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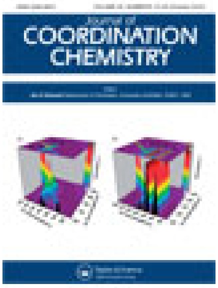

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Syntheses, crystal structures, and spectroscopic properties of copper(II) complexes with 3,14-diethyl-2,6,13,17-tetraazatricyclo(16.4.0.0^{7,12})docosane

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Syntheses, crystal structures, and spectroscopic properties of copper(II) complexes with 3,14-diethyl-2,6,13,17-tetraazatricyclo(16.4.0.0^{7,12})docosane

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$[Cu(L)(NO_3)_2]$ (**1**) and $[Cu(L)(H_2O)_2](SCN)_2$ (**2**) [L = 3,14-diethyl-2,6,13,17-tetraazatricyclo(16.4.0.0^{7,12})docosane] have been prepared and structurally characterized by single-crystal X-ray diffraction at 100 K. For these constrained macrocycle complexes, copper(II) exists in a tetragonally distorted octahedral environment with the four nitrogen atoms of the macrocyclic ligands and two oxygen atoms from either nitrate or water in axial positions. The macrocyclic ligands in both complexes adopt the most stable *trans*-III conformation. The Cu–N distances are 2.021(2)–2.047(2) Å and typical but the axial ligands are weakly coordinating, with Cu–O bond lengths, 2.506(2) Å for **1** and 2.569(2) Å for **2**, due to the pseudo Jahn–Teller effect. The crystals are stabilized by a 3-D network by intra and intermolecular hydrogen bonds that are formed among the secondary nitrogen hydrogen atoms and nitrate in **1**, and intermolecular hydrogen bonds are formed by water and thiocyanates in **2**. The electronic absorption and IR spectral properties are also discussed.

Keywords: Crystal structure; Spectroscopic properties; Copper(II); Macrocyclic ligand; *trans*-III Conformation

1. Introduction

Macrocyclic ligands and their metal complexes have been of interest for enzyme mimics [1, 2], waste-water treatment [3], catalysis [4], and fluorescent sensors [5–7]. Different neutral donors have been incorporated into the macrocyclic ligand backbone [8–10]; 1,4,8,11-tetraazacyclotetradecane (cyclam: AMD1498), xylyl-biscyclam (AMD3100), and their metal complexes have been reported to exhibit anti-HIV effects and to stimulate activity of stem cells from bone marrow [11–13]. The cyclam derivatives inhibit the entry of the virus into white cells by binding to CXCR4, a chemokine receptor in the outer membrane. The strength of binding to the CXCR4 receptor correlates with anti-HIV activity. These 14-membered macrocyclic ligands have a moderately flexible structure and can adopt both planar (*trans*) and folded

