15.274(6)$ Å, $\alpha = 76.18(3)^\circ$, $\beta = 82.7(3)^\circ$, $\gamma = 82.31(3)^\circ$, and $Z = 2$. The crystal structure of the title complex reveals that the two-dimensional bimetallic layers are constructed of $\text{Cu}^{\text{II}}\text{Mn}^{\text{II}}$ - Cu^{II} chains linked together by carboxylate bridge and hydrogen bonds help to produce a novel three-dimensional channel-like structure. The magnetic susceptibility measurements (5–300 K) were analyzed by means of the Hamiltonian $\hat{H} = -2J\hat{S}_{\text{Mn}}(\hat{S}_{\text{Cu1}} + \hat{S}_{\text{Cu2}})$, leading to $J = -17.4 \text{ cm}^{-1}$.

Introduction

The design of metal-containing building blocks to spontaneously assembly into interesting molecular architectures is of considerable interest in view of the nature of magnetic exchange interactions between metal ions through bridging ligands.¹ A successful strategy leading to one-, two-, and three-dimensional (1D, 2D, 3D) systems is the use of metal cations to link reactively stable coordination compounds containing potential bridging blocks, i.e., the “complex as

ligand” approach. These anionic precursors are particularly suitable for designing heterobinuclear complexes or heterobimetallic chain compounds and have played an important role in the development of molecular magnetism.^{2–7}

Symmetrically *N,N'*-disubstituted oxamidate derivatives are known to be versatile organic ligands which can chelate as well as bridge the metal ions to construct discrete and extended structures, depending on the *cis* or *trans* conformation (Scheme 1).^{8,9} By suitable choice of the terminal groups bonded to the M ion in a Cu–M heterobinuclear complex, the formation of *cis*-oxamidato-bridged heteromolecular units can be used as a “complex as ligands”, following a stepwise

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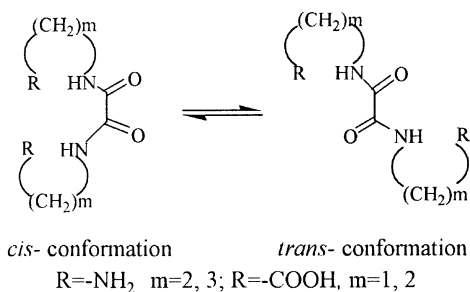
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Scheme 1. Symmetrically *N,N'*-Disubstituted Oxamidate Derivatives

strategy to synthesize new large clusters with special spin topologies.¹⁰ When the bricks have two different bridges,^{1f,3,4,7,11b} the units can be linked together to give 1- and 2D heterometallic supramolecular coordination polymers on one hand. On the other hand, the bistridentate character of this kind of ligand in trans conformation allows the formation of *trans*-oxamidato-bridged binuclear copper units which behave as building blocks to be linked together by other bridging groups, such as azide,¹² cyanate,¹³ 4,4'-bipyridine,¹⁴ pyrimidine,^{14,15} carboxylate,¹⁶ cyanide,¹⁷ hydroxyl ion,¹⁸ etc., to construct extended 1D or 2D homobimetallic polymers. Indeed, as pointed by Kahn,¹¹ to explore further this area of alternating bimetallic chains, it seems interesting to utilize dissymmetrical copper(II) precursors. So far, only two copper(II) precursors of this kind have been both structurally and magnetically characterized owing to synthetic difficulties: $[\text{Cu}(\text{obze})]^{2-}$ ^{7,11a} (obze = oxamido-

N-benzoato-*N'*-ethanoato); $[\text{Cu}(\text{obzp})]^{2-}$ ^{11b,c} (obzp = oxamido-*N*-benzoato-*N'*-propionato).

Here we report the preparation of a new dissymmetrical ligand *N*-benzoato-*N'*-(2-aminoethyl)oxamido (H_3oxbe), its copper(II) precursor, $\text{Na}[\text{Cu}(\text{oxbe})] \cdot 1.5\text{H}_2\text{O}$, and a 3D supramolecular coordination polymer $\{[\text{Cu}(\text{oxbe})]\text{Mn}(\text{H}_2\text{O})\}_n \cdot n\text{DMF} \cdot n\text{H}_2\text{O}$. Its magnetic properties are also investigated.

Experimental Section

Materials. All chemicals were of reagent grade and obtained commercially without further purification.

