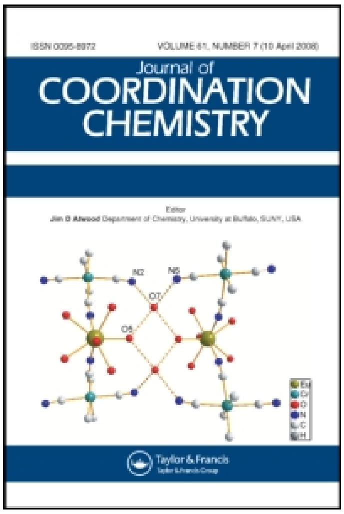

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SYNTHESIS AND CRYSTAL STRUCTURE OF OXAMIDATO-BRIDGED BINUCLEAR COPPER(II) COMPLEXES

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The compounds [Cu(oxpn)] (1), [(bpy)(H_2O)Cu(μ-*cis*-oxpn)Cu(H_2O)]·$2NO_3$·$2H_2O$ (2) and [(Him)(NO_3)Cu(μ-*trans*-oxpn)Cu(Him)(NO_3)] (3), where oxpn is the dianion of *N,N′*-bis(3-aminopropyl)oxamide, bpy is bipyridine and Him is imidazole, were prepared and characterized by elemental analysis and IR spectra. Complex (2) was also studied by thermochemical analysis and its structure determined by X-ray crystallography. The structure of complex (2) consists of binuclear copper(II) molecules in which the copper(II) atoms are bridged by an oxamidato group in the *cis* conformation resulting a copper–copper distance of 5.21 Å. Both copper(II) ions are in square-pyramidal surroundings with almost coplanar basal planes and a water molecule occupying the apical positions. The N atoms of the oxamidato moiety are trigonal. Two lattice water molecules together with the two coordinated ones hydrogen bond with nitrate ions.

Keywords: Copper(II); bipyridine; oxamidate; crystal structure; IR spectra; thermochemistry

INTRODUCTION

The synthesis of polymetallic coordination complexes, particularly those having two- or three-dimensional and supramolecular structures, is of current interest for inorganic chemists seeking to design new molecular materials with unusual magnetic and electrical properties.[1–3] A study of spin

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* Corresponding author.

exchange in polynuclear metal complexes in view of the nature of the bridging groups and stereochemical factors has been continuing in our laboratory.[4–6] The oxpn^{2-} ligand [H_2oxpn = *N,N'*-bis(3-aminopropyl)-oxamide] is a well known member of the *N,N'*-disubstituted oxamides with its coordination chemistry having been explored in the last decade.[8–11] The great versatility of oxpn^{2-} as a ligand is based on the bidentate character of the mononuclear complexes, which can be used as chelating units towards a second metal ion to form binuclear complexes in the *cis* conformation and the adoption of a conformation change from *cis* to *trans* to form symmetric binuclear complexes. We have previously reported the structure of a binuclear copper(II) complex, [Cu_2(*trans*-oxpn)$(Him)_2(NO_3)$], in which oxpn is a bis-tridentate in *trans* conformation, bridging two copper(II) ions.[6] In this paper, we report a binuclear copper(II) complex in which oxpn^{2-} bridges two copper ions in the *cis* conformation.

EXPERIMENTAL

Physical Measurements

Analyses for C, H and N were carried out with a Perkin-Elmer Analyzer, Model 240. IR spectra were recorded on a Perkin-Elmer Paragon 100 spectrophotometer with KBr discs. The X-ray crystal structure determination was carried out on a Rigaku AFC7R diffractometer. Thermochemical studies were carried out on a Perkin-Elmer 7 Series system under N_2 flow (50 cm^3 min^{-1}) and the heating rate of 20°C min^{-1}.

Preparation of [Cu(oxpn)] (1)

To a solution of 20 mmol of 1,3-propylenediamine in 50 cm^3 of ethanol cooled in an ice bath was added dropwise a solution of 10 mmol of diethyl oxalate in 30 cm^3 of ethanol. The mixture was heated to reflux for 2 h and then cooled. Then, 10 mmol of $Cu(NO_3)_2 \cdot 4H_2O$ in 30 cm^3 of ethanol was added with stirring followed by 20 mmol of NaOH in 20 cm^3 of water. The mixture was stirred at 70°C for 1 h and then filtered. Red [Cu(oxpn)] was obtained by filtration after distilling some of the solvent. *Anal.* Calcd. for $C_8H_{16}N_4O_2Cu$ (%): C, 36.45; H, 6.10; N, 21.25. Found: C, 36.36; H, 6.14; N, 21.09.

