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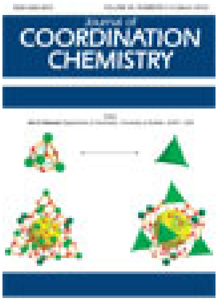

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A new oxamido-bridged dinuclear copper(II) complex with large antiferromagnetic exchange interactions

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A new oxamido-bridged dinuclear compound $[Cu_2(\mu\text{-pmox})(DMF)_4] \cdot 2ClO_4$ (**1**) (H_2pmox = *N*,*N*′-bis-(2-methylpyridyl)oxalamide, DMF = dimethylformamide) was synthesized and structurally characterized. The five-coordinate Cu(II) is bridged by oxamido groups and further cross-linked by C–H···O hydrogen bonds between the uncoordinated oxygen of perchlorate and methyl of DMF. The complex was also characterized by infrared spectroscopy and magnetic measurement. The copper complex exhibits strong antiferromagnetic interactions *via* the *trans* oxamido bridge with *J* of $-414\,\mathrm{cm}^{-1}$, where *J* is the exchange parameter in the isotropic Hamiltonian $H = -JS_1S_2$.

Keywords: Copper(II) complex; Oxamido-bridged; Crystal structure; Hydrogen bonds; Antiferromagnetic

1. Introduction

Functional metal–organic frameworks and polymeric compounds have received attention for their interesting structures and applications in magnetism, optical, selective absorption, separation, gas storage, electrical conductivity, ion exchange, and catalytic applications, which may lead to promising new materials [1–3]. Magnetism of transition metal complexes is of ongoing interest, not only for understanding magnetic interactions and magneto-structural correlations in molecular systems, but also for developing molecule-based magnetic materials [4, 5]. The versatile ligands, *N*,*N*′-bis(substituted)oxamides are thoroughly applied in molecular magnetic studies for their abilities to construct homo- and heterometallic complexes with various structures [6, 7]. Paramagnetic metal ions can efficiently exchange magnetic interactions through oxamido bridges [8]. *N*,*N*′-bis(2-pyridylmethyl)oxamide can bridge the metal ions *via* oxamido adopting either *cis*- or *trans*- conformation, also *via* pyridyl as a bis(pyridyl) bridge (scheme 1). Dinuclear copper(II) complexes with oxamidato bridges have been much studied [9–11], and their magnetic behavior is reasonably well-understood. To a large extent, the magnetic coupling is satisfactorily rationalized in the basis of overlap of magnetic orbitals.

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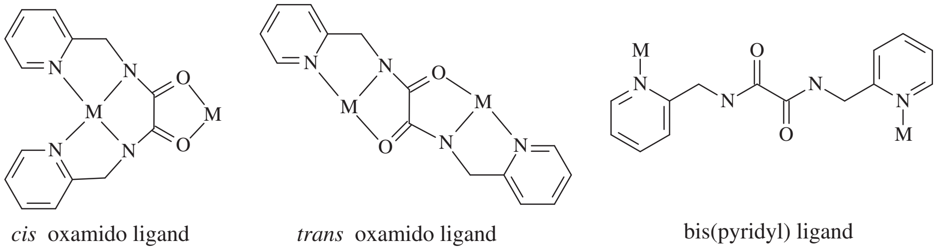


Scheme 1. The three bridging conformations of H_2pmox or pmox^{2-}. M represents a metal ion.

So far, studies dealing with the formation of oxamidato H_2pmox complexes are scarce [12, 13]. Here we report the synthesis, crystal structure, and the magnetic properties of a new dinuclear copper(II) complex $[Cu_2(\mu\text{-pmox})(DMF)_4] \cdot 2ClO_4$ (**1**). This complex exhibited expected strong antiferromagnetic interactions *via* the *trans* oxamido bridge with J of $-414\,cm^{-1}$.

