

A Dimeric Copper(II) Complex of Oxalate and Oxamide Dioxime Ligands: Synthesis, Crystal Structure, Thermal Stability, and Magnetic Properties

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The dimeric copper(II) complex $[\text{Cu}(\text{C}_2\text{O}_4)(\text{H}_2\text{oxado})(\text{H}_2\text{O})]_2$ (**1**), where H_2oxado = oxamide dioxime, has been synthesized in water and characterized by elemental and thermal analyses, IR spectroscopy, and single-crystal X-ray diffraction. Complex **1** is composed of two neutral $[\text{Cu}(\text{C}_2\text{O}_4)(\text{H}_2\text{oxado})(\text{H}_2\text{O})]$ entities connected by Cu–O bonds between oxalate oxygen atoms and copper(II) ions, thereby producing a centrosymmetric dimer, with the Cu(II) centers exhibiting a strongly distorted octahedral coordination. Neighboring dimers are hydrogen-bonded through O–H···O interactions leading overall to a layer structure. Thermal analyses of complex **1** showed two significant weight losses corresponding to the coordinated water molecules, followed by the decomposition of the network. Variable-temperature (10–300 K) magnetic susceptibility measurements revealed very weak antiferromagnetic interactions ($\theta = -0.86$ K from Curie–Weiss law behavior) within the dinuclear unit.

Key words: Oxalate, Oxamide Dioxime, Cu(II) Complex, Crystal Structure

Introduction

One of the current challenges in the field of materials science is the design and synthesis of new flexible organic-inorganic materials with interesting properties [1–3]. In this regard, oxalatocopper(II) complexes have received growing attention over the past few years, owing to their fascinating network topologies and potential applications in molecular-based magnets [4–6]. Moreover, such complexes could have potential applications as precursors for the synthesis of copper-containing superconducting ceramics [7].

Recently, mixed-ligand copper(II) complexes of the general formula $[\text{CuL}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})] \cdot x\text{H}_2\text{O}$ (L = 2,2'-bipyridyl [8], 1,10-phenanthroline [9], or di-2-pyridyl-

amine [10]) have been synthesized and characterized with the aim of gaining a better understanding of the coordination chemistry of copper in different ligand environments. Replacement of a terminal ligand in such complexes with an oxamide dioxime molecule (H_2oxado) is expected to induce new structural architectures, given the large number of potential hydrogen-bond donating groups of this N, N' -chelating molecule. This flexible ligand has recently shown excellent features in the construction of hydrogen-bonded lattice networks [11, 12].

In this paper, we report the synthesis, characterization and crystal structure of an unexpected copper(II) oxalato-oxamide dioxime complex made up of layers of dimers of neutral $[\text{Cu}(\text{C}_2\text{O}_4)(\text{H}_2\text{oxado})(\text{H}_2\text{O})]$ units.

Experimental Section

Materials and physical measurements

All reactions were carried out in distilled water as the solvent. Chemicals were used as received. The starting compounds, $\text{K}_2[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$ and oxamide dioxime (H_2oxado), were prepared according to the methods of Kirschner [13] and Ephraim [14], respectively. Elemental analysis (C, H, N) was performed on a Vario EL (Heraeus) CHNS analyzer. The infrared spectrum was recorded on a Perkin-Elmer (System 2000) FT-IR spectrometer with a pressed KBr pellet in the scan range $4000\text{--}400\text{ cm}^{-1}$. Thermal analyses (TGA and TDA) were performed with a Mettler Toledo TGA/SDTA 851 thermal analyzer. The powdered sample (*ca.* 15 mg) was heated from 25 to $600\text{ }^\circ\text{C}$ with a rate of $10\text{ }^\circ\text{C min}^{-1}$ in dry nitrogen gas flowing at 60 mL min^{-1} . The melting points were measured in open capillary tubes using an Electrothermal 9100 apparatus. Magnetic susceptibility data were recorded using a Quantum Design MPMS-5XL SQUID magnetometer as a function of temperature (10 to 300 K). Experimental data were corrected for sample holder (PTFE capsules) and diamagnetic contributions calculated from tabulated values ($\chi_{\text{dia}}(1) = -0.995 \times 10^{-4}\text{ cm}^3\text{ mol}^{-1}$).