Preparation of $[Cu_2(bipy)(\mu\text{-}cis\text{-}oxpn)(H_2O)_2] \cdot 2NO_3 \cdot 2H_2O$ (2)

Some 2.41 g (10 mmol) of $Cu(NO_3)_2 \cdot 4H_2O$ was dissolved in 40 cm^3 of ethanol followed by the addition of 1.56 g (10 mmol) of 2,2′-bipyridine, with stirring. The mixture solution was heated for 1 h at 75°C, then 20 cm^3 of an aqueous solution containing 2.64 g (10 mmol) of [Cu(oxpn)] was slowly added with continuous stirring for 0.5 h at 75°C. The resulting solution was filtered and slowly cooled to room temperature. After several days, well-shaped, dark blue, single crystals were obtained. *Anal.* Calcd. for $C_{18}H_{32}N_8O_{12}Cu_2$ (%): C, 31.81; H, 4.75; N, 16.49. Found: C, 31.75; H, 4.82; N, 16.50.

Preparation of $[Cu_2(Him)_2(\mu\text{-}trans\text{-}oxpn)(NO_3)_2]$ (3)

Some 2.41 g (10 mmol) of $Cu(NO_3)_2 \cdot 4H_2O$ was dissolved in 40 cm^3 of ethanol followed by 0.67 g (10 mmol) of imidazole with stirring. To the mixture was added 20 cm^3 of an aqueous solution containing 2.64 g (10 mmol) of [Cu(oxpn)] with continuous stirring for 0.5 h at room temperature. The resulting solution was filtered and well-shaped, dark blue, single crystals were obtained after standing for several days. *Anal.* Calcd. for $C_{14}H_{24}N_{10}O_8Cu_2$ (%): C, 28.62; H, 4.12; N, 23.85. Found: C, 28.54; H, 4.32; N, 23.75.

Crystal Structure Determination of Complex (2)

A dark blue crystal of complex (2) having approximate dimensions 0.20 × 0.20 × 0.30 mm was mounted on glass fibre. All measurements were made on a Rigaku AFC7R diffractometer with graphite-monochromated MoKα radiation and a 12 kW rotating anode generator. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 20° carefully centred reflections in the range $13.9° < 2\theta < 21.1°$. The data were collected using the ω–2θ scan technique. Of the 4292 reflections which were collected, 3948 were unique ($R_{int} = 0.090$). The linear absorption coefficient, μ, for MoKα radiation is 16.4 cm^{-1}. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods[15] and expanded using Fourier techniques.[16] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. A summary of data collection and structure refinement details is given in Table I; final atomic positional parameters, and selected bond lengths and angles are given in Tables II and III, respectively.

TABLE I Crystal data and structure refinement details for 2

Compound	$[Cu_2(II)(bpy)(cis\text{-}oxpn)(H_2O)_2]\cdot 2NO_3\cdot 2H_2O$
Color/shape	Dark blue/ prismatic
Empirical formula	$C_{18}H_{32}Cu_2N_8O_{12}$
Formula weight	679.59
Temperature	293 K
Crystal system	Monoclinic
Space group	$P2_1/c$
No. of reflections used for unit cell determination (2θ range)	20 (13.9°–21.1°)
a (Å)	8.656(2)
b (Å)	17.843(3)
c (Å)	18.024(5)
β (°)	102.62(2)
V (Å^3)	2716(1)
Z	4
$D_{calc.}$ (g cm^{-3})	1.662
μ(MoKα) (cm^{-1})	16.40
F(000)	1400
Diffractometer	Rigaku AFC7R
Radiation	MoKα ($\lambda = 0.71069$ Å) graphite monochromated
Scan type	ω–2θ
Scan width	$(1.78 + 0.30 \tan\theta)°$
$2\theta_{max}$	50°
No. of reflections measured	Total: 4292; unique: 3948 ($R_{int} = 0.090$)
No. observations ($I > 2.5\sigma(I)$)	2367
No. variables	361
Reflection/ parameters ratio	6.56
Residuals: R; R_w	0.045; 0.049
S	1.69
Max. peak in final diff. map	0.39 eÅ^{-3}