2. Experimental

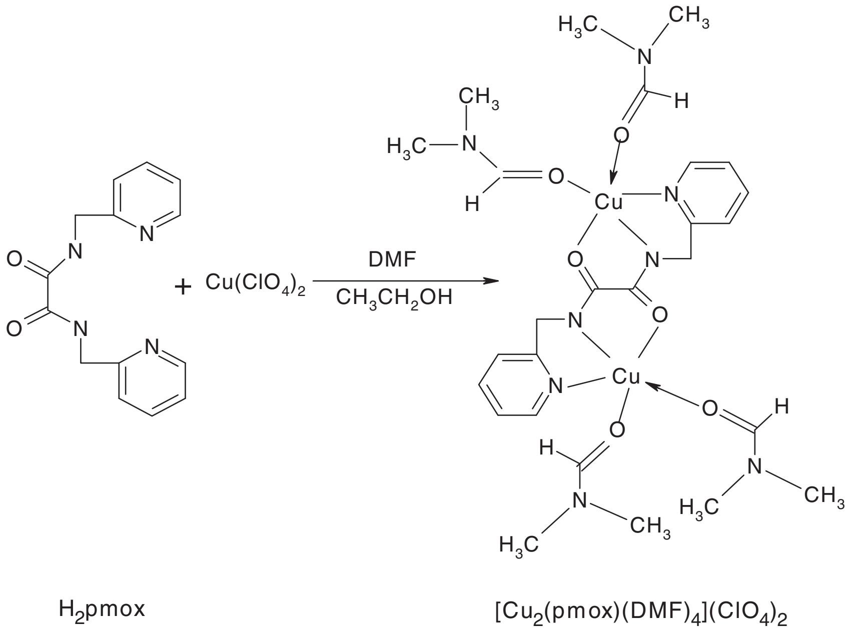
2.1. *Materials and general methods*

Solvents for syntheses (analytical grade) were used without purification. $Cu(ClO_4)_2$ was prepared in a modified method. H_2pmox was prepared according to the literature method [14]. Elemental analyses were carried out with a Perkin-Elmer analyzer model 240. Infrared (IR) spectra were recorded as KBr pellets on a Bruker TENSOR 27 infrared spectrophotometer from 4000 to $400\,cm^{-1}$. Variable-temperature magnetic susceptibilities were measured on a Quantum Design MPMS 5 S SQUID magnetometer from 2 to 300 K with an applied field of 1000 Oe. Diamagnetic corrections were made with Pascal's constants for all constituent atoms [15].

Safety note: *Perchlorate salts of metal complexes with organic ligands are potentially explosive. In general, when non-coordinating agents are required, every attempt should be made to substitute anions such as the fluoro sulfonates for the perchlorates. If a perchlorate must be used, only small amounts of material should be prepared and this should be handled with great caution.*

2.2. *Syntheses*

2.2.1. Preparation of $[Cu_2(\mu\text{-pmox})(DMF)_4] \cdot 2ClO_4$ (1). An ethanol solution (6 mL) of $Cu(ClO_4)_2 \cdot 6H_2O$ (185.2650 mg, 0.5 mmol) was carefully layered onto a DMF solution (7 mL) of H_2pmox (67.5725 mg, 0.25 mmol). The synthetic route of **1** is shown in scheme 2. Pale-blue single crystals suitable for X-ray diffraction analysis were obtained after 6 days. Yield: 58%. Elemental analysis (%) calculated for $C_{26}H_{40}Cl_2Cu_2N_8O_{14}$ ($M = 886.64$): C, 35.22; H, 4.55; N, 12.64. Found (%): C, 35.25; H, 4.43; N, 12.71.



Scheme 2. The synthetic route of **1**.

FT-IR (KBr, cm^{-1}): 3089 (w), 2931 (m), 2885 (w), 1664br, (vs), 1609 (w), 1567 (w), 1485 (m), 1436 (m), 1410 (s), 1350 (m), 1329 (m), 1285 (m), 1256 (m), 1093br, (vs), 880 (w), 770 (m), 718 (w), 702 (m), 627 (s), 547 (m), 496 (m).