Synthesis of H_3oxbe . A 50 mmol (6.83 g) portion of ethyl oxalyl chloride in 10 mL of THF (THF = tetrahydrofuran) was added dropwise into a 40 mL THF solution of 50 mmol (6.86 g) of anthranilic acid. After 1 h, 30 mL of absolute ethanol was further added and the mixture was added dropwise into the solution which contained 30 mL of absolute ethanol and 30 mL of ethylenediamine at 0 °C. The resulting solution was stirred for 2 h, and H_3oxbe was precipitated as a white powder and washed with water and dried under vacuum at 100 °C. Yield: 10 g, 80%. Anal. Calcd for $\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}_4$: C, 52.60, H, 5.21, N, 16.70. Found: C, 52.58; H, 5.22; N, 16.73. IR (KBr, cm^{-1}): ν_{NH_2} 3307; $\nu_{\text{C=O}}$ (oxamidate group) 1636 cm^{-1} ; $\nu_{\text{as}(\text{COO})}$ (ν_{COOH} un-ionized) 1700 cm^{-1} .

Synthesis of the Copper(II) Precursor. An 8 mmol (2.00 g) amount of H_3oxbe and 24 mmol (0.96 g) of NaOH were dissolved in 100 mL of water/ethanol (v/v = 1:1). A 10 mL volume of aqueous solution containing 8 mmol (1.36 g) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was then added. The resulting violet-red solution was filtered and concentrated to 20 mL. Ethanol was then added slowly into the filtrate, and $\text{Na}[\text{Cu}(\text{oxbe})] \cdot 1.5\text{H}_2\text{O}$ precipitated as a red polycrystalline powder and was washed with ethanol and dried under vacuum at room temperature. Yield: 2.6 g, 90%. Anal. Calcd for $\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}_{5.5}\text{NaCu}$: C, 36.51; H, 3.62; N, 11.62; Cu, 17.56. Found: C, 36.44; H, 3.68; N, 11.69; Cu, 17.46. IR (KBr, cm^{-1}): ν_{NH_2} 3314 cm^{-1} ; $\nu_{\text{C=O}}$ 1649 cm^{-1} .

Synthesis of the Title Compound. A 1 mmol (0.362 g) amount of $\text{Na}[\text{Cu}(\text{oxbe})] \cdot 1.5\text{H}_2\text{O}$ was dissolved in 50 mL of water, and a solution containing 0.5 mmol (0.122 g) of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ was then added. The title compound was precipitated as a red polycrystalline powder and then recrystallized from DMF to give dark green crystals, which were suitable for X-ray crystal analysis. Yield: 0.41 g, 95%. Anal. Calcd for $\text{C}_{28}\text{H}_{38}\text{N}_8\text{O}_{12}\text{Cu}_2\text{Mn}$: C, 39.07; H, 4.45; N, 13.02; Cu, 14.77; Mn, 6.38. Found: C, 39.16; H, 4.99; N, 13.18; Cu, 14.75; Mn, 6.42. IR (KBr, cm^{-1}): ν_{NH_2} 3315 cm^{-1} ; $\nu_{\text{C=O}}$ 1647 cm^{-1} .

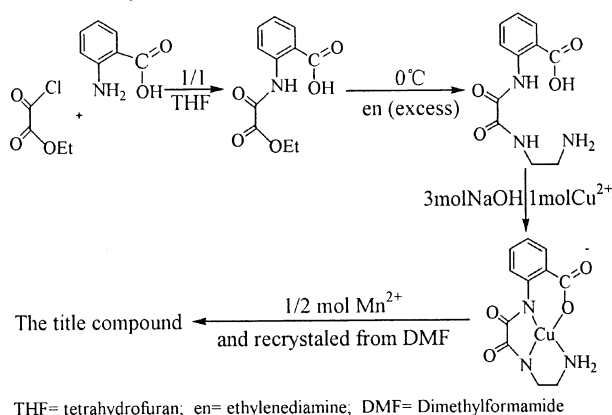
The synthesis route is shown in Scheme 2.

