

SYNTHESIS AND CHARACTERIZATION OF A THIOCYANATE BRIDGED DINUCLEAR CU(II) COMPLEX CONTAINING MACROCYCLIC LIGAND DERIVED FROM PYRIDINE-2, 6-DICARBOXALDEHYDE AND 1, 2-BIS(2-AMINOETHOXY) ETHANE

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ABSTRACT

The cyclic (2+2) template condensation of pyridine-2,6-dicarboxaldehyde with 1,2-Bis(2-aminoethoxy) ethane using $\text{Pb}(\text{SCN})_2$ gave dinuclear lead (II) complex, $\text{Pb}_2\text{L}_1(\text{SCN})_4$, where L_1 is a tetra-Schiff-base macrocycle. The transmetallation treatment of $\text{Pb}_2\text{L}_1(\text{SCN})_4$ with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ yield the complex, $[\text{Cu}_2\text{L}_1(\text{SCN})_3(\text{ClO}_4)]$ which has been characterized by elemental analysis, IR, ESI-MS spectroscopy and X-ray crystallography. On the basis of spectral data, different geometry of Cu^{2+} has been suggested.

Key words: Macrocylic complexes, Spectroscopic studies, 1,2-bis(2-aminoethoxy) ethane, X-ray crystallography

INTRODUCTION

Dinuclear metal complexes in which metal centers are in close proximity are of current interest as model of metalloproteins (Eawards *et al.* 1992). Macrocylic ligands are widely recognized as functional molecules that can bring out the full potential of accommodated metal ions. A number of excellent examples of universal ligands such as crown ethers (Gokel *et al.* 2004), porphyrins (Hambright 1971) and saturated (or unsaturated) macrocylic polyamines (Kimura 1992, Zhang *et al.* 1997), their chemical properties and functions as metal complexes have been systematically enhanced by the facile and diverse chemical modification of their macrocylic frameworks. The study of macrocylic ligands and their complexes has been a very active area of research interest for many years which continues to expand. Hence, the design and study of well-disposed metal-containing macrocycles with desirable properties still continues to be important. The template condensation reaction lies at the heart of macrocylic chemistry (Curtis 1968) and have been widely used for synthesis of macrocylic complexes where,

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generally the transition metal ions are used as templating metal agents (Niasari *et al.* 2006). Macrocyclic complexes find use in DNA recognition and oxidation (Muller *et al.* 1993) and detecting tumor lesions (Kosmos *et al.* 1992). Considering these factors, in this paper present authors report the synthesis and characterization of a new type of thiocyanate bridged macrocyclic dinuclear Cu(II) complex (Fig. 1.). The crystal structure of the complex is also reported.

MATERIALS AND METHODS

Elemental analysis was carried out at the Instrumental Research Center on JM10 MICROCORDER made by J. Science laboratory Co., Ltd. IR Spectra were recorded on an Excalibur Series JASCO FT/IR 3000MX/UMA250 spectrometer in the range 4000-400/cm⁻¹ as KBr pellets. NMR spectra were measured on a Bruker Avance^{III}-400 with CDCl₃ as solvent. The positive-ion ESI-mass spectrum of complexes was obtained with a Quattro micro API spectrometer manufactured by Waters. X-ray measurement was performed on a Rigaku Saturn CCD area detector at Li was first prepared by condensation pyridine-216-discardox aldehyde with 1,2-bis(2-amino ethony) ethane which was subsequently treated with Pb (SCN)₂ to yield pb₂ Li (SCN)₄ by the method as reported in the literature (Alam *et al.* 2011). Pyridine-2,6-dicarboxaldehyde and Pb₂L₁(SCN)₄ were prepared by method reported by Alam *et al.* (2011).. All measurements were performed at room temperature (25 ± 2 °C).

