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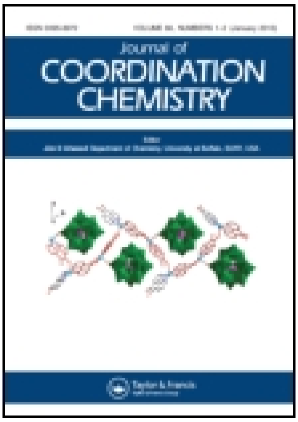

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Di-radical dinuclear copper complex: synthesis, structure, and magnetic properties

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Di-radical dinuclear copper complex: synthesis, structure, and magnetic properties

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The reaction of $Cu(Ac)_2{\cdot}4H_2O$ with 2-[(3,5-dichloro-2-hydroxy-benzylidene)-amino]-2hydroxymethyl-propane-1,3-diol (H_4L) and 4,4′-bipyridyl-N,N′-dioxide (4,4′-bipy-NO) in DMF under solvothermal conditions leads to the formation of a di-radical dinuclear copper complex [Cu_2(4,4′-bipy-NO)(dcdmap)$_4$] (**1**) (dcdmap is the anion of 2,4-dichloro-6dimethylaminomethyl-phenol, synthesized by an *in situ* reaction). Compound **1** was characterized by elemental analysis, IR spectroscopy, and X-ray single-crystal diffraction. Complex **1** displays dominant anti-ferromagnetic interaction between oxyradicals and copper ion and oxyradical.

Keywords: Radical ligand; Crystal structure; Magnetic properties

1. Introduction

Metal complexes of radicals have been actively pursued as components of new molecular magnetic materials [1–4]. An advantage of paramagnetic ligands is that direct magnetic exchange coupling between metal and ligand spins is possible. Various 2-pyridyl-substituted ligands containing paramagnetic 1,5-dimethyl-3-(2,2′-bipyridin-6-yl)-6-oxoverdazyl (bipyvd) [1], *N*-tert-butyl-n-4-pyridylaminoxyl (4NOpy) [2], nitronyl nitroxide (NN) [5–7], imino nitroxide (IN) [8, 9], oxoverdazyl (VD) [10, 1], and dithiadiazolyl (DTDA) [11, 12] groups form chelate rings where a radical center is directly bonded to the metal ion (scheme 1). Heteroaromatic rings have a weaker stabilizing effect than phenyl, as indicated by the fact that intact pyridyl-NOs are not isolable [13]. A paramagnetic bridging ligand, 4,4′-bipyridyl-N,N′-dioxide (4,4′-bipy-NO) [14, 15], is a synthetic target whose stability would be improved owing to an additional aromatic ring and π-conjugation. Furthermore, NO has some advantage. The spin density on the ligating O of 4,4′-bipy-NO is assumed to be almost twice as large as that of other conventional radicals such as ArNN [16, 17], because of the almost half size of the spin delocalizable π-conjugation in the radical

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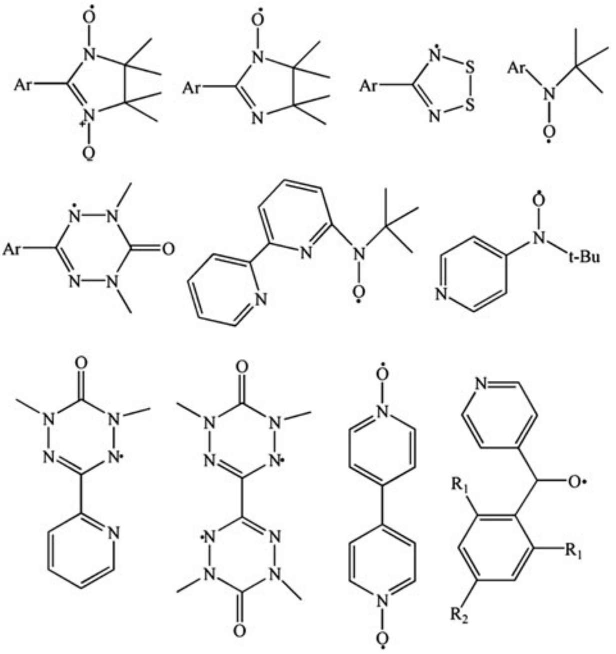

Scheme 1. Radical ligands.

groups (which also leads to the undesired instability of ArNO). Magnetic exchange coupling is proportional to the spin densities at the interacting atoms [18]. Thus, ArNO radicals are promising to bestow stronger exchange coupling to metal-radical hybrid solids. Herein, we constructed a di-radical dinuclear copper complex [Cu_2(4,4′-bipy-NO)(dcdmap)$_4$] (**1**) by an *in situ* reaction.