Physical Measurements. Elemental analyses for C, H, and N were carried out on a Perkin-Elmer elemental analyzer, model 2400II. The metal contents were determined by EDTA titration. The infrared spectrum was recorded on Avater-360 spectrometer using KBr pellets in 400–4000 cm^{-1} . UV–vis spectra were recorded on a α spectrometer in the 200–800 nm range. X-band EPR spectra were recorded on a Varian E-115 EPR spectrometer. Thermogravimetric analysis was carried out on the Perkin-Elmer-7 type analyzer in a nitrogen atmosphere, and the complex was heated to 600 °C at a heating rate of 10 °C/min. Magnetic measurement was carried out on polycrystalline samples with a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

Crystal Structure Determination and Refinement. A dark green single crystal (0.40 × 0.28 × 0.16 mm³) of the title complex

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Scheme 2. Synthetic Route



THF= tetrahydrofuran; en= ethylenediamine; DMF= Dimethylformamide

Table 1. Crystal and Structure Refinement Data for the Title Complex

empirical formula	$C_{28}H_{38}N_8O_{12}Cu_2Mn$
fw	860.68
cryst syst	triclinic
space group	$P\bar{1}$
a , Å	9.260(4)
b , Å	12.833(5)
c , Å	15.274(6)
α , deg	76.18(3)
β , deg	82.75(3)
γ , deg	82.31(3)
V , Å ³	1738.4(12)
Z	2
D_c , g cm ⁻³	1.644
λ (Mo K α), Å	0.710 73
μ (Mo K α), mm ⁻¹	1.642
T , K	293(2)
R1 [$I > 2\sigma(I)$] ^a	0.0566
wR2 ^b	0.1176

^a $R1 = \sum(|F_o| - |F_c|) / \sum|F_o|$. ^b $wR2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

was selected and mounted on Siemens P4 diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.710 73$ Å). Data were collected at room temperature to a θ_{max} of 25.00° with a total 7611 reflections collected including 6112 independent reflections ($R_{int} = 0.0249$). A summary of the crystallographic data is given in Table 1. The structure was solved with the heavy-atom method and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the *SHELXTL-97* program.¹⁹ A full-matrix least-squares refinement on F^2 was carried out using the *SHELXTL-97* program. The final agreement factor values are $R1 = 0.0566$ and $wR2 = 0.1176$ ($I > 2\sigma(I)$). The DMF molecule coordinated to the Cu1 atom appeared to be disordered. Selected bond distances and angles are given in Table 2.

Results and Discussion

IR Spectra. The ligand H₃oxbe exhibits one $\nu_{C=O}$ vibration of the oxamidate group at ca. 1636 cm⁻¹,²⁰ one $\nu_{as(COO)}$ vibration band at ca. 1700 cm⁻¹ (ν_{COOH} un-ionized),²¹ and the bands of the ν_{N-H} group (oxamidate group) at ca. 2955, 3017, and 3083 cm⁻¹. These bands are all missing in the

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Table 2. Selected Bond Length (Å) and Angles (deg) for the Title Complex

Mn—O(6) ^{#1}	2.114(4)	Mn—O(3)	2.182(4)
Mn—O(8)	2.194(4)	Mn—O(4)	2.195(4)
Mn—O(W1)	2.207(5)	Mn—O(7)	2.211(4)
Cu(1)—O(1)	1.881(4)	Cu(1)—N(2)	1.914(5)
Cu(1)—N(1)	1.976(5)	Cu(1)—N(3)	2.032(5)
Cu(1)—O(9)	2.433(6)	Cu(2)—O(5)	1.933(4)
Cu(2)—N(5)	1.941(5)	Cu(2)—N(4)	1.972(5)
Cu(2)—N(6)	2.027(5)	Cu(2)—O(2) ^{#2}	2.299(5)
O(1)—C(7)	1.257(7)	O(2)—C(7)	1.238(7)
O(2)—Cu(2) ^{#3}	2.299(5)	O(3)—C(8)	1.255(7)
O(4)—C(9)	1.248(7)	O(5)—C(18)	1.279(7)
O(6)—C(18)	1.247(7)	O(6)—Mn ^{#4}	2.114(4)
O(7)—C(19)	1.256(6)	O(8)—C(20)	1.283(6)
N(1)—C(2)	1.420(7)	N(1)—C(8)	1.331(7)
N(2)—C(9)	1.304(7)	N(4)—C(19)	1.322(7)
N(4)—C(13)	1.428(7)	C(1)—C(7)	1.525(9)
C(8)—C(9)	1.527(8)	C(12)—C(18)	1.508(8)
C(19)—C(20)	1.527(8)		
O(6) ^{#1} —Mn—O(3)	94.41(17)	O(6) ^{#1} —Mn—O(8)	97.63(16)
O(3)—Mn—O(8)	167.92(15)	O(6) ^{#1} —Mn—O(4)	167.91(16)
O(3)—Mn—O(4)	76.35(15)	O(8)—Mn—O(4)	91.84(15)
O(6) ^{#1} —Mn—O(W1)	85.69(18)	O(3)—Mn—O(W1)	92.16(18)
O(8)—Mn—O(W1)	89.69(16)	O(4)—Mn—O(W1)	86.87(19)
O(6) ^{#1} —Mn—O(7)	95.52(16)	O(3)—Mn—O(7)	101.81(16)
O(8)—Mn—O(7)	76.15(14)	O(4)—Mn—O(7)	94.03(17)
O(W1)—Mn—O(7)	165.83(16)	O(1)—Cu(1)—N(2)	164.6(2)
O(1)—Cu(1)—N(1)	94.62(19)	N(2)—Cu(1)—N(1)	84.5(2)
O(1)—Cu(1)—N(3)	96.0(2)	N(2)—Cu(1)—N(3)	82.9(2)
N(1)—Cu(1)—N(3)	166.2(2)	O(1)—Cu(1)—O(9)	93.2(2)
N(2)—Cu(1)—O(9)	101.9(20)	N(1)—Cu(1)—O(9)	103.3(2)
N(3)—Cu(1)—O(9)	84.8(2)	O(5)—Cu(2)—N(5)	158.4(2)
O(5)—Cu(2)—N(4)	92.20(19)	N(5)—Cu(2)—N(4)	83.5(20)
O(5)—Cu(2)—N(6)	97.75(19)	N(5)—Cu(2)—N(6)	82.01(19)
N(4)—Cu(2)—N(6)	162.5(2)	O(5)—Cu(2)—O(2) ^{#2}	95.00(19)
N(5)—Cu(2)—O(2) ^{#2}	106.64(19)	N(4)—Cu(2)—O(2) ^{#2}	99.90(18)
N(6)—Cu(2)—O(2) ^{#2}	93.52(19)		

