

Scientific paper

Synthesis, Crystal Structure and Spectroscopic Studies of Copper Complexes with Tridentate Schiff Base Ligand

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Abstract

Four Cu(II) complexes [CuLX], where X = NO₃ (**1**), Br (**2**), Cl (**3**), ClO₄ (**4**) and L = benzoylacetoneacetohydrazid tridentate Schiff base, HL, have been synthesized and characterized by elemental analysis, FT-IR, UV-Vis spectroscopy. The structure of compound **1**, has been determined by single-crystal X-ray diffraction analysis. The structure of **1** is a mononuclear species, the coordination geometry around the copper(II) ion is four coordinated square planar, L acts as a tridentate ligand which forms one five-membered and one six-membered chelate rings with the Cu(II) metal center, and the fourth position at the Cu ion is occupied by the NO₃ anion. The nitrate ions play role in the H bonding network. In fact the amide NH groups act as H donor towards the nitrate oxygen. The formation of the copper complexes in solution was monitored by a UV/Vis titration experiment. The results revealed that the complexes were of the composition (ligand/metal) 1:1 in solution.

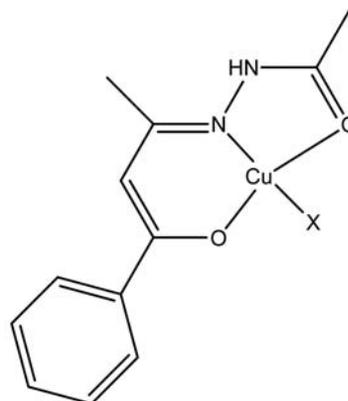
Keyword: Copper complex, mononuclear, tridentate Schiff base, formation constant, square planer.

1. Introduction

Schiff bases are an important class of ligands in inorganic chemistry and have remained a main and popular area of research due to their simple synthesis, interesting chemistry and diverse range of applications.^{1,2} The Schiff bases have played an important role in the improvement of coordination chemistry as they readily form stable complexes with most of the transition metals. Transition metal complexes of Schiff bases have attracted many researchers due to their formation of stable compounds and their potent biological activities such as antifungal, antibacterial, anticancer and herbicidal applications.^{1–8} The coordination chemistry of copper(II) complexes has received increased attention over the last decades. This is mainly due to their interesting characteristics in the fields of coordination chemistry and biological systems. Copper complexes containing Schiff base ligands have been reported as good models for a variety of enzymes.^{9–12}

In previous study,¹³ we reported the syntheses and crystal structures of mono- and di-nuclear copper(II) com-

plexes bearing salicylaldehydesemicarbazone tridentate Schiff bases ligand. The main goal of this study was the synthesis and characterizations of some new mononuclear complexes with a benzoylacetoneacetohydrazid tridentate



X = NO₃, (**1**); Br, (**2**); Cl, (**3**); ClO₄, (**4**)

Scheme 1. The structure of Cu complexes

Schiff bases ligand, CuLX (L = tridentate ligand and X = Cl, Br, NO₃, ClO₄), (Scheme 1). These compounds were characterized by elemental analysis, FT–IR, UV–Vis spectroscopy and X-ray crystallography. In addition, the formation constants, K_f , were determined spectrophotometrically. The effects of the anion ligands, X on the formation constants complexes were studied.

2. Experimental

2.1. Reagents

All chemicals were used as supplied by Merck and Fluka without further purification.

2.2. Physical Measurements

Infrared spectra were taken with an Equinox 55 Bruker FT-IR spectrometer using KBr pellets in the 400–4000 cm⁻¹ range. Absorption spectra were determined using GBC UV-Visible Cintra 101 spectrophotometer with 1 cm quartz, in the range 200–1100 nm at 25 °C. Elemental analyses (C, H, N) were performed by using a CHNS-O 2400II PARKIN-ELMER elemental analyzer.

2.3. UV-Vis Measurements

For purpose of the molar ratio method,^{14,15} a series of solutions has been prepared in which metal ion concentration has kept constant (1.0×10^{-2} M), while that of ligand has been varied for covering the molar ratios [ligand]/[Cu(II)] = 0.0–3.0 The spectra of all solutions prepared have been recorded within the wavelength range 400–1100 nm.