RESULTS AND DISCUSSION

Crystal Structure

The structure of complex (2) consists of $[(H_2O)Cu(\mu\text{-}cis\text{-}oxpn)Cu(bpy)(H_2O)]^{2+}$ cations with two water molecules coordinate to each copper atom on the same side, as shown in Figure 1. Each copper atom has a slightly distorted square-pyramidal environment with an oxygen atom of H_2O in the apical site with bond distances of 2.273(5) and 2.448(5) Å for Cu1–O3 and Cu2–O12, respectively. Cu1 is displaced by 0.166 Å out of the basal plane defined by O1, O2, N1 and N2 atoms towards the apical position. In the molecule, two N atoms of a bpy ligand coordinate to the Cu1 atom in the basal plane with an average Cu–N distance of 1.98 Å and two O atoms of the [Cu(oxpn)] complex-ligand chelate the Cu(II) atom with an average Cu–O distance of 1.944 Å, forming two five-membered chelate rings with the N1–Cu–N2 and O1–Cu–O2 bond angles being 81.5° and 85.8°,

TABLE II Final atomic positions and equivalent isotropic thermal parameters

Atom	*x/a*	*y/b*	*z/c*	*Beq* (Å^2)
Cu(1)	0.1830(1)	0.52463(5)	0.10700(4)	2.95(2)
Cu(2)	−0.0882(1)	0.52935(5)	0.33806(4)	2.85(2)
O(1)	0.1366(6)	0.5993(3)	0.1779(3)	3.4(1)
O(2)	0.0577(5)	0.4566(3)	0.1539(2)	3.0(1)
O(3)	0.4182(6)	0.4894(3)	0.1821(3)	4.0(1)
O(4)	0.3629(8)	0.3695(4)	0.2775(4)	6.4(2)
O(5)	0.389(1)	0.2521(4)	0.2920(4)	8.9(2)
O(6)	0.3991(8)	0.3021(4)	0.1856(4)	7.3(2)
O(7)	0.5899(9)	0.0525(5)	0.1144(4)	8.3(2)
O(8)	0.4387(7)	0.1410(4)	0.0623(4)	6.3(2)
O(9)	0.6105(8)	0.0940(4)	0.0068(4)	7.1(2)
O(10)	0.4270(7)	0.1069(3)	0.2303(3)	5.9(2)
O(11)	0.2412(6)	0.3386(3)	0.4138(3)	5.1(2)
O(12)	0.1343(5)	0.4806(3)	0.4339(3)	3.9(1)
N(1)	0.2744(6)	0.5965(3)	0.0446(3)	2.9(1)
N(2)	0.2022(6)	0.4563(3)	0.0227(3)	3.0(1)
N(3)	0.0206(6)	0.6009(3)	0.2819(3)	2.8(1)
N(4)	−0.1129(7)	0.6055(3)	0.4166(3)	3.5(2)
N(5)	−0.0563(6)	0.4585(3)	0.2580(3)	2.8(1)
N(6)	−0.2404(7)	0.4614(3)	0.3765(3)	3.6(2)
N(7)	0.3827(9)	0.3076(5)	0.2501(4)	5.0(2)
N(8)	0.547(1)	0.0956(4)	0.0612(5)	4.9(2)
C(1)	0.3074(9)	0.6677(4)	0.0619(4)	3.9(2)
C(2)	0.377(1)	0.7139(4)	0.0163(4)	4.1(2)
C(3)	0.414(1)	0.6840(4)	−0.0474(4)	4.2(2)
C(4)	0.3835(9)	0.6099(4)	−0.0648(4)	3.4(2)
C(5)	0.3110(8)	0.5665(4)	−0.0176(4)	2.8(2)
C(6)	0.2683(8)	0.4866(4)	−0.0310(4)	2.7(2)
C(7)	0.2971(8)	0.4451(4)	−0.0913(4)	3.1(2)
C(8)	0.2516(9)	0.3702(5)	−0.0963(4)	4.0(2)
C(9)	0.182(1)	0.3393(4)	−0.0419(4)	4.2(2)
C(10)	0.160(1)	0.3838(5)	0.0170(4)	4.0(2)
C(11)	0.0620(8)	0.5691(4)	0.2244(4)	3.0(2)
C(12)	0.0183(7)	0.4874(4)	0.2112(4)	2.6(2)
C(13)	0.067(1)	0.6789(4)	0.2977(4)	4.0(2)
C(14)	−0.014(1)	0.7129(4)	0.3560(5)	5.7(3)
C(15)	−0.010(1)	0.6719(5)	0.4247(5)	6.1(3)
C(16)	−0.0911(8)	0.3777(4)	0.2519(4)	3.4(2)
C(17)	−0.228(1)	0.3574(5)	0.2856(6)	6.8(3)
C(18)	−0.228(1)	0.3791(5)	0.3622(5)	6.2(3)

