

Synthesis, structures, and properties of two new binuclear complexes based on carboxyl-substituted nitronyl nitroxide: $[M_2(\text{NITpBA})_4(\text{H}_2\text{O})_2]$ (M = Zn and Cu)

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ABSTRACT

Two new binuclear complexes, $[M_2(\mu\text{-NITpBA})_4(\text{H}_2\text{O})_2]$ (M = Zn 1 and Cu 2) [where NITpBA = 2-(4-carboxyl-phenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-oxide], were synthesized and characterized. Magnetic susceptibility measurements revealed antiferromagnetic exchange interactions in the two complexes.

Keywords: Binuclear Complex; Carboxyl-Substituted; Nitronyl Nitroxide; Antiferromagnetic Exchange

1. INTRODUCTION

The past decade has triggered fast-growing interests in nitronyl nitroxide radicals (NITR) as building blocks in the engineering of molecular-based magnet. The reasons are mainly that they are the most stable paramagnetic ligands, even in combination with metal ions where they can also act as bridging ligands [1]. Carboxylate bridges mediate exchange interactions between coordinated metal centres [2,3]. Metal complexes with bridging carboxylates as well as stable organic radical ligands are of considerable interest to the field of molecular magnetism [4]. In an effort to bring together the two areas of research, carboxyl-substituted nitronyl nitroxide, as an important anionic ligand, was deemed favorable for the realization in reactions with metal ions. To the best of our knowledge, to prepare transition metal complexes with nitronyl nitroxide-substituted carboxylate ligands, many investigations on the scope have been recently performed, but the related reports are very scarce [5,6]. The only structurally characterized transition metal compounds are 1D-chain systems in which two nitronyl

nitroxides NITpBA^- are coordinated with two metal centers via one NO-group and a monodentate carboxylate group [7,8]. Miller's group even reported on copper (II) compounds with NITpBA^- assumed to be in a bidentate-bridging mode, but did not provide structural information on the related radical-metal compounds [9]. Rentschle's group examined the reaction of NITpBAH with different metal salts, bases, and terminal capping coligands following with various methods but could not isolate any dimeric compounds. Ligand exchange reaction of NITpBAH with copper (II) acetate hydrate, however, leads to the desired system. Recrystallization from hot dimethylsulfoxide/methanol (2:1) leads to formation of small green-blue crystals $\text{Cu}_2(\mu\text{-NITpBA})_4/\text{H}_2\text{O}/\text{dmsO}$ [10].

With the purpose of obtaining materials with unusual molecular high nuclearity spin clusters, we were interested in the preparation of carboxylate-bridged metal complexes with pendant organic radical substituents. In this paper, we present the simple synthesis and properties of two new metal-radical binuclear complexes $[M_2(\mu\text{-NITpBA})_4(\text{H}_2\text{O})_2]$ (M = Zn 1 and Cu 2).

2. EXPERIMENTAL

2.1. General

All reagents used in the synthesis were of analytical grade without further purification. 2-(4-carboxyl-phenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-oxide was prepared by the literature method [11]. Elemental analyses (C, H, and N) were carried out with a Perkin Elmer 240 C elemental analyzer. IR spectra were recorded from 400 to 4000 cm^{-1} on an Avatar-360 spectrophotometer using KBr pellets. Variable-temperature magnetic susceptibilities were measured with a MPMS-7SQUID magnetometer at a magnetic field of 2000 G. Diamagnetic corrections were made with Pascal's con-

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stants for all constituent atoms.

2.2. Synthesis of $[M_2(\mu\text{-NITpBA})_4(\text{H}_2\text{O})_2]$ (M = Zn 1 and Cu 2)

2.2.1. $[\text{Zn}_2(\mu\text{-NITpBA})_4(\text{H}_2\text{O})_2]$ 1

NITpBAH (0.4 mmol, 0.1076 g) was dissolved in 4 mL 0.2 M NaOH. The complex 1 was synthesized by the addition of NITpBA⁻ and ZnCl₂ (0.2 mmol, 0.0275 g) to 30 mL of methanol-water. The mixture was stirred for 2 h and then filtered. The resulting blue filtrate was kept at room temperature for slow evaporation. After a few days, dark blue crystals of compound 1 suitable for X-ray analysis were obtained. Anal. Found: C, 53.12; H, 5.30; N, 8.61% Calcd. for C₅₆H₆₈N₈O₁₈Zn₂ (1): C, 52.83; H, 5.39; N, 8.81%. IR (KBr disk): 1612 cm⁻¹ (ν_{as}COO⁻), 1413 cm⁻¹ (ν_sCOO⁻), 1355 cm⁻¹ (νNO).

