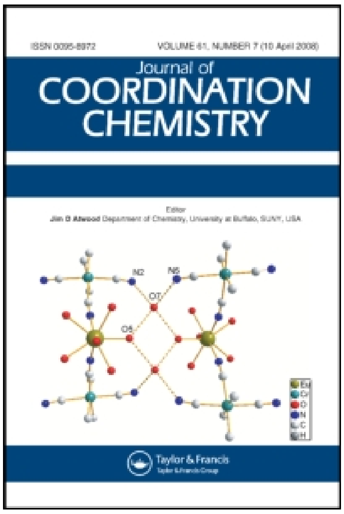

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Synthesis, crystal structure, magnetic and spectroscopic properties of $\{[\mathrm{Cu(oxbe)(py)}]_2\mathrm{Ni(py)}_2\}\cdot 2\mathrm{Dmf}$ complex of dissymmetrical oxamidate

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SYNTHESIS, CRYSTAL STRUCTURE, MAGNETIC AND SPECTROSCOPIC PROPERTIES OF $\{[Cu(oxbe)(py)]_2Ni(py)_2\} \cdot 2DMF$ COMPLEX OF DISSYMMETRICAL OXAMIDATE

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The trinuclear complex $\{[Cu(oxbe)(py)]_2Ni(py)_2\} \cdot 2DMF$ has been prepared and characterized by elemental analysis, IR and electronic spectra and magnetic susceptibility, where H_3oxbe is the dissymmetrical ligand *N*-benzoato-*N′*-(2-aminoethyl) oxamido, py = pyridine, DMF = dimethylformamide. The molecular structure of this complex is centrosymmetrical and has an extended oxamido-bridged structure consisting of two pyramidal copper(II) and one octahedral nickel(II) ions. The central Ni(II) and two terminal Cu(II) ions are antiferromagnetically coupled, $J = -60.2\,\mathrm{cm}^{-1}$.

Keywords: Centrosymmetrical; Oxamido-bridged; Copper(II); Nickel(II); Trinuclear complex; Antiferromagnetically coupled

INTRODUCTION

Molecular magnetism has developed rapidly since the 1980s [1–3], with particular emphasis on heterobimetallic complexes. The magnetic interaction between two non-equivalent paramagnetic centers may lead to situations which cannot be encountered in species containing only one kind of center [4]. Journaux *et al.* [5] proposed that obtaining polynuclear complexes is mainly based on the following synthetic schemes: (1) the self-assembly method, (2) the use of a polynucleating ligand, and (3) the use of complexes as ligands.

One of the best strategies to obtain heterobimetallic systems is the ‘‘complex as ligand’’ approach, *i.e.*, using as precursors mononuclear complexes that contain potential donors for another metal ion. Copper(II) complexes of bis(oxamato), such as $[Cu(pba)]^{2-}$, $[Cu(pbaOH)]^{2-}$, and $[Cu(opba)]^{2-}$ [pba = 1,3-propylenebis(oxamato), pbaOH = 2-hydroxy-1,3-propylenebis(oxamato), opba = *O*-phenylbis(oxamato)] are

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good examples of "complex as ligand". From these precursors, it was possible to design binuclear and trinuclear complexes [4,6–10], linear and zigzag chains [10–13], two-dimensional networks with an interlocked structure [14–16], and ladder compounds [17,18] through rational assembly.

Symmetrically *N*,*N*′-disubstituted oxamidate derivatives are also known to be versatile organic ligands which can chelate as well as bridge metal ions to construct discrete and extended structure, depending on their adoption of the cis- or trans-conformation [19]. Owing to synthetic difficulties, only two dissymmetric oxamidate copper(II) precursors have been both structurally and magnetically characterized by Kahn and coauthors: $[Cu(obze)]^{2-}$ [20] and $[Cu(obzp)]^{2-}$ [21]. More recently [22], a new copper(II) precursor of this kind has been reported. Through the "complex as ligand" approach, we have obtained a 3D supramolecular coordination polymer $\{[Cu(oxbe)]Mn(H_2O)[Cu(oxbe)(DMF)]\}_n \cdot n\text{DMF} \cdot n\text{H}_2\text{O}$, and a 2D supramolecular compound $\{[Cu(oxbe)]_2Co(H_2O)_2\} \cdot 2DMF \cdot DMA$ [23]. Now we have used this copper(II) precursor $[Cu(oxbe)]^-$ as the ligand to react with nickel(II) in the presence of py forming a new discrete trinuclear complex $\{[Cu(oxbe)(py)]_2Ni(py)_2\} \cdot 2DMF$. Here, we report the synthesis, crystal structure, magnetic and spectroscopic properties of $\{[Cu(oxbe)(py)]_2Ni(py)_2\} \cdot 2DMF$.