Synthesis of [Cu₂L₁(SCN)₃(ClO₄)]: About 150 ml methanol was heated at 60°C for 30 minutes to which 0.222 g (0.1945 mmol) of Pb₂L₁(SCN)₄ was added and heating was continued for another 30 minutes. Cu(ClO₄)₂·6H₂O (0.144g, 0.39 mmol plus slight excess) was added to the solution. The reaction mixture was refluxed for 2 hours at 70°C resulting a green solution. After filtration the solution was concentrated in rotary evaporator until crystallization begun. Recrystallization from acetonitrile and diethyl ether gave an emerald green crystal. Yield = 34%, Calc. for C₂₉H₃₄ClCu₂N₉O₈S₃: C, 38.90; H, 3.83; N, 14.08%. Found: C, 38.94; H, 3.81; N, 14.08 %. IR (KBr): ν(SCN) 2075/cm, 2098/cm, ν(C = N)Py 1589/cm, ν(ClO₄⁻) 1091/cm, 813/cm (SCN), 786/cm (SCN), 667/cm ν(ClO₄⁻), 621/cm ν(ClO₄⁻).

Crystal structure determination: The block type crystals of complex, [Cu₂L₁(SCN)₃(ClO₄)] are so stable in air that the single crystal was mounted in a capillary without coating. Data collection was performed on a Rigaku Saturn CCD area detector with graphite monochromated Mo-Kα radiation. Indexing was performed from 0 images that were exposed for 0 seconds. The crystal-to-detector distance was 45.31 mm. The structure was solved by direct methods (Altomare *et al.* 1994) and expanded using Fourier techniques (Beurskens *et al.* 1999). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of

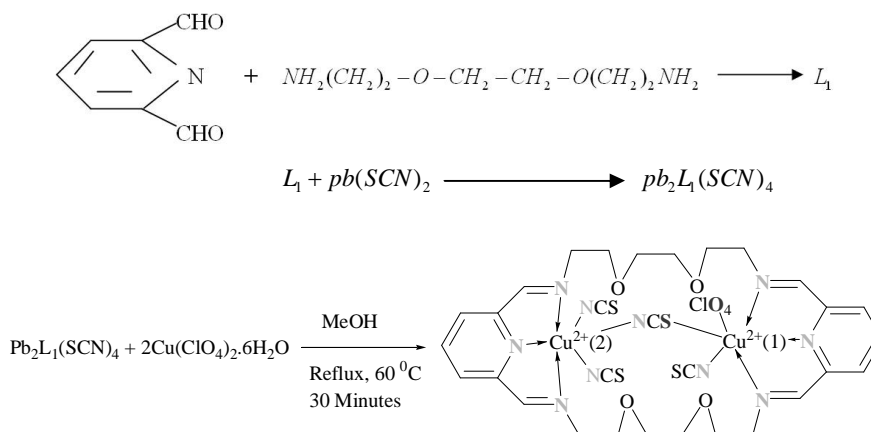
full-matrix least-squares refinement on F^2 was based on 9391 observed reflections and 503 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.0324$$

$$wR^2 = [\sum (w (F_o^2 - F_c^2)^2) / \sum w(F_o^2)]^{1/2} = 0.0742$$

RESULTS AND DISCUSSION

The blocked type crystalline thiocyanate bridged complex of macrocyclic ligand L_1 with Cu^{2+} was prepared in 34% yield by the reaction of $Pb_2L_1(SCN)_4$ with an excess of copper perchlorate in methanol solution. Replacement of Pb^{2+} ion from the macrocycle was effected readily as judged by instantaneous color change on mixing of reactants. The analytical data showed the suggested formula for macrocyclic complex as $[Cu_2L_1(SCN)_3(ClO_4)]$, where, $L_1 =$ Schiff's base type macrocyclic ligand ($C_{26}H_{34}N_6O_4$).



Scheme1. Preparation of $[Cu_2L_1(SCN)_3(ClO_4)]$ complex.

The formation of $[Cu_2L_1(SCN)_3(ClO_4)]$ complex was confirmed by ESI-MS spectrometry. The data were in good agreement with the formation of macrocyclic frame. Measured and calculated isotope patterns of the complex ion are shown in Fig. 1.

