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CRYSTAL STRUCTURE AND SPECTROSCOPIC PROPERTIES OF ISOTHIOCYANATO[(3,14-DIMETHYL-2,6,13,17-TETRAAZATRICYCLO(16.4.0.0^{7,12})DOCOSANE)]COPPER(II) THIOCYANATE

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A new complex $[Cu(L^1)(NCS)]SCN$, where $L^1 = $ 3,14-dimethyl-2,6,13,17-tetraazatricyclo(16.4.0.0^{7,12})docosane is prepared and characterized by single crystal X-ray crystallographic analysis. The complex crystallizes in the triclinic space group $P\bar{1}$ with two mononuclear formula units in a cell of dimensions $a = 7.9681(2)$, $b = 8.8644(2)$, $c = 18.8165(5)$ Å, $\alpha = 76.758(70)$, $\beta = 78.490(2)$ and $\gamma = 77.679(2)°$. The Cu(II) ion is five-coordinate in an axially elongated square pyramidal environment, with the four amine N atoms at the equatorial positions and the N atom of one thiocyanate at an apical site. The macrocyclic cyclam moiety adopts a stable *trans*-III configuration. The Cu—N basal plane bond length has a mean value of 2.037(2) Å. The coordinated Cu—NCS bond length is 2.322(3) Å. The N atom of the thiocyanate anion is connected to the macrocyclic ligand of the cation via an NH…N(CS) hydrogen bond. The UV-visible absorption and IR spectral properties are also discussed.

INTRODUCTION

Macrocyclic compounds are very significant for their excellent applications in both biological science and materials science and technology. Macrocycles with either C-alkyl or N-alkyl groups on the polyaza macrocyclic ring and their transition metal complexes have attracted considerable attention because of their structural and chemical properties, which are quite different from those of the corresponding unalkylated macrocycic system [1—4]. It has been reported that 1,4,8,11-tetraaza-cyclotetradecane (cyclam: AMD1498), xylyl-biscyclam (AMD3100) and their complexes exhibit anti-HIV activity and mobilize the activity of stem cells from the bone marrow [5—7]. The cyclam derivatives and their complexes inhibit the entry of the virus into white blood cells by binding to the chemokine receptor CXCR4 in the outer membrane. The anti-HIV activity is correlated to the binding strength of the cyclam derivatives to the CXCR4 receptor. The 14-membered tetraaza macrocyclic ligand has a fairly flexible structure, and it can adopt both planar (*trans*) and folded (*cis*) configurations. There are five configurational *trans* isomers for the macrocycle, which differ in the chirality of the *sec*-NH centers. The *trans*-I, *trans*-II and *trans*-V configurations can fold to form *cis*-I, *cis*-II and *cis*-V isomers, respectively [8, 9]. The configuration of the macrocyclic ligand and the orientations of

the N—H bonds are very important factors influencing co-receptor recognition. As a result, understanding the coordination behavior and the configuration of the cyclam derivative has become important for the improved design and advancement of new highly effective anti-HIV compounds that particularly target alternative events in the HIV replicative cycle. Thus, modification of the tetraazamacrocyclic ligands is necessary in order to control the electronic and geometrical properties of the coordinated metal centers. Various constrained cyclam ligands containing two 1,2-diaminocyclohexanediamine subunits and two methyl or ethyl groups at the carbon atoms are illustrated in Scheme 1.

L^1:R_1 = Me, R_2 = H
L^2:R_1 = Me, R_2 = Benzyl
L^3:R_1 = Me, R_2 = 1-Naphthylmethyl
L^a:R_1 = Et, R_2 = H
L^b:R_1 = Et, R_2 = Benzyl
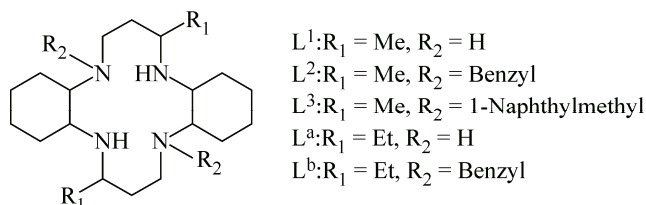
Scheme 1. Structures of various macrocyclic ligands