respectively, comparable to those found in a similar binuclear complex.[7] Bond distances and bond angles of [Cu(oxpn)] moiety are similar to those found in the mononuclear complex.[10] The Cu···Cu distance of 5.21 Å is somewhat smaller than that found in $[Cu_2(Him)_2(\mu\text{-}trans\text{-}oxpn)(NO_3)_2]$ (5.24 Å).[6] The six atoms of the oxamidato moiety, O1, O2, N3, N5, C11 and C12, are planar with a mean deviation of 0.0035 Å. The three atoms around N3 and those around the N5 lie in a plane with the sum of bond angles being 360°. This fact, together with the bond distances involved and the planarity

TABLE III Selected inter-atomic distances (Å) and bond angles (°)

Cu(1)–O(1)	1.947(4)	Cu(2)–N(6)	2.021(6)
Cu(1)–O(2)	1.941(4)	O(1)–C(11)	1.284(7)
Cu(1)–O(3)	2.273(5)	O(2)–C(12)	1.281(7)
Cu(1)–N(1)	1.981(5)	C(11)–C(12)	1.511(9)
Cu(1)–N(2)	1.983(6)	N(3)–C(11)	1.298(8)
Cu(2)–O(12)	2.448(5)	N(3)–C(13)	1.459(9)
Cu(2)–N(3)	1.989(5)	N(5)–N(12)	1.277(7)
Cu(2)–N(4)	2.007(6)	N(5)–C(16)	1.472(8)
Cu(2)–N(5)	1.983(5)		
O(1)–Cu(1)–O(2)	85.8(2)	Cu(1)–O(2)–C(12)	110.8(4)
O(1)–Cu(1)–O(3)	94.9(2)	Cu(1)–N(1)–C(1)	125.4(5)
O(1)–Cu(1)–N(1)	95.5(2)	Cu(1)–N(1)–C(5)	114.4(5)
O(1)–Cu(1)–N(2)	170.7(2)	C(1)–N(1)–C(5)	120.0(6)
O(2)–Cu(1)–O(3)	94.6(2)	Cu(1)–N(2)–C(6)	115.2(5)
O(2)–Cu(1)–N(1)	169.4(2)	Cu(1)–N(2)–C(10)	125.7(5)
O(2)–Cu(1)–N(2)	95.6(2)	Cu(2)–N(3)–C(11)	111.7(5)
O(3)–Cu(1)–N(1)	95.8(2)	Cu(2)–N(3)–C(13)	130.7(4)
O(3)–Cu(1)–N(2)	94.1(2)	C(11)–N(3)–C(13)	117.5(6)
N(1)–Cu(1)–N(2)	81.5(2)	Cu(2)–N(4)–C(15)	117.4(4)
O(12)–Cu(2)–N(3)	101.5(2)	Cu(2)–N(5)–C(12)	113.2(5)
O(12)–Cu(2)–N(4)	86.1(2)	Cu(2)–N(5)–C(16)	128.3(4)
O(12)–Cu(2)–N(5)	94.2(2)	C(12)–N(5)–C(16)	118.1(6)
O(12)–Cu(2)–N(6)	90.9(2)	Cu(2)–N(6)–C(18)	117.0(4)
N(3)–Cu(2)–N(4)	93.4(2)	O(1)–C(11)–N(3)	127.1(6)
N(3)–Cu(2)–N(5)	83.2(2)	O(1)–C(11)–C(12)	116.5(6)
N(3)–Cu(2)–N(6)	167.4(2)	N(3)–C(11)–C(12)	116.4(6)
N(4)–Cu(2)–N(5)	176.7(2)	O(2)–C(12)–N(5)	128.4(6)
N(4)–Cu(2)–N(6)	89.2(2)	O(2)–C(12)–C(11)	116.1(6)
N(5)–Cu(2)–N(6)	94.1(2)	N(5)–C(12)–C(11)	115.5(6)
Cu(1)–O(1)–C(11)	110.3(4)		

