Journal of Structural Chemistry. Vol. 59, No. 4, pp. 975-980, 2018.
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A TEMPLATE-DIRECTED APPROACH FOR THE SYNTHESIS OF A NEW MONO-CONDENSED SCHIFF BASE COMPLEX OF COPPER(II)

S. Thakurta[1] and G. Pilet[2]

In this paper, the formation of Schiff base compounds has been explained by the templating effect of a metal ion modulated by counter anions. It is shown that a dicondensed Schiff ligand can utilize the N_2O_2 compartment to form a stable copper complex. However, in the presence of a strongly coordinating thiocyanate ion, the dicondensed ligand is converted to the corresponding monocondensed ligand to yield a square planar copper(II) complex coordinated by the NNO donor set of the Schiff base and the terminal thiocyanate coligand. This template approach provides a methodology to trap the monocondensed ligand HL^2 [2-((E)-(3-aminopropylimino)methyl)-6-methoxyphenol] as its Cu(II) compound [CuL^2(NCS)]. We report herein the crystal structure and spectroscopic studies of this newly synthesized complex.

DOI: 10.1134/S0022476618040339

Keywords: template synthesis, monocondensed ligand, copper(II), crystal structure, hydrogen bonding.

INTRODUCTION

Although the di-Schiff base ligands formed by the 1:2 condensation of several diamines with salicylaldehyde and their derivatives have been well known for many years. The corresponding monocondensed Schiff bases are not explored much. The development of routes to unsymmetrical N,O donor ligands is of interest since such ligands may be useful in preparing synthetic analogues of the metal-binding sites of zinc and copper proteins [1]. The synthesis of monocondensation products of diamines and salicylaldehyde derivatives, often referred to as “half units”, where one primary amine group forms an imine bond and another is unchanged, is quite challenging. One convenient method is the condensation with a large excess of diamines in chloroform, as described by Costes et al. [2], but problems of purification appear formidable. Recent studies reveal that the stability of a Schiff base during a particular reaction can be rationalized in terms of the geometrical preferences of the corresponding metal ion and coordinating ability of the counter anion [3-6]. This cation/anion directed templated approach is an effective synthetic methodology because a templating agent contains the required information to organize a collection of building blocks so that they can be linked together in a specific manner [7]. In our previous research on the use of metal templates, the stability and coordination behavior of NNO donor mono- and NNOO donor bis-Schiff base ligands were monitored upon their reaction with cobalt perchlorate [8]. In a similar work, we reported the difference in the coordination behavior of a dicondensed Schiff base ligand upon the reaction with two different metal ions: copper(II) and cobalt(III) [9].

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[1] Department of Chemistry, Prabhu Jagatbandhu College, Howrah, West Bengal, India; sthakurtaju@yahoo.co.in.
[2] Groupe de Cristallographie et Ingénierie Moléculaire, Laboratoire des Multimatériaux et Interfaces UMR 5615 CNRS – Université Claude Bernard Lyon 1, Cedex, France. The text was submitted by the authors in English. *Zhurnal Strukturnoi Khimii*, Vol. 59, No. 4, pp. 1013-1017, May-June, 2018. Original article submitted November 23, 2016.

In this work, we investigate the influence of a strongly coordinating counter anion on copper(II) compounds of Schiff bases derived from the condensation of 1,3-diaminopropane and 3-methoxysalicyaldehyde. The dicondensed H_2L^1 ligand N,N′-bis(3-methoxysalicylidenimino)-1,3-diamino-propane resulted in complex $[CuL^1(H_2O)]$ (**1**) in which the central copper ion occupies the N_2O_2 compartment of the ligand [10]. However, in the presence of a thiocyanate ion, the tetradentate ligand H_2L^1 undergoes partial hydrolysis to the monocondensed ligand 2-((E)-(3-aminopropylimino)methyl)-6-methoxyphenol (HL^2), which results in a new complex $[CuL^2(NCS)]$ (**2**) upon its reaction with a copper(II) ion. The observations have been explained by the templating effect of Cu(II) modulated by the counter anion. Complex **2** has been completely characterized by the elemental analysis, FT-IR, UV–Vis spectroscopy, and the single crystal X-ray diffraction analysis.

EXPERIMENTAL

Materials. All the chemicals and solvents employed for the synthesis were of analytical grade. 1,3-Diaminopropane and 3-methoxy-2-hydroxybenzaldehyde were purchased from Aldrich Co., USA and $Cu(NO_3)_2 \cdot 3H_2O$ was from Merck, India Ltd. Sodium thiocyanate (Aldrich, USA) was used as received.