The chemical properties and geometries of copper(II) complexes with macrocyclic ligands are influenced by structural characteristics such as stereochemistry, chelate ring size, and substituent type. In previous papers, we reported the preparation and X-ray 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^- = NO_3^-, ClO_4^-), in which the copper(II) ions have a tetragonally distorted octahedral geometrical environment with four N atoms of the macrocyclic ligand in equatorial positions and O atoms of two counter-anions in axial positions [10, 11]. The macrocyclic ligands adopted their most stable *trans*-III configuration. The constrained ligand, containing two cyclohexane rings and methyl groups at the carbon atoms, often shows different coordination behaviors from those of the transition metal complexes of the parent cyclam ligand. The copper(II) ion may be tetracoordinated in a roughly square planar coordination somewhat distorted toward a tetrahedral geometry [1]. The macrocyclic backbone in the copper(II) complex can adopt a less stable *trans*-I (RSRS) configuration. However, in most cases the marcrocyclic skeleton adopts the most stable *trans*-III configuration [2, 3].

Anionic species play very important roles in chemistry, medicine, catalysis, molecular assembly, and biology, yet their binding characteristics have not received much recognition [13]. Cu(II) is especially prone to the formation of five-coordinate complexes with the thiocyanate group, in a somewhat distorted trigonal bipyramidal or square pyramidal geometry environment [12—14].

As part of our ongoing research, we describe herein the preparation, structural and spectroscopic properties of $[Cu(L^1)(NCS)]SCN$ (Scheme 2), with the purpose of elucidating the effect of a counter anion on the coordination environment around the Cu^{2+} ion.
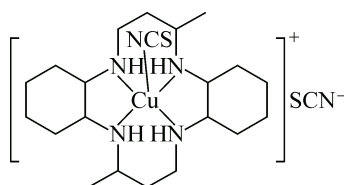

Scheme 2. Chemical structure of $[Cu(L^1)(NCS)]SCN$

EXPERIMENTAL

Materials and synthesis. The macrocycle cocrystal, 3,14-dimethyl-2,6,13,17-tetraazatricyclo(16.4.0.0^{7,12})docosane(1-napthalenyl)methanol, and $[Cu(L^1)(NO_3)_2]$ were prepared according to published procedures [10, 15]. All other chemicals were purchased from commercial sources and used without further purification. The solvents were of reagent grade, and were purified by the usual methods.

Preparation of [Cu(L^1)(NCS)]SCN. [Cu(L^1)(NO$_3$)$_2$] (0.068 g, 0.13 mmol) was dissolved in 10 ml of MeOH and H$_2$O (1:1 v/v). Ammonium thiocyanate (0.02 g, 0.26 mmol) was added to the solution. The mixture was heated to reflux for 30 min at 65 °C (Scheme 3). The resulting pink colored solution was filtered and kept stand at room temperature for several days to allow the formation of pink crystals suitable for X-ray structural analysis Yield: ca. 65 %. C$_{22}$H$_{40}$CuN$_6$S$_2$: calcd. C 51.18, H 7.81, N 16.28, S 12.42 %; found: C 51.29, H 7.86, N 16.22 %. UV/Vis: λ$_{max}$ (CH$_3$CN:H$_2$O, 1:1 v/v): 512 nm (155 M$^{-1}\cdot$cm^{-1}). IR (KBr): $\overline{ν}$ = 3132 s ($ν$ NH), 2938 vs and 2868 s ($ν$ CH), 2049 vs ($ν_{as}$ CN), 1464 m and 1453 s (δ CH$_2$), 1388 s, 1308 m, 1273 m, 1221 w, 1174 m, 1095 vs, 1067 s, 1012 s, 966 m, 905 m (ρ CH$_3$), 890 vw and 846 w (γ NH), 800 m (ρ CH$_2$), 733 m ($ν$ CS), 667 w, 598 w, 552 w, 427 w cm^{-1}.
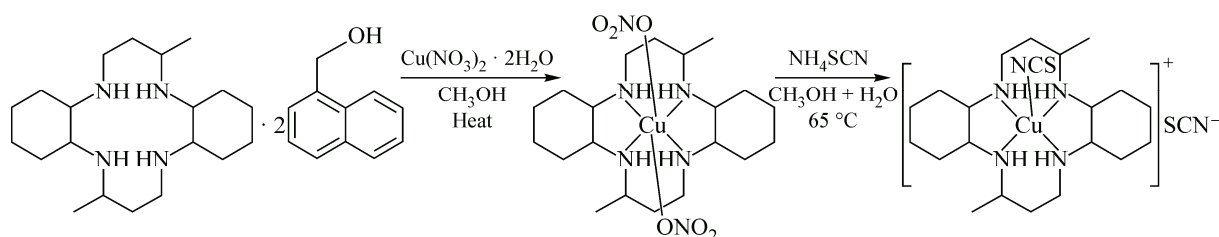
Scheme 3. Synthesis of [Cu(L^1)(NCS)]SCN

Physical measurements. The UV-Visible absorption spectrum was recorded on a Shimadzu UV-1800 UV/Visible spectrophotometer. The mid-infrared spectrum was obtained using a KBr pellet on 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.