EXPERIMENTAL

Materials and Methods

All regents used in the synthesis were of analytical grade. The perchlorate complex of nickel ion is prepared by a general method. Elemental analyses for C, H and N were carried out on a Perkin–Elmer instrument, model 2400II. The metal contents were determined by EDTA titration. The infrared spectrum was recorded on an Avater-360 spectrophotometer using KBr pellets in the range 400–4000 cm^{-1}. UV-Vis spectra were recorded on HEΛIOS α spectrophotometer in the 200–900 nm range. Magnetic measurements were carried out on polycrystalline samples with an MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

Preparation of the Complexes

The ligand oxbe and its copper(II) mononuclear complex $Na[Cu(oxbe)] \cdot 1.5H_2O$ were obtained as described in the literature [22].

Synthesis of the Title Complex

1 mmol (0.362 g) of $Na[Cu(oxbe)] \cdot 1.5H_2O$ was dissolved in 50 cm^3 water and a solution containing 0.5 mmol (0.183 g) of $Ni(ClO_4)_2 \cdot 6H_2O$ in 5 cm^3 methanol was then added slowly with continuous stirring for 2 h, affording a red precipitate, which was filtered, washed with water, and dried in a desiccator containing silica gel. Well-shaped blue single crystals of this complex were obtained by slow evaporation of pyridine into the DMF solution containing the crude product. Yield: 80%. Anal. Calcd. for

TABLE I Crystal data and structure refinement for the title complex

Molecular formula	$C_{48}H_{54}N_{12}O_{10}Cu_2Ni$
Molecular weight	1144.82
Crystal system	Monoclinic
Space group	$P2(1)/n$
a (Å)	10.932(7)
b (Å)	15.839(10)
c (Å)	16.140(10)
β (°)	108.142(12)
V (Å^3)	2656(2)
Z	2
D_c (g cm^{-1})	1.432
λ (Mo Kα) (Å)	0.71073
μ (Mo Kα)(mm^{-1})	1.211
T (K)	293(2)
$R1[(I > 2\sigma)]^a$	0.0582
$wR2^b$	0.1021

$^aR1 = \|F_0| - |F_c\|/|F_0|$; $^bwR2 = [w(|F_0|^2 - |F_c|^2)^2/\Sigma(F_0{}^2)^2]^{1/2}$.

$C_{48}H_{54}N_{12}O_{10}Cu_2Ni$(%): C, 50.36; H, 4.75; N, 14.68; Cu, 11.10; Ni, 5.13. Found: C, 50.38; H, 4.72; N, 14.72; Cu, 11.13; Ni, 5.11.

Caution: Although no problem was encountered in this work, the nickel perchlorate complex is potentially explosive and should only be handled in small quantities.

X-ray Structure Determination and Refinement of the Title Complex

A blue single crystal ($0.20 \times 0.15 \times 0.10\,mm^3$) of the title complex was selected, and intensity data were collected in the 2θ range of 3.08–51.96° at room temperature on a Bruker Smart 1000CCD area detector equipped with graphite-monochromated Mo Kα radition ($\lambda = 0.71073$ Å). Empirical absorption corrections were applied using the SADABS program. The structure was solved by direct methods and refined by full-matrix methods on F^2 with anisotropic thermal parameters for all nonhydrogen atoms [24]. The hydrogen atoms of solvent molecules were not added, and the other hydrogen atoms were located geometrically and refined isotropically.

Pertinent crystallographic data and structure refinement parameters are summarized in Table I.

RESULTS AND DISCUSSION

IR and Electronic Spectra

The $\nu_{C=O}$ vibration (oxamidate group and ionized carboxylate group) at $1649\,cm^{-1}$ for $Na[Cu(oxbe)] \cdot 1.5H_2O^{22}$ was shifted to higher frequencies in the trinuclear complex ($1665\,cm^{-1}$). This shift has often been used as proof of the existence of the oxamido-bridge.