The IR spectra of the complex indicate that the macrocycle has remained unchanged during the metal exchange reaction. There is no absorption at 3200 - 3400/cm indicates that no hydrolysis to amine and carbonyl compound had occurred. Complex $[Cu_2L_1(SCN)_3(ClO_4)]$ showed two strong bands at 2098 and 2075/cm are due to Cu-NCS-Cu bridging (Kazuo 2008, Mitchel *et al.* 1960) mode and Cu-NCS mode, respectively. The strong band 1589 is assigned to $\nu(C=N)$ vibration (Drew *et al.* 1977, Drew *et al.* 1979).

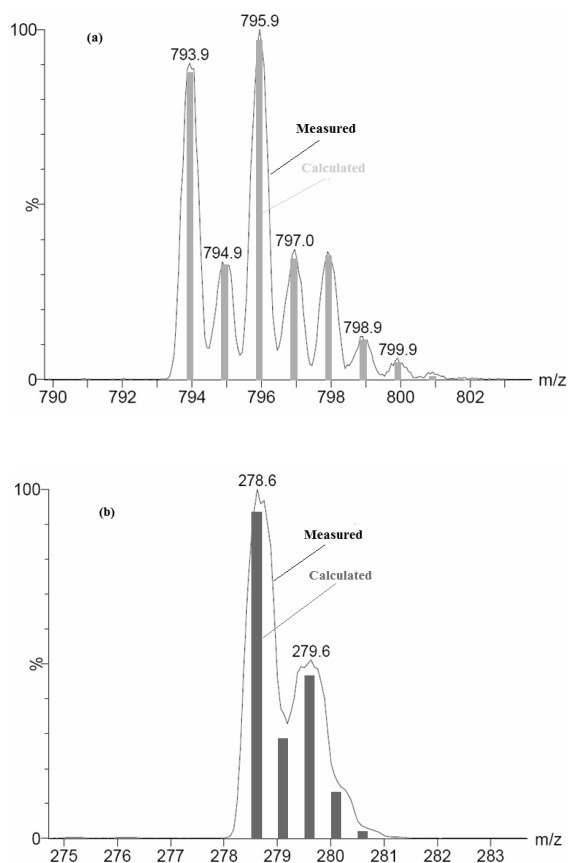


Fig. 1. ESI-MS spectra of (a) $[\text{Cu}_2\text{L}_1(\text{SCN})_3]^+$ and (b) $[\text{Cu}_2\text{L}_1]^{2+}$ ion measured in CH_3CN .

The two strong bands of ClO_4^- appeared at 1110 and 1090/ cm^{-1} indicated the presence of uni-dentate perchlorate ion (Lewis *et al.* 1975). The observed bands at 621 and 667/ cm^{-1} also support the presence of coordinated ClO_4^- ion (Lewis *et al.* 1975). Crystal data and details pertaining to the data collection are given Table 1.

The crystal structure of $[\text{Cu}_2\text{L}_1(\text{SCN})_3(\text{ClO}_4)]$ is shown in Fig. 2. The macrocycle L_1 binds two copper ions $[\text{Cu}(1)\text{-Cu}(2)$ 6.064 Å] (Drew *et al.* 1981) into the ring to afford copper pairs in which a SCN^- unit bridged. The two metal ions have different coordination geometry. One $\text{Cu}^{2+}(2)$ ion has a five coordination (distorted square pyramidal) geometry attained by imine $[\text{Cu}(2)\text{-N}(4)$ 2.057(2) Å, $\text{Cu}(2)\text{-N}(6)$ 2.064 Å], pyridine $[\text{Cu}(2)\text{-N}(5)$ 1.951 Å], bridged thiocyanate nitrogen $[\text{Cu}(2)\text{-N}(9)$ 2.003 Å], and nonbridged thiocyanate nitrogen $[\text{Cu}(2)\text{-N}(8)$ 1.987 Å]. On the other hand $\text{Cu}^{2+}(1)$ ion attained six coordination (octahedral) by imine $[\text{Cu}(1)\text{-N}(1)$ 2.081 Å, $\text{Cu}(1)\text{-N}(3)$ 2.070 Å], pyridine $[\text{Cu}(1)\text{-N}(2)$ 1.926 Å], nonbridged thiocyanate $[\text{Cu}(1)\text{-N}(7)$ 1.906 Å],