2.2.2. $[\text{Cu}_2(\mu\text{-NITpBA})_4(\text{H}_2\text{O})_2]$ 2

The complex 2 was prepared in a procedure similar to complex 1 except that ZnCl₂ was replaced by CuCl₂. Dark blue crystals were obtained expectedly. Anal. Found: C,

52.53; H, 5.16; N, 8.74% Calcd. for C₅₆H₆₈N₈O₁₈Cu₂ (2): C, 52.98; H, 5.40; N, 8.83%. IR (KBr disk): 1610 cm⁻¹ (ν_{as}COO⁻), 1407 cm⁻¹ (ν_sCOO⁻), 1350 cm⁻¹ (νNO).

2.2.3. X-Ray Data Collection and Structure Determination

X-ray diffraction intensities were collected on a Bruker Smart CCD diffractometer equipped with a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) by using a ω - φ scan technique at room temperature. Absorption correction were applied using SADABS program [12]. The structures were solved by direct methods with SHELXS-97 program [13] and refined with SHELXS-97[14] by full matrix least-squares technique on F². All the non-hydrogen atoms were refined with anisotropic temperature parameters. Hydrogen atoms of organic ligands were fixed in ideal positions. The relevant parameters of the crystal structures for complex 1 and 2 are listed in **Table 1**, and the selected bond lengths and bond angles are given in **Tables 2** and **3**, respectively.

Table 1. Crystal data and structure refinement for the two complexes 1 and 2.

	1	2
Formula	C ₅₆ H ₆₈ N ₈ O ₁₈ Zn ₂	C ₅₆ H ₆₈ N ₈ O ₁₈ Cu ₂
Formula weight	1271.92	1268.26
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>
Unit cell dimensions (Å, °)		
<i>a</i>	10.415(2)	10.392(2)
<i>b</i>	12.770(3)	12.650(3)
<i>c</i>	22.987(5)	23.116(5)
β	98.02(3)	97.85(3)
Volume (Å ³), <i>Z</i>	3027.3(11), 2	3010.5(10), 2
F(000)	1328	1324
θ range for data collection (°)	1.83 to 28.40	1.84 to 28.40
Limiting indices	-13 ≤ <i>h</i> ≤ 13 -15 ≤ <i>k</i> ≤ 16 -30 ≤ <i>l</i> ≤ 30	-13 ≤ <i>h</i> ≤ 13 -16 ≤ <i>k</i> ≤ 16 -30 ≤ <i>l</i> ≤ 30
Reflections collected	51,237	52,552
Independent reflections	7419 [R(int) = 0.1174]	7505 [R(int) = 0.0545]
Completeness (%)	97.9	99.3
Goodness-of-fit on F ²	1.021	1.014
Final <i>R</i> indices (<i>I</i> > 2 σ(<i>I</i>))	<i>R</i> ₁ = 0.0771, <i>wR</i> ₂ = 0.1852	<i>R</i> ₁ = 0.0594, <i>wR</i> ₂ = 0.1582
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1399, <i>wR</i> ₂ = 0.2293	<i>R</i> ₁ = 0.0896, <i>wR</i> ₂ = 0.1785

Table 2. Selected bond distances (Å) and angles (°) for the complex 1.

Bond distances			
Zn(1)-Zn(1)#1	2.9672(12)	O(6)-C(15)	1.254(6)
Zn(1)-O(1W)	1.964(4)	N(1)-O(3)	1.275(7)
Zn(1)-O(2)#1	2.025(3)	N(2)-O(4)	1.298(16)
Zn(1)-O(5)	2.025(4)	O(8)-N(4)	1.288(5)
Zn(1)-O(1)	2.030(4)	O(7)-N(3)	1.276(6)
Zn(1)-O(6)#1	2.035(4)	N(4)-C(22)	1.340(6)
O(1)-C(1)	1.246(7)	C(22)-N(3)	1.354(6)
O(2)-C(1)	1.249(6)	N(1)-C(8)	1.233(8)
O(5)-C(15)	1.244(6)	C(8)-N(2)	1.447(13)
Bond angles			
C(1)-O(2)-Zn(1)#1	130.0(4)	O(2)#1-Zn(1)-O(6)#1	90.03(16)
C(15)-O(6)-Zn(1)#1	132.3(3)	O(5)-Zn(1)-O(6)#1	158.99(16)
O(1W)-Zn(1)-O(2)#1	100.2(2)	O(1)-Zn(1)-O(6)#1	87.75(17)
O(1W)-Zn(1)-O(5)	104.5(2)	O(1W)-Zn(1)-Zn(1)#1	171.23(17)
O(2)#1-Zn(1)-O(5)	87.60(16)	O(2)#1-Zn(1)-Zn(1)#1	77.48(12)
O(1W)-Zn(1)-O(1)	101.2(2)	O(5)-Zn(1)-Zn(1)#1	83.94(11)
O(2)#1-Zn(1)-O(1)	158.59(17)	O(1)-Zn(1)-Zn(1)#1	81.38(13)
O(5)-Zn(1)-O(1)	86.91(16)	O(6)#1-Zn(1)-Zn(1)#1	75.16(11)
O(1W)-Zn(1)-O(6)#1	96.5(2)	C(1)-O(1)-Zn(1)	124.4(4)