2.4. X-ray Crystallography

Diffraction images were measured at 200 K on a Nonius Kappa CCD diffractometer using Mo $K\alpha$, graphite monochromator ($\lambda = 0.71073$ Å) and data extracted using the DENZO/SCALEPACK package.¹⁶ The structures were solved by direct methods with the SIR92,¹⁵ and CRYSTALS software used to prepare material for publication.¹⁸ Atomic coordinates, bond lengths and angles and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. Crystallographic data for the complex **1** are summarized in Table 1.

2.5. Syntheses

2.5.1. Syntheses of Schiff Base Ligand, HL

The benzoylacetoneacetohydrazid tridentate Schiff base, HL, was prepared by condensation an equimolar amount of benzoylacetone (20 mmol, 3.24 g) and acetohydrazid (20 mmol, 1.48g) in methanol (30 ml). The mixture was refluxed for 2 hour during which a light yel-

Table 1. Crystallographic data of the complex **1**

Compound	1
Chemical formula	C ₁₂ H ₁₃ CuN ₃ O ₅
Formula weight	342.80
Temperature (K)	200
Space group	Monoclinic, $P\bar{1}$
Unit cell dimensions	
<i>a</i> (Å)	7.0013 (1)
<i>b</i> (Å)	2568.9198 (2)
<i>c</i> (Å)	11.1957 (3)
α (°)	85.5868 (14)
β (°)	72.8773 (15)
γ (°)	87.7203 (14)
<i>V</i> (Å ³)	666.10 (3)
<i>F</i> (000)	350
<i>D</i> _{calc} (g cm ⁻³)	1.709
Crystal size (mm)	0.38 × 0.19 × 0.15 mm
μ (mm ⁻¹)	1.67
θ range (°)	2.6–30
Limiting indices	–9 ≤ <i>h</i> ≤ 9 –12 ≤ <i>k</i> ≤ 12 –15 ≤ <i>l</i> ≤ 15
R [$F^2 > 2\sigma(F^2)$]	0.031
wR (F^2) (all data)	0.080

$$* w = 1/[\sigma^2(F^2) + (0.05P)^2 + 0.4P], \text{ where } P = (\max(F_o^2, 0) + 2F_c^2)/3$$

low precipitate was formed. The reaction mixture was then cooled to room temperature and the solid compound formed was filtered. The compound was recrystallized from warm acetone. Yield 67%. IR (KBr, cm⁻¹): $\nu_{C=N} = 1610$, $\nu_{C=O} = 1650$. Electronic spectra in acetone: λ_{\max} (nm), (log ϵ): 333 (2.66), 232 (4.29).

2.5.2. Syntheses of Complexes, 1–4

A CuX₂, (X = NO₃, Br, Cl, ClO₄), (2 mmol) was added to a solution of HL ligand (2 mmol, 0.434 g) in methanol (30 mL) and the resulting solution was stirred at room temperature for 2–12 h (dependent on X). The resulting green solution was filtered and allowed to crystallize at room temperature.

CuLNO₃, 1. After many days, green precipitates appeared upon slow evaporation of the solvents at room temperature. The resulting green precipitates were collected by filtration and recrystallized from methanol/2-propanol (1:1 v/v) and were washed with ethanol and dried in air. Yield 75%. Anal. Calcd. for C₁₂H₁₃CuN₃O₅: C, 42.05; H, 3.82; N, 12.26 Found: C, 41.60; H, 3.61; N, 12.22. IR (KBr, cm⁻¹): $\nu_{C=N} = 1560$, $\nu_{C=O} = 1591$. Electronic spectra in CH₃OH: λ_{\max} (nm), (log ϵ): 687 (1.94), 370 (4.47), 242 (4.57).

CuLBr, 2. Green needle shaped crystals appeared upon slow evaporation of the solvents at room temperature, and were washed with ethanol and dried in air. Yield 67%. Anal. Calcd. for C₁₂H₁₃BrCuN₂O₂: C, 39.96; H,

3.63; N, 7.77. Found: C, 40.26; H, 3.46; N, 7.83. IR (KBr, cm^{-1}): $\nu_{\text{C=N}} = 1550$, $\nu_{\text{C=O}} = 1589$. Electronic spectra in CH_3OH : λ_{max} (nm), ($\log \epsilon$): 683 (1.92), 375 (5.04), 237 (4.99).