^a Symmetry transformations used to generate equivalent atoms: #1, $x - 1, y, z$; #2, $x + 1, y - 1, z$; #3, $x - 1, y + 1, z$; #4, $x + 1, y, z$.

spectrum of the mononuclear complex because of the loss of the protons of both the COOH and N—H (oxamidate group) groups, indicating the formation of the mononuclear Cu(II) complex. It must be stressed that one new sharp strong band observed in the mononuclear (1649 cm⁻¹) and trinuclear complex (1647 cm⁻¹) is the result of overlapping between $\nu_{as(COO)}$ of the ionized carboxylate group and the vibration of the oxamidate group ($\nu_{C=O}$) acting in a bidentate mode. In addition, the —NH₂ vibration at ca. 3307 cm⁻¹ for H₃-oxbe was present for all complexes and with small shift (3314 and 3315 cm⁻¹ for the mono- and trinuclear complex, respectively). Such a red shift indicates that the nitrogen of —NH₂ coordinates to the copper ion. The presence of a strong and broad absorption at ca. 3450 cm⁻¹ in the infrared spectra of mono- and trinuclear complexes is indicative of the presence of a hydrogen-bonded lattice and/or coordinated water molecules.²² No peak can be assigned unambiguously to metal—ligand vibrations in the range below 600 cm⁻¹, since the ligand itself has several absorptions in this region.

Electronic Spectra. The diffuse reflectance spectrum of the mononuclear compound exhibits a very broad peak around 18.80×10^3 cm⁻¹, which is consistent with the tetracoordination of a nearly square planar geometry. This

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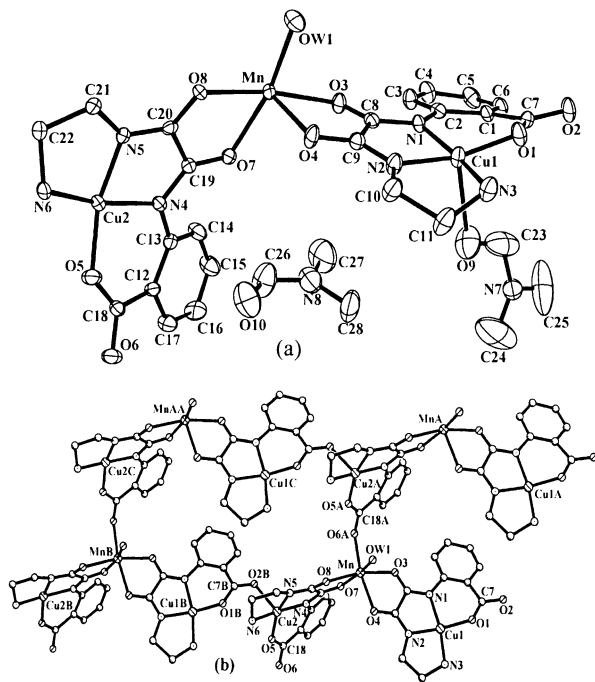