of the oxamidato ligand, reveals that N3 and N5 atoms and the π-carbonyl electrons are delocalized to form a conjugated system. The C11–C12 bond distance of 1.511 Å suggests a single bond, very close to those observed in other oxamidato-bridged copper(II) complexes. The distances between O3 and O4, O4 and O11, O5 and O10, O7 and O10 and O11 and O12 of 1.851(8), 2.928(8), 2.868(9), 2.929(1) and 2.748(7) Å, respectively, suggest hydrogen bonding interactions as shown in Figure 1. Hydrogen bonds are also found between O3 and $O10^{i}$ (2.786(8) Å; i, symmetry code: $1-x$, $0.5+y$, $0.5-z$), O7 and $O12^{ii}$ (3.001(8) Å; ii, symmetry code: $1-x$, $-0.5+y$, $0.5-z$), O8 and $O11^{iii}$ (2.868(8) Å; iii, symmetry code: x, $0.5-y$, $-0.5+z$) and O9 and $O12^{iv}$ (3.015(9) Å; iv, symmetry code: $1-x$, $-0.5+y$, $0.5-z$) as shown in Figure 2.

IR Spectra

For the mononuclear complex [Cu(oxpn)], two strong absorption peaks are observed at 3190 and 3125 cm^{-1}, attributed to $\nu(NH_2)$. Six strong

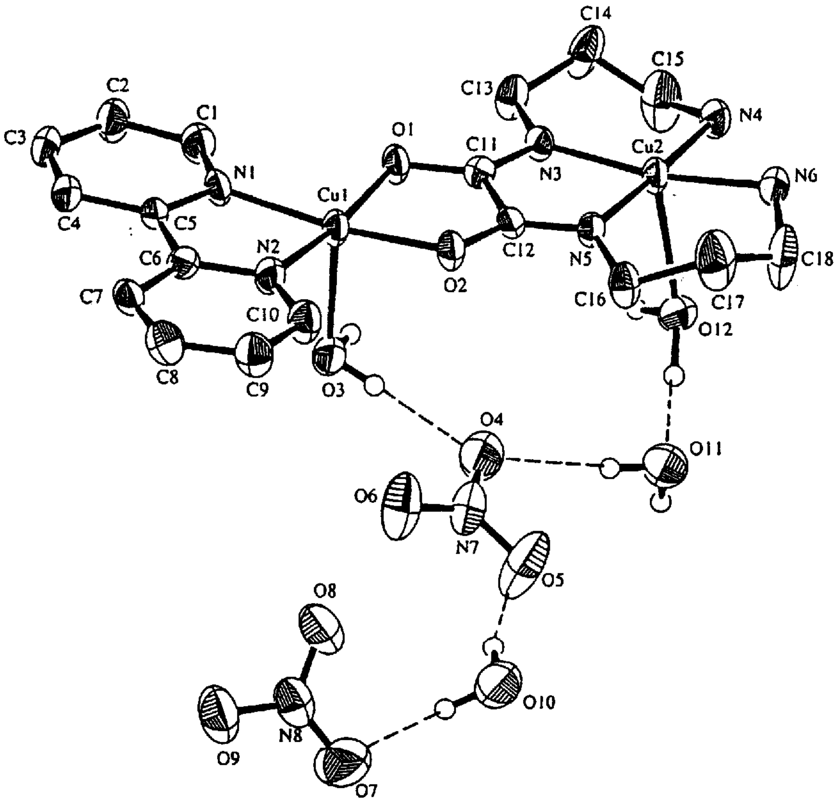

FIGURE 1 Crystal structure of $[(bpy)(H_2O)Cu(\mu\text{-}cis\text{-}oxpn)Cu(H_2O)] \cdot 2NO_3 \cdot 2H_2O$ (thermal ellipsoids at 50% probability level). Hydrogen atoms (excluding those of water molecules) are omitted for clarity.

absorptions in the range $2932\text{–}2842\,cm^{-1}$ are indicative of the CH_2 groups for the complex. A strong and broad peak centred at $1586\,cm^{-1}$ is assigned to ν_{asym} of the amidato moiety (amide I band). Two medium-intensity bands at 1355 and $717\,cm^{-1}$ correspond with ν_{sym}(NCO) and δ(CO) deformation modes, respectively. A large shift of the absorption peak for the amidato moiety toward lower frequencies is observed, compared with the free ligand H_2oxpn ($1640\,cm^{-1}$).[12] This is due to the coordination of the N atom to the central Cu atom which leads to a lower C=O bond order. For complex (2), a broad and strong band centred at $3426\,cm^{-1}$ can be assigned to the OH stretch of the lattice and the coordinated water molecules. A broad band at *ca.* $3240\,cm^{-1}$ is attributed to $\nu(NH_2)$. The ν_{asym}(NCO) (amide I) and ν_{sym}(CO) modes of the oxamidato group at 1627 and $1314\,cm^{-1}$ are