Synthesis of the complex. A solution of 1,3-diaminopropane (0.08 mL, 1 mmol) was added to a methanol solution of 3-methoxysalicylaldehyde (0.304 g, 2 mmol). The mixture was then refluxed for 45 min and filtered. The filtrate was added dropwise to a clear solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.930 g, 1 mmol) in methanol (25 mL), and immediately an intense blue colored solution was produced. The solution was heated to boiling followed by the addition of sodium thiocyanate (0.81 g, 1 mmol) in a minimum volume of methanol. The solution on being concentrated in the open atmosphere yielded brown, needle-shaped single crystals after four days.

Anal. Calc. for C12 H15 Cu1 N3 O2 S1 (328.88): C 43.84, H 4.60, N 12.78. **Found:** C 43.88, H 4.54, N 12.71%.

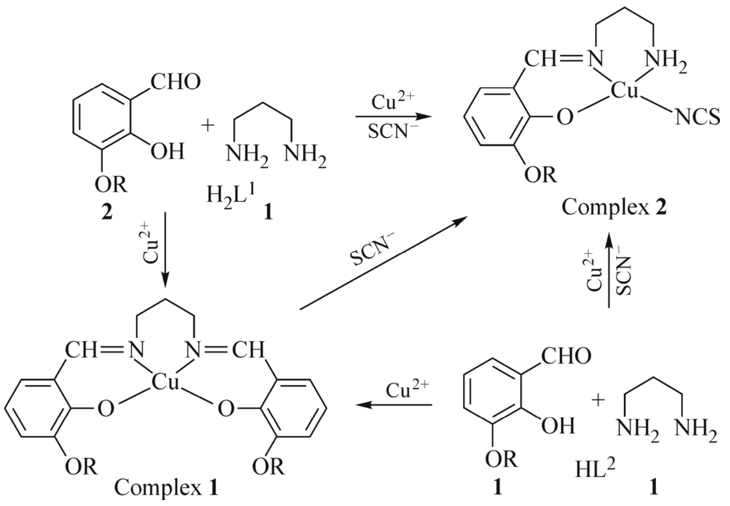
Physical measurements. The FT-IR spectra (4000-200 cm^{-1}) of the complexes were recorded on a Perkin Elmer Spectrum RX I FT-IR system with a solid KBr disc. The electronic spectra were recorded on a Perkin Elmer Lambda-40 UV/Vis spectrometer using HPLC grade acetonitrile as a solvent. C, H, N microanalyses were carried out with a Perkin Elmer 2400 II elemental analyzer.

X-ray crystallographic data collection and structure refinement. The air stable single crystal of complex **2** ($C_{12}H_{15}Cu_1N_3O_2S_1$, $M = 328.88$) has dimensions of 0.02×0.02×0.10 mm with a monoclinic crystal system and the $C2/c$ (No. 15) space group: $a = 20.691(5)$ Å, $b = 7.212(5)$ Å, $c = 18.629(5)$ Å, $\beta = 106.537(5)°$, $V = 2665(2)$ Å^3, $Z = 4$, $D_{calc} = 1.639$ g cm^{-3}, $\mu = 1.796$ mm^{-1}, $F(000) = 1352$.

Intensity data were collected on the single crystals of complex **2** at 293 K on an Oxford Diffraction XCALIBUR diffractometer equipped with a molybdenum X-ray tube and a graphite monochromator (λ/MoK_α = 0.71069 Å, θ = 2.6 to 29.3°). The CrysAlis RED [11] program was used for the data reduction. The structure was solved by direct methods using the SIR97 program [12] and refined by full-matrix least-squares methods with CRYSTALS programs [13]. Data collection: Total = 27638, Unique Data = 3368, $R_{int} = 0.058$. The final refinement factors are $R_1 = 0.0485$ and $wR_2 = 0.0524$ for 2702 observed reflections with $I > 2\sigma(I)$; Goodness-of-fit = 1.1223. All the H atoms were generated geometrically and included in the refinement in the riding model.

RESULTS AND DISCUSSION

Synthetic procedures and discussion. Two types of ligands H_2L^1 and HL^2 are prepared by refluxing 1,3-diaminopropane and 3-methoxysalicylaldehyde in 1:2 and 1:1 ratios, respectively. The ligands are not isolated and the methanol solutions are used for the syntheses of the complexes. In order to understand the correlation between the ligands as the starting material and the complexes as the products, the synthesis is carried out in different sets (Scheme 1).



Scheme 1.

