Int. J. Chem. Sci.: 13(2), 2015, 593-604
ISSN 0972-768X
www.sadgurupublications.com

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

M. A. SUBHAN[a], K. S. RYOO and J. H. CHOI[*]

Department of Chemistry, Andong National University, ANDONG 760-749, SOUTH KOREA
[a]Department of Chemistry, Shah Jalal University of Science and Technology,
SYLHET, BANGLADESH

ABSTRACT

The synthesis, molecular structure, IR and UV-visible spectral properties of $[Cu(L^1)](NCS)_2{\cdot}2H_2O$, where L^1 = 3,14-dimethyl-2,6,13,17-tetraazatricyclo(16.4.0.0^{7,12})docosane were reported. The complex crystallized in the triclinic space group $P\bar{1}$ with one mononuclear formula unit in a cell of dimensions a = 8.594 (2), b = 8.775 (2), c = 9.875 (2) Å, α = 76.456 (7)^o, β = 71.215 (5)^o and γ = 76.364 (7)^o. The copper (II) ion had a distorted square-planar environment with the four N atoms of the macrocyclic ligand in equatorial positions. The macrocyclic ligand adopts the most stable *trans*-III conformation. The mean Cu-N distance of 2.038 (7) Å was normal, but the elongation of Cu…NCS bond, 3.037 (7) Å may be due to the peudo Jahn-Teller effect and the strong in-plane ligand field. The crystal was stabilized by a three-dimensional network of hydrogen bonds among secondary N hydrogens, N atoms of NCS^- and O or H atoms of water molecules.

Key words: Crystal structure, Spectroscopic properties, Copper(II) complex, Macrocyclic ligand, *Trans*-III configuration.

INTRODUCTION

The transition metal complexes with macrocyclic ligands have attracted considerable attention because of their diverse applications focused on enzyme mimics[1,2], waste-water treatment[3], catalysis[4], fluorescent sensor[5-7], biomedicine[8]. In recent years, it has been reported that the 1,4,8,11-tetraazacyclotetradecane (cyclam: AMD1498), xylyl-biscyclam (AMD3100) and their complexes exhibit *anti*-HIV activity[9-11]. The cyclam derivatives and their complexes inhibit the entry of the virus into white cells by binding to CXCR4, a

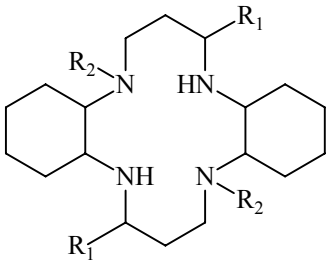
[*]Author for correspondence; E-mail: jhchoi@anu.ac.kr

chemokine receptor in the outer membrane. The strength of binding to the CXCR4 receptor correlates with *anti*-HIV activity.

The 14-membered tetraaza macrocyclic ligand has a moderately flexible structure, and 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 centres. The *trans*-I, *trans*-II and *trans*-V configurations can fold to form *cis*-I, *cis*-II and *cis*-V isomers, respectively[12,13].

The configuration for the macrocyclic ligand and the orientations of the N–H bonds are very important factors for co-receptor recognition[9-11]. Therefore, knowledge of coordination behavior and configuration of the cyclam derivative has become important in the improved design and development of new highly effective *anti*-HIV drugs that specially target alternative events in the HIV replicative cycle.

The various constrained cyclam ligands containing two 1,2-diaminocyclo hexanediamine sub units and two methyl or ethyl groups on 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

The chemical properties and geometries of copper(II) complexes of macrocyclic ligands are influenced by the structural characteristics such as stereochemistry, chelate ring size, and substituent. Previously we have 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; $X^- = NO_3^-$, ClO_4^-), in which the copper(II) ions have tetragonally distorted octahedral environment with the four N atoms of the macrocyclic ligand in equatorial positions and the O atoms of two counter-anions in axial positions[14,15]. In these two Cu(II) complexes, the macrocyclic ligands adopted their most stable *trans*-III configuration. The constrained ligand containing two cyclohexane

rings and methyl groups on the carbon atoms has often shown different coordination behaviors from those of the transition metal complexes with the parent cyclam ligand. In particular, the 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 the copper(II) ion was tetracoordinated in a roughly square planar somewhat distorted towards tetrahedral geometry.[16]