Crystal structure analysis. A pink crystal was mounted with inert oil on top of a glass fiber. Single crystal X-ray diffraction data were collected at 100 K on a Bruker SMART 1K CCD diffractometer using graphite—monochromated Mo$K_α$ radiation (λ = 0.71073 Å). The unit cell parameters were determined using SMART and refined based on the positions of all strong reflections using SAINT [16]. Absorption correction was applied by SADABS [17] based on symmetry-equivalent and repeated reflections. The crystal structure was solved by direct method using SIR97 [18] and refined by the full-matrix least-squares on F^2 using SHELXTL [19]. Molecular graphics were produced using X—SEED [20]. Both thiocyanates are disordered over two positions; the one covalently bonded to the copper atom is disordered such that the major component (84.2 %) is connected through the nitrogen end whereas the minor component is connected through the sulfur end. Pairs of distances (i.e., S—C, N—C) were restrained to 0.01 Å of each other. The anisotropic temperature factors were restrained to be nearly isotropic. Other non-hydrogen atoms were refined anisotropically; hydrogen atoms were first located in a difference map, and then N—H hydrogen atoms were freely refined and C—H hydrogen atoms were constrained to ride on the parent carbon atom, with C—H = 0.95—1.00 Å and U_{iso}(H) = 1.2U_{eq}(C). The crystallographic data and refinement parameters are summarized in Table 1.

RESULTS AND DISCUSSION

Structure description. The title complex crystallizes in the triclinic space group $P\overline{1}$ with two formula units, a = 7.9681(2), b = 8.8644(2), c = 18.8165(5) Å, α = 76.758(70), β = 78.490(2) and γ = 77.679(2)°. The crystal structure consists of square pyramidal [Cu(L^1)(NCS)]$^+$ cations and SCN$^-$ anions. Ellipsoid plot of the complex together with the atomic labelling is illustrated in Fig. 1. The square pyramidal coordination polyhedron consists of the nitrogen atoms of L^1 below the Cu^{2+} ion in the basal positions and the nitrogen atom of a thiocyanate ligand in the apical position. The macrocyclic skeleton adopts the most stable *trans*-III (RRSS) configuration, which is quite different from the *trans*-I (RSRS) configuration in [Cu(L^2)](ClO$_4$)$_2$ [1]. Selected bond lengths and angles and their standard deviations are given in Table 2.

Crystal data and structure refinement for [Cu(L^1)(NCS)]SCN

Formula weight	516.26
Temperature, K	100 (2)
Crystal system	Triclinic
Space group	$P\overline{1}$
a, b, c, Å	7.9681(2), 8.8644(2), 18.8165(5)
α, β, γ, deg.	76.758(2), 78.490(2), 77.679(2)
V, Å^3	1247.96(5)
Z	2
Calculated density, g/cm^3	1.374
Crystal size, mm	0.30×0.25×0.20
μ, mm^{-1}	1.06
Reflections collected / independent, (R_{int})	9822 / 5518, (0.027)
Transmission factors	0.741—0.815
Refined parameters	300
R ($F^2 > 2\sigma$)	0.043
R_w (F^2, all data)	0.110
GOOF on F^2	1.03
Max and min electron density, e/Å^3	0.91 and −0.82