Symmetry codes: #1: x + 1, y, z + 2.

Table 3. Selected bond distances (Å) and angles (°) for the complex 2.

Bond distances			
Cu(1)-Cu(1)#1	2.6457(1)	O(6)-C(15)	1.253(4)
Cu(1)-O(2)#1	1.952(2)	O(5)-C(15)	1.253(4)
Cu(1)-O(1)	1.955(3)	O(3)-N(1)	1.248(9)
Cu(1)-O(5)	1.960(2)	N(2)-O(4)	1.275(6)
Cu(1)-O(6)#1	1.971(2)	O(7)-N(3)	1.279(5)
Cu(1)-O(1W)	2.121(3)	N(4)-O(8)	1.271(4)
O(2)-C(1)	1.255(4)	N(4)-C(22)	1.340(5)
O(1)-C(1)	1.254(5)	C(22)-N(3)	1.339(5)
Bond angles			
C(1)-O(2)-Cu(1)#1	124.1(2)	O(1)-Cu(1)-O(1W)	96.67(14)
C(15)-O(6)-Cu(1)#1	124.8(2)	O(5)-Cu(1)-O(1W)	100.95(14)
O(2)#1-Cu(1)-O(1)	167.82(12)	O(6)#1-Cu(1)-O(1W)	90.97(14)
O(2)#1-Cu(1)-O(5)	88.99(12)	O(2)#1-Cu(1)-Cu(1)#1	83.00(9)
O(1)-Cu(1)-O(5)	88.35(12)	O(1)-Cu(1)-Cu(1)#1	84.96(9)
O(2)#1-Cu(1)-O(6)#1	90.66(12)	O(5)-Cu(1)-Cu(1)#1	86.15(8)
O(1)-Cu(1)-O(6)#1	89.49(12)	O(6)#1-Cu(1)-Cu(1)#1	81.96(8)
O(5)-Cu(1)-O(6)#1	168.05(11)	O(1W)-Cu(1)-Cu(1)#1	172.74(13)
O(2)#1-Cu(1)-O(1W)	95.51(14)		

Symmetry codes: #1: x, y + 2, z.

3. RESULTS AND DISCUSSION

3.1. Description of Crystal Structures

Crystal analysis show that compounds 1 and 2 are iso structural. They crystallize in the monoclinic system, $P2_1/c$ (No.14) space group, which are different from that lecture [10] (triclinic system, space group P_1). The asymmetric unit consists of one-half of a dimeric metal ion bridged by O-carboxyl from four nitronyl nitroxide. The two halves are related to each other through a center of inversion located in the middle of the M-M axis. The coordination geometry of Zn (II) and Cu (II) lies at the center of the distorted octahedral geometry formed by five oxygen atoms, which come from four equivalent nitroxide ligand, one water molecule, and the M-M distances of the neighboring metal atoms is [Zn1-Zn1(A) 2.9672 Å and Cu1-Cu1(A) 2.6457Å], which is rather short and may be regarded as the normal M-M bonding range[15,16]. Their molecular structures are depicted in **Figures 1** and **2**, respectively.