When the methanol solution of the dicondensed Schiff base ligand H_2L^1 is added to a methanol solution of Cu(II) nitrate salt, the ligand remains intact in complex **1**. When the same reaction is carried out in the presence of thiocyanate, we obtain complex **2** in which the corresponding tridentate mono-condensed Schiff base ligand HL^2 is present. Similarly, HL^2 on addition to methanol solution of $Cu(NO_3)_2$ yields exclusively complex **1**, but in presence of SCN^-, it results complex **2**. Interestingly, when a methanol solution of sodium thiocyanate is added to the solution of complex **1**, it transforms into complex **2**. Thus, it is obvious that the nature of Schiff bases present in the complexes does not depend upon the ratios of the diamine:carbonyl compounds used for their preparation; instead the counter anions present in the Cu(II) salt dictate their composition.

The formation of the Schiff base compounds has been explained by the templating effect of Cu(II) modulated by the counter anions. In general, Cu(II) prefers to be coordinated with a dinegetive, tetradentate ligand to satisfy its charge and four coordination sites. On the other hand, the thiocyanate ion that have similar crystal field stabilization energy as the Schiff base, occupies a coordination site, leaving the other three sites to be coordinated by a Schiff base and that can be achieved most efficiently by a mononegetive, tridentate Schiff base ligand. It is concluded that the di-condensed Schiff ligands are stable enough to form the copper complexes, while they are converted to the corresponding mono-condensed ligands to yield the copper(II) complexes with thiocyanate as terminal co-ligand. This provides a methodology to trap the mono-condensed ligand as its Cu(II) compound.

Description of the crystal structure of complex [Cu(L^2)(NCS)] (2). The perspective view of complex **2** with the atom labeling scheme is shown in Fig. 1. The monocondensed ligand (HL^2) offers the N4 imine nitrogen atom, the N1 primary amine nitrogen atom, and the O14 phenolic oxygen atom as the coordinating sites. The crystal structure features a four-coordinate copper centre with the NNO donor set of the Schiff base. The N-coordinated thiocyanato ligand completes the coordination of the Cu(II) centre to a square planar geometry. However, the square plane is somewhat distorted, which is manifested in the deviations of *trans* angles from 180° and *cis* angles from 90° (Table 1), as well as in a certain “twisting” of the square, which can be interpreted as a (minor) distortion towards the tetrahedral geometry. Thus, the N1/Cu1/N4 plane forms a dihedral angle of 16.43° with the O14/Cu1/N21 plane. The central copper atom deviates from the mean plane defined by N4, N1, O14, and N21 atoms by 0.056 Å. The terminal thiocyanate ligand bound through its nitrogen atom is almost linear and shows a bent coordination mode with metal (N21–C22–S23/Cu1–N21–C22 = 178.7(3)/165.7(3)°). The six-membered chelate ring CuC_3N_2, incorporating the trimethylene fragment from the starting diamine, assumes an *envelope* conformation and the $CuOC_3N$ chelate ring is almost planar. The fact that the Cu–N(amine) bond is longer than the Cu–N(imine) bond is quite evident from the difference in hybridization states (sp^2 for imine N and sp^3 for free NH_2). The Cu–N(thiocyanato) bond length is in agreement with the reported literature values for similar complexes [14]. Selected bond lengths and angles of complex **2** are summarized in Table 1.

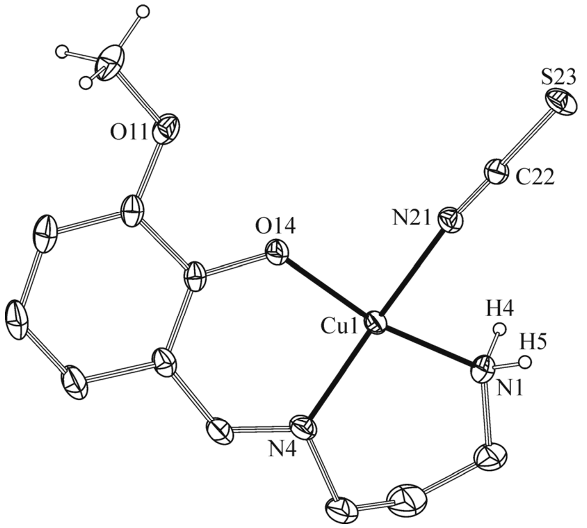


Fig. 1. ORTEP view of complex **2** with the atom labeling scheme. Thermal ellipsoids are drawn at the 40% probability level.