2.3. *X-ray crystallographic study*

Crystallographic data were collected on a Bruker Smart CCD diffractometer at 113(2) K using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and corrected for Lorentz and polarization effects. The frames were integrated with Bruker SAINT software and the data were corrected for absorption using SADABS [16]. The structure was solved by direct methods using SHELXS-97 [17]. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F^2 using SHELXL-97 [18]. Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters. The perchlorate appears to be disordered. Crystal data and structure refinement parameters are listed in table 1. Selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. *Crystal structure*

A perspective view of the asymmetric unit along with the atom-labeling scheme is shown in figure 1. One molecule of **1** is composed of a cationic dinuclear unit

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

Empirical formula	$C_{26}H_{40}Cl_2Cu_2N_8O_{14}$
Formula weight	886.64
Temperature (K)	113(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*P2(1)/c*
Unit cell dimensions (Å, °)	
a	15.492(3)
b	7.2649(15)
c	16.884(3)
α	90
β	109.96(3)
γ	90
Volume (Å^3), *Z*	1786.1(6), 2
Calculated density (g cm^{-3})	1.649
Absorption coefficient (mm^{-1})	1.417
F(000)	912
Crystal size (mm^3)	0.20 × 0.08 × 0.06
θ range for data collection (°)	2.47–25.02
Index ranges	$-18 \leq h \leq 17$; $-7 \leq k \leq 8$; $-20 \leq l \leq 20$
Reflection collected/unique	12327/3136 [$R_{\text{int}} = 0.0767$]
Completeness to $\theta = 25.02$ (%)	99.6
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Observed reflections [$I > 2\sigma(I)$]	2218
Data/restraints/parameter	3136/80/277
Max. and min. transmission	0.9198 and 0.7648
Goodness-of-fit on F^2	1.018
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0596$, $wR_2 = 0.1284$
R indices (all data)	$R_1 = 0.0754$, $wR_2 = 0.1396$
Largest difference peak and hole (e Å^{-3})	0.758 and −0.993

Table 2. Selected bond lengths (Å) and angles (°) for **1**.[a]

Cu(1)–N(2)	1.908(4)	N(2)–C(7)	1.297(5)
Cu(1)–O(3)	1.956(3)	N(2)–C(6)	1.444(5)
Cu(1)–O(1)#1	1.992(3)	N(3)–C(8)	1.319(6)
Cu(1)–N(1)	2.004(3)	N(3)–C(10)	1.448(6)
Cu(1)–O(2)	2.281(3)	N(3)–C(9)	1.458(6)
O(1)–C(7)	1.280(5)	N(4)–C(11)	1.305(6)
O(2)–C(8)	1.243(5)	N(4)–C(13)	1.460(5)
O(3)–C(11)	1.252(5)	N(4)–C(12)	1.464(6)
N(1)–C(5)	1.346(5)	C(1)–C(2)	1.381(6)
N(1)–C(1)	1.349(5)	C(7)–C(7)#1	1.513(8)
N(2)–Cu(1)–O(3)	168.09(13)	O(1)#1–Cu(1)–N(1)	164.86(13)
N(2)–Cu(1)–O(1)#1	84.58(13)	N(2)–Cu(1)–O(2)	104.00(13)
O(3)–Cu(1)–O(1)#1	95.86(12)	O(3)–Cu(1)–O(2)	87.85(12)
N(2)–Cu(1)–N(1)	81.40(14)	O(1)#1–Cu(1)–O(2)	94.69(11)
O(3)–Cu(1)–N(1)	96.70(13)	N(1)–Cu(1)–O(2)	94.19(13)

[a] Symmetry code: #1 $-x$, $-y+1$, $-z+1$.

$[Cu_2(\mu\text{-pmox})(DMF)_4]^{2+}$, and two ClO_4^-. The dinuclear unit is centrosymmetric and the inversion center stands at the middle of the C7–C7A bond. The environment of each copper is surrounded by three oxygen atoms (O(1 A), O(2) and O(3)) and two nitrogen atoms (N(1) and N(2)) occupying the vertices of a distorted square-based pyramid.

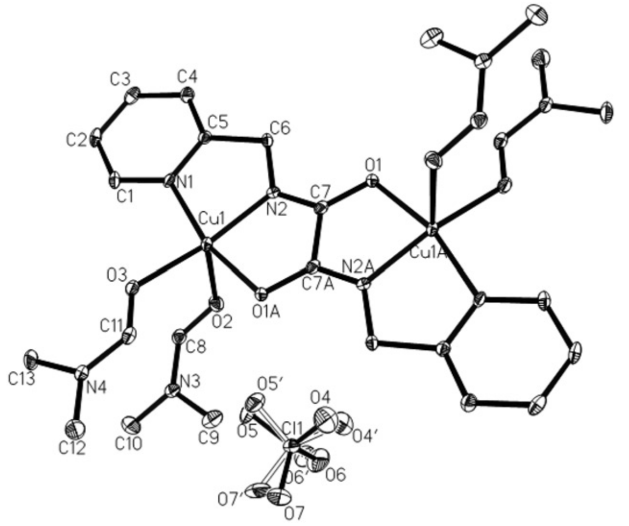


Figure 1. ORTEP drawing of the molecular unit of **1**. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