In complex 1, the C1-O1 and C1-O2 bonds from the same carboxylate group are equal to 1.246 and 1.249 Å, respectively, whereas the distance of C15-O5 and C15-O6 are of 1.244 and 1.254 Å, respectively. The Ph-COO bonds of 1.5093 Å are close to that reported in the literature [11]. The C-C bond lengths of the phenyl rings show no alternation and are located in the aromatic region ranging from 1.361 to 1.394 Å. The Zn-O_{water} distance of 1.964 Å is shorter than that of Zn-O whose oxygen atoms are from Ph-COO⁻. Four oxygen atoms from Ph-COO⁻ of the nitroxide ligand compose the equatorial plane. The O5-Zn1-O6A angle in the equatorial plane is 158.99°, and the O1-Zn1-O2A angle is equal to 158.59°. The O1W-Zn1-Zn1A angle in the axial position is 171.23°. The Zn (II) center is displaced by 0.324 Å from the basal O4-plane toward the axial oxygen atom from H₂O. The fragment O4-N2-C8-N1-O3 is non-planar, and it forms a dihedral angle of 65.1° with the plane of the phenyl ring (C6-C5-C4). Conversely, the fragment O8-N4-C22-N3-O7 is nearly planar and forms a dihedral angle of 35.1° with the plane of the phenyl ring (C19-C18-C20). The IR spectrum shows the N-O stretching vibration of the NITpBA at 1355 cm⁻¹ as well as the antisymmetric ν_{as} COO⁻ and the symmetric ν_s COO⁻ stretching mode of the caroxyl group at 1612 and 1413 cm⁻¹, respectively, in accordance with a bidentate-bridging mode [10,17,18].

In complex 2, the Cu1-Cu1A distance is 2.6457 Å, which is a typical value for dimeric copper (II) carboxylate adducts [19,20]. The Cu-O_{water} distance of 2.121 Å is longer than that of Cu-O whose oxygen atoms come from Ph-COO⁻. The Cu (II) core is displaced by 0.205 Å from the basal O4-plane toward the axial oxygen atom of the solvent. Mean deviation from base O4-plan

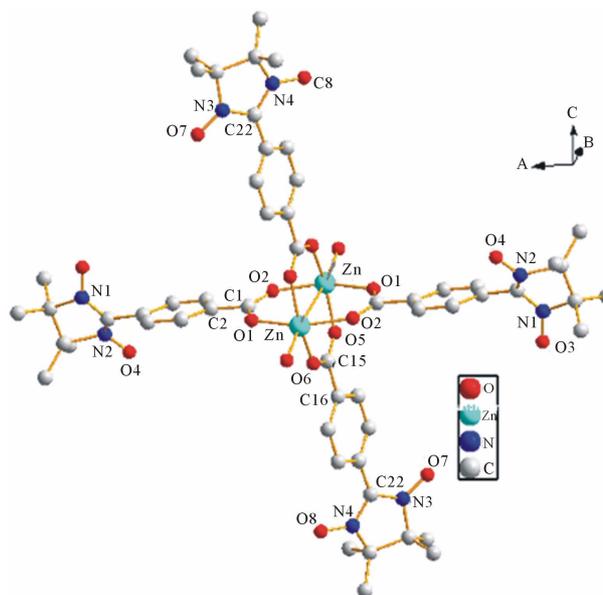


Figure 1. View of the moiety of the complex 1 [Zn₂(NITpBA)₄(H₂O)₂]. All hydrogen atoms are omitted for clarity.

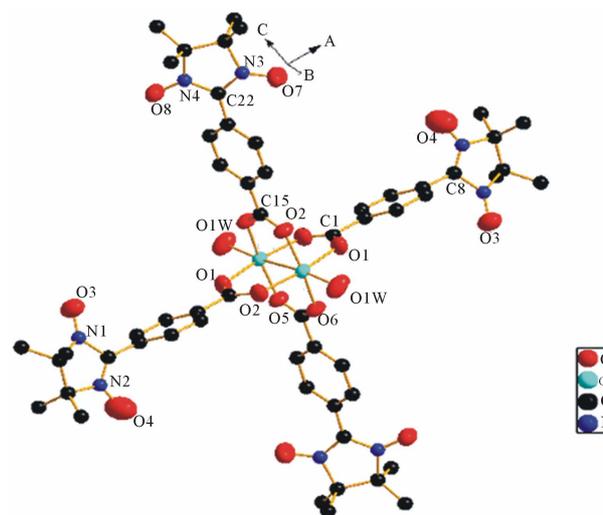


Figure 2. View of the moiety of the complex 2 [Cu₂(NITpBA)₄(H₂O)₂]. All hydrogen atoms are omitted for clarity.

is 0.0009 Å. The fragment O4-N2-C8-N1-O3 is non-planar, where the mean deviation from the plane is 0.0676 Å, and forms a dihedral angle of 86.1° with the plane of the phenyl ring (C4-C5-C6). The fragment O8-N4-C22-N3-O7 is nearly planar, and the plane for ms a dihedral angle of 36.4° with the phenyl ring (C19-C18-C20). The product shows IR absorptions at 1350, 1407 and 1610 cm⁻¹, respectively.