TABLE 1. Selected Bond Distances (Å) and Angles (deg.) for **2**

Bond Lengths	Å	Bond Angles	deg.
Cu1–O14	1.908(3)	O14–Cu1–N1	163.41(12)
Cu1–N1	2.013(3)	O14–Cu1–N4	92.88(12)
Cu1–N4	1.964(3)	O14–Cu1–N21	86.76(11)
Cu1–N21	2.000(3)	N1–Cu1–N4	96.00(12)
N21–C22	1.158(4)	N1–Cu1–N21	86.34(12)
S23–C22	1.624(3)	N4–Cu1–N21	172.07(12)

The uncondensed amine group also exhibits an intermolecular hydrogen bonding interaction, and thereby it plays a significant role in the stabilization of the complex. One of the two hydrogen atoms on N1, H4 is involved in a strong hydrogen bond with the phenolic oxygen atom (O14a) of the deprotonated Schiff base ligand of a neighboring centrosymmetrically related unit (1/2–*x*, 1/2–*y*, –*z*) forming an H-bonded dimeric entity (Fig. 2). The N1–H4…O14a angle is 164° and the donor (N1)-acceptor (O14a) distance is 2.976(4) Å. The Cu…Cu distance between the two H-bonded units (3.53 Å) is shorter than the two neighboring non-hydrogen bonded units. The H-bonding parameters are given in Table 2.

IR spectra. The solid state FT-IR spectrum of complex **2** is fully consistent with its single crystal structure. The strong $\nu_{C=N}$ stretching vibration at 1598 cm^{-1} is shifted considerably towards lower frequencies compared to that of the free Schiff base ligand (1641 cm^{-1}), indicating the coordination of the imino nitrogen atom to the central metal centre [15]. Ligand coordination to the metal centre is substantiated by prominent bands appearing at nearly 455 cm^{-1} and 375 cm^{-1}, which can be attributed to ν(M–N), and ν(M–O), respectively. The bands at 2930 cm^{-1} can be correlated to the alkyl C–H bond stretching of the methoxy group. The bands at 3295 cm^{-1}, 3292 cm^{-1}, and 3127 cm^{-1} for complex **2** may be assigned to ν(N–H) stretching vibrations of the NH_2 group. The presence of more than two bands in this region indicates the unequal involvement of the two H atoms in the hydrogen bonding. The sharp single peak at 2084 cm^{-1} corresponds to the N-bonded thiocyanate group.

Electronic spectra. The electronic spectral data for complex **2** in the HPLC grade acetonitrile solvent are in good agreement with its geometry [16]. Complex **2** shows a broad band centered at 355 nm, which is a typical *d-d* band for Cu(II) in the square planar environment [17]. The intense band in the 225-245 nm region can be attributed to the charge transfer transition from the coordinated unsaturated ligand to the metal ion (LMCT).

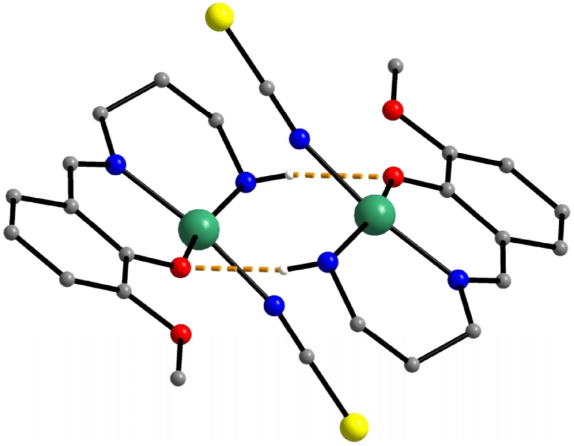


Fig. 2. Representation of the asymmetric unit of **2** containing the hydrogen bonded dimer. Dashed lines indicate hydrogen bonds.

TABLE 2. Hydrogen Bonding Parameters for **2**

D–H…A	*d*(D–H) Å	*d*(H…A) Å	*d*(D…A) Å	∠(DHA), deg.
N1–H4…O14	0.8600	2.1400	2.976(4)	164.00

CONCLUSIONS

In this work, the monocondensed ligand (HL^2) has been prepared conveniently as the Cu(II) compound [CuL^2(NCS)] (**2**) by the reaction of 1,3-diaminopropane, Cu(II), and 3-methoxy salicylaldehyde, followed by the reaction with a large excess of NaNCS. The observations indicate that the counter anions of metal salt play a very important role in the stability and hydrolysis of the Schiff base during the compound formation.

CIF file containing complete information on the studied structure was deposited with CCDC, deposition number 1509732, and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif.

S. Thakurta gratefully acknowledges Prof. (Dr.) Samiran Mitra of Jadavpur University for his valuable suggestions. We thank Jadavpur University, Kolkata, India for supporting this study.

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