Synthesis

An aqueous solution (20 mL) of H_2oxado (0.12 g, 1 mmol) was added to a blue solution of $\text{K}_2[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$ (0.35 g, 1 mmol) in 40 mL of warm water. The mixture was stirred at $50\text{ }^\circ\text{C}$ for 1 h. After cooling to room temperature, the resulting solution was filtered, and the filtrate was allowed to stand undisturbed at room temperature for about one week. Blue-greenish single crystals (0.25 g) suitable for X-ray diffraction were isolated by filtration, washed with ethanol (3 mL) and dried in air. Yield 69%. M. p. $> 230\text{ }^\circ\text{C}$. – Elemental analysis for $\text{C}_8\text{H}_{16}\text{Cu}_2\text{N}_8\text{O}_{14}$ (575.39): calcd. C 16.70, H 2.80, N 19.47; found C 16.87, H 2.73, N 19.07. – Characteristic IR absorptions (KBr, cm^{-1}): $\nu = 3475(\text{w}), 3162(\text{w}), 1692(\text{m}), 1621(\text{m}), 1493(\text{s}), 1416(\text{m}), 1370(\text{s}), 891(\text{m})$. – Room-temperature magnetic moment: $2.62\text{ }\mu_{\text{B}}$ per dimer.

X-Ray crystallography

A blue-greenish crystal with approximate dimensions of $0.16 \times 0.15 \times 0.02\text{ mm}^3$ was mounted in random orientation on a glass fiber. Intensity data were collected at $T = 100\text{ K}$ on a Gemini kappa-geometry diffractometer with graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). The structure was solved by Direct Methods with the program SIR97 [15] and refined by full-matrix least-squares calculations [16] based on F^2 . All non-hydrogen atoms were refined anisotropically. The positions of hydro-

Table 1. Summary of crystal data and numbers pertinent to data collection and structure refinement for complex **1**.

Empirical formula	$\text{C}_8\text{H}_{16}\text{Cu}_2\text{N}_8\text{O}_{14}$
M_r	575.39
Crystal size, mm^3	$0.16 \times 0.15 \times 0.02$
Crystal system	triclinic
Space group	$P\bar{1}$
$a, \text{\AA}$	6.503(1)
$b, \text{\AA}$	7.560(1)
$c, \text{\AA}$	9.670(2)
α, deg	70.98(1)
β, deg	83.36(1)
γ, deg	78.38(1)
$V, \text{\AA}^3$	439.60(13)
Z	1
$D_{\text{calcd.}}, \text{g cm}^{-3}$	2.17
$\mu (\text{MoK}\alpha), \text{mm}^{-1}$	2.5
$F(000)$	290
hkl range	$-9 \leq h \leq 8, -10 \leq k \leq 10,$ $-13 \leq l \leq 13$
θ range for data collection, deg	3.8–29.5
Reflections collected / unique / R_{int}	7220 / 2174 / 0.058
Data / restraints / parameters	2174 / 0 / 145
Final R_1 / wR_2 [$I > 2\sigma(I)$]	0.0170 / 0.0416
Final R_1 / wR_2 (all data)	0.0182 / 0.0419
GOF	1.16
Largest diff. peak / hole, $\text{e}\cdot\text{\AA}^{-3}$	1.28 / -1.19

gen atoms were added in idealized geometrical positions. Crystal data and structure refinement parameters are given in Table 1.

CCDC 908428 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Crystal structure of **1**

The synthetic approach was used with the aim of obtaining the mononuclear complex $[\text{Cu}(\text{C}_2\text{O}_4)(\text{H}_2\text{oxado})]\cdot x\text{H}_2\text{O}$ according to our previous work [17]. However, the unexpected dinuclear copper(II) complex $[\text{Cu}(\text{C}_2\text{O}_4)(\text{H}_2\text{oxado})(\text{H}_2\text{O})_2]$ was obtained. The propensity to form the dinuclear rather than the simple complex might be related to the lattice energy of the dimers which is apparently much more favorable than that of the monomer. This dinuclear complex is an air-stable blue-greenish solid practically insoluble in ethanol and acetone, and moderately soluble in water.