2. Experimental

2.1. *General*

All chemicals were commercially available and used as received without purification. The C, H, N microanalyses were carried out with a PE 2400 series II elemental analyzer. FT–IR spectra were recorded from KBr pellets at 4000–400 cm^{-1} on a Bio-Rad FTS-7 spectrophotometer. The crystal structure was determined on a Bruker Smart Apex CCD area-detector diffractometer using SHELXS-97 and SHELXL-97 for structure solution and refinement, correspondingly. Magnetization measurements were carried out with a Quantum Design PPMS model 600 magnetometer working under an applied field of 5 T for **1**.

2.2. *Solvothermal syntheses*

Preparation of H_4L and 4,4′-bipy-NO: 2-[(3,5-dichloro-2-hydroxybenzylidene)amino]-2hydroxymethyl-propane-1,3-diol (H_4L) was prepared according to a literature procedure

[19], and 4,4′-bipyridyl-N,N′-dioxide (4,4′-bipy-NO) was prepared according to a literature procedure [14, 15].

2.3. *[Cu₂(4,4′-bipy-NO)(dcdmap)₄] (1)*

A mixture of H_4L (0.295 g, 1 mM), 4,4′-bipy-NO (0.188 g, 1 mM), $Cu(Ac)_2{\cdot}4H_2O$ (0.248 g, 1 mM), triethylamine (0.6 mL), and DMF (8.0 mL) was placed in a Teflon-lined stainless steel vessel and heated to 120 °C for 5 days. The autoclave was cooled over a period of 8 h at a rate of $10\,°C\,h^{-1}$. Blue block crystals of **1** were obtained by filtration, washed with ethanol, and dried in air. Phase-pure crystals of **1** were collected by manual separation. Yield 0.181 g (31.22% based on Cu). Elemental analysis for **1**: $C_{46}H_{48}Cl_8Cu_2N_6O_6$, Calcd C 46.36; H 4.06; N 7.05%; Found: C 46.32; H 4.11; N 7.08%. IR data for **1** (KBr, cm^{-1}): 3431(m), 2976(w), 1583(w), 1459(s), 1356(m), 1178(m), 1022 (w), 751(m), 544(w) (figure S1).

2.4. *X-ray crystallography*

Intensity data for **1** were collected at 296 K on a Bruker Smart Apex CCD area-detector diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using the ω-θ scan mode from $1.44 \leqslant \theta \leqslant 25.01°$. Raw frame data were integrated with SAINT [20]. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on F^2 using SHELXS-97 [20]. An empirical absorption correction was applied with SADABS [20]. All non-hydrogen atoms were refined anisotropically. Hydrogens were set in calculated positions and refined by a riding mode with a common

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

Formula	$C_{46}H_{48}C_{l8}Cu_2N_6O_6$
Fw	1191.58
T (K)	296(2)
Cryst. syst.	Triclinic
Space group	$P\bar{1}$
a (Å)	8.978(1)
b (Å)	10.361(1)
c (Å)	14.303(1)
α/°	81.518(4)
β/°	83.452(4)
γ/°	72.860(4)
V/Å^3	1254.0(2)
Z	1
D_{calcd}/g cm^{-3}	1.578
μ/mm^{-1}	1.328
θ Range/°	1.44 to 25.01
Reflection collected	4371
Unique reflection	3535
R_{int}	0.0175
GOF	1.042
R_1 $[I \geqslant 2\sigma(I)]^{[a,b]}$	0.0408
wR_2 (all data)$^{[a,b]}$	0.0811
Residues/e Å^{-3}	0.375 and −0.215

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

thermal parameter. All calculations and graphics were performed with SHELXTL [20]. Crystal data and details of the structure determination are given in table 1.