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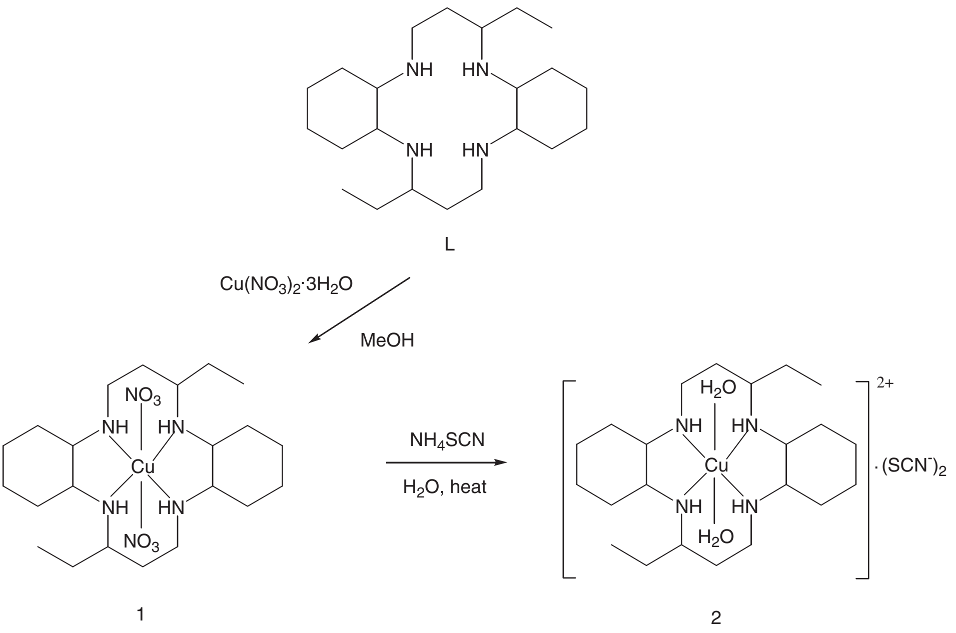
(*cis*) configurations. There are five configurational *trans* isomers for these types of macrocycles, which differ in the chirality of the *sec*-NH centers [14, 15]. The *trans*-I, *trans*-II, and *trans*-V configurations also can fold to form *cis*-I, *cis*-II, and *cis*-V isomers, respectively [16]. The configuration for the macrocyclic ligand and the orientations of the N–H bonds are very important for CXCR4 chemokine receptor recognition [11–13]. Therefore, understanding of coordination behavior and configuration of cyclam derivatives have become important in improved design and development of new highly effective anti-HIV drugs that specifically target alternative events in the HIV replicative cycle. The chemical properties and geometries of copper(II) complexes of macrocyclic ligands are influenced by structural characteristics, such as stereochemistry, chelate ring size, and substituents. To control the electronic properties of the coordinated metal centers modification of the tetraazamacrocyclic ligands is necessary. Constrained ligands containing two cyclohexane rings and methyl or ethyl groups on the carbons have shown different coordination behavior from those of transition metal complexes with the parent cyclam. Previously, we reported the crystal structures of $[Cu(L^1)X_2]$ (L^1 = 3,14-dimethyl-2,6,13,17-tetraazatricyclo(16.4.0.0^{7,12})docosane; X = H_2O, NO_3, ClO_4), in which copper(II) has a tetragonally distorted octahedral environment with the four nitrogen atoms of the macrocyclic ligand in basal positions and two oxygen atoms of either water or counter-anions in apical positions [17–20]. In these three Cu(II) complexes, the macrocyclic ligands adopt their most stable *trans*-III configuration. However, crystallographic analysis of $[Cu(L^2)](ClO_4)_2$ [L^2 = 2,13-dibenzyl-5,16-dimethyl-2,6,13,17-tetraazatricyclo(16.4.0.0^{7,12})docosane] showed that copper(II) is four-coordinate in a square plane distorted toward tetrahedral [21]. The macrocyclic backbone in this copper(II) complex adopts the less stable *trans*-I (RSRS) configuration in which the two benzyl substituents lie on the same side of the square plane of the macrocycle. The perchlorates are not bonded to copper(II). For $[Cu(L^3)](ClO_4)_2 \cdot 2CH_3CN$ [L^3 = 2,13-bis(1-naphthylmethyl)-5,16-dimethyl-2,6,13,17-tetraazatricyclo(16.4.0.0^{7,12})docosane], the two pendant naphthylmethyl groups are *trans* to each other and the macrocycle skeleton adopts the most stable *trans*-III configuration [22]. Two perchlorates are each linked to the cation *via* hydrogen bonds instead of coordination. Investigations of various constrained cyclam ligands containing 1,2-diaminocyclohexanediamine subunit have proved instructive, allowing correlation of the modifications of the ligand and coordination geometries [17–22]. More recently, we found that L^1 and $[Zn(L^1)(OAc)_2] \cdot 0.5H_2O$ were active toward viral strains HIV-1 (IIIB) and HIV-2 (ROD). With cytotoxic concentrations of $> 100\,\mu mol\,L^{-1}$, they showed high activity and low levels of toxicity to cells [23]. In our study, we introduced two methyl or ethyl substitutions on the macrocycle for steric hindrance, which may provide interesting electronic effect as well as applications in medicine [17–24]. The anionic species also play important roles in chemistry, medicine, catalysis, molecular assembly, and in biology, yet their binding characteristics have not received much recognition [25, 26].

As part of our ongoing investigation, herein we describe syntheses of $[Cu(L)(NO_3)_2]$ (**1**) and $[Cu(L)(H_2O)_2](SCN)_2$ (**2**) [L = 3,14-diethyl-2,6,13,17-tetraazatricyclo (16.4.0.0^{7,12})docosane] and report the crystal structures and spectroscopic properties of the complexes to elucidate the conformation of macrocyclic ligand L, coordination behavior, and packing force of water, thiocyanate, and nitrate. L contains cyclam in the diethyl substituted backbone with two 1,2-diaminocyclohexanediamine subunits (scheme 1).



Scheme 1. Chemical structure of macrocycle L and syntheses of **1** and **2**.

