



Synthesis and Crystal Structure of a Mixed Ligand Copper(II) Complex with Tridentate Schiff Base

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Abstract

A dimeric thiocyanato bridged copper(II) complex $[\text{Cu}_2(\text{L})_2(\text{NCS})_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$, (**I**) where L is 2-[(2-piperazine-1-ylethylimino)methyl]phenolate, have been synthesized and the molecular structures have been determined by X-ray crystallography. Copper(II) shows square pyramidal coordination in **I** with one O and two N atoms of the tridentate ligands in mer orientations and the fourth coordination sites of basal planes are occupied by the N atom of the thiocyanate. The fifth coordination site of central copper(II) is occupied by a symmetry related S of thiocyanate at the apical position, thereby creating centrosymmetric dimers. Two $[\text{CuL}(\text{NCS})]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$ moieties are connected through two end-to-end thiocyanato (N,S) bridges to compose the dimeric unit.

Keywords: Schiff base, Cu(II) dimer, IR, X-ray structure.

Introduction

Transition metal complexes with Schiff base ligands are of continuing interest for many years. First row transition metal complexes of acyclic Schiff base ligands including copper have received much attention due to their important catalytic, magnetic and biological properties in addition to the structural diversity [1–3]. Thiocyanate, a pseudohalide, bridges the metal centers in a 1,3 coordination mode where both nitrogen and sulphur atoms produce double or single thiocyanate bridging complexes [4-5]. In this communication we describe the synthesis and characterization of a mixed ligand end-to-end thiocyanato bridged copper(II) dimer $[\text{Cu}_2(\text{L})_2(\text{NCS})_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (**I**) containing a tridentate (NNO) Schiff base ligand 2-[(2-piperazine-1-ylethylimino)methyl]phenolate (HL) shown in Fig. 1.

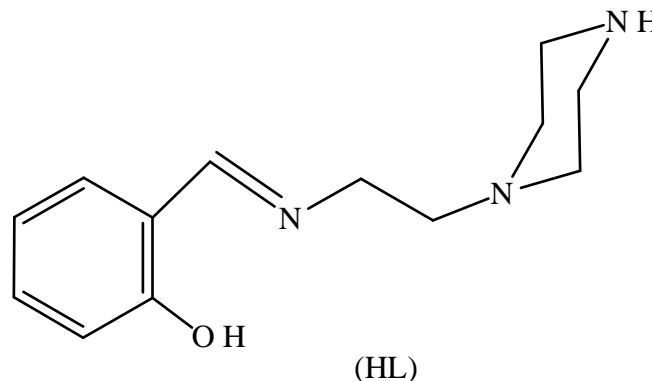


Fig. 1. Schiff base ligand 2-[(2-piperazine-1-ylethylimino)methyl]phenol (HL)

Experimental

All chemicals were of reagent grade and were used without further purification. Elemental analysis for C, H and N was performed using a PerkinElmer model 2400 Series II elemental analyzer. IR spectra were recorded on a Shimadzu 8400S FT-IR spectrophotometer with KBr discs (4000–400 cm^{-1}).

Caution! Although no problems were encountered in the present work, compounds of perchlorate salts containing organic ligands are potentially explosive. Therefore, only a small amount of these materials should be used at a time and handled with proper care.

Synthesis of $[\text{Cu}_2(\text{L})_2(\text{NCS})_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$. The tridentate Schiff base ligand (HL) was obtained by the usual method of condensation of salicylaldehyde with 1-(2-aminoethyl) piperazine in 1:1 M ratio in methanol. The ligand was not isolated. A methanol solution (10ml) of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.37 g, 1 mmol) was added to it (1 mmol) and stirred for 15 minutes. Ammonium thiocyanate (0.076 g, 1 mmol) dissolved in same volume of methanol added with constant stirring. Stirring was continued and green precipitate started to separate after half an hour were collected by filtration, washed with Et_2O and finally dried. The product was recrystallized from acetonitrile. The yield was 40%. For $\text{C}_{28}\text{H}_{46}\text{Cl}_2\text{Cu}_2\text{N}_8\text{O}_{14}\text{S}_2$ Anal. Calcd., %: C, 34.29; H, 4.73; N, 11.42. Found, %: C, 34.42; H, 4.71; N, 11.45.