The macrocyclic backbone in the copper(II) complex adopts a less stable *trans*-I (RSRS) configuration in which the two benzyl group sustituents lie on the same side of the square plane of macrocycle N donors. However, in case of $[Cu(L^3)](ClO_4)_2 \cdot 2CH_3CN$ [L^3 = 2, 13-bis(1-naphthylmethyl)-5,16-dimethyl-2,6,13,17-tetraazatricyclo(16.4.0.0^{7,12})docosane], two functional pendant 1-naphthalenylmethyl groups were *trans* to each other, and the marcrocyclic skeleton adopted the most stable *trans*-III configuration[17]. Anionic species play very important roles in chemistry, medicine, catalysis, molecular assembly and in biology, yet their binding characteristics have not received much recognition.

As part of our current research on such compounds, in the presnt paper, we describe on the synthesis, structural and spectral properties of the copper(II) complex with the constrained macrocycle (L^1), water molecules and thiocyanate anions in order to obtain conclusive information concerning configuration of marcocyclic ligand, coordination behavior and packing force of water molecule and the thiocyanate anionic group.

EXPERIMENTAL

Materials and synthesis

The starting material, $[Cu(L^1)(NO_3)_2] \cdot 3H_2O$ were prepared according to a published procedures[14]. All other chemicals were purchased from commercial sources and were used without further purification. The solvents were of reagent grade, and were purified by the usual methods.

0.069 g (0.12 mmol) of $[Cu(L^1)(NO_3)_2] \cdot 3H_2O$ and 0.02 g (0.026 mmol) of NH_4SCN was dissolved in 10 mL of water and acetonitrile (1:1). The mixture was heated at 100^{o}C for 30 min. The resulting solution was filtered and cooled to room temperature. The solution was kept in an open beaker for crystallization. After one day pink crystals suitable for X-ray analysis were obtained. Yield: 62%. *Anal.* Found: C, 48.29; H, 8.16; N, 15.63; O, 5.34; S, 11.27%. Calc. for $Cu(C_{20}H_{40}N_4)(NCS)_2 \cdot 2H_2O$: C, 47.84; H, 8.03; N, 15.22; O, 5.79; S, 11.61%. Visible spectral data for an aqueous solution, λ_{max} in nm (ε in M^{-1} cm^{-1}): 511.2 (102), IR spectrum (KBr, cm^{-1}): 3479 s and 3435 s (ν OH), 3235 vs and 3129 s (ν NH), 2933

vs and 2865 s (ν CH), 2061 vs and 2046 vs (ν_{as} CN), 1636 m (δ H_2O), 1464 m and 1447 m (δ CH_2), 1394 m, 1338 m, 1310 m, 1271 m, 1218 m, 1171 m, 1094 vs, 1012 s, 970 m, 906 m (ρ CH_3), 890 m and 842 w (γ NH), 786 m (ρ CH_2), 875 m and 755 m (ν CS), 667 w, 646 w (ρ_w H_2O), 596 w, 482 m (δ NCS), 448 w.

Physical measurements

The visible absorption spectrum of aqueous solution was recorded on a Shimadzu UV-1800 UV/Visible spectrophotometer. The mid-infrared spectrum was obtained using a KBr pellet on a Thermo Nicolet 5700 FT-IR spectrometer. Analyses for C, H, N, O and S were performed on a Carlo Erba 1108 Elemental Vario EL analyzer.