2. Experimental

All chemicals were purchased from commercial sources and used without purification. The solvents were of reagent grade and purified by the usual methods. L was prepared according to a published procedure [27]. Anal. Calcd for $C_{22}H_{44}N_4$ (%): C, 72.47; H, 12.16; N, 15.37. Found (%): C, 72.58; H, 12.05; N, 15.60. IR spectrum (KBr, cm^{-1}): 3288 vs, 3272 vs and 3250 m (ν NH), 2930 vs and 2853m (ν CH), 1591 m, 1456 s and 1173 m (δ CH_2), 1363 s, 1266 m, 1215 w, 1124 vs, 1092 s, 926 w (ρ CH_3), 910 m, 866 m and 856 w (γ NH), 820 m and 800 m (ρ CH_2), 771 s, 746 m, 569 w, 545 w, 523 w, 463 w, 446 w.

2.1. *Preparation of [Cu(L)(NO$_3$)$_2$] (1)*

Complex **1** was synthesized according to the method shown in scheme 1. $Cu(NO_3)_2{\cdot}3H_2O$ (0.242 g, 1.0 mmol) and 0.073 g (0.2 mmol) of L were dissolved in 10 mL of MeOH. The mixture was refluxed for 30 min giving violet complex. The product was filtered off and air dried. Recrystallization of the product from hot acetonitrile and water (1 : 1) gave violet single crystals suitable for X-ray analysis. Yield: ~60%. Anal. Calcd for $C_{22}H_{44}N_6O_6Cu$ (%): C, 47.86; H, 8.03; N, 15.22. Found (%): C, 47.58; H, 8.04; N, 15.31. UV-Vis data λ_{max} (H_2O): 510 nm (111 ε in $(mol\,L^{-1})^{-1}\,cm^{-1}$); IR spectrum (KBr, cm^{-1}): 3197 vs and 3136 s (ν NH), 2940 vs and 2860 m (ν CH), 1767 w, 1456 s, and 1166 m (δ CH_2), 1385 vs (ν_{as} NO_2), 1333 s (ν_s NO_2), 1276 m, 1097 s, 1025 m (ν NO), 970 m, 917 w (ρ CH_3), 900 m, 880 m and 838 w (γ NH), 823 m and 797 m (ρ CH_2), 637 w, 599 w, 548 w, 517 w, 434 w.

2.2. *Preparation of [Cu(L)(H$_2$O)$_2$](SCN)$_2$ (2)*

Cu(L)(NO$_3$)$_2$ (0.067 g, 0.12 mmol) and 0.02 g (0.0.26 mmol) of NH$_4$SCN were dissolved in 10 mL of water and acetonitrile (1 : 1). The mixture was heated at 100°C for 30 min. The resulting pink solution was filtered and cooled to room temperature. The solution was kept in an open beaker for crystallization. After one day violet crystals suitable for X-ray analysis were obtained. Yield: ~70%. Anal. Calcd for $C_{26}H_{48}N_6S_2O_2Cu$ (%): C, 49.66; H, 8.34; N, 14.48; S, 11.05. Found (%): C, 49.57; H, 8.32; N, 14.66; S, 11.01. UV-Vis data λ_{max} (H$_2$O): 509 nm (87 € in (mol L^{-1})$^{-1}$ cm^{-1}); IR spectrum (KBr, cm^{-1}): 3466 w and 3421 (ν OH), 3172 s and 3125 w (ν NH), 2940 vs and 2860 m (ν CH), 2360 w, 2051 vs (ν_{as} CN), 1716 s, 1636 w (δ H$_2$O), 1446 s and 1156 w (δ CH$_2$), 1384s, 1219 m, 1092 m, 965 s, 914 w (ρ CH$_3$), 900 m, 879 m and 847 w (γ NH), 823 w and 797 m (ρ CH$_2$), 751 m (ν CS), 637 w, 529 w, 480 w and 467 m (δ SCN).

2.3. *Physical measurements*

UV-Vis absorption spectra were recorded with a Cary 5000 UV-Vis-NIR Spectrophotometer. The mid-IR spectra were obtained from a KBr pellet with a JASCO 460 plus series FT-IR spectrometer. Analyses for C, H, N, and S were performed on a Carlo Erba 1108 Elemental Vario EL analyzer.