Figure 1. (a) ORTEP view of the dissymmetric segment of the title complex. (b) Molecular rectangle of the complex, showing the coordination environment around Mn, Cu(1), and Cu(2). DMF molecules were omitted for clarity.

fact is in accordance with the EPR spectra. The electronic spectrum of the trinuclear complex shows a broad-band absorption in the visible region with a maximum at $17.73 \times 10^3 \text{ cm}^{-1}$, and the frequency is lower than that of the mononuclear compound. Such a red shift of the d–d band may be attributed to the decreased planarity of the $[\text{CuN}_3\text{O}]$ chromophore and/or due to the square pyramidal CuN_3O_2 chromophore in DMF solution. The d–d bands of the $[\text{MnO}_6]$ chromophore, due to spin-forbidden transitions, are all too weak to be observed or are obscured by the d–d bands of Cu(II).

Besides the d–d bands, the spectrum of the mononuclear complex displays more intense bands centered at ca. 29.4×10^3 , 32.5×10^3 , and $42.4 \times 10^3 \text{ cm}^{-1}$, which can be assigned to $\pi(\text{ligand}) \rightarrow \text{Cu}(\text{II})(d_{x^2-y^2})$ LMCT and internal ligand $\pi \rightarrow \pi^*$ transitions, respectively.²¹ And the spectrum of the trinuclear species is the same as that of mononuclear one in this range.

Thermal Properties. Thermogravimetric analyses (TGA) show that the mononuclear compound loses 7.50% in the 25–150 °C temperature range, corresponding to the loss of one and a half water molecules for the mononuclear compound (expected, 7.46%). The title compound loses 21.10% of total weight in the 25–250 °C temperature range, corresponding to loss of two water molecules and two DMF molecules for the formula unit (expected, 21.17%). We also found that the title compound decomposes at about 340 °C, and the temperature is higher than that of the mononuclear compound (at about 290 °C). This indicates that the title compound is more stable than the mononuclear compound.

Description of the Crystal Structure. The structure unit of the title complex is shown Figure 1. Each unit consists of

a heterotrimeric neutral molecule, one DMF molecule disordered and bonded to the Cu1 atom, the other DMF molecule, and one water molecule involved in a network with hydrogen bonds. Two oxamidate anions act as bridges between the central and the outer metal ions. The environment of the central Mn^{2+} ion has a distorted octahedral geometry with four coplanar bonds of nearly equivalent length (Mn–O(3), 2.182(4) Å; Mn–O(4), 2.195(4) Å; Mn–O(8), 2.194(4) Å; Mn–O(6)[#], 2.114(4) Å) and two longer apical bonds (Mn–O(7), 2.211(4) Å; Mn–O(W1), 2.207(5) Å). The equatorial atoms deviate significantly from the plane (O(3), 0.0956 Å; O(4), –0.0959 Å; O(8), 0.0799 Å; O(6)[#], –0.0796 Å, respectively), the Mn atom being close to the least-squares plane through these atoms (O(3), O(4), O(8), O(6)[#]) and deviating by 0.0552 Å. The Cu(1) and Cu(2) atoms are all distorted square pyramidal with CuN_3O_2 surroundings. Two copper atoms are displaced 0.1901 and 0.2876 Å from the equatorial plane toward the apical position, respectively. Each copper atom occupies an inner site of the trideprotonated ligand with a CuN_3O environment in equatorial plane. A nitrogen atom from one DMF molecule occupies the apical position of Cu(1) atom with a apical bond length of 2.443(6) Å. And the apical position of Cu(2) atom is occupied by a “free” carboxylate oxygen atom from centrosymmetrically related chain with a $\text{Cu(2)–O(2)}^\#$ apical bond length 2.2995 Å. The equatorial plane of Cu(1) (N(1), N(2), N(3), O(1)) and the equatorial plane of Cu(2) (N(4), N(5), N(6), O(5)) make angles of 130.6 and 57.1° with the bridge plane (Mn: O(3), O(4), O(8), O(6)[#]) and 94.0° with each other. The distances of Mn–Cu(1), Mn–Cu(2), and Cu(1)–Cu(2) are 5.440, 5.490, and 9.672 Å, respectively.