Crystal structure analysis

A pink crystal of title complex was mounted with inert oil on the top of a glass fibre. Table 1 summarizes the crystallographic experimental data. Single-crystal X-ray diffraction data were collected at 200 K on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). Data collection and integration were performed with COLLECT[18] and EvalCCD.[19] Absorption corrections were applied by SADABS[20] based on symmetry-equivalent and repeated reflections. The structure was solved by direct methods using SIR97[21] and refined by full-matrix least-squares on F^2 using SHELXTL.[22] Molecular graphics were produced using DIAMOND-3.[23] Non-hydrogen atoms were refined anisotropically; hydrogen atoms were first located in a difference map, 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).

Table 1: Crystallographic data for $[Cu(L^1)](NCS)_2 \cdot 2H_2O$

Chemical formula	$CuC_{22}H_{40}N_6O_2S_2$
M_r	548.26
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	200 (2)
a, b, c (Å)	8.594 (2), 8.775 (2), 9.875 (3)
α, β, γ (°)	76.456 (7), 71.215 (5), 76.364 (7)
V (Å^3)	675.0 (3)
Z	1

Cont…

Chemical formula	**$CuC_{22}H_{40}N_6O_2S_2$**
Radiation source	Mo *K*α radiation
μ (mm^{-1})	0.993
Crystal size (mm)	0.31× 0.21 × 0.20
Data collection	CCD area detector diffractometer
T_{min}, T_{max}	0.8261, 0.7482
No. of independent reflections	2641
R_{int}	0.0474
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.1245, 0.3878, 1.371
No. of reflections	2641
No. of parameters	152
No. of restraints	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	1.205, -1.726

RESULTS AND DISCUSSION

Crystallography

The title complex crystallizes in the space group $P\bar{1}$ of the triclinic system with one mononuclear formula unit in a cell of dimensions a = 8.594 (2), b = 8.775(2), c = 9.875(2) Å, α = 76.456(7)°, β = 71.215(5)° and γ = 76.364(7)°. The molecule structure of the complex comprises one $[Cu(L^1)]$ $(NCS)_2$ and two hydrated water molecules in the chemical formula. The stereochemistry of the copper(II) complex may be considered as square planar or tetragonally octahedral, depending upon whether or not the out of plane N atoms of NCS groups are considered to be bonded to copper atom[24,25]. Selected bond lengths and angles are listed in Table 2.

Table 2: Selected bond distances (Å) and angles (°) for $[Cu(L^1)](NCS)_2 \cdot 2H_2O$

Cu1–N1	2.021 (7)	Cu1 – N2	2.055 (7)
N1–C9^i	1.470 (10)	N2 – C6	1.471 (11)
N1–C1	1.490 (11)	N2 – C7	1.512 (10)
C1–C2	1.506 (13)	C9 – N1^i	1.470 (10)

Cont…

C1–C6	1.577 (11)	C5 – C6	1.545 (13)
C2–C3	1.519 (14)	C7 – C8	1.490 (13)
C3–C4	1.543 (13)	C8 – C9	1.533 (13)
C4–C5	1.552 (14)	C9 – C10	1.520 (12)
C1S–N1S	1.139 (18)	S1S – C1S	1.679 (17)
N1–Cu1–N2	85.6 (3)	N1–Cu1–N2^{i}	94.4 (3)
C1–N1–Cu1	109.7 (5)	C6–N2–Cu1	106.4 (5)
C9^{i}–N1–Cu1	121.9 (6)	C7–N2–Cu1	115.7 (5)
N1–C1–C2	115.3 (7)	N1–C1–C6	106.4 (6)
N2–C6–C5	112.7 (7)	N2–C6–C1	108.4 (7)
N1^{i}–C9–C8	110.0 (7)	N1^{i}–C9–C10	109.8 (7)
C6–N2–C7	113.7 (6)	C8–C7–N2	112.0 (7)
C9^{i}–N1–C1	113.4 (7)	C5–C6–C1	110.0 (7)
C1–C2–C3	111.6 (7)	C6–C5–C4	110.0 (7)
C2–C1–C6	109.4 (7)	C7–C8–C9	116.0 (7)
C2–C3–C4	110.9 (8)	C10–C9–C8	112.6 (8)
C3–C4–C5	109.8 (8)	N1S–C1S–S1S	174.6 (11)

Symmetry code: (i) $-x+1, -y+1, -z+1$

An ellipsoid plot of the complex cation together with the atomic labelling is illustrated in Fig. 1. The hydrogen atoms are shown as small spheres of arbitrary radii.