The four Cu—N distances are not siginifically different and their mean value of 2.037(2) Å is in good agrement with the values found for related complexes (Table 3) [1, 10, 11, 21—27]. The coordination geometry around Cu(II) is a distorted square pyramid, with the metal center protruding out of the N4 plane by 0.208(2) Å toward the nitrogen atom of the apical isothiocyanato group. The *trans*-basal angles N1—Cu1—N3 = 172.18(9)° and N2—Cu1—N4 = 168.14(9)° are similar to those expected for square pyramidal Cu(II) complexes. The axial Cu1—N5 linkage of the isothiocyanato group is not perfectly perpendicular to the CuN4 plane with four N—Cu1—N5 angles ranging from 91.13(10) to 100.70(11)°. However, the isothiocyanato and thiocyanato units are disordered. Thus, there are two kinds of copper(II) coordination geometries because of the disorder. The axial Cu1—N5 bond of 2.322(3) Å with the isothiocyanato group is longer by about 0.285 Å than the equatorial Cu1—N
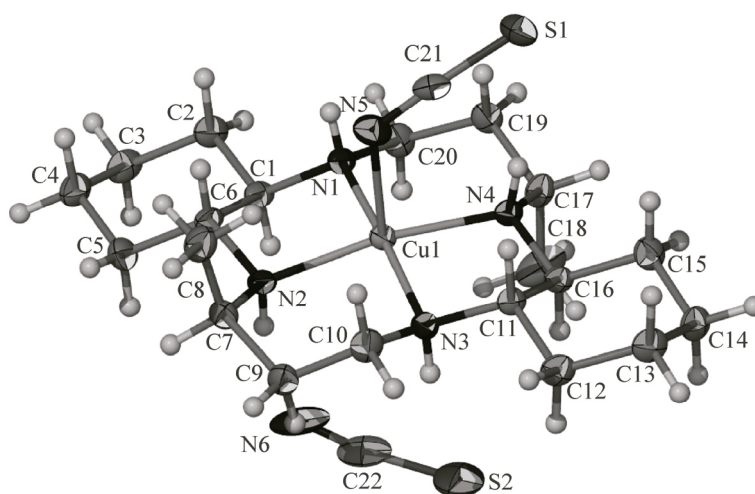

Fig. 1. A perspective view (50 % probability level) of [Cu(L^1)(NCS)]SCN with an atom numbering scheme

Table 2

Selected bond distances (Å) *and angles* (deg.) *for* [Cu(L^1)(NCS)]SCN

Cu1—N1	2.0319(19)	Cu1—N2	2.045(2)	N1—Cu1—N2	84.51(8)	N3—Cu1—N1	172.18(9)
Cu1—N3	2.0179(19)	Cu1—N4	2.052(2)	N3—Cu1—N2	93.84(8)	N3—Cu1—N4	84.13(8)
Cu1—N5	2.322(3)	Cu1—S1′	2.756(6)	N1—Cu1—N4	95.91(8)	N1—Cu1—N5	92.33(11)
N5—C21	1.169(4)	S1—C21	1.646(3)	N2—Cu1—N4	168.14(9)	N2—Cu1—N5	100.70(11)
N6—C22	1.167(8)	S2—C22	1.657(7)	N3—Cu1—N5	95.48(11)	N4—Cu1—N5	91.13(10)
				N6—C22—S2	171(2)	N5—C21—S1	175.2(3)

Table 3

Selected bond distances (Å) *and configurations of some metal complexes with constrained macrocyclic ligands*

Compound	M—N	M—X	Configuration	Reference
[Cu(L^1)(NO$_3$)$_2$]·3H$_2$O	2.021(2)—2.029(2)	2.746(2)	*trans*-III	[22]
[Cu(L^1)(NO$_3$)$_2$]	2.007(2)—2.044(2)	2.463(2)	*trans*-III	[10]
[Cu(L^1)(ClO$_4$)$_2$]	2.005(2)—2.048(2)	2.623(2)	*trans*-III	[11]
[Cu(L^1)(bip)$_2$]	2.015(2)—2.037(2)	2.534(2)	*trans*-III	[25]
[Cu(L^1)(H$_2$O)$_2$]Cl$_2$	2.017(2)—2.038(2)	2.649(2)	*trans*-III	[23]
[Cu(L^1)(H$_2$O)$_2$](BF$_4$)$_2$·2H$_2$O	2.028(2)—2.028(2)	2.693(3)	*trans*-III	[24]
[Cu(L^1)(N$_3$)]ClO$_4$·H$_2$O	2.030(3)—2.054(3)	2.254(4)	*trans*-III	[21]
[Zn(L^1)(NCS)]SCN	2.074(11)—2.197(10)	2.028(11)	*trans*-III	[28]
[Cu(L^1)(NCS)]SCN	2.013(2)—2.052(2)	2.322(3)	*trans*-III	[This work]
[Cu(L^2)(NO$_3$)$_2$]	1.999(7)—2.095(7)	2.919(7)	*trans*-III	[24]
[Cu(L^2)](ClO$_4$)$_2$	1.990(4)—2.050(4)	3.496(3)	*trans*-I	[1]
[Cu(L^3)](ClO$_4$)$_2$·2CH$_3$CN	2.030(3)—2.081(2)	3.264(3)	*trans*-III	[27]
[Cu(L^a)(ClO$_4$)$_2$]	2.016(2)—2.040(2)	2.762(2)	*trans*-III	[26]
[Cu(L^a)(NO$_3$)$_2$]	2.014(2)—2.047(2)	2.506(2)	*trans*-III	[2]
[Cu(L^a)(H$_2$O)$_2$](SCN)$_2$	2.021(2)—2.046(2)	2.569(2)	*trans*-III	[2]