The molecular structure and crystallographic atom numbering of complex **1** are shown in Fig. 1. Se-

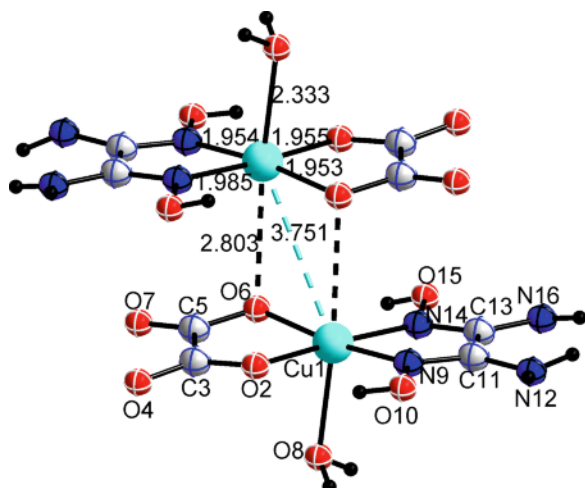


Fig. 1 (color online). ORTEP plot of complex **1** with displacement ellipsoids drawn at 50% probability level. H atoms are shown as spheres of arbitrary radius. Symmetry code: (i) $-x+1, -y+1, -z+1$.

Table 2. Selected bond lengths (Å) and angles (deg) for complex **1**^a.

Atoms	Distance	Atoms	Angle
Cu1–O6 ⁱ	2.803(3)	O6 ⁱ –Cu1–O2	99.17(12)
Cu1–O2	1.954(3)	O6 ⁱ –Cu1–O6	77.36(13)
Cu1–O6	1.953(3)	O2–Cu1–O6	84.54(13)
Cu1–O8	2.334(3)	O6 ⁱ –Cu1–O8	164.63(10)
Cu1–N9	1.954(4)	O2–Cu1–O8	87.47(13)
Cu1–N14	1.985(4)	O6–Cu1–O8	89.59(13)
O2–C3	1.271(5)	O6 ⁱ –Cu1–N9	94.37(14)
C3–O4	1.240(5)	O2–Cu1–N9	94.67(15)
C3–C5	1.540(7)	O6–Cu1–N9	171.43(17)
C5–O6	1.305(5)	O8–Cu1–N9	98.92(15)
C5–O7	1.220(5)	O6 ⁱ –Cu1–N14	82.47(14)
O8–H83	0.901	O2–Cu1–N14	174.28(15)
O8–H81	0.814	O6–Cu1–N14	101.17(15)
N9–O10	1.391(5)	O8–Cu1–N14	92.29(15)
N9–C11	1.298(6)	N9–Cu1–N14	79.72(16)
O10–H101	0.831	Cu1 ⁱ –O6–Cu1	102.64(13)
C11–N12	1.336(6)	Cu1–O8–H83	115.2
C11–C13	1.489(6)	Cu1–O8–H81	109.9
N12–H121	0.849	H83–O8–H81	97.8
N12–H122	0.859	Cu1–N9–O10	128.8(3)
C13–N14	1.299(6)	N9–O10–H101	106.5
C13–N16	1.328(5)	N9–C11–N12	124.9(4)
N14–O15	1.400(5)	N9–C11–C13	113.5(4)
O15–H151	0.823	N14–C13–N16	124.9(4)
N16–H161	0.861	Cu1–N9–C11	117.2(3)
N16–H162	0.856	O10–N9–C11	113.9(4)

^a Symmetry transformation used to generate equivalent atoms: (i) $-x+1, -y+1, -z+1$.

lected bond lengths and bond angles are listed in Table 2. The structure determination revealed that the dinuclear complex forms layers. In the neutral $[\text{Cu}(\text{C}_2\text{O}_4)(\text{H}_2\text{oxado})(\text{H}_2\text{O})]$ entities the oxalate dianion and the oxamide dioxime each form five-membered rings with the copper atom. The first $[\text{Cu}(\text{C}_2\text{O}_4)(\text{H}_2\text{oxado})(\text{H}_2\text{O})]$ unit is linked to the second by an oxalate oxygen atom O6 which appears in the axial position of the second copper site, Cu1^{i} , the $\text{Cu1–O6}^{\text{i}} / \text{Cu1}^{\text{i}}\text{–O6}$ contacts being 2.803(3) Å. These long $\text{Cu1–O6}^{\text{i}} / \text{Cu1}^{\text{i}}\text{–O6}$ contacts are indicative of the weakness of the dimerization interaction in the complex. The $\text{Cu1}\cdots\text{Cu1}^{\text{i}}$ separation within the dimer is 3.751 Å. Similar dimerized structure types were found in the salts $[\text{C}_5\text{H}_6\text{N}]_2[\text{Cu}(\text{C}_2\text{O}_4)_2]\cdot\text{H}_2\text{C}_2\text{O}_4$ ($\text{Cu}\cdots\text{Cu}$: 3.697(7) Å; axial contact: 2.893(3) Å) [18] and $[\text{C}_6\text{H}_{14}\text{N}_2][\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$ ($\text{Cu}\cdots\text{Cu}$: 3.818(8) Å; axial contact: 2.906(10) Å) [19]. The two equatorial oxalate oxygen atoms [O2, O6] surround the Cu1 atom in a bidentate and symmetrical mode with bond lengths $\text{Cu1–O2} / \text{Cu1–O6} = 1.953(3)$ Å while the oximino nitrogen atoms [N9, N14] from the oxamide dioxime ligand are connected to Cu1 in a bidentate and unsymmetrical mode with bond lengths $\text{Cu1–N9} = 1.954(4)$ and $\text{Cu1–N14} = 1.985(4)$ Å. The axially coordinated water molecules of the dimeric entity are *trans* to each other according to the centrosymmetry. The distance of the copper atom from the coordinated water oxygen atom O8 is 2.334(3) Å. The coordination sphere around the copper center can be described as a strongly distorted octahedron. There are no unusual bond lengths or bond angles in the oxamide dioxime [11, 12] or oxalate ligands [3, 11, 12].