The basal plane is built by carbonyl oxygen O(1 A), amide nitrogen N(2) and pyridyl nitrogen N(1) of the oxamidate and one carbonyl oxygen O(3) of DMF. An oxygen O(2) from the other DMF is apical. Bond length between copper and the axial oxygen is long: Cu(1)–O(2) = 2.281 Å. The Cu(1)–N(1) bond distance (2.004(3) Å) is significantly larger than the other equatorial distances (1.908(4) Å, 1.992(3) Å, 1.956 Å for Cu(1)–N(2), Cu(1)–O(1)#1 and Cu(1)–O(3), respectively). The mean displacement of the four atoms from this plane is 0.0377 Å. The copper lies −0.1617 Å out of this mean basal plane. Two copper(II) ions are bridged by deprotonated oxamido, $pmox^{2-}$, which exhibits a *trans* conformation with an inversion center at the middle of the carbon–carbon (amide) bond. Two five-membered chelate rings are around each copper(II) with somewhat depressed values for the two copper–oxamidate angles (averages 84.6° and 84.6° for N(2)–Cu(1)–O(1 A) and O(1)–Cu(1 A)–N(2 A), respectively). The oxamidato bridge is planar as observed in other oxamidate-bridged copper complexes [19–23]. The copper-copper separation through $pmox^{2-}$ is 5.205 Å, which is very close to other copper complexes bridged by oxamidato ligands [24–26].

Comparing neutral H_2pmox, the bond lengths of the oxamide group in the deprotonated $pmox^{2-}$ are significantly different [27]. The deprotonated $pmox^{2-}$ has better conjugation than H_2pmox. The carbonyl bond length of $pmox^{2-}$ (1.280 Å) is longer than that of H_2pmox (1.218 Å), while the C–C bond and amide bond length of $pmox^{2-}$ (1.513 Å, 1.297 Å, respectively) are shorter than that of H_2pmox (1.525 Å, 1.338 Å, respectively). The oxamide $pmox^{2-}$ is almost planar with mean plane deviation of 0.0320 Å.

As depicted in figure 2, one binuclear molecule links with four other binuclear units *via* C–H···O hydrogen bonds between oxygen of perchlorate and the methyl of DMF forming the supramolecular structure of **1** (figure 3). The detailed description on C–H···O hydrogen bonds in the structure is listed in table 3.

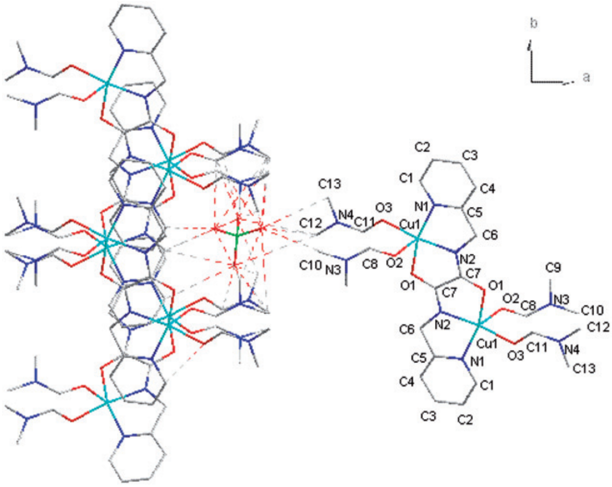


Figure 2. The schematic structure of C–H···O hydrogen bonds in **1** observed along the *c*-axis.