Through the bonds of Mn–O(6)[#] and $\text{Cu(2)–O(2)}^\#$, asymmetric units are linked to form two chains, which construct the layer 2D network structure as depicted in Figures 1b and 2. This is the first structure in which 2D bimetallic chains are constructed by the bridging dissymmetric oxamidate ligand. The Mn and Cu(2A) atoms are bridged by one carboxylato bridge (O(5A)C(18A)O(6A)), with Mn–Cu(2A) separation 5.596 Å. The equatorial plane of Cu(2A) (N(4A), N(5A), N(6A), O(5A)) and the equatorial plane of Mn (O(3), O(4), O(8), O(6A)) make angles of 18.0 and 127.7° with the plane of carboxylate and of 112° with each other. The Mn and Cu(2A) atoms deviate from the plane of the carboxylato bridge (O(5A)C(18A)O(6A)) by 1.3964 and 0.2302 Å, respectively. The Cu(1B) and Cu(2) atoms are also bridged by another carboxylato bridge (O(1B)C(7B)O(2B)), with Cu(1B)–Cu(2) separation of 5.130 Å. The equatorial plane of Cu(2) (N(4), N(5), N(6), O(5)) and the equatorial plane of Cu(1B) (N(1B), N(2B), N(3B), O(1B)) make angles of 76.9 and 14.7° with the plane of carboxylate and of 94.1° with each other.

Extended networks can be assembled by both coordination and hydrogen bonds, in principle; the assembly of lower dimensionality polymers via hydrogen-bonding interactions can obtain higher dimensionality networks. A space-filling representation of the title complex illustrated in Figure 2c clearly demonstrates the formation of a nanoscopic rectangular cavity with an approximate dimension of $13 \times 4 \text{ Å}$,

Table 3. Hydrogen Bonds for the Title Complex

D-H	$d(D-H)$, Å	$d(H\cdots A)$, Å	<DHA, deg	$d(D\cdots A)$, Å	A	sym code
O(W1)-H(W1A)	0.850	1.961	169.56	2.801	O(10)	$x - 1, y, z$
O(W1)-H(W1B)	0.850	1.977	153.72	2.765	O(W2)	$x - 1, y - 1, z$
O(W2)-H2(WA)	0.850	2.032	155.03	2.825	O(5)	$-x + 2, -y - 1, -z + 2$
O(W2)-H2(WB)	0.850	1.956	159.28	2.767	O(8)	$-x + 1, -y - 1, -z + 2$
N(3)-H(3A)	0.900	2.110	159.71	2.970	O(W2)	$-x + 1, -y, -z + 2$
N(6)-H(6A)	0.900	2.176	136.38	2.895	O(1)	$x + 1, y - 1, z$
N(6)-H(6B)	0.900	2.354	163.57	3.227	O(8)	$-x + 1, -y - 2, -z + 2$

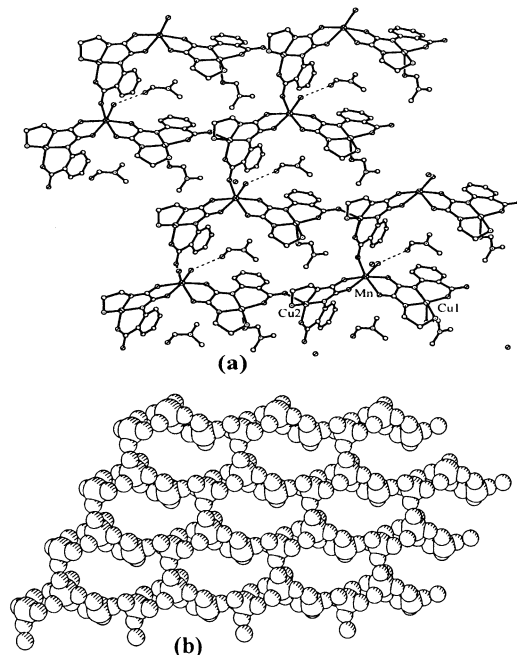


Figure 2. (a) Top view of the bimetallic chain of the complex perpendicular to the ab plane. (b) Space-filling model showing the molecular rectangle of the title complex.