CuLCl, 3. Green precipitate appeared upon fast evaporation of the solvent on a rotary evaporator, and were washed with ethanol and dried in air. Yield 38%. Anal. Calcd. for $\text{C}_{12}\text{H}_{13}\text{ClCuN}_2\text{O}_2$: C, 45.58; H, 4.14; N, 8.83. Found: C, 45.36; H, 4.08; N, 8.98. IR (KBr, cm^{-1}): $\nu_{\text{C=N}} = 1556$, $\nu_{\text{C=O}} = 11591$. Electronic spectra in CH_3OH : λ_{max} (nm), ($\log \epsilon$): 685 (1.90), 345 (4.64), 290 (4.85).

CuLClO₄, 4. Green precipitates appeared upon slow evaporation of the solvents at room temperature. The resulting green precipitates were collected by filtration and recrystallized from methanol/2-propanol (2:1 v/v) and were washed with ethanol and dried in air. Yield 40%. Anal. Calcd. for $\text{C}_{12}\text{H}_{13}\text{ClCuN}_2\text{O}_6$: C, 37.90; H, 3.45; N, 7.37. Found: C, 37.87; H, 3.81; N, 7.62. IR (KBr, cm^{-1}): $\nu_{\text{C=N}} = 1561$, $\nu_{\text{C=O}} = 1557$. Electronic spectra in CH_3OH : λ_{max} (nm), ($\log \epsilon$): 685 (1.83), 376 (4.42), 246 (4.68).

3. Result and Discussion

3.1. Description of Crystal Structures the Complex 1

Single crystals of complex **1** suitable for X-ray were obtained from saturation solution of **1** in methanol/2-propanol. The complex crystallized in the triclinic space group P1. The molecular structure of the copper complex with labeling of selected atoms is shown in Fig. 1. Selected bond lengths and angles are listed in Table 2.

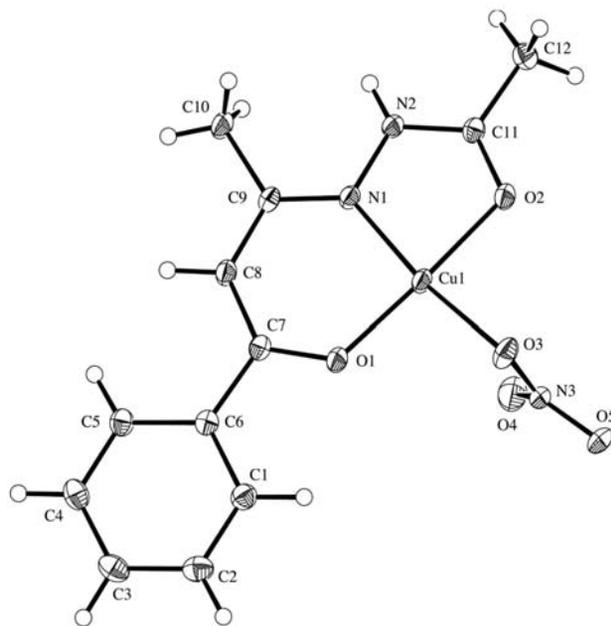


Fig. 1. The molecular structure of **1** with labelling of selected atoms, ellipsoids shows 30% probability levels.

The coordination geometry around the copper(II) ion in complex **1** is four coordinated square planer. In complex **1**, L acts as a tridentate ligand which forms one five-membered and one six-membered chelate rings with the Cu(II) metal center, and the fourth position at the Cu ion is occupied by the NO_3 anion.

Table 2. Selected bond lengths (Å) and angles (°) in complex **1**

Cu1–O1	1.8836 (12)	O1–Cu1–O2	175.16 (5)
Cu1–O2	1.9587 (12)	O1–Cu1–O3	93.37 (5)
Cu1–O3	1.9756 (12)	O2–Cu1–O3	90.83 (5)
Cu1–N1	1.9140 (12)	O1–Cu1–N1	93.83 (5)
C7–O1	1.2960 (18)	O2–Cu1–N1	82.21 (5)
C11–O2	1.2587 (19)	O3–Cu1–N1	171.07 (6)
C9–N1	1.3135 (19)	Cu1–O3–N3	108.57 (10)
C11–N2	1.3340 (19)	O3–N3–O4	118.18 (14)
N1–N2	1.3850 (18)	O5–N3–O4	123.31 (17)

The Cu1–O1, Cu1–O2 and Cu1–N1 bond lengths are 1.8836(12), 1.9587(12) and 1.9140(12) Å, respectively, which are good agreement with analogous square-planer Cu(II) complexes observed in the literature.^{13,19–21} The imine double bond distance of C9–N1 = 1.3135(19) Å that is similar to values reported for other Schiff base copper complexes.^{8,21,22} The angles Cu(II) with two donor atoms in the cis position at complex **1**, is in the range 82.21(5)–93.83(5)° and with two donor atoms in the trans position is in the range 171.07(6)–175.16(5)°, respectively (Table 2).