2.4. *X-ray structure determination*

X-ray diffraction data on crystals of **1** (0.30 × 0.3 × 0.10 mm) and **2** (0.30 × 0.10 × 0.05 mm) were collected at 100(2) K on an Agilent Technologies SuperNova Dual diffractometer with an Atlas detector using Mo-Kα radiation so that $\theta_{max} = 27.5°$. The data set was reduced and corrected for absorption effects using CrysAlis PRO [28]. The structures of **1** and **2** were solved by direct-methods with SHELXS-97 [29] and refinement (anisotropic displacement parameters, hydrogen atoms in the riding model approximation and a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (0.030P)^2 + 0.841P]$ for $P = (F_o^2 + 2F_o^2)/3$) was on F^2 by means of SHELXL-97 [29]. The amino and water hydrogen atoms were located in a difference Fourier map and refined with distance restraints of N–H 0.88 ± 0.01 and O–H 0.84 ± 0.01 Å; their temperature factors were refined. The crystallographic data and the final refinement details are given in table 1. Molecular graphics were produced using DIAMOND-3 [30].

3. Results and discussion

3.1. *X-ray crystallography*

Complexes **1** and **2** crystallize in the triclinic space group $P\bar{1}$ and monoclinic space group $P2_1/c$, respectively. The structure of **1** comprises one [Cu(L)(NO$_3$)$_2$] and **2** comprises [Cu(L)(H$_2$O)$_2$]$^{2+}$ and two SCN$^-$ anions, in agreement with the chemical formula derived from microanalyses. Selected bond lengths and angles are listed in table 2.

Table 1. Crystallographic data and structure refinement for **1** and **2**.

	1	**2**
Molecular formula	$C_{22}H_{42}CuN_6O_6$	$C_{26}H_{48}CuN_6O_2S_2$
Formula weight	552.17	580.34
Temperature (K)	100(2)	100(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	7.9468(4)	10.8375(4)
b	9.1175(4)	8.8860(3)
c	9.8268(5)	15.6435(6)
α	72.826(4)	90
β	71.768(4)	109.327(4)
γ	69.839(4)	90
Volume (Å^3), Z	620.63(5), 1	1421.60(9), 2
Calculated density (Mg m^{-3})	1.477	1.356
Absorption coefficient (mm^{-1})	0.93	0.95
Crystal size (mm^3)	0.30 × 0.30 × 0.10	0.3 × 0.10 × 0.05
Reflections collected	5400	7060
Independent reflection	2766 [R(int) = 0.057]	3172 [R(int) = 0.037]
Min. and max. transmission	0.768 and 0.913	0.764 and 0.954
Goodness-of-fit on F^2	1.04	1.07
Final R indices [$F^2 > 2\sigma$] R_1, wR_2	0.042, 0.117	0.043, 0.100
Largest difference map peak and hole (e Å^{-3})	1.01 and −0.82	0.39 and −0.45

Ellipsoid plots of the complexes with atom labeling is illustrated in figures 1 and 2, respectively.

The macrocyclic skeletons in both complexes adopt the most stable *trans*-III conformation, quite different from the configuration of [Cu(L^2)](ClO_4)$_2$. The geometry of copper(II) in [Cu(L^2)](ClO_4)$_2$ is approximately square planar but somewhat distorted toward tetrahedral. The macrocyclic backbone in this copper complex adopts the slightly less stable *trans*-I conformation where the two benzyls lie on the same side of the square plane of the macrocycle [21].

Cu–N distances [2.014(2)–2.047(2) Å] for **1** and [2.021(2)–2.046(2) Å] for **2** are within the expected range and comparable to those observed in related complexes, e.g., for [Cu(L^1)(NO_3)$_2$] · 3H_2O [2.021(2)–2.029(2) Å] [17], [Cu(L^1)(NO_3)$_2$] [2.007(2)–2.044(2) Å] [18], [Cu(L^1)(ClO_4)$_2$] [2.005(2)–2.048(2) Å] [15], [Cu(L)(ClO_4)$_2$] [2.016(2)–2.040(2) Å] [27], and [Cu(L^1)(bip)$_2$] [2.015(2)–2.037(2) Å] [31].

The stereochemistry of copper(II) may be considered as square planar or tetragonally octahedral, depending upon whether or not the out of plane oxygen atoms of water are bonded to copper [32, 33]. The concept of semi-coordinated bond was introduced to describe a situation where the polyatomic anion or ligand occupy the long tetragonal position in an otherwise square planar copper(II) complex with an atom in the range of 2.5–3.0 Å [8–10, 33]. The apical Cu–O bonds, 2.506(2) Å for **1** and 2.569(2) Å for **2**, are longer than the corresponding bond lengths in [Cu(L^1)(NO_3)$_2$] [2.463(2) Å], [Cu(cyclam)(H_2O)$_2$]F_2 · 4H_2O [2.484(6) Å], [Cu(cyclam)(DMF)$_2$](PF_6)$_2$ [2.399(2) Å], [Zn(L^1)(H_2O)$_2$]Cl_2 [2.388(3) Å], [Zn(L^1)(NO_3)$_2$] [2.3123(12) Å], and [Zn(L^1)(OAc)$_2$] · 1/2H_2O [2.294(1) Å] but are shorter than those of [Cu(L^1)(NO_3)$_2$] · 3H_2O [2.746(2) Å], [Cu(L^1)(H_2O)$_2$](BF_4)$_2$ · 2H_2O [2.693(3) Å], and [Cu(L^1)(H_2O)$_2$]Cl_2 [2.649(2) Å] (table 3) [17–23, 34–38]. The copper(II) geometries in **1** and **2** are described