The coordination geometry around the copper(II) ion reveals tetrahedrally distorted square planar coordination environment with four N atoms from the macrocycle. The copper atom is situated on the centre of inversion of the triclinic cell containing just one copper complexe per unit cell. The two methyl 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. The two hydrogen atoms attached to C1 and C6 atoms are also *anti* with respect to the five-membered chelate ring. The macrocyclic skeleton adopts the most stable *trans*-III (RRSS) configuration. The Cu–N distances [2.020(7)–2.056(7) Å] are within the expected range, and comparable to those observed in similar copper(II) complex systems such as $[Cu(L^1)(NO_3)_2]\cdot 3H_2O$ [2.021(2)–2.029(2) Å][14], $[Cu(L^a)(NO_3)_2]$ [2.014(2)–2.047(2)Å][26],

$[Cu(L^2)](ClO_4)_2$ [1.990(4)–2.050(2) Å][16], and $[Cu(L^3)](ClO_4)_2{\cdot}2CH_3CN$ [2.030(3)–2.081(2) Å].[17] The Cu-N bond lengths of the teritiary amines in $[Cu(L^2)](ClO_4)_2$ and $[Cu(L^3)](ClO_4)_2{\cdot}2CH_3CN$ are slightly longer than those of the secondary amines, which may be attributed to the steric hindrance of the benzyl or 1-naphthylmethyl groups[16,17].

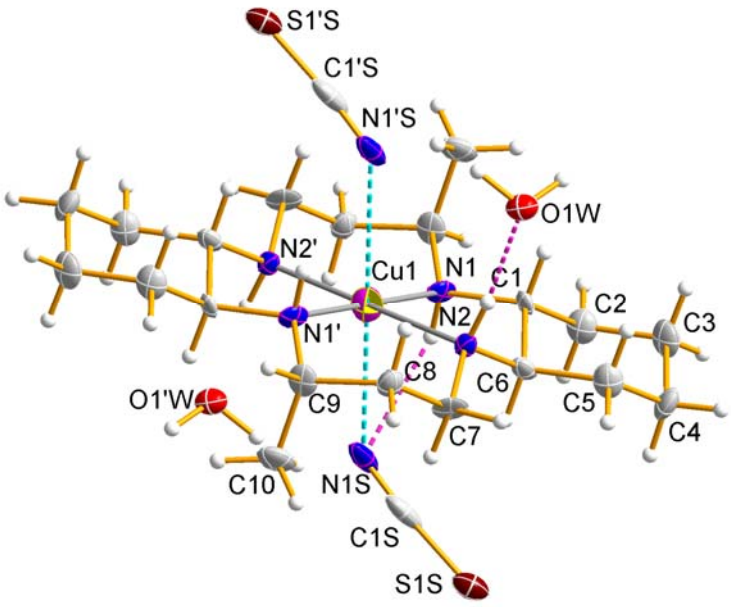


Fig. 1: A perspective view (50% probability level) of $[Cu(L^1)](NCS)_2{\cdot}2H_2O$ with the atom-numbering scheme. Dashed lines represent hydrogen bond interaction N–H···O (purple) and very weak interaction Cu···NCS (cyan), respectively.