The nitrate ions play a significant role in the H bonding network. In fact the amide NH groups act as H donor towards the nitrate oxygen (Fig. 2). The major hydrogen bonding with the corresponding lengths and angle are listed in Table 3.

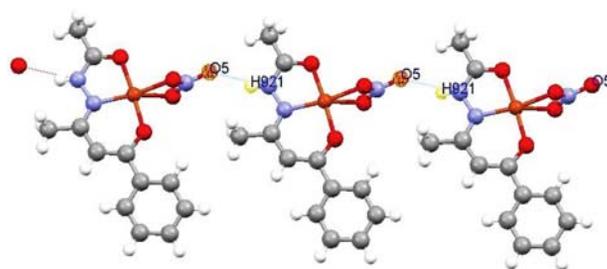


Fig. 2. The hydrogen bonding in complex **1** shown as dotted line

Table 3. Hydrogen bonding (Å) and angles (°) for complex **1**

D–H...A	D–H	H...A	D...A	D–H...A
N2–H921...O15 ^{vii}	0.83(3)	2.04(3)	2.84(2)	161(2)

Symmetry codes: (vii) x, y+1, z.

3. 2. Infrared Spectra

A comparison of the spectra of the free ligand and complexes indicates that the ligand is coordinated to the copper center. The IR spectrum of free tridentate ligand, HL, shows band at 1214, 1610 and 1650 cm^{-1} , which are assigned as $\nu\text{C-O}$, $\nu\text{C=N}$ and $\nu\text{C=O}$, respectively. The strong $\nu\text{C=N}$ band at 1550–1560 cm^{-1} for complexes 1–4 and $\nu\text{C=O}$ band is shifted approximately $\sim 50 \text{ cm}^{-1}$ toward lower energy in comparison to the free ligand, which indicates coordination of the imine nitrogen atom and carbonyl group to the copper ion.²³ Conversely, the $\nu\text{C-O}$ band is shifted toward higher energies compared with the free ligand, which suggests coordination of the deprotonated phenolic oxygen to the copper ion in the complexes 1–4.^{24,25}

3. 3. The Formation Constant of Copper Complexes

The formation of the copper complexes in solution was monitored by a UV/Vis titration experiment. Fig. 3 shows the changes in the absorption spectra of the copper bromide upon increasing the concentration of HL ligand in methanol. The absorption spectrum of the metal ion exhibits a band with a maximum at 905 nm, the absorbance of this band decreases and a new band appears at around 680 nm upon increasing the $[\text{HL}]/[\text{Cu}^{2+}]$ ratio. An apparent isosbestic point appears at around 780 nm, indicating the formation of a metal–ligand coordination compound. Furthermore, the Fig. 4 shows a maximum at $[\text{ligand}]/[\text{metal}] = 1$, which indicates the formation of a 1:1 complex in solution.

The mean K_f values obtained for the metal complexes under investigation are given in Table 4.

The formation constants of the copper complexes

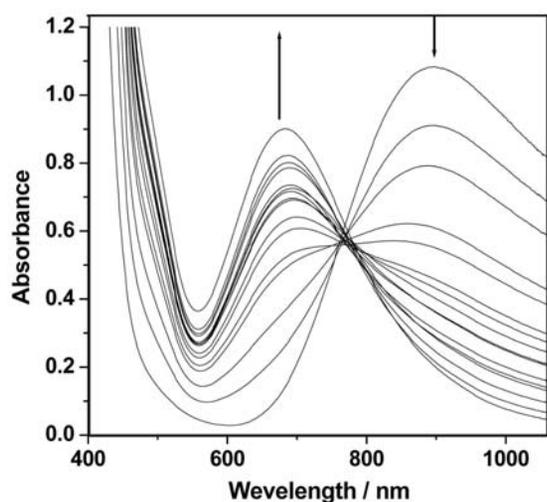


Fig. 3. Change of absorption spectra of the copper(II) bromide upon increasing the concentration of HL ligand in methanol.