3. Results and discussion

3.1. *Synthesis*

[Cu_2(4,4′-bipy-NO)(dcdmap)$_4$] was synthesized by H_4L, 4,4′-bipy-NO, and $Cu(Ac)_2 \cdot 4H_2O$ in DMF. The ligand 2-[(3,5-dichloro-2-hydroxy-benzylidene)amino]-2-hydroxymethylpropane-1,3-diol (H_4L) underwent an *in situ* reaction to form 2,4-dichloro-6dimethylaminomethyl-phenol (Hdcdmap) during the solvothermal process, as shown in scheme S1. The reaction using 2,4-dichloro-6-methylaminomethyl-phenol instead of H_4L only affords unknown white precipitates, though 2,4-dichloro-6-dimethylaminomethyl-phenol (Hdcdmap) can be formed by an *in situ* reaction. Herein, the structure of dcdmap in the synthesis system seems to be the most important synthetic parameter in formation of **1**.

3.2. *Crystal structure*

Single-crystal X-ray structure analysis reveals that **1** crystallizes in the triclinic space group $P\bar{1}$. As shown in figure 1, **1** is a centro-symmetric dinuclear complex. The molecule can be viewed as two [Cu(dcdmap)$_2$] units connected by a bridging 4,4′-bipy-NO. Copper(II) is five-coordinate by two O and two N from two different dcdmap ligands, one O from 4,4′-bipy-NO, forming a slightly distorted square pyramid where O from 4,4′-bipy-NO lies in the apical position. The apical Cu1–O3 distance (2.445(1) Å) is significantly longer than the Cu1–O, N distances within the basal plane (table 2), indicating that the bridging

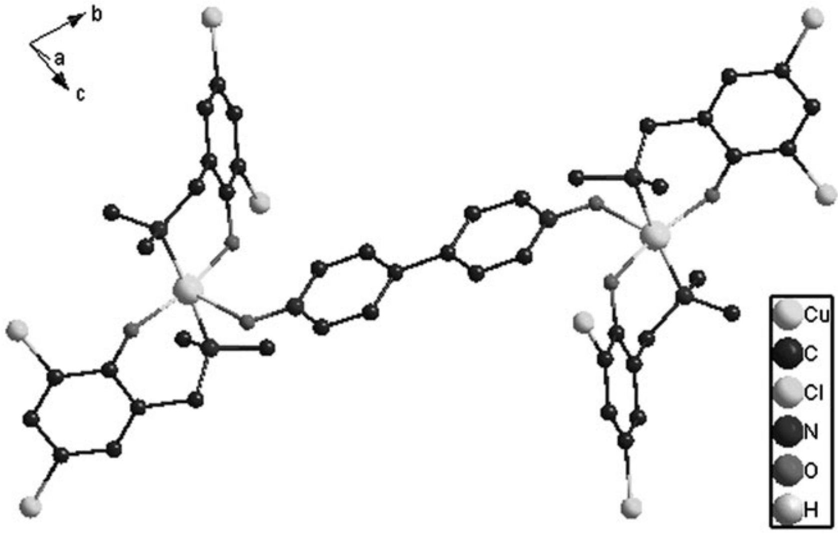

Figure 1. The structure of **1**.

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

Cu1–O1	1.916(2)	Cu1–N1	2.049(2)
Cu1–O2	1.929(2)	Cu1–N2	2.063(2)
Cu1–O3	2.445(1)	N1–Cu1–N2	172.98(9)
O1–Cu1–O2	165.4(1)	O1–Cu1–N1	86.16(8)
O2–Cu1–N1	92.20(8)	O1–Cu1–N2	91.79(7)
O2–Cu1–N2	88.09(7)		

Cu1–O3 interaction is a weak coordination bond [21, 22]. Each pair of Cu(II) ions is bridged by 4,4′-bipy-NO to form a dinuclear compound. The Cu…Cu distance of 13.280 (1) Å is longer than the copper … copper distance in other dimeric copper(II) 4,4′-bipy-NO complexes (11.830–12.977 Å) [23–25]. The complex further constructed a 1-D chain through C–H…Cl hydrogen bonds (C18–H18…Cl3^{i}, 3.574(1) Å, symmetry code: (i) *x*, 1 +*y*, *z*) and C-H…O hydrogen bonds (C21–H21…O3^{ii}, 3.439(1) Å, symmetry code: (ii) 3/2–*x*, 2–*y*, 3/2–*z*) (figure 2).