Crystal structure determination. Diffraction-quality crystals were obtained by cooling acetonitrile solution of **I** at 4 °C. A green block-like specimen of $\text{C}_{28}\text{H}_{46}\text{Cl}_2\text{Cu}_2\text{N}_8\text{O}_{14}\text{S}_2$, approximate dimensions 0.080 mm \times 0.140 mm \times 0.200 mm was mounted onto quartz fibers, and the X-ray diffraction intensity data were measured at 153 K with a Bruker Kappa diffractometer equipped with a CCD detector, employing MoK radiation ($\lambda = 0.71073 \text{ \AA}$), with the SMART suite of programs [6]. All data were processed and corrected for Lorentz and polarization effects with SAINT [7] and for absorption effects with SADABS [8]. Structural solution and refinement were carried out with the SHELXTL suite of programs [9]. The structures were solved by direct methods or Patterson maps to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The ratio of minimum to maximum apparent transmission was 0.767. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7630 and 0.8940. The crystallographic data and experimental details for structural analysis of the complex are summarized in Table 1. Selected bond parameters are collected in Table 2. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no 1471367); deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>.

Table 1. Crystallographic data and structure refinement parameters of **I**

Parameter	Value
<i>F</i> _w	980.82
Crystal shape/color	Block/green
Crystal siz, mm	0.200 \times 0.140 \times 0.080
Crystal system	monoclinic
Space group	<i>C2/c</i>
<i>a</i> , Å	25.1158(17)
<i>b</i> , Å	12.3230(7)
<i>c</i> , Å	12.8634(9)
<i>r</i> , deg	90
<i>s</i> , deg	105.034(3)
<i>x</i> , deg	90
<i>V</i> , Å ³	3845.0(4)
<i>Z</i>	8
λ , Å	0.71073
μ , cm^{-1}	1.430
$T_{\text{min}}/T_{\text{max}}$	0.69/0.89
Temp, K	153.0(2)
Measured reflections	29748
Unique reflections	5196
Observed reflections	3814
Parameters/restraints	265/7
Goodness of fit on F^2	1.026
R_1 , wR_2 (<i>I</i> \geq 2 (<i>I</i>))*	0.0469, 0.1188
R_1 , wR_2 (all data)*	0.0744, 0.1388

$$*R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}.$$

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Cu(1)–N(1)	1.924(2)	Cu(1)–N(2)	2.154(3)
Cu(1)–N(4)	1.942(2)	Cu(1)–O(1)	1.931(2)
Cu(1)–S(1A)	2.9140(9)		
Angle	, deg	Angle	, deg
N(4)Cu(1)N(1)	172.6(1)	N(4)Cu(1)O(1)	90.3(1)
N(1)Cu(1)O(1)	92.7(1)	N(4)Cu(1)N(2)	92.3(1)
N(1)Cu(1)N(2)	83.8(1)	O(1)Cu(1)N(2)	171.00(9)
N(4)Cu(1)S(1A)	89.97(8)	N(1)Cu(1)S(1A)	96.77(8)
O(1)Cu(1)S(1A)	91.86(7)	N(2)Cu(1)S(1A)	96.77(7)

* Symmetry code for (A): $-x, y, 1/2-z$

Results and Discussion

The reaction of copper(II) perchlorate, ammonium thiocyanate and tridentate Schiff base (HL) in 1:1:1 ratio in methanol resulted a novel end-to-end thiocyanato-bridged dimeric copper(II) compound **I**. Two $[\text{CuL}(\text{NCS})](\text{ClO}_4)(\text{H}_2\text{O})_2$ moieties are connected through two end-to-end thiocyanato (N,S) bridges to compose the dimeric unit and secondary nitrogen atom of piperazinyl ring coordinates one extra proton (L = aminoethylpiperazineH) and stays away from the coordination. The complex has been characterized by microanalytical and single crystal X-ray diffraction studies. In the IR spectra, the distinct band due to azomethine (C=N) group at 1637 cm^{-1} was noticed. The band at 1091 cm^{-1} is indicative of the presence of ClO_4^- anion. The strong band at 2129 cm^{-1} indicates the presence of thiocyanate group.