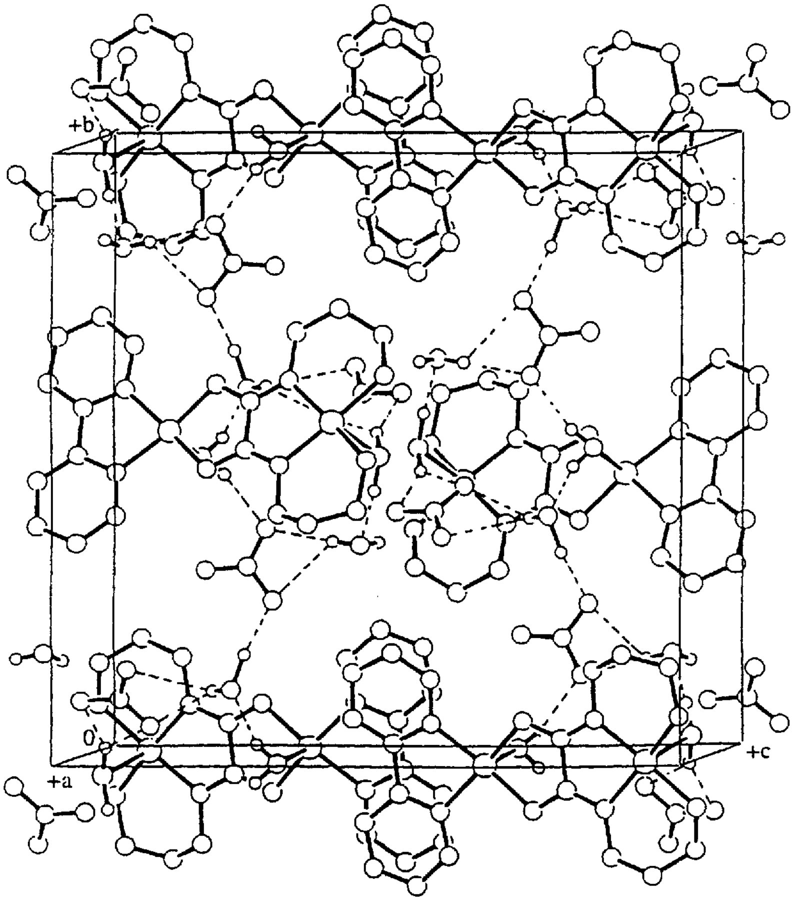

FIGURE 2 A view of the molecular packing of $[(bpy)(H_2O)Cu(\mu\text{-}cis\text{-}oxpn)Cu(H_2O)]\cdot 2NO_3\cdot 2H_2O$.

diagnostic of the bis-bidentate behaviour of the oxamide. Compared with (**1**), the amide I band of (**2**) shifts considerably toward higher frequency ($41\,cm^{-1}$). Bands at 2399 (weak), 1383 (weak) and $827\,cm^{-1}$ are diagnostic of nitrate ions.[13] The IR spectrum of complex (**3**) has a sharp and strong absorption at $1622\,cm^{-1}$ (amide I band) and a medium-intensity peak at $1325\,cm^{-1}$ (ν_{sym}(NCO) stretch) as well as a triplet at 3304, 3225 and $3151\,cm^{-1}$ ($\nu(NH_2)$ stretches). The shift toward higher frequencies of amide I band is consistent with the oxamidato bridge in a *cis* conformation. The position of the amide I band is quite sensitive to the different coordination modes of H_2oxpn in its copper(II) complexes. Since amide I band is due to a composite NCO oxamidato vibration, differences in the bond order of the NCO skeleton would account for the shifting of this band.[14]

Thermogravimetric Study of Complex (2)

Complex (2) loses lattice and coordinated water molecules from about 50°C, ending at about 100°C with a weight loss of 9.5%. The water-free residue is stable in the range 100–290°C. Then organic ligands are lost at 290°C (weight loss 69.5%). At about 300°C, the weight of the black solid residual is in agreement with that required for CuO (21%).

Acknowledgements

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Supplementary Material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-125665.

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