3.3. *Magnetic studies*

The magnetic susceptiblity of **1** was measured on crushed single crystals. The dc susceptibility was measured under an applied field of 1 kOe at 2 to 300 K (see figure 3). The value of $\chi_m T$ at room temperature is 1.05 cm^{3}Kmol^{-1}, which is significantly smaller than that expected for two non-interacting $S = 1/2$ Cu(II) ions and two $S = 1/2$ radicals (1.5 cm^3 KM^{-1} for $g = 2$) [19]. But the $\chi_m T$ value is slightly higher than the value of 0.9 cm^3 KM^{-1} for a reported tetranuclear copper complex [Cu$_4$L^{1}Cl$_2$(OH)$_2$](ClO$_4$)$_2$ (H$_2$L^1 = 13,27-dichloro-6,20-bis-(2-phenyl amino-ethyl)-3,6,9,17,20,23-hexaaza-tricyclo[23.3.1.1^{11,15}]triaconta-1(28),2,9,11,13,15(30),16, 23, 25(29),26-decaene-29,30-diol**)** [26]. The $\chi_m T$ slowly falls on cooling to a value of 0.84 cm^3 KM^{-1} at 16 K, after which the values rapidly decrease to 0.61 cm^3 KM^{-1} at 2 K. This indicates the occurrence of an antiferromagnetic intramolecular interaction between radicals and Cu(II) ions and radicals.

The temperature dependence of the reciprocal susceptibility $\chi_m{}^{-1}$ vs. T above 50 K follows the Curie–Weiss law ($\chi_m = C/(T - \theta)$) with a Weiss constant $\theta = -17.148(1)$ K and Curie constant $C = 1.087(1)$ cm^3 KM^{-1} (figure 4). The larger negative Weiss constant also indicates dominant intramolecular anti-ferromagnetic interaction between radicals and Cu(II) ion and

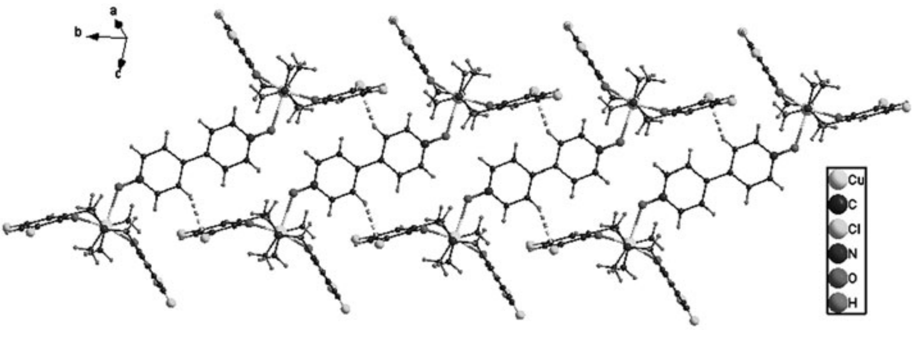

Figure 2. The 1-D chain of **1**.

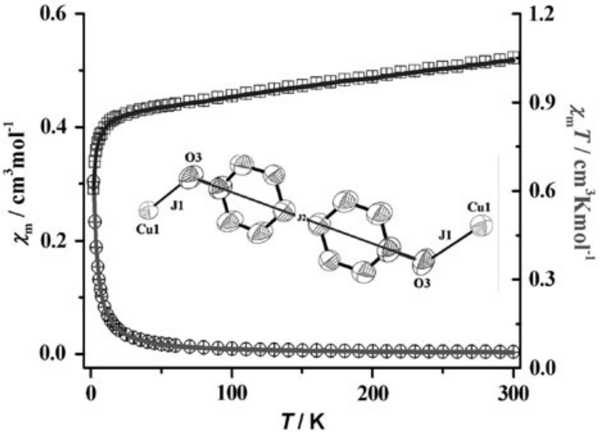

Figure 3. Plot of $\chi_M T$ and χ_M vs. T measured in a 1000 Oe field for **1**. The solid lines repesent the best fits of data between 300 and 2 K as described in the text.