The projection of the structure onto the *ac* plane is shown in Fig. 2. In the crystal, N–H \cdots O hydrogen bonds involving oxalate O atoms (O4, O7) and amino N atoms (N12, N16) of the oxamide dioxime link dimers $[\text{Cu}(\text{C}_2\text{O}_4)(\text{H}_2\text{oxado})(\text{H}_2\text{O})]_2$ into layers parallel to the *bc* plane. The layers are further hydrogen-bonded through the aqua ligand O atom (O8), forming a three-dimensional network. The distances and angles of the hydrogen bonds are listed in Table 3. These intra- and intermolecular hydrogen bonds holding the $[\text{Cu}(\text{C}_2\text{O}_4)(\text{H}_2\text{oxado})(\text{H}_2\text{O})]$ molecules together (Fig. 3, Table 3) are responsible for producing a material with low solubility.

The structure of complex **1** has a number of noteworthy aspects. To the best of our knowledge, no ex-

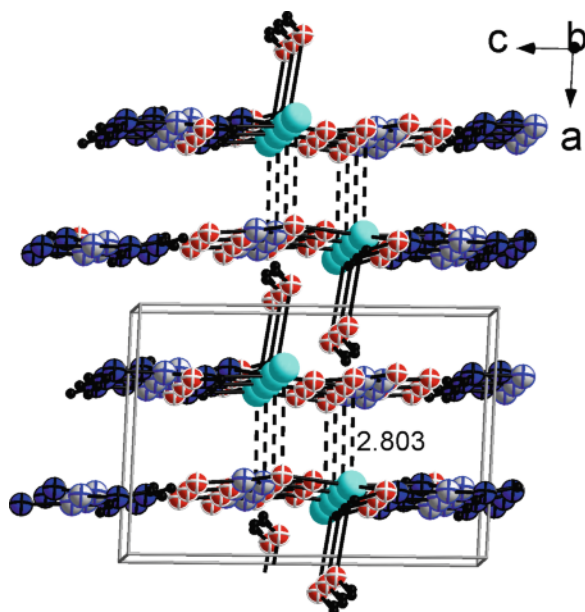


Fig. 2 (color online). Structure of complex **1** projected onto the *ac* plane highlighting layers of $[\text{Cu}(\text{C}_2\text{O}_4)(\text{H}_2\text{oxado})(\text{H}_2\text{O})]$ units. The long Cu–O contacts within the dimers are shown in dashed lines.

Table 3. Hydrogen bond lengths (Å) and bond angles (deg) for complex **1**^a.