(secondary amine) bonds. The Cu1—S1′ bond of 2.75(6) Å can also be considered as a semi-coordinated bond. The distances between Cu1 and N5 or S1′ are longer than the Zn—NCS bond length of 2.028(2) Å in the structure of [Zn(L^1)(NCS)]SCN [28]. The elongated square pyramidal geometry is common for five-coordinate Cu(II) complexes containing non-equivalent ligands, and the distortion arises from the pseudo Jahn—Teller effect operative on the d^9 metal center [29]. However, the Cu1…N6 3.744 Å distance and Cu1…S2′ 4.179 Å distance indicate that N6 and S2′ are not involved in coordination. The Cu1—N5—C21 angle of 116.18(3)° is more bent than the corresponding angles in [Cu(cyclam)(NCS)]SCN (167.3°) [15] and [Zn(L^1)(NCS)]SCN (131.2°) [28]. The five-membered chelate rings have a *gauche* conformation in which the N1—Cu1—N2 and N3—Cu1—N4 angles are 84.51(8) and 84.13(8)°, respectively. The six-membered rings adopt stable *chair* conformations with N1—Cu1—N4 and N2—Cu1—N3 angles of 95.91(8) and 93.84(8)°, respectively. The mean bite distance (2.735 Å) of the five-membered ring is smaller than that (3.000 Å) of the six-membered ring. The methyl groups are attached axially as substituents to the six-membered ring in the chair conformation, while the substitution of the five-membered ring by the methylene C atoms of the fused cyclohexane ring is equatorial; the cyclohexane ring also adopts the chair conformation. The mean C—N and C—C distances in the macrocyclic ligand are typical for macrocyclic tetraamine complexes, while the C—N—C and C—C—N angles are also typical. However, the N—C distances involving the coordinated nitrogen atoms are slightly longer than the corresponding N—C distances of the free ligand [15, 30].

Hydrogen-bonding geometry (Å, deg.) *for* [Cu(L^1)(NCS)]SCN

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···N6	0.88(4)	2.14(4)	2.998(19)	165(3)

The isothiocyanato group and thiocyanate anion are slightly bent with an N5—C21—S1 bond angle of 175.2(3)° and an N6—C22—S2 bond angle of 171.(3)°, respectively. The uncoordinated thiocyanate remains outside the coordination sphere. Thus there is no weak interaction with the copper atom below the basal plane. However, the N6 atom of the thiocyanate anion forms a hydrogen bond with the secondary NH group of the macrocycle (Fig. 1 and Table 4).

Spectroscopic properties. The UV-visible electronic spectrum (Fig. 2) in CH$_3$CN:H$_2$O, 1:1 v/v shows one broad *d—d* band at 19530 cm^{-1}. The absorption maximum ν_{max} of the complex is very similar to those of [Cu(L^1)(ClO$_4$)$_2$] and [Cu(L^1)(NO$_3$)$_2$]·3H$_2$O with maximum values at 19 530 and 19 570 cm^{-1}, respectively [12, 13]. Based on the low ε value for this transition, it is confirmed that the band is due to *d—d* transition. The maximum absorption bands are consistent with the presence of a Cu(II)—N$_4$ chromophore in a square planar arrangement with very weak axial interaction [2]. The electronic spectroscopic properties are associated with the pseudo Jahn—Teller effect operating in the *d^9* system, confirmed from the crystal structures that show a significantly elongated axial Cu…NCS distance compared to the relatively short equatorial Cu—N bonds.