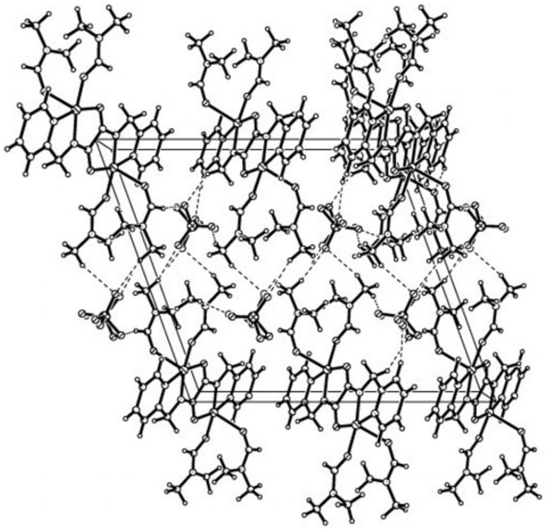


Figure 3. The crystal packing of **1** viewed along the *b*-axis. Dashed lines are hydrogen bonds.

3.2. *IR spectrum*

IR spectra of the complex agree with the structure features described above. The sharp strong N–H stretch (amide group) at 3288 cm^{-1} in the spectrum of free H_2pmox is missing in the spectrum of the dinuclear complex because of loss of amide protons, which agrees with the crystal structure. The bands at 2931 and 2885 cm^{-1} can be assigned to C–H stretch of $–CH_3$ of DMF. The broad strong band at *ca* 1664 cm^{-1} can be attributed to overlap of ν(C=O) (oxamide) and ν(C=O) (formamide). The occurrence of ν(C–N) at 1609 cm^{-1} supports the presence of bridging oxamidato.

Table 3. C–H···O hydrogen bonds in the crystal structure of **1**.

C–H···O	C–H (Å)	H···O (Å)	C···O (Å)	C–H···O (°)
C(2)–H(2)···O(2) $^{x,y-1,z}$	0.950	2.428	3.318	156.0
C(4)–H(4)···O(5)$'^{-x,-0.5+y,0.5-z}$	0.980	2.507	3.366	150.4
C(8)–H(8)···O(4) $^{x,y-1,z}$	0.950	2.561	3.427	151.8
C(8)–H(8)···O(4)$'$ $^{x,y-1,z}$	0.950	2.348	3.269	163.0
C(6)–H(6 A)···O(4)$'^{-x,-0.5+y,0.5-z}$	0.980	2.471	3.341	146.4
C(10)–H(10 A)···O(7) $^{x,y-1,z}$	0.980	2.873	3.512	161.4
C(10)–H(10B)···O(7) $^{-x+1,-y+1,-z+1}$	0.980	2.576	3.512	159.8
C(10)–H(10B)···O(7)$'^{-x+1,-y+1,-z+1}$	0.980	2.417	3.380	167.4
C(12)–H(12 A)···O(6) $^{x,0.5-y,0.5+z}$	0.980	2.362	3.315	163.8
C(12)–H(12B)···O(7)$'^{-x+1,-y+1,-z+1}$	0.980	2.456	3.378	156.6
C(13)–H(13 A)···O(6)$'$ $^{x,0.5-y,0.5+z}$	0.980	2.391	3.337	161.9

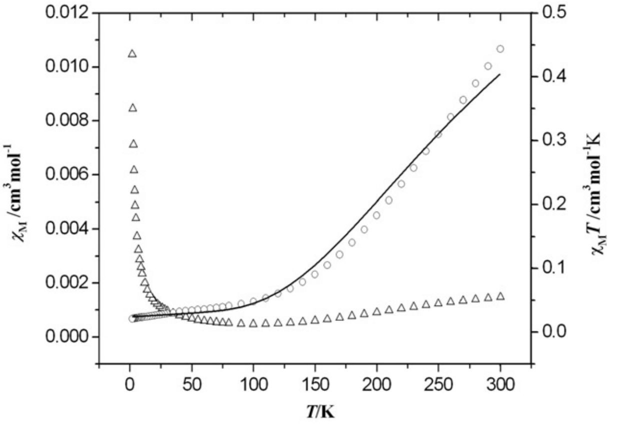


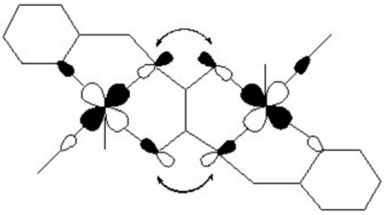
Figure 4. Plots of χ_M (triangle for experimental data) and $\chi_M T$ (open circle for experimental data) *vs.* T for **1**. Solid line represents the best fit obtained.