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

1			
Cu1–N1	2.014(2)	Cu1–N2	2.047(2)
Cu1–O1	2.506(2)	O1–N3	1.260(2)
O2–N3	1.254(2)	O3–N3	1.244(2)
N1–Cu1–N2	84.65(6)	N1–Cu1–N2$^{\mathrm{i}}$	95.35(6)
N1–Cu1–O1	91.38(6)	N2–Cu1–O1	100.16(5)
N1–Cu1–O1$^{\mathrm{i}}$	88.62(6)	N3–O1–Cu1	128.69(12)
C1–N1–Cu1	107.96(11)	N2–Cu1–O1$^{\mathrm{i}}$	79.84(5)
C6–N2–Cu1	107.88(11)	C9$^{\mathrm{i}}$–N1–Cu1	115.94(12)
O2–N3–O1	119.65(15)	C7–N2–Cu1	121.06(12)
O3–N3–O2	120.58(17)	O3–N3–O1	119.77(17)
2			
Cu1–N1	2.046(2)	Cu1–N2	2.021(2)
Cu1–O1W	2.569(2)	S1–C12	1.644(3)
N2–Cu1–N1	84.47(8)	N2–Cu1–N1$^{\mathrm{i}}$	95.53(8)
N2–Cu1–O1W	86.88(7)	N2$^{\mathrm{i}}$–Cu1–O1W	93.12(7)
N1$^{\mathrm{i}}$–Cu1–O1W	81.06(7)	N1–Cu1–O1W	98.94(7)
C7–N2–Cu1	117.89(14)	C1–N1–Cu1	107.57(13)
C6–N2–Cu1	107.61(13)	C9$^{\mathrm{i}}$–N1–Cu1	120.04(15)

[a]Symmetry codes $^{\mathrm{i}}$ $-x+1, -y+1, -z+1$ for **1**; $^{\mathrm{i}}$ $-x+1, -y+1, -z+1$ for **2**.

Figure 1. A perspective view (50% probability level) of [Cu(L)$(NO_3)_2$] (**1**) with the atom-numbering scheme.

as tetragonally distorted with four nitrogen atoms from the macrocycle and two oxygen atoms of nitrate or water. The tetragonally elongated geometry is common to six-coordinate Cu(II) complexes involving non-equivalent ligands, and the distortion arises from the pseudo Jahn–Teller effect operative on the d^9 metal center [39, 40].

The nitrates in **1** have slightly distorted trigonal planar geometry due to hydrogen-bonding interactions and interaction with copper(II). The longer O1–N3 bond reflects coordination to copper. The two ethyl groups on the six-membered chelate rings and the two $-(CH_2)_4-$ parts of the cyclohexane backbones are *anti* with respect to the macrocyclic plane. As usually observed, the five-membered chelate rings adopt a *gauche* conformation whereas the six-membered rings are in chair conformations. Ethyl groups are attached axially as substituents to the chair six-membered rings, while substitution

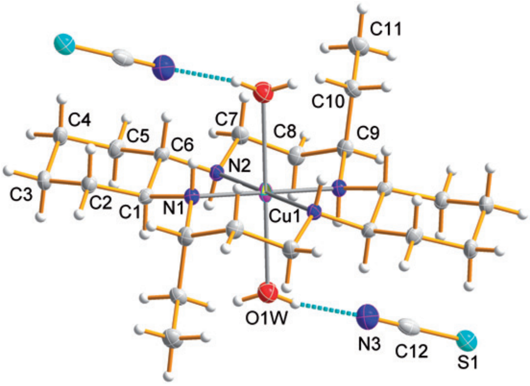


Figure 2. A perspective view (50% probability level) of $[Cu(L)(H_2O)_2](SCN)_2$ (**2**) with the atom-numbering scheme.