In the title complex, one NCS group is bonded to the copper atom at a distance of 2.322(3) Å, giving a square pyramidal stereochemistry. For the square pyramidal geometry, the order of one-electron energy levels is established as *e* (*xz, yz*) < *b$_2$* (*xy*) < *a$_1$* (*z^2*) < *b$_1$* (*x^2 − y^2*). The ^2D term of the free copper(II) ion (3*d^9*) in an octahedral field splits into an upper $^2T_{2g}$ level and a lower ^2E_g level. The ^2E_g and $^2T_{2g}$ levels for the square pyramidal distorted copper(II) complexes will split into $^2B_1$, $^2A_1$, $^2B_2$, and ^2E states. The observed band has a slightly asymmetric profile. In order to obtain some points of reference for the splitting of the band, the absorption band was deconvoluted into two components by using Gaussian curves (dotted line), as shown in Fig. 2. Deconvolution of the experimental band pattern yielded maxima at 14 835 and 20 250 cm^{-1}, respectively. The two *d—d* transition components are tentatively assigned to the following transitions, in order of increasing energy, $^2B_1 \rightarrow ^2B_2$ and $^2B_1 \rightarrow ^2E$ [31, 32]. Much weaker, lower energy absorptions at 10 255 cm^{-1} may be due to the $^2B_1 \rightarrow ^2A_1$ transition. The energy level sequence will depend on the degree of square-pyramidal distortion arising due to the ligand-field effect. The energy of the transitions originating from the *xz*, *yz*, and *xy* orbitals for amine donors exhibiting only σ interactions is independent of the axial ligands. The electronic spectroscopic properties are in agreement with crystal structures that show an elongated axial Cu…NCS distance compared to the relatively short equatorial Cu—N bonds.
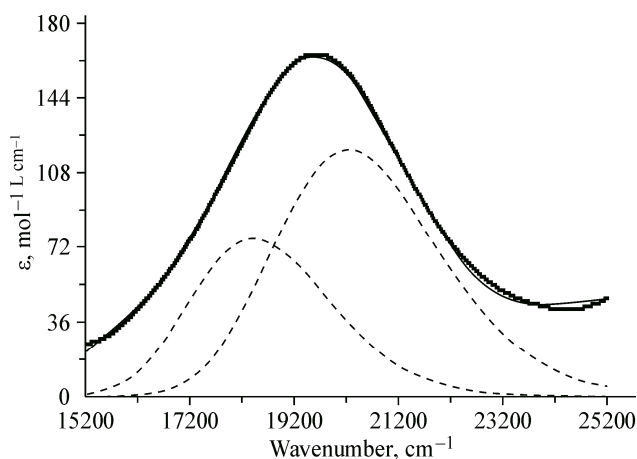
The FT-infrared spectrum of the complex shows strong bands in the regions 3250—3050 and 3000—2850 cm^{-1} due to the symmetric and antisymmetric N—H and C—H stretching modes, respectively. The lowering of the ν(N—H) frequency (3132 cm^{-1}) compared to that (3291 cm^{-1}) of the free ligand L^1 can be explained by coordination and hydrogen bonding of the secondary amine groups. The very intense band at 2049 cm^{-1} is assigned to the

Fig. 2. Visible absorption spectrum of [Cu(L^1)(NCS)]SCN in solution and the resolved overlapping peaks (dotted curves)

v(CN) frequency of thiocyanate [33]. It is well known that the *trans* isomer shows two groups of bands, a doublet near 890 cm^{-1} arising from the secondary amine vibration and a single band near 800 cm^{-1} due mainly to the methylene vibration. However, the *cis* isomer exhibits at least three bands in the 890—830 cm^{-1} region due to the N—H wagging modes, while the methylene vibration splits into two peaks in the 830—790 cm^{-1} region [34—38]. Two bands at 890 and 846 cm^{-1} and a single absorption band at 800 cm^{-1} are assigned to the N—H wagging and CH$_2$ rocking frequencies, respectively. The three absorptions in the secondary amine and methylene vibrational regions are consistent with the *trans*-III configuration of the constrained cyclam ligand. These wagging and rocking deformation bands are not significantly affected by differing counter anions and central metal ions [2, 8, 9].

CONCLUSIONS

The electronic absorption and infrared spectroscopic properties of [Cu(L^1)(NCS)]SCN are in agreement with the X-ray crystallography results, which shows that the Cu(II) complex is in a distorted square pyramidal geometry, with four amine N atoms in equatorial positions and one NCS group in an axial position The macrocyclic skeleton adopts the most stable *trans*-III configuration. The uncoordinated thiocyanate anion remains outside the coordination sphere and it is attached to the Cu(II) complex cation by a hydrogen bond. The crystal structure is stabilized by the hydrogen bond between the secondary N hydrogen atoms of the macrocyclic ligand and the N atom of SCN$^-$ counter anion.

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 891182. 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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