The structural representation of **I** with the atom-numbering scheme is shown in Fig. 2. Cu (II) centers are square-pyramidal coordinated equatorially by one oxygen atom O(1) and two nitrogen atoms, N(1) and N(2), of the Schiff base ligand and a nitrogen atom, N(4), of one of the bridging thiocyanate, defining the basal plane, and with one symmetry related ($-x, y, 1/2-z$) thiocyanate S atom, S(1A), occupying the apical position. Deviation of the Cu atom from the

least-squares plane defined by the four basal donor atoms is 0.13 Å . Each of the coordinating atoms O(1), N(1), N(2) and N(4) deviates 0.02 Å from the least-square basal plane. The Addison parameter (trigonality index, $\tau = (\alpha - \beta)/60$, where α and β are the two largest L–M–L angles of the coordination sphere) [10] is 0.027 , and this confirms the square-pyramidal geometry ($\tau = 0$ infers a perfect square pyramid and $\tau = 1$ infers a perfect trigonal bipyramid). Sum of the different angles around the metal centre in the equatorial plane is $\sim 359.1^\circ$. The bond length and angles are comparable to those observed in other related copper(II) compounds [11–14]. Five membered chelate ring, Cu(1)–N(1)–C(8)–C(9)–N(2), incorporating the piperazine fragment from the starting diamine assumes a twist-boat conformation with puckering parameters $Q(2) = 0.423(3)\text{ Å}$ and $\phi(2) = 267.7(3)^\circ$. The bridging NCS⁻ groups in the complex are quasi-linear and shows bent coordination modes with copper atoms (N(4)–C(14)–S(1)/Cu(1)–N(4)–C(14)/Cu(1)–S(1)–C(14)ⁱ = $179.3(3)^\circ / 175.6(2)^\circ / 93.4(1)^\circ$). While the Cu–N and Cu–O bond lengths fall in the range $1.924\text{--}2.154\text{ Å}$, the Cu–S bond distance of 2.914 Å is comparatively larger as expected. The two Cu(II) centres are separated by a distance of 5.65 Å .

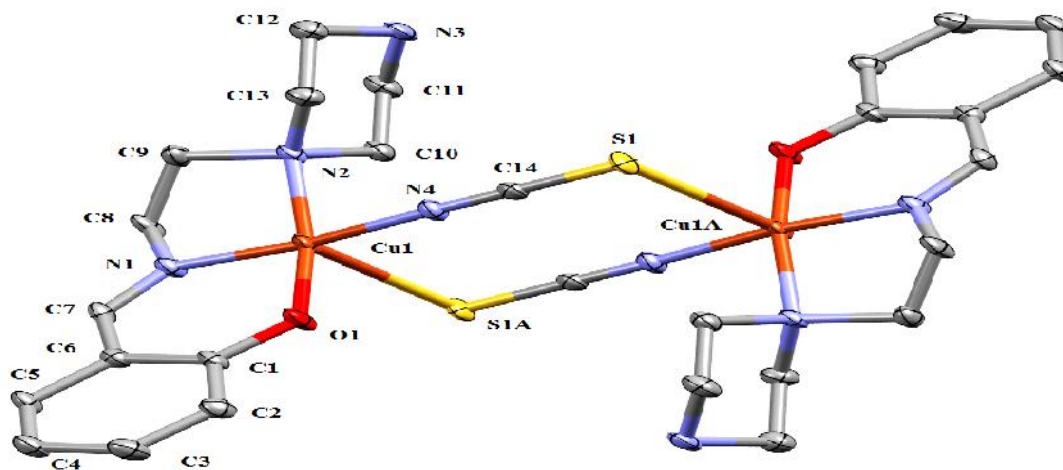


Fig. 2. ORTEP view of **I** with atom labelling scheme showing 50% probability thermal ellipsoids for all non-hydrogen atoms

In summary, synthesis and characterization of a mixed ligand copper (II) complex containing a tridentate NNO Schiff base ligand has been discussed. Structural studies reveal that I is a thiocyanato-bridged binuclear species in which each copper(II) ion adopts a distorted square pyramidal geometry. Interestingly, in a similar Schiff base, piperidine moiety in the amine part instead of piperazine resulted in a polymeric EE thiocyanato bridged Cu(II) complex [4].

Acknowledgments

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