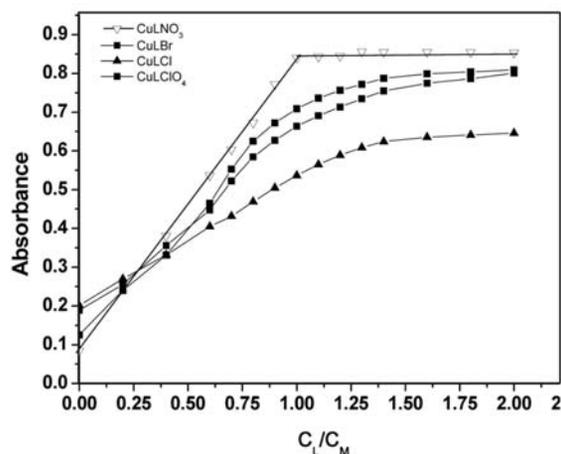


Fig. 4. The plot of absorbance at 680 nm vs. the $[\text{HL}]/[\text{Cu}^{2+}]$ ratio.

Table 4. The formation constants data of CuLX complexes

X	NO_3	Br	Cl	ClO_4
$\log K_f$	5.38 ± 0.09	3.68 ± 0.06	3.11 ± 0.03	3.77 ± 0.03

accord with mole ratio plots of complexes (Fig. 4). The complexes 2–4 were less completely formed at the equivalence point, their mole ratio plot was curved and the molar ratio was difficult to determine (Fig. 4). The weaker the complex, the greater is the curvature and the more uncertain is the identification of the molar ratio of the components of the complex.^{26,27}

This is in somewhat in agreement with classification of “hard and soft acids and bases” (HSAB),²⁸ however, other factors might as well be involved. This order indicating that a steric factor is effective.

4. Conclusion

In this paper we have designed tridentate Schiff base ligand that is suitable for yielding stable complexes of copper(II) with empirical formula $[\text{CuLX}]$. The crystal structure of the mononuclear $[\text{CuL}(\text{NO}_3)]$ complex revealed that the coordination geometry around the copper(II) ion is four coordinated square planar.

The formation constants of the copper complexes in solution were monitored by a UV/Vis titration experiment. The mole ratio plot shows a maximum at $[\text{ligand}]/[\text{metal}] = 1$, which indicates the formation of a 1:1 complex in solution. From a comparison of the anions (X) used, it can be concluded that the nature of X ion is reflected in the stability of the complexes. The $[\text{CuL}(\text{NO}_3)]$ complex is the most stable complex formed. The difference in formation constants of complexes is obvious and their stability follows the order: $\text{NO}_3^- > \text{ClO}_4^- > \text{Br}^- > \text{Cl}^-$.

5. Supplementary material

The deposition number of the studied complex **1** is CCDC 963047. This data can be obtained free-of-charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data-request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033.

6. Acknowledgments

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Povzetek

Štirje Cu(II) kompleksi [CuLX], z X = NO₃ (**1**), Br (**2**), Cl (**3**), ClO₄ (**4**) in L = tridentatna Schiffova baza benzoilacetohidrazid, HL, so bili sintetizirani in okarakterizirani z elementno analizo, FT-IR in UV-Vis spektroskopijo. Struktura spojine **1** je bila določena z monokristalno rentgensko difrakcijo. Struktura spojine **1** enojedrna, koordinacijska geometrija okoli bakrovega(II) iona je kvadratno-planarna, ligand L je tridentatni ligand, ki z Cu(II) kovinskim centrom tvori en petčlenski in en šestčlenski kelatni obroč, medtem ko je četrto koordinacijsko mesto zasedeno z NO₃ anionom. Nitratni ioni sodelujejo pri tvorbi H vezi. NH skupina je donor H-vezi in nitratni kisik akceptor. Tvorba bakrovih kompleksov v raztopini je bila spremljana z UV/Vis titracijskim eksperimentom. Rezultati razkrivajo, da imajo kompleksi v raztopini sestavo 1:1 (ligand/metal).