The Cu1…N1S distance of 3.037(7) Å is much longer than the axial bond lengths of $[Cu(L^1)(NO_3)_2]$ [2.463(2) Å][27], $[Cu(L^1)(ClO_4)_2]$ [2.623(2) Å][15], $[Cu(L^1)(H_2O)_2](BF_4)_2{\cdot}2H_2O$ [2.693(3)Å][28], $[Zn(L^1)(NCS)]SCN$ [2.028(2) Å][29] and $[Zn(L^1)(OAc)_2]{\cdot}0.5H_2O$ [2.294(2) Å].[30] The thiocyanate group is very weakly connected axially by nitrogen atom N1S and slightly bent with N1S-C1S-S1S angle of 174.9(11)°. The bonding between copper(II) and the NCS ligand is bent with Cu1-N1S-C1S angle of 130.35(10)°. The bent Cr-N-C conformation may be due to steric or packing effects. The Cu1…N1S bond is not perpendicular to the CuN_4 plane, the actual angles N1S-Cu1-N1 and N1S-Cu1-N2 being 107.77(3) and 89.06(3)°, respectively. The five-membered chelate ring has *gauche* conformation in which the N1-Cu1-N2 angle is 85.7(3)°. The six-membered ring adopts stable chair conformation with the N1-Cu1-$N2^i$ [(i) $-x+1, -y+1, -z+1$] angle of 94.3(3)°. The bite distance [2.772(7) Å] of the five-membered ring is smaller than that [2.988(7) Å] of

six-membered ring. The methyl groups are attached axially as substituents to the chair six-membered ring, while the substitution of the five-membered ring by methylene C atoms of the fused cyclohexane ring is equatorial; the cyclohexane ring is also chair conformation, with the N atoms in equatorial positions. The mean C–N and C–C distances in the macrocyclic ligand are typical for macrocyclic tetraamine complexes. 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[31]. The uncoordinated water molecules remain outside the coordination sphere and they are linked to the NCS group and macrocyclic ligand through hydrogen bonds. Both the hydrogen on secondary N1 and N2 of macrocyclic ligand are involved in N-H…O and N-H…N type interactions with water molecule and NCS group. Table 3 contains the distances and angles of hydrogen bonds. The crystal structure is stabilized by these intra and intermolecular hydrogen bondings.

Table 3: Hydrogen-bonding geometry (Å, °) for $[Cu(L^1)](NCS)_2 \cdot 2H_2O$

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*2···N1*S*^{i}	0.98	2.08	2.834 (16)	133
N1—H1···N1*S*	0.93	2.39	3.092 (13)	133
N2—H2···O1*W*	0.93	1.96	2.884 (10)	174

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1

Electronic absorption spectroscopy

The visible absorption spectrum of $[Cu(L^1)](NCS)_2 \cdot 2H_2O$ were recorded in aqueous solution (Fig. 2). The complex shows one broad *d-d* band at 19570 cm^{-1} in aqueous solution. Based on the low value of Є for this transition, it is generally confirmed that the band can be assigned to *d-d* transition. The observed band has 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.

The contribution from outside bands was subtracted for more accurate Gaussian line-shape analysis. Deconvolution of the experimental band pattern yielded maxima at 18520 and 19815 cm^{-1}. UV/Vis data correspond to a type-III square planar structure in solution[32].

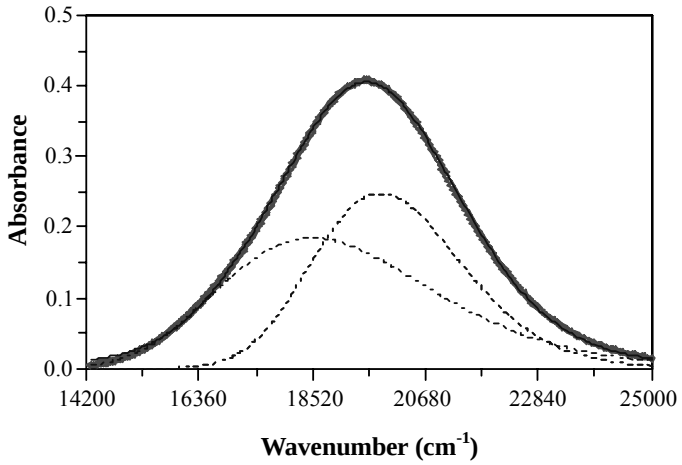


Fig. 2: Visible absorption spectrum (solid line) of $[Cu(L^1)](NCS)_2 \cdot 2H_2O$ in aqueous solution