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	<(DHA)
O10–H101...O2	0.83	2.52	3.108(7)	129
O10–H101...O15 ⁱⁱ	0.83	2.15	2.830(7)	138(1)
N12–H121...O7 ⁱⁱⁱ	0.85	2.13	2.943(7)	161(1)
N12–H122...O4 ^{iv}	0.86	2.21	3.051(7)	166(1)
O15–H151...O8 ^v	0.82	1.82	2.633(7)	172(1)
N16–H161...O10 ^{vi}	0.86	2.45	3.236(7)	152(1)
N16–H162...O4 ^{iv}	0.86	2.06	2.912(7)	172(1)
O8–H83...O6 ^v	0.90	1.82	2.605(7)	145(1)
O8–H81...O4 ^{vii}	0.81	1.87	2.683(7)	176(1)

^a Symmetry transformations used to generate equivalent atoms: (ii) $x, y+1, z$; (iii) $x, y, z+1$; (iv) $x, y-1, z+1$; (v) $-x, -y+1, -z+1$; (vi) $x, y-1, z$; (vii) $-x, -y+2, -z+1$.

ample of the same type involving both oxalate and α, β -dione dioxime ligands in the ratio 1 : 1 seems to have been reported hitherto. Furthermore, the most closely related systems described previously [18, 19] are salts in essence with a chain-like structure of anionic entities. By contrast, the present compound features solely neutral dimeric species in a layer-like structure resulting from strong hydrogen bonding between neighboring dimers.

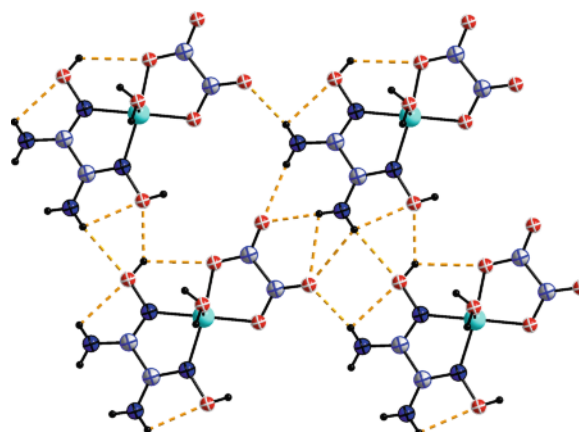


Fig. 3 (color online). Intra- and intermolecular hydrogen bonds holding the $[\text{Cu}(\text{C}_2\text{O}_4)(\text{H}_2\text{oxado})(\text{H}_2\text{O})]$ units together in the *ab* plane.

IR spectrum of **1**

The IR spectrum of complex **1** exhibits weak absorption bands centered at $3475\text{--}3162\text{ cm}^{-1}$ attributable to $\nu_{\text{N-H}}$ and $\nu_{\text{O-H}}$ vibrations involved in hydrogen bonding [20]. The medium-size bands appearing at 1692, 1639 and 1621 cm^{-1} are attributed to $\nu_{\text{C=O}}$, $\nu_{\text{C=N}}$ and δ_{HNH} vibrations [21]. The strong band at 1493 cm^{-1} can be assigned to the symmetric stretching absorption of the carboxylate groups of the oxalato ligand [22], and the band appearing around 1416 cm^{-1} to the $\nu_{\text{C-N}}$ vibrations. Strong to medium well-resolved bands appear at 1370 cm^{-1} ($\nu_{\text{C-O}}$), at 1254 cm^{-1} ($\nu_{\text{N-O}}$) and at 891 cm^{-1} ($\nu_{\text{C-C}}$) [22].

Thermal analysis of **1**

The results of the thermal analyses (TGA and DTA) of complex **1** are depicted in Fig. 4. The thermogram (Fig. 4 a) exhibits no mass loss up to 120°C , thus confirming the absence of solvate water in the complex. Between 121 and 160°C , a first mass loss of 6% (calcd. 6.3%) is observed, which reasonably is attributed to the release of the coordinated water molecules. For this step, an endothermic peak with $T_{\text{max}} = 152.7^\circ\text{C}$ on the DTA curve (Fig. 4 b) is observed. A second step of 58% mass loss (calcd. 57.8%) finally occurs between $243\text{--}246^\circ\text{C}$ with a corresponding exothermic peak with $T_{\text{max}} = 244.7^\circ\text{C}$, which corresponds to the release of a combined mass summarized as $4\text{N}_2 + 4\text{CO}_2 + 6\text{H}_2\text{O}$.

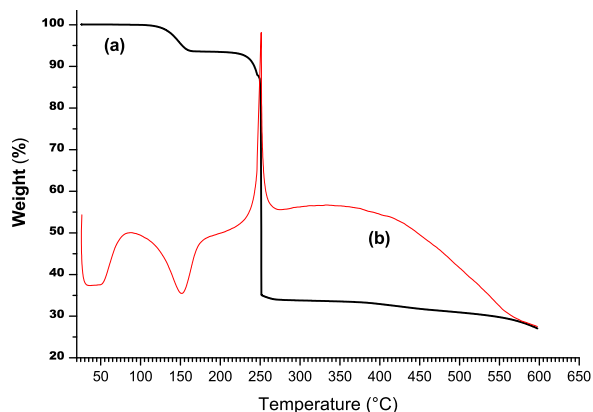


Fig. 4 (color online). TGA (curve a) and DTA (curve b) of complex **1**.