bridged thiocyanate sulfur [Cu(1)-S(3) 2.002 Å], and perchlorate oxygen [Cu(1)-O(7) 2.657 Å].

Table 1. Crystallographic data and details of the structure determinations for [Cu₂L₁(SCN)₃(ClO₄)].

Empirical formula	C ₂₉ H ₃₄ ClCu ₂ N ₉ O ₈ S ₃
Formula weight	895.37
Crystal color, habit	Colorless, prism
Crystal dimensions	0.45 × 0.44 × 0.42 mm
Crystal system	Monoclinic
Lattice type	Primitive
Detector position	45.31 mm
Pixel size	0.137 mm
Lattice parameters	$\alpha = 11.8661(16)$ Å $\beta = 11.5475(16)$ Å $\gamma = 26.930(4)$ Å $\beta = 93.0340(19)$ o $V = 3684.8(9)$ Å ³
Space group	$P2_1/n$ (Roma # 14)
Z value	4
Dcalc	1.614 g/cm ³
F ₀₀₀	1832.00
m(MoK α)	14.572/cm
Goniometer	Rigaku AFC10
Radiation	MoK α ($\lambda = 0.71075$ Å) graphite monochromated
$2\theta_{\text{max}}$	54.9°
No. of reflections measured	Total: 14573 Unique: 8332 ($R_{\text{int}} = 0.034$)
Refinement	Full-matrix least-squares on F^2
Function minimized	$\sum w (F_o^2 - F_c^2)^2$
Least squares weights	$1/[0.0003F_o^2 + 1.0000s(F_o^2)]/(4F_o^2)$
No. observations ($I > 2.00s(I)$)	9391
No. variables	503
Goodness of fit indicator	1.010
Max shift/error in final cycle	0.000
Maximum peak in final diff. map	0.65 e-/Å ³
Minimum peak in final diff. map	-0.79 e-/Å ³

Concerning bond distances, the copper(II)-imine nitrogen bonds (average 2.068 Å) and copper(II)-pyridine nitrogen bonds (average 1.939 Å) fall well within the range of distances observed for typical copper-nitrogen (Drew *et al.* 1981) coordination compounds.

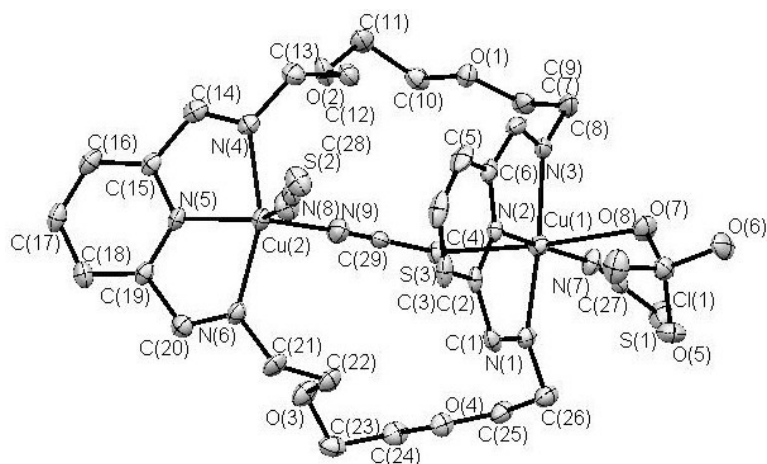


Fig. 2. ORTEP presentation of $[\text{Cu}_2\text{L}_1(\text{SCN})_3(\text{ClO}_4)]$ complex.