Infrared spectroscopy

The FT-infrared spectrum of the newly synthesized cupper(II) complex is given in Fig. 3. The two absorptions at 3479 and 3435 cm^{-1} and the doublet near 1623 cm^{-1} are due to the symmetric OH stretching and deformation of hydrate H_2O molecule. The FT-infrared spectrum shows strong bands in the regions 3240–3080 cm^{-1} 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 (3235 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.

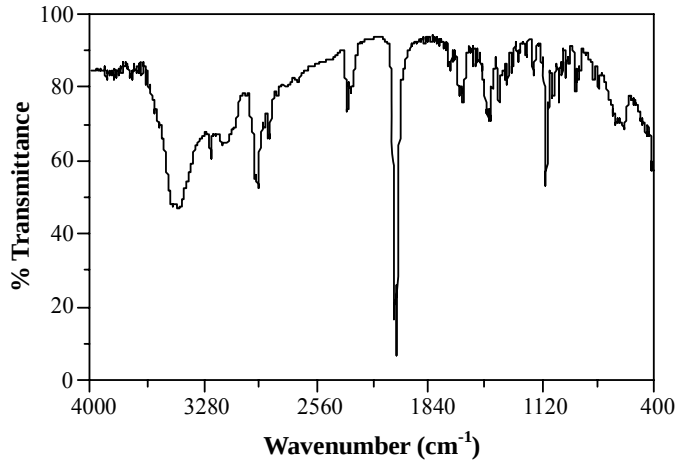


Fig. 3: FT-infrared spectrum of $[Cu(L^1)](NCS)_2 \cdot 2H_2O$.

The very intense bands at 2061 and 2046 cm^{-1} are assigned to ν(CN) frequency of thiocyanate group.[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 only one 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 842 cm^{-1} and a single absorption band at 786 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.[12,39,40]

In conclusion, the spectroscopic properties of $[Cu(L^1)](NCS)_2 \cdot 2H_2O$ are in agreement with X-ray crystallographic results, which shows that the complex adopts tetrahedrally distorted square planar CuN_4 (*trans*-III configuration) arrangement with two NCS groups occupying symmetric sites above and below the square coordination plane. The anion and complex cation are linked by hydrogen bond and weak Cu…NCS interaction. The uncoordinated water molecules remain outside the coordination sphere and they are attached to the complex only by hydrogen bonds. The crystal is stabilized by the hydrogen bonds among the secondary N hydrogens of macrocyclic ligand, N atom of NCS^- and O or H atoms of water molecule.

Suppelementary 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 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).

REFERENCES

1. F. Wuerthner and J. Rbek, Angew. Chem. Int. Ed. Engl., **34**, 446 (1995).
2. T. Koike and E. Kimura, J. Am. Chem. Soc., **113**, 8935 (1991).
3. F.Cuenot, M. Meyer, A. Bucaille and R. Guilard, J. Mol. Liq., **118**, 89 (2005).
4. W. Nam and J. S. Valentine, J. Am. Chem. Soc., **115**, 1772 (1993).

5. M. H. Lim and S. Lippard, Acc. Chem. Res., **40**, 41 (2007).

6. E. Tamanini, K. Flavin, M. Motevalli, S. Piperno, L.A. Gheber, M. H. Todd and M. Watkinson, Inorg. Chem., **49**, 3789 (2010).

7. V. Kubicek and E. Toth, Adv. Inorg. Chem., **61**, 63 (2009).

8. D. Parker, Chem. Soc. Rev., **19**, 271 (1990).

9. G. C. Valks, G. McRobbie, E. A. Lewis, T. J. Hubin, T. M. Hunter, P. Sadler, C. Pannecouque, E. De Clercq and S. J. Archibald, J. Med. Chem., **49**, 6162 (2006).