Table 3. Selected bond distances (Å) and configurations of some copper(II) complexes with constrained macrocyclic ligands.

Compound	Cu–N	Cu–O	Configuration	Reference
$[Cu(L^1)(NO_3)_2]\cdot 3H_2O$	2.021(2)–2.029(2)	2.746(2)	*trans*-III	[17]
$[Cu(L^1)(NO_3)_2]$	2.007(2)–2.044(2)	2.463(2)	*trans*-III	[18]
$[Cu(L^1)(ClO_4)_2]$	2.005(2)–2.048(2)	2.623(2)	*trans*-III	[19]
$[Cu(L^1)(bip)_2]$	2.015(2)–2.037(2)	2.534(2)	*trans*-III	[31]
$[Cu(L^1)(H_2O)_2]Cl_2$	2.017(2)–2.038(2)	2.649(2)	*trans*-III	[36]
$[Cu(L^1)(H_2O)_2](BF_4)_2\cdot 2H_2O$	2.028(2)–2.028(2)	2.693(3)	*trans*-III	[20]
$[Cu(L^2)(NO_3)_2]$	2.018(7)–2.085(7)	2.873(7)	*trans*-III	[20]
$[Cu(L^2)](NO_3)_2$	1.999(7)–2.095(7)	2.964(7)	*trans*-III	[20]
$[Cu(L^2)](ClO_4)_2$	1.990(4)–2.050(4)	3.496(3)	*trans*-I	[21]
$[Cu(L^3)](ClO_4)_2\cdot 2CH_3CN$	2.030(3)–2.081(2)	3.264(3)	*trans*-III	[22]
$[Cu(L)(ClO_4)_2]$	2.016(2)–2.047(2)	2.762(2)	*trans*-III	[27]
$[Cu(L)(NO_3)_2]$ (**1**)	2.014(2)–2.047(2)	2.506(2)	*trans*-III	This work
$[Cu(L)(H_2O)_2](SCN)_2$ (**2**)	2.021(2)–2.046(2)	2.569(2)	*trans*-III	This work

of the five-membered rings by methylene carbons of the fused cyclohexane rings is equatorial; the cyclohexane rings are also in a chair conformation, with nitrogen atoms in equatorial positions. The mean C–N and C–C distances, and C–N–C and C–C–N angles in the macrocyclic ligand are typical for macrocyclic tetramine complexes [17–22].

In **1**, both hydrogen atoms on N1 and N2 of the macrocycle are involved in N–H···O interactions with NO_3^-. One oxygen atom of NO_3^- is semi-coordinated to Cu(II) and the other two are involved in hydrogen-bonding through inter and intramolecular hydrogen-bonding networks. In **2**, the S1–C12 and N3–C12 bond lengths, and the S1–C12–N3 bond angles are normal for thiocyanate [41]. The uncoordinated SCN^- anions remain outside the coordination sphere [Cu1–N3 (2.484 Å) and Cu1–S1 (4.812 Å)] and are linked to coordinated water only through hydrogen bonds. Further distances and symmetry codes are given in table 4. The crystal structures of **1** and **2** are stabilized by these various hydrogen bonds.

Table 4. Hydrogen-bonding geometry (Å, °) for **1** and **2**.

D–H···A	D–H	H···A	D···A	D–H···A
1				
N1–H1···O2	0.87(1)	2.14(1)	2.993(2)	165(2)
N2–H2···O1^{i}	0.87(1)	2.40(2)	2.943(2)	121(2)
2				
O1*W*–H11···N3	0.84(1)	1.99(1)	2.810(3)	166(3)
O1*W*–H12···S1^{i}	0.83(1)	2.45(1)	3.277(2)	174(3)

Symmetry codes: ^{i} $-x+1$, $-y+1$, $-z+1$ for **1**; ^{i} $-x+1$, $y-1/2$,$-z+3/2$ for **2**.

The Cu1–O1 and Cu1–O1W bonds are not perpendicular to the CuN_4 plane with the N1–Cu1–O1 and N2–Cu1–O1 angles being 91.38(6) and 100.16(5)° in **1** and N1–Cu1–O1W and N2–Cu1–O1W angles in **2** are 98.94(7) and 86.88(7)°, respectively. The tetragonality ratio, $T = R_{eq}/R_{ax}$, where R_{eq} and R_{ax} are the average equatorial Cu–N and axial Cu–O bond distances, is used as a measure of tetragonal distortion. The calculated values of the tetragonality factors, T are 0.810 and 0.792 in **1** and **2**, respectively, close to calculated mean *ca* 0.8 for a number of such copper(II) complexes [42].