The diffuse reflectance spectrum of the title complex exhibits a broadband absorption in the visible region with a maximum at 566 nm, consistent with five-coordinated copper(II) with an intermediate geometry between ideal square pyramidal and trigonal bipyramidal, and the frequency is lower than that of the mononuclear complex

(532 nm). Such a red shift of the d–d band may be attributed to the decreased planarity of the [CuN_3O] chromophore and/or to the square pyramidal CuN_4O chromophore. It should be stressed that the $^3A_2(Ni) \rightarrow {}^3T_1(Ni)$ d–d transition of an octahedral [NiN_2O_4] chromophore should also be observed in the above range, but may be obscured by the d–d band of Cu(II). A weak band at around 760 nm is attributed to the spin-forbidden transition $^3A_2(Ni) \rightarrow {}^1E_2(Ni)$, which is activated by an exchange mechanism [25,26]. Besides the d–d bands, the spectrum of the title complex displays two more intense bands centered at 308 nm and 345 nm, which can be assigned to πligand → Cu(II)$d_{x^2-y^2}$ LMCT and internal ligand π–π^* transitions, respectively [27].

Crystal Structure

The neutral molecule is depicted in Fig. 1 and selected bond lengths and bond angles are listed in Table II. The crystal structure of the title complex consists of a trinuclear neutral molecule, and two DMF molecules that are involved in weak coordination. The structure of the title complex is centrosymmetric with the nickel(II) ion located at the inversion center. Two oxamidates act as bridges between the central and the outer metal ions.

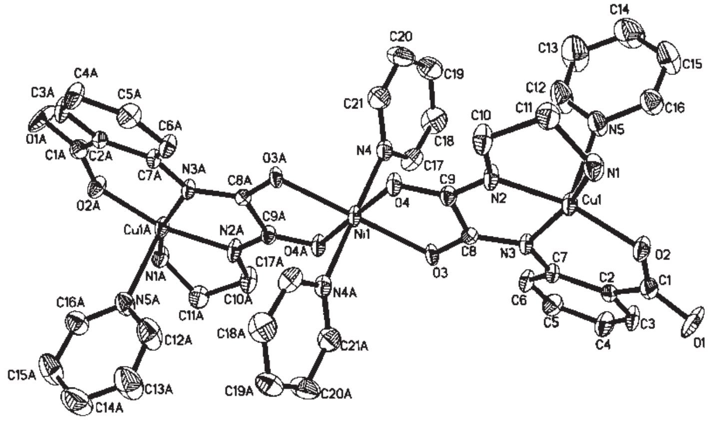

FIGURE 1 The molecular structure of Complex 2; DMF molecules omitted for clarity.

TABLE II Bond length (Å) and angles (°) around the metal atoms for the title complex

Cu(1)–O(2)	1.912(4)	Cu(1)–N(2)	1.913(4)
Cu(1)–N(3)	1.988(4)	Cu(1)–N(1)	2.052(5)
Cu(1)–N(5)	2.292(6)	Ni(1)–O(4)	2.046(3)
Ni(1)–O(3)	2.080(4)	Ni(1)–N(4)	2.088(6)
O(2)–Cu(1)–N(2)	164.5(2)	O(2)–Cu(1)–N(3)	94.8(2)
N(2)–Cu(1)–N(3)	83.6(2)	O(2)–Cu(1)–N(1)	96.4(2)
N(2)–Cu(1)–N(1)	81.7(2)	N(3)–Cu(1)–N(1)	161.4(2)
O(2)–Cu(1)–N(5)	96.8(2)	N(2)–Cu(1)–N(5)	98.8(2)
N(3)–Cu(1)–N(5)	99.1(2)	N(1)–Cu(1)–N(5)	94.2(2)
O(3)–Ni(1)–O(4)	82.0(2)	O(4)–Ni(1)–N(4)	90.0(2)
O(3)–Ni(1)–N(4)	87.9(2)		

The central nickel(II) ion is octahedrally coordinated by two pairs of oxamide oxygens and two py molecules in trans positions. The Ni–O (2.05–2.08 Å) and Ni–N (2.09 Å) distances are all consistent with the literature [28,29]. Each copper atom shows five coordination in the form of a square pyramid with the trideprotonated ligand [N(1), N(2), N(3), O(2)] in the plane and the nitrogen [N(5)] of the py molecule at the apex. The Cu–N(1) bond distance (2.052 Å) is longer than Cu–N(2) (1.913 Å) and Cu–N(3) (1.988 Å), consistent with the greater basicity of the deprotonated amido group. The apex bond Cu–N(5) (2.292 Å) is much longer than the other two kinds, suggesting that the py is more weakly coordinated to the copper. Compared with similar supramolecular complexes previously reported by us [22,23], the title compound has higher steric hindrance because of the coordination of pyridine. Though there are many aromatic rings, neither π–π stacking interactions nor hydrogen bonds have been found in the complex $\{[Cu(oxbe)(py)]_2Ni(py)_2\} \cdot 2DMF$.