Bands of pyridyl rings are at 1567, 1485 and 1436 cm^{-1}. Strong and broad peak at 1093 cm^{-1} arises from perchlorate.

3.3. *Magnetic properties*

The temperature dependence of the magnetic susceptibilities for **1** was measured from 2 to 300 K with an applied field of 1000 Oe. Plots of χ_M and $\chi_M T$ per mol copper(II) of **1** *versus* T are shown in figure 4. The $\chi_M T$ value of **1** at room temperature is 0.44 cm^3 mol^{-1} K, slightly higher than the spin-only value 0.38 cm^3 mol^{-1} K for Cu(II) owing to mixing of angular momentum from excited states *via* spin–orbit coupling [28, 29]. Upon cooling, the $\chi_M T$ value decreases sharply, indicating a very strong antiferromagnetic interaction between the binuclear copper(II) ions.

The magnetic data for **1** were fitted by the Bleaney–Bowers equation for a dinuclear copper(II) complex with the interaction Hamiltonian defined as $H = -JS_1S_2$,



Scheme 3. The magnetic orbitals for **1**. The strong antiferromagnetic interaction is due to the favorable orientation of the magnetic orbitals.

where $S_1 = S_2 = 1/2$ [30].

$$\chi_M = (2N\beta^2g^2/kT)[3 + \exp(-J/kT)]^{-1}(1 - \rho) + (N\beta^2g^2/2kT)\rho + N_\alpha$$

where J is the exchange coupling parameter describing the magnetic interaction between the binuclear copper(II) ions, ρ is the percentage of the paramagnetic impurities, N_α is the temperature-independent paramagnetism ($N_\alpha = 120 \times 10^{-6}\,\mathrm{cm^3\,mol^{-1}}$), and N, β, and k have their usual meaning. A least-squares fit of all experimental data leads to $J = -414\,\mathrm{cm^{-1}}$, $\rho = 0.0245$ and $g = 2.2$ with an agreement factor $R = \Sigma(\chi_{\mathrm{obsd}} - \chi_{\mathrm{calcd}})^2/\Sigma\chi_{\mathrm{obsd}}{}^2$ of 1.3×10^{-4}.

The large J value is expected. Scheme 3 illustrates the magnetic orbitals for **1**, which is similar to that of the oxalate-bridged dinuclear complex $[(\mathrm{tmen})(\mathrm{H_2O})\mathrm{Cu}(\mathrm{C_2O_4})\mathrm{Cu}(\mathrm{H_2O})(\mathrm{tmen})](\mathrm{ClO_4})_2 \cdot 1.25\mathrm{H_2O}$ (tmen = N,N,N',N'-tetramethylenediamine, $J = -385.4\,\mathrm{cm^{-1}}$) proposed by Kahn [31]. As described by Kahn, when the magnetic orbitals have large in-plane overlap, the complex exhibits a strong antiferromagnetic interaction, while if orbitals on the copper(II) ions were rotated 90°, the antiferromagnetic interaction would "be negligible" [31]. The molecular structure of **1** is similar to that of $[(\mathrm{tmen})(\mathrm{H_2O})\mathrm{Cu}(\mathrm{C_2O_4})\mathrm{Cu}(\mathrm{H_2O})(\mathrm{tmen})](\mathrm{ClO_4})_2 \cdot 1.25\mathrm{H_2O}$. Copper(II) ion is in a square-pyramidal environment and the oxamidato oxygen and nitrogen occupy the equatorial plane inducing the favorable orientation of the magnetic orbitals, which contributes to the large antiferromagnetic exchange interaction of **1**. The oxamidato bridge is very effective in transmitting the exchange interaction between two copper(II) ions separated by more than 5.2 Å and the antiferromagnetic exchange interaction of the oxamidato bridge is stronger than that of oxalate bridge due to the smaller energy gap between the metal orbital and the ligand orbitals [32–36]. Selected magneto-structural data for the complexes containing oxamidato-bridged binuclear copper(II) reported are listed in table 4. The obtained J value for **1** is close to that of $[\mathrm{Cu_2(pmox)(dapm)_2(NO_3)_2} \cdot 6\mathrm{H_2O}]_n$ (table 4, complex **4**) [37]. It seems that the magnitude of the antiferromagnetic exchange interaction between copper(II) ions is not directly related to the distance between copper(II) ions.