3.2. *IR spectroscopy*

FT-IR spectra of **1** and **2** exhibit bands at 3470–3420 cm^{-1} and near 1630 cm^{-1} due to ν(O–H) and δ(H–O–H) modes of KBr disc surface moisture and coordinated water. The absorptions at 3220–3120 cm^{-1} and 3000–2850 cm^{-1} are assigned to N–H and C–H stretches, respectively [8–10]. The lowering of ν(N–H) compared to those (3288, 3272 and 3250 cm^{-1}) of free ligand can be explained by coordination and hydrogen-bonding of the secondary amine. Nitrate can coordinate to a metal as monodentate, chelating bidentate, and bridging [43]. In **1**, absorptions at 1384, 1333, and 1025 cm^{-1} correspond to ν(NO) of nitrate. By applying Lever's separation method [44], the splitting of 21 cm^{-1} in the combination bands ($\nu_1 + \nu_4$) at 1767 and 1746 cm^{-1} supported monodentate nitrate. Complex **2** has a single ν(CN) at 2051 cm^{-1} and a weak ν(CS) in its IR spectrum, characteristic of ionic isothiocyanate [41].

IR spectroscopy is often useful in assigning *cis* and *trans* isomers of transition metal complexes with cyclam derivatives [15, 16, 45]. The *trans* isomer shows two groups of bands, overlapping peaks near 890 cm^{-1} arising from the secondary amine vibration and only one band near 800 cm^{-1} due to the methylene vibration. However, the *cis* isomer exhibits at least three bands at 890–830 cm^{-1} due to N–H vibrations, while the methylene vibration splits into two peaks at 830–790 cm^{-1} [46–49]. The two bands at 880–840 cm^{-1} are assigned to NH vibration but the IR spectra also exhibit two bands at 823 and 791 cm^{-1} in the CH_2 rocking frequency region. These N–H vibration and CH_2 rocking bands are not significantly affected by the different counter-anions and central metal [15, 16]. However, the rule must be applied with caution because these vibrations can be affected by crystal packing or other absorptions of anions if we do not have exact information on the crystal structure and geometry of the complex.

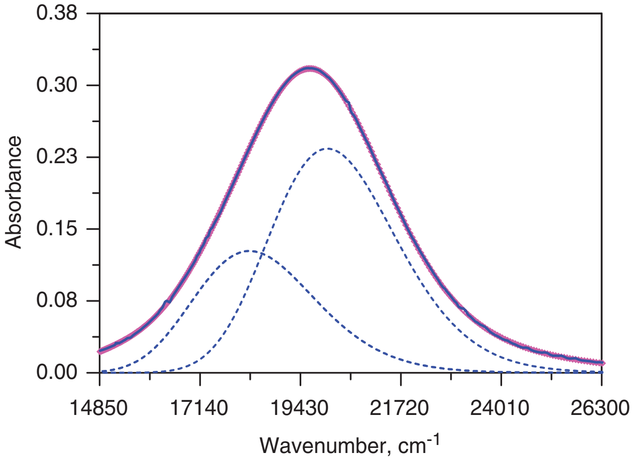


Figure 3. The visible spectrum of **1** in aqueous solution and the resolved overlapping peaks (dotted curves).