Magnetic Properties

The magnetic susceptibility of the title complex was measured in the temperature range 5–300 K on an MPMS-7 SQUID magnetometer. The room temperature value for μ_{eff} (3.40 B.M. where μ_{eff} is the effective magnetic moment) is lower than expected for uncoupled Cu(II)–Ni(II)–Cu(II) trinuclear ions (4.11 B.M.). Upon cooling, the μ_{eff} value decreases steadily approaching almost zero. A plateau of 0.45 B.M. is reached at about 20 K. The temperature behavior of the magnetic susceptibility of the complex clearly indicates that the $S = 1$ state of the nickel(II) is antiferromagnetically coupled to the terminal $S = 1/2$ state of the copper(II) ions [28].

On the basis of the isotropic spin Hamiltonian $\hat{H} = -2J(\hat{S}_{\text{Cu1}}\hat{S}_{\text{Ni}} + \hat{S}_{\text{Cu2}}\hat{S}_{\text{Ni}})$, the expression of the magnetic susceptibility for a Cu(II)–Ni(II)–Cu(II) system is

$$\chi_{\text{M}} = \frac{2N\beta^2 g^2}{K(T-\theta)}\left[\frac{1 + 5\exp(4J/KT) + \exp(2J/KT)}{3 + 5\exp(4J/KT) + \exp(-2J/KT) + 3\exp(2J/KT)}\right].$$

The agreement with the observed magnetic susceptibility is good, except at low temperature where the calculated values are lower than the experimental ones. The discrepancy is probably due to paramagnetic impurities, whose contribution becomes relevant when the compound is diamagnetic. In order to overcome it, we introduce ρ to take into account the presence of such impurities. Thus, the expression of the magnetic susceptibility for this system becomes

$$\chi'_{\text{M}} = \chi_{\text{M}}(1-\rho) + \frac{N\beta^2 g^2}{3KT}\left[2 \times \frac{1}{2}\left(\frac{1}{2}+1\right) + 1 \times (1+1)\right]\rho + N_\alpha$$

where N_α is the temperature-independent paramagnetism ($400 \times 10^{-6}\ \text{cm}^3\,\text{mol}^{-1}$). The best fit to the experimental data gives $J = -60.2\ \text{cm}^{-1}$, $g = 2.06$, $\theta = 0.472$ K, $\rho = 1.02 \times 10^{-2}$. The agreement factor $R = \sum(\chi_{\text{obsd}} - \chi_{\text{cacld}})^2 / \sum \chi^2_{\text{obsd}}$ is 4.93×10^{-4}, which corresponds to good agreement as shown in Fig. 2. The calculated J value is very close to those previously reported for other Cu(II)–Ni(II) complexes [28,30,31], and $[Cu(oxbe)Ni(phen)_2]ClO_4 \cdot 3H_2O$ ($J = -57.1\ \text{cm}^{-1}$) [32].

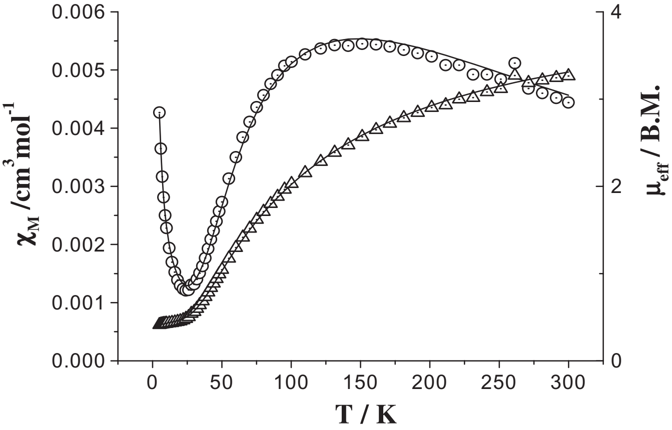

FIGURE 2 χ_M versus T and μ_{eff} versus T plots for the title complex.

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Supplementary Data

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. 208281. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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