The perchlorate ion is weakly coordinated to Cu(1) through a single oxygen atom with separation (Lewis *et al.* 1975) of 2.657 Å fall within the range 2.56 to 2.83 Å. The bond distance between copper-thiocyanate bridged nitrogen [Cu(2)-N(9) 2.003 Å] is slightly longer than copper-non bridged thiocyanate nitrogen bond (average 1.945 Å). Again the C-N bond distance [C(29)-N(9) 1.167 Å] in bridging thiocyanate group slight longer than that in nonbridged mode [C(27)-N(7) 1.161 Å or C(28)-N(8) 1.161 Å]. Both of these variations in bond distances confirm bridging of one SCN⁻ unit. The selected bond lengths and bond angles are listed in Tables 2 and 3, respectively.

Table 2. Selected bond lengths (Å) for $[\text{Cu}_2\text{L}_1(\text{SCN})_3(\text{ClO}_4)]$.

Cu(1)-N(1)	2.081(2)	Cu(1)-S(3)	2.002(2)	Cu(2)-N(4)	2.057(2)
Cu(1)-N(2)	1.926(19)	Cu(2)-N(5)	1.951(19)	N(7)-C(27)	1.161(3)
Cu(1)-N(3)	2.070(19)	Cu(2)-N(6)	2.064(19)	N(8)-C(28)	1.161(3)
Cu(1)-N(7)	1.906(2)	Cu(2)-N(8)	1.987(2)	N(9)-C(29)	1.167(3)
Cu(1)-O(7)	2.657(19)	Cu(2)-N(9)	2.003(2)		

Table 3. Selected bond angles (°) for $[\text{Cu}_2\text{L}_1(\text{SCN})_3(\text{ClO}_4)]$.

N(1)-Cu(1)-N(2)	78.91(8)	N(1)-Cu(1)-N(3)	156.47(8)	N(5)-Cu(2)-N(6)	78.41(8)
N(1)-Cu(1)-N(7)	99.83(8)	N(2)-Cu(1)-N(3)	78.66(8)	N(5)-Cu(2)-N(9)	121.79(8)
N(2)-Cu(1)-N(7)	172.48(8)	N(3)-Cu(1)-N(7)	101.47(8)	N(6)-Cu(2)-N(9)	97.39(8)
O(7)-Cu(1)-S(3)	172.28(8)	N(7)-Cu(1)-S(3)	89.40(8)	N(5)-Cu(2)-N(8)	128.75(8)
N(4)-Cu(2)-N(5)	78.59(8)	N(4)-Cu(2)-N(6)	156.90(8)	N(6)-Cu(2)-N(8)	97.85(8)
N(4)-Cu(2)-N(8)	94.79(8)	N(4)-Cu(2)-N(9)	156.90(8)	N(8)-Cu(2)-N(9)	109.42(9)

CONCLUSIONS

The macrocyclic ligand L₁ showed di-nucleating properties toward Cu²⁺. Elemental analysis and mass spectra data confirm the formation of macrocyclic complex [Cu₂L₁(SCN)₃(ClO₄)]. Both infrared and X-ray crystallographic data have confirmed the octahedral geometry of one Cu²⁺(1), while distorted square pyramidal for the other Cu²⁺(2). Perchlorate ion employed to attach as a coordination site rather than its usual counter ionic nature. One of the thiocyanate was found as a bridging ligand between two Cu²⁺ while the other two are monodentate through nitrogen coordination to different Cu²⁺.

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SUPPLEMENTARY INFORMATIONS

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC). Copies can be obtained free of charge via www.ccdc.cam.ac.uk/ or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0)1223 762911 or e-mail: deposit@ccdc.cam.ac.uk), quoting the deposition numbers CCDC 826014 ([Cu₂L₁(SCN)₃(ClO₄)]).

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