3.3. *Electronic absorption spectroscopy*

The visible spectra of **1** and **2** in aqueous media reveal a single broad absorption with maxima at 19,605 and 19,635 $\mathrm{cm^{-1}}$, respectively. The absorption maxima $\nu_{\max}$ of these two complexes in solution are similar to those of $[\mathrm{Cu(cyclam)(NO_3)_2}]$, $[\mathrm{Cu(L^1)(NO_3)_2}]\cdot 3\mathrm{H_2O}$, $[\mathrm{Cu(L^1)(ClO_4)_2}]$, $[\mathrm{Cu(cyclam)(H_2O)_2}]\mathrm{F_2}\cdot 4\mathrm{H_2O}$, and $[\mathrm{Cu(L^1)(H_2O)_2}](\mathrm{BF_4})_2\cdot 2\mathrm{H_2O}$ with maxima at 19,570, 19,570, 19,530, 19,605, and 19,530 $\mathrm{cm^{-1}}$, respectively [17, 35, 50]. The similar position and shape of the absorption bands suggest a similar *trans*-$\mathrm{Cu^{II}N_4O_2}$ chromophore in a tetragonally elongated octahedral geometry. In **1** and **2**, two nitrato groups and water molecules bind weakly to the copper(II) ion in apical positions. For tetragonal octahedral geometry, the order of one-electron energy levels is e_{g} $(xz, yz) < b_{2\mathrm{g}}$ $(xy) < a_{1\mathrm{g}}$ $(z^2) < b_{1\mathrm{g}}$ $(x^2\text{–}y^2)$. The ^2D term of the free copper(II) ion ($3\mathrm{d}^9$) in an octahedral field splits into an upper $^2T_{2\mathrm{g}}$ level and a lower $^2E_{\mathrm{g}}$ level. The $^2E_{\mathrm{g}}$ and $^2T_{2\mathrm{g}}$ levels for a tetragonally distorted copper(II) complex split into $^2B_{1\mathrm{g}}$, $^2A_{1\mathrm{g}}$, $^2B_{2\mathrm{g}}$, and $^2E_{\mathrm{g}}$ states [10, 51]. The observed band has a slightly asymmetric profile. To obtain some points of reference for the splitting of the band, the absorption was deconvoluted into two components by using Gaussian curves (dotted line), as shown in figures 3 and 4. Deconvolution of the experimental band pattern yielded maxima at 18,215 and 20,400 $\mathrm{cm^{-1}}$ for **1**, whereas maxima are found at 18,320 and 20,015 $\mathrm{cm^{-1}}$ for **2**. The two d–d transition components are tentatively assigned to $^2B_{1\mathrm{g}}\rightarrow{}^2B_{2\mathrm{g}}$ and $^2B_{1\mathrm{g}}\rightarrow{}^2E_{\mathrm{g}}$ [51, 52]. Much weaker, lower energy absorptions at 10,355 and 10,890 $\mathrm{cm^{-1}}$ for **1** and **2** may be due to the $^2B_{1\mathrm{g}}\rightarrow{}^2A_{1\mathrm{g}}$ transition. The energy level sequence depends on the degree of tetragonal distortion arising due to the ligand-field effect. The energy of transitions originating from the *xz*, *yz*, and *xy* orbitals for amine donors with only σ-interactions is independent of the axial ligands. The electronic spectroscopic properties are in agreement with the crystal structures, which show elongated axial Cu$\cdots$O distances compared to relatively short equatorial Cu–N bonds.

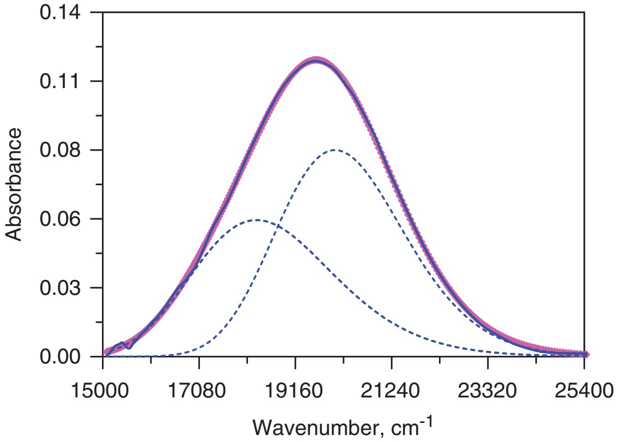


Figure 4. The visible absorption spectrum of **2** in aqueous solution and the resolved overlapping peaks (dotted curves).

4. Conclusion

Elemental analyses, UV-Vis and IR spectroscopic properties of **1** and **2** are in agreement with the results obtained from X-ray crystallography, which show that the two complexes adopt an elongated tetragonal octahedral geometry with a square planar CuN_4 (in which the macrocycle adopts the stable *trans*-III configuration) and two nitrates or water molecules occupying sites above and below the square plane. The Cu–N and Cu–ONO_2 bond lengths are 2.014(2)–2.047(2) Å and 2.506(2) Å in **1** while the Cu–N and Cu–OH_2 bond distances are 2.021(2)–2.046(2) Å and 2.569(2) Å in **2**. The crystals of the complexes are stabilized by hydrogen bonds between secondary NH, NO_3^-, H_2O, and SCN^-. Understanding of crystal packing force, coordination mode, and geometry between copper(II)-constrained cyclam complexes and other molecules may be useful to develop new effective anti-HIV drugs and stem cell mobilizers.

Supplementary material

Crystallographic data, tables of atomic coordinates and displacement parameters, and full lists of bond lengths and angles have been deposited in CIF format with the Cambridge Crystallographic Data Centre, CCDC 793593 and 793990 for structures of **1** and **2**, respectively. Copies of this information may 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 or www: http://www.ccdc.cam.ac.uk).

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