4. Conclusion

By using the flexible N,N'-bis(2-pyridylmethyl)oxamide ($\mathrm{H_2pmox}$), a new oxamidato-bridged binuclear Cu(II) complex $[\mathrm{Cu_2(\mu\text{-}pmox)(DMF)_4}] \cdot 2\mathrm{ClO_4}$ (**1**) has been

Table 4. Selected magneto-structural data for complexes containing oxamidato-bridged binuclear copper(II).

Complex	Cu···Cu (Å)	Donor set[a]	*g*	*J* (cm^{-1})	References
1	5.205	O_2N_2O	2.2	−414	This work
2	5.323	ON_3N	2.1	−285.1	[38]
3	5.255	ON_3O	2.09	−558.1	[39]
4	5.31	ON_3O	2.09	−437.57	[14]
5	5.272	O_2N_2O	2.13	−338	[40]
6	5.244	O_2N_2O	2.10	−305	[41]
7	5.190	O_2N_2O	2.04	−393	[41]
8	5.271	ON_3N	2.10	−335	[42]
9	5.20	ON_3N	2.10	−582	[43]
10	5.29	ON_3N	2.01	−480	[19]
11	5.202	ON_3O	2.10	−591	[19]
12	5.306	ON_3O	2.12	−560	[20]
13[b]	5.195	N_4O/O_2N_2O	2.26	−439	[9]

[a] The first four atoms comprise the basal plane and the fifth occupies the apical position.

[b] Oxamidato bridge adopts the *cis* conformation.

2:$[Cu_2^{II}(L_1)Cu^I(CN)_3]$
3:$[Cu_2(L_2)(H_2L_2)(H_2O)_2(ClO_4)_2{\cdot}2(C_2H_6O)]_n$
4:$[Cu_2(pmox)(dapm)_2(NO_3)_2 \cdot 6H_2O]_n$
5:$[Cu_2(L_3)(L_4)(H_2O)_2 \cdot H_2O]_n$
6:$[Cu_2(L_3)(O_2CMe)_2] \cdot 2H_2O$
7:$[Cu_2(L_3)\ (NO_3)_2]$
8:[$Cu_2(L_2)(L_5)_2 \cdot 2ClO_4]_n$
9:$[Cu_2(L_2)(L_6)_2 \cdot 2ClO_4]_n$
10:$[Cu_2(L_7)(N_3)_2]_n$
11:$[Cu_2(L_7)(N_3)_2(H_2O)_2]$
12:[$Cu_2(L_7)(NCO)_2(H_2O)_2]$
13:$[Cu(L_3)Cu(L_8)] \cdot 2ClO_4$

H_2L_1 = *N*,*N*′-bis(dipropylenetriamine)oxamide); H_2L_2 = *N*,*N*′-bis(2-aminoethyl)oxamide; dapm = 4,4′-diaminodiphenylmethane; H_2L_3 = *N*,*N*′-bis(3-aminopropyl)oxamide; H_2L_4 = 3,4-dihydroxycyclobut-3-ene-1,2-dione; L_5 = 4,4′-bipyridine; L_6 = pyrimidine; H_2L_7 = *N*,*N*′-bis[2-(dimethylamino)ethyl]oxamide; L_8 = 2,2′-bipyridyl.

synthesized. Single-crystal X-ray diffraction analysis reveals that Cu(II) ion is in a five-coordinate square pyramid, bridged by oxamido groups in *trans* formation with Cu···Cu distance of 5.205 Å. A very strong antiferromagnetic coupling with *J* of –414 cm^{-1} is observed in this binuclear complex. The magnitude of the antiferromagnetic interaction between copper(II) ions in this complex is compared with that of other complexes containing oxamidato-bridged binuclear copper(II) unit. It seems that the magnitude of the antiferromagnetic exchange interaction between copper(II) ions is not directly related to the distance between copper(II) ions.

Supplementary material

CCDC 846685 for **1** contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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