3.2. Magnetic Properties

We have then examined the temperature dependences of

$\chi_M T$ and χ_M for complex 1 and 2 in order to analyze the exchange coupling in this six-spin system. Temperature dependences of the molar magnetic susceptibility for two complexes were measured in a temperature range of 2 K to 300 K at a magnetic field of 2000 G. The results are given in **Figures 3** and **4**, respectively.

For complex 1, the $\chi_M T$ at room temperature has a value of $1.535 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$, which is close to the expected value for uncoupled spins of $S = 4/2$ ($1.5 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$) for two zinc centers and four nitronyl nitroxide radical-ligands. It was regarded as a tetra-radical system to evaluate the exchange coupling constants. The $\chi_M T$ value decreases slowly and reaches $1.43 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ at 100 K as the temperature is lowered, and subsequently decreases rapidly during further lowering of temperature. Based on the structural results, it undergoes a major magnetic interaction in the present system, in which the exchange interaction of NITpBA radicals through Zn (II) core exists [21]. The result indicates that a weak anti-ferromagnetic exchange interaction is predominant, which is agreement with literatures [22,23].

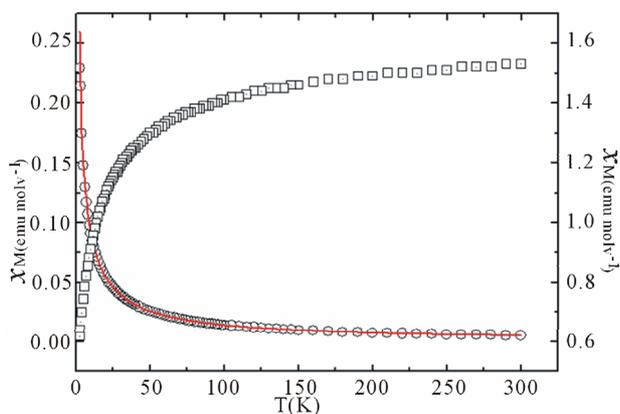


Figure 3. Temperature dependence of χ_M (\circ) and $\chi_M T$ (\square) vs T for the complex 1

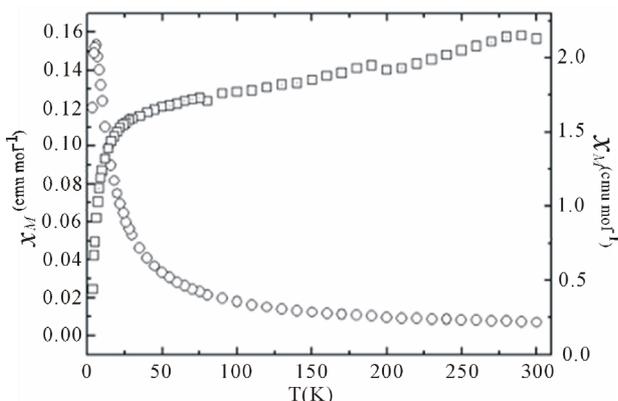


Figure 4. Temperature dependence of χ_M (\circ) and $\chi_M T$ (\square) vs T for the complex 2

For complex 2, the $\chi_M T$ value at room temperature is $2.14 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$, which is significantly lower than that of the expected value for six uncoupled spins of $S = 1/2$ ($2.25 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$) for two copper centers and four nitronyl nitroxide. The result indicates that a strong anti-ferromagnetic exchange interaction is predominant. The result is in accord with those reported [10,24].

4. CONCLUSION

Two new binuclear complexes formulae of $[\text{M}_2(\mu\text{-NITpBA})_4(\text{H}_2\text{O})_2]$ ($\text{M} = \text{Zn } 1$ and $\text{Cu } 2$) [where NITpBA = 2-(4-carboxyl-phenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-oxide)] were synthesized and structurally characterized. The simple procedure of the NITpBAH with metal chloride yielded dimeric complexes 1 and 2. The temperature dependences of the magnetic susceptibility show dominant intramolecular anti-ferromagnetic exchange interaction in complexes 1 and 2. According to the result of the complex 1, it demonstrates that the magnitude of the intramolecular magnetic exchange has little relationship with the crystal system and space group.

5. ACKNOWLEDGEMENTS

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APPENDIX A. SUPPLEMENTARY DATA

Detailed crystallographic data in CIF format for the title complex are available from Cambridge Crystallographic Data Center (CCDC ID: 876210 and 876209). CIF deposits may now be made using our new online service: https://www.ccdc.cam.ac.uk/services/structure_deposit.