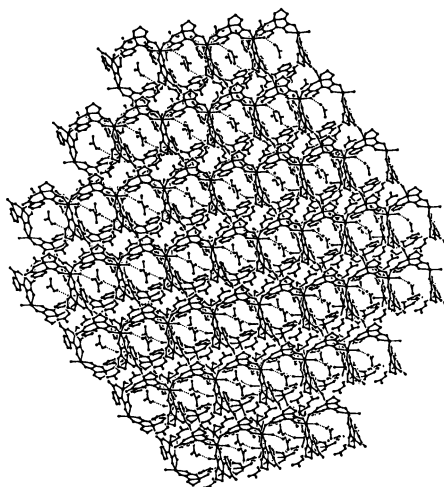


Figure 3. 3D channel-like structure.

which is occupied by the guest molecule DMF. The 2D layers are further connected by several kinds of hydrogen bonds to yield a novel 3D channel-like material, as depicted in Figure 3.

Hydrogen Bonds. A list of hydrogen bonds is given in Table 3. The guest DMF molecule is hydrogen bonded to the water coordinated to the Mn atom of the adjacent molecule, with $O(W1)\cdots O(10)$ distance of 2.801 Å ($x - 1, y, z$). The water coordinated to the Mn atom is also linked

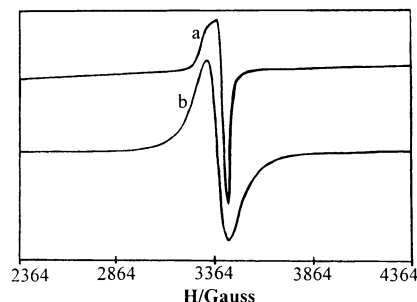


Figure 4. Powder X-band EPR spectra of complexes at room-temperature: (a) mononuclear; (b) trinuclear.

to the O(W2) through a hydrogen bond with $O(W1)\cdots O(W2)$ distance of 2.765 Å ($x - 1, y - 1, z$). O(W2) is also linked to the other layer O(5), O(8), and N(3) atoms with $O(W2)\cdots O(5)$ distance of 2.825 Å ($-x + 2, -y - 1, -z + 2$), $O(W2)\cdots O(8)$ distance of 2.767 Å ($-x + 1, -y - 1, -z + 2$), and $O(W2)\cdots N(3)$ distance of 2.970 Å ($-x + 1, -y, -z + 2$), respectively. The N(6) atom is linked to O(1) and O(8) atoms of the adjacent molecules with $N(6)\cdots O(1)$ distance being 2.895 Å and $N(6)\cdots O(8)$ distance being 3.227 Å ($-x + 1, -y - 2, -z + 2$). Through $O(W1)-H\cdots O(10)$, $O(W1)-H\cdots O(W2)-H\cdots O(5)$, $O(W1)-H\cdots O(W2)-H\cdots O(8)$, $O(W1)-H\cdots O(W2)\cdots H-N(3)$, $N(6)-H\cdots O(1)$, and $N(6)-H\cdots O(8)$ hydrogen bonds, the whole molecular structure can be seen as a 3D structure.

Electron Paramagnetic Resonance Spectra. The EPR spectra are shown in Figure 4. The EPR spectra of the mononuclear species for a polycrystalline powder at room temperature, exhibiting two types of g values, g_{\perp} and g_{\parallel} , have been used²³⁻²⁵ to distinguish unambiguously between $d_{x^2-y^2}$ and d_{z^2} ground states for which $g_{\parallel} > g_{\perp}$ and $g_{\perp} > g_{\parallel} \approx 2.00$, respectively. The X-band room-temperature EPR spectrum of polycrystalline samples of mononuclear complex is axial giving $g_{\parallel} = 2.081$, $g_{\perp} = 2.068$, and $g_{\parallel} > g_{\perp}$, and the hyperfine structure is not observed. These g -values confirm the presence of CuN_3O chromophores of geometry close to square planar with a basically $d_{x^2-y^2}$ ground state for the Cu(II) ion, as suggested by electronic spectroscopy. The powder EPR spectra of the trinuclear compound at room temperature are obviously different from the mononuclear fragment, showing a single and symmetrical resonance center at $g = 2.068$ without a detectable half-field transition. It is difficult to quantitatively interpret this band. Qualitatively, however, it is clear that these features reflect the exchange coupling

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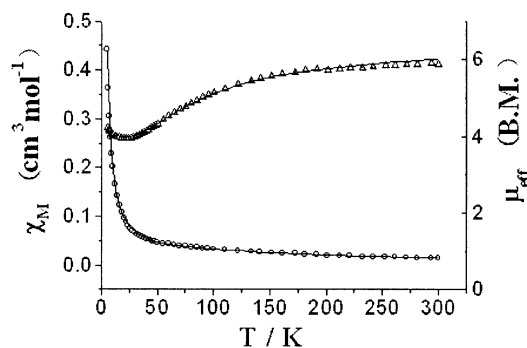