radical. This pattern is compatible with moderate anti-ferromagnetic coupling which is different from the orbital model previously described for the copper-radical complex [Cu(6bpyNO)Cl$_2$], where 6bpyNO is 2,2′-bipyridin-6-yl *tert*-butyl nitroxide [3]. Inspection of the molecular structure reveals two main exchange pathways: J_1, the interaction between copper ion and radical, J_2, the interaction between radicals. The linear paramagnetic ion and radicals give the Van Vleck equation (1) [27] based on the Hamiltonian: $\hat{H} = -2J_1(\hat{S}_1\hat{S}_2 + \hat{S}_3\hat{S}_4) - 2J_2\hat{S}_2\hat{S}_3$.

$$\chi_M = \frac{2Ng^2\beta^2}{kT} \times \frac{5e^{a/kT} + e^{b/kT} + e^{c/kT} + e^{d/kT}}{5e^{a/kT} + 3e^{b/kT} + 3e^{c/kT} + 3e^{d/kT} + e^{h/kT} + e^{f/kT}} \tag{1}$$

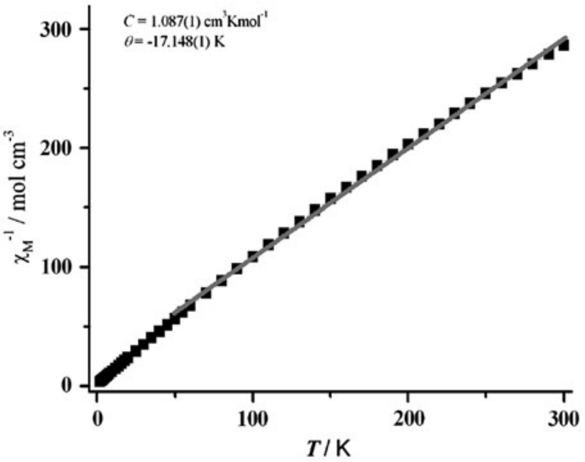

Figure 4. Plot of $\chi_M{}^{-1}$ vs. T for **1**. The solid line represents a fit of data in the temperature range 50–300 K.

where $a = J_1 + 0.5J_2$, $b = 0.5J_2 - J_1$, $c = -0.5J_2 - (J_1^2 + J_2^2)^{0.5}$, $d = (J_1^2 + J_2^2)^{0.5} - 0.5J_2$, $h = -J_1 - 0.5J_2 - (4J_1^2 - 2J_1J_2 + J_2^2)^{0.5}$, $f = (4J_1^2 - 2J_1J_2 + J_2^2)^{0.5} - J_1 - 0.5J_2$. The best fitting gave: $g = 2.05$, $J_1 = -\ 1.874\,\mathrm{cm}^{-1}$, $J_2 = -0.125\,\mathrm{cm}^{-1}$ with

$$R = \frac{\sum[(\chi_{\mathrm{M}}T)_{\mathrm{calc}} - (\chi_{\mathrm{M}}T)_{\mathrm{obs}}]^2}{\sum(\chi_{\mathrm{M}}T)^2_{\mathrm{obs}}} = 5.2 \times 10^4.$$

Further evidence of *anti*-ferromagnetic coupling between radicals and copper ion and radical was observed in the variable-field magnetization curve in figure S2. At low fields from 0 to 2 *T*, the magnetization of **1** sharply increases. Above 4 *T*, the magnetization increases continually and does not saturate until 5 *T*.

4. Conclusion

We have synthesized a di-radical dinuclear copper complex with the composition $[Cu_2(4,4'\text{-bipy-NO})(dcdmap)_4]$ (**1**), where dcdmap is the anion of 2,4-dichloro-6dimethyl-aminomethyl-phenol which was synthesized by an *in situ* reaction. Magnetic measurements show that **1** displays dominant anti-ferromagnetic interactions between copper ion and radical and very weak ferromagnetic interactions between radicals.

Supplementary material

CCDC 875356 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via http://www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; Fax: +44 1223 336 033; or E-mail: deposit@ccdc.cam.ac.uk.

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