Magnetic susceptibility measurements of **1**

The corrected molar susceptibility, χ_M^{corr} , was used to calculate the effective magnetic moment, μ_{eff} , according to Eq. 1:

$$\mu_{\text{eff}} = 2.82[\chi_M^{\text{corr}}T]^{1/2}\mu_B \quad (1)$$

(μ_B = Bohr magneton)

The effective magnetic moment at room temperature of **1** was measured to be $2.62 \mu_B$ per dimer, which is comparable to the values found in $[\text{Cu}_2(\text{dpyam})_4(\mu\text{-C}_2\text{O}_4)](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ ($2.62 \mu_B$ per dimer) [23] and $[\text{Cu}_2(\text{dpyam})_4(\mu\text{-C}_2\text{O}_4)](\text{BF}_4)_2 \cdot 3\text{H}_2\text{O}$ ($2.64 \mu_B$ per dimer) [23]. Furthermore this value is very close to the spin-only value calculated of $2.45 \mu_B$ for two uncoupled Cu(II) spin 1/2 centers. The thermal variation of the molar susceptibility of complex **1** is shown in Fig. 5 as the reciprocal susceptibility (χ_M^{-1}) versus T . This reciprocal susceptibility was fitted to the Curie-Weiss law, yielding a Weiss constant $\theta = -0.86$ K. This small negative Weiss constant suggests very weak antiferromagnetic interactions at low temperatures in the solid state [24]. Geiser *et al.* have reported on a similar coordination mode of copper with oxalate ligands in the compound pyridinium bis(oxalato)cuprate(II)-oxalic acid that also shows weak antiferromagnetic coupling ($\theta = -3.6$ K) [18]. As mentioned by Geiser *et al.*, the appearance of small antiferromagnetic coupling reflected in the negative Weiss constant cannot readily be explained because any of the conceivable exchange pathways involves orthogonal orbitals that could suggest a slightly ferromagnetic interaction [18]. Therefore,

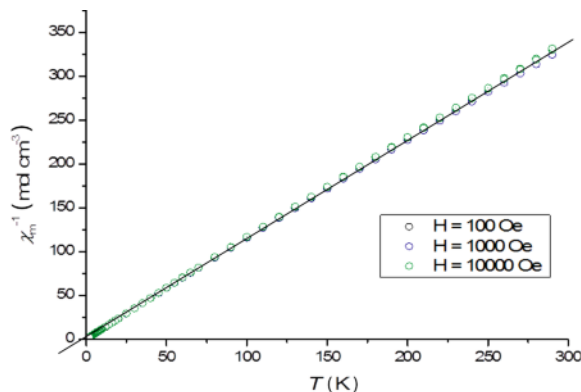


Fig. 5 (color online). Temperature-dependent magnetic behavior of **1**, showing the χ_M^{-1} vs. T curve. The solid line corresponds to the theoretical curve.

the observed very weak antiferromagnetism in this type of compounds may be associated with dipolar coupling mechanisms, either of an intra- or an inter-chain type. The synthesis and systematic study of similar compounds and of their magnetic properties at very low magnetic fields and temperatures will be very useful for the understanding of this unusual behavior.

Conclusion

In summary, the compound $[\text{Cu}(\text{C}_2\text{O}_4)(\text{H}_2\text{oxado})(\text{H}_2\text{O})_2]$, obtained from aqueous solution as blue-greenish crystals, is a novel dimeric layer-like copper(II) complex involving oxalate ions, oxamide dioxime and coordinated water molecules, with extensive hydrogen-bonding interactions stabilizing the 3-dimensional network. Thermal analysis showed that the compound is stable up to *ca.* 120 °C. Magnetic susceptibility data revealed very weak antiferromagnetic spin exchange interactions within the dinuclear unit. Preliminary observations from our laboratory suggest that the method illustrated for the preparation of this complex may be applied systematically to fabricate a whole range of homologous α, β -dione dioxime compounds. More data on analogous compounds should probably provide insights for a detailed understanding of their magnetic interactions.

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