Figure 5. χ_M versus T and μ_{eff} versus T plots for the title complex.

between Cu^{2+} and Mn^{2+} ions. According to Kambe's approach,²⁶ three spins $S_{\text{Cu}(1)}^{2+} = 1/2$, $S_{\text{Cu}(2)}^{2+} = 1/2$, and $S_{\text{Mn}}^{2+} = 5/2$ couple to yield the total spin states of $S = 3/2$, $5/2$, $5/2$, and $7/2$. On the basis of Boltzmann's distribution, these states are both populated at room temperature owing to weak interactions. Thus, this broad-bond signal may be ascribed to a complex in these spin states.

Magnetic Properties. The magnetic susceptibility was measured in the temperature range 5–300 K on a MPMS-7 SQUID magnetometer. The room-temperature value for μ_{eff} ($5.99 \mu_{\text{B}}$, where μ_{eff} is the effective magnetic moment) is slightly smaller than that expected for uncoupled $\text{Cu}(1)(\text{II})$, $\text{Cu}(2)(\text{II})$, and $\text{Mn}(\text{II})$ trinuclear ions. Upon cooling, the μ_{eff} value decreases regularly, approaching a minimum around 25 K with $\mu_{\text{eff}} = 4.11 \mu_{\text{B}}$, which indicates the ground state $S = 3/2$ is thermally populated. Finally the μ_{eff} value increases as temperature is further lowered to 5 K, which possibly is due to the ferromagnetic interaction between trinuclear units.

From a magnetic viewpoint, there are three kinds of magnetic interactions for the present systems, namely, (i) $\text{Cu}(1)^{\text{II}}-\text{Mn}^{\text{II}}-\text{Cu}(2)^{\text{II}}$ through oxamidate bridges, (ii) $\text{Cu}(1\text{B})^{\text{II}}-\text{Cu}(2)^{\text{II}}$ through a carboxylate bridge ($\text{O}(1\text{B})\text{C}(7\text{B})\text{O}(2\text{B})$), and (iii) $\text{Mn}^{\text{II}}-\text{Cu}(2\text{A})^{\text{II}}$ through a carboxylate bridge ($\text{O}(5\text{A})\text{C}(18\text{A})\text{O}(6\text{A})$), as shown in Figure 1b. We take this bimetallic chain system as an isolated heterobinuclear

complex with only (i) $\text{Cu}(1)^{\text{II}}-\text{Mn}^{\text{II}}-\text{Cu}(2)^{\text{II}}$ through two oxamidate bridges and take (ii) and (iii) into account in the Θ value. The magnetic analysis was then carried out by using the theoretical expression of the magnetic susceptibility deduced from the spin Hamiltonian $\hat{H} = -2J\hat{S}_{\text{Mn}}(\hat{S}_{\text{Cu}(1)} + \hat{S}_{\text{Cu}(2)})$. The expression of the magnetic susceptibility for a CuMnCu system is

$$\chi_M = \{(Ng^2\beta^2)/[4K(T - \Theta)]\}[A/B] + N_\alpha \quad N_\alpha = 120 \times 10^{-6}$$

$$A = 84 \exp(5J/KT) + 35 \exp(-2J/KT) + 10 \exp(-7J/KT) + 35$$

$$B = 4 \exp(5J/KT) + 3 \exp(-2J/KT) + 2 \exp(-7J/KT) + 3$$

where J is the exchange integral between Mn and Cu(1) or Cu(2) ions. The best fitting for the experimental data gives $J = -17.4 \text{ cm}^{-1}$, $g = 2.02$, and $\Theta = 0.69$. Agreement factor $R = \sum(\chi_{\text{obsd}} - \chi_{\text{cacld}})^2 / \sum\chi_{\text{obsd}}^2$ is 8.38×10^{-5} , which corresponds to a good agreement as can be seen in Figure 5.

The J value is negative, suggesting that an antiferromagnetic interaction among the copper ions is operative. $\Theta > 0$, indicating the interaction between trinuclear units is ferromagnetic, which is also consistent with the μ_{eff} value increasing as temperature is lowered from 25 to 5 K.

The quality of the fittings for the equation stopped us from looking for an alternative model and taking into account the interaction through the carboxylate bridge and other interactions.

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Supporting Information Available: Tables listing detailed crystallographic data, complete lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters and X-ray data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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