10. X. Liang and P. J. Sadler, Chem. Soc. Rev., **33**, 246 (2004).

11. L. Ronconi and P. J. Sadler, Coord. Chem. Rev., **251**, 1633 (2007).

12. J. H. Choi, Inorg. Chim. Acta, **362**, 4231 (2009).

13. M. A. Subhan, J. H. Choi and S. W. Ng, Z. Anorg. Allg. Chem., **637**, 2193 (2011).

14. J. H. Choi, T. Suzuki and S. Kaizaki, Acta Crystallogr. Sect. E, **62**, m2383 (2006).

15. J. H. Choi, K. S. Ryoo and K. M. Park, Acta Crystallogr. Sect. E, **63**, m2674 (2007).

16. J. H. Choi, W. Clegg and R. W. Harrington, J. Chem. Crystallogr., **40**, 80 (2010).

17. J. H. Choi, W. Clegg and G. S. Nichol, Z. Anorg. Allg. Chem., **636**, 1612 (2010).

18. R. W. W. Hooft, Collect, Nonius BV, Delft (1999).

19. A. J. M. Duisenberg, L. M. J. Kroon-Batenburg and A. M. M. Schreurs, J. Appl. Crystallogr., **36**, 220 (2003).

20. G. M. Sheldrick, SADABS, University of Göttingen, Germany (2003).

21. A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guargliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, J. Appl., **32**, 115 (1999).

22. G. M. Sheldrick, Acta Crystallogr. Sect. A, **64**, 112 (2008).

23. K. Brandenburg and H. Putz, Diamond-3, University of Bonn, Germany (2012).

24. P. Comba, P. Jurisic, Y. D. Lampeka, A. Peters, A. I. Prikhod'ko and H. Pritzkow, Inorg. Chim. Acta **324**, 99 (2001).

25. J. Reedijk, Transition Met. Chem., **6**, 195 (1981).

26. J. H. Choi, M. A. Subhan and S. W. Ng, W, J. Coord. Chem., **65**, 3481 (2012).

27. J. H. Choi, M. A. Subhan and S. W. Ng, Acta Crystallogr. Sect. E, **68**, m190 (2012).

28. J. H. Choi, T. Joshi and L. Spiccia, Z. Anorg. Allg. Chem., **638**, 146 (2012).

29. K. Y. Choi, I. H. Suh and J. C. Kim, Polyhedron, **16**, 1783 (1997).

30. A. Ross, J. H. Choi, T. M. Hunter, C. Pannecouque, S. A. Moggach, S. Parsons, E. De Clercq and P. J. Sadler, Dalton Trans., **41**, 6408 (2012).

31. J. H. Choi, W. Clegg, R. W. Harrington, H. M. Yoon and Y. P. Hong, Acta Crystallogr. Sect. E**, 62**, o644 (2006).

32. A. B. P. Lever, Inorganic Electronic Spectroscopy, 2nd Ed., Elsevier, Amsterdam (1984) p. 570.

33. J. H. Choi and S. H. Lee, J. Mol. Struct., **832**, 84 (2009).

34. C. K. Poon and K. C. Pun., **19**, 568 (1980).

35. J. H. Choi, Chem. Phys., **256**, 29 (2000).

36. J. H. Choi, Spectrochim. Acta Part A, **56**, 1653 (2000).

37. J. H. Choi, I. G. Oh, T. Suzuki and S. Kaizaki, J. Mol. Struct., **694**, 39 (2004).

38. J. H. Choi, I. G. Oh, R. Linder and T. Schönherr, Chem. Phys., **297**, 7 (2004).

39. C. K. Poon and K. C. Pun, J. Chem. Soc. Dalton Trans., 858 (1976).

40. M. A. Subhan and J. H. Choi, Spectrochim. Acta Part A, **123**, 410 (2014).

Accepted : 16.04.2015