

Synthesis and Characterization of Two New Copper (II) Complexes

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ABSTRACT

The reaction between $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with bis[(2S,3R)-bicyclo[2.2.2]octane-2,3-dicarbonitrile], (BCODCN) and bis[(2S,3R)-bicyclo[2.2.2]octane-2,3-diamine], (BCODA) produced two new ionic complexes. One of them is bis[(2S,3R)-bicyclo[2.2.2]octane-2,3-dicarbonitrile]copper(II) nitrate, $[\text{Cu}(\text{BCODCN})_2]^{2+}$, that is easily synthesized in a nearly quantitative yield using a direct reaction of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and (BCODCN). Another is bis[(2S,3R)-bicyclo[2.2.2]octane-2,3-diamine]copper(II) nitrate, $[\text{Cu}(\text{BCODA})_2]^{2+}$, that has been synthesized by reaction of (BCODA) with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. These compounds were characterized by IR, UV/Visible techniques. The electronic and vibrational spectra of $[\text{Cu}(\text{BCODCN})_2]^{2+}$ and $[\text{Cu}(\text{BCODA})_2]^{2+}$ have been measured and studied.

Key Words: Synthesis, Characterization, Bis[(2S,3R)-bicyclo[2.2.2]octane-2,3-dicarbonitrile]copper(II)nitrate, Bis[(2S,3R)-bicyclo[2.2.2]octane-2,3-diamine]copper (II) nitrate.

INTRODUCTION

In principle, the central transition metal atoms of different soft and hard Lewis acidity usually need to be satisfied in the most suitable fashion. Copper containing ligands are known to form stable complexes with class b metal ions, such as gold(I) [1,2] and se(II) [3]. Copper is an important element present in several cell types with essential functions in the human body, participating in various biochemical and biological cycles. Complexes of copper with nitrogen ligand are of considerable interest due to broad spectrum of biological activities [4-6]. Schiff base ligands are considered "privileged ligands" because they are easily prepared by the condensation between aldehydes and imines. There has been a considerable interest in the coordination chemistry of Schiff-base ligands, because of their feasibility to make various kinds of metal complexes [7,8] and to stabilize them in various oxidation states. The Schiff base complexes have been used as models for biological systems [9,10]. In this paper, the synthesis

and characterization of copper (II) complexes of Schiff base ligands, (BCODCN) and (BCODA) are reported and characterized by UV-Vis and IR spectra. (BCODCN) and (BCODA) compounds are capable to form complexes with transition metal ions in the form Schiff bases.

The spectroscopic data of the complexes indicate that the copper (II) ions are coordinated by the nitrogen atoms (C=N) and (NH₂) of the ligands. Formula of synthesized complexes is [CuL₂]²⁺ in than L = nitrogen ligand.

We have managed to prepare three new complexes of copper (II) that have not been synthesized and reported so far.

MATERIALS AND METHODS

Acetonitrile (Fluka, P.A.) was distilled several times from phosphorus pentaoxide before using, thereby reducing its water content to <4 ppm. Cu(NO₃)₂.3H₂O (Merck, p.a.) were used. Solvents were purified by standard methods. Infrared spectra were recorded as KBr disks on a Shimadzu model 420 spectrophotometer. Microanalyses were carried out using a Heraeus CHN-O- Rapid analyzer. The UV/Visible measurements were made on an Uvicon model 922 spectrometer. The percent compositions of elements were obtained from the Microanalytical Laboratories, Department of Chemistry, OIRC, Tehran.

Synthesis of Bis[(2S,3R)-bicyclo[2.2.2]octane-2,3-dicarbonitrile]copper(II)nitrate:

[Cu(BCODCN)₂]²⁺ was prepared by dissolving Cu(NO₃)₂.3H₂O (2.41 gr, 10 mmol) in MeCN and adding this solution to a solution of (BCODCN) ligand (3.2 gr, 20 mmol) in MeCN under stirring at room temperature until a green precipitate was formed. After 3 hours stirring, the mixture was filtered, washed with ether and dried at room temperature. The complex is soluble in polar solvents, such as DMSO, DMF, and chloroform but not soluble in hexane, benzene. m.p 109 °C. Anal. calc. for C₂₀H₂₄N₆O₆Cu: C, 47.28; H, 4.72; N, 16.55. Found: C, 47.19; H, 4.62; N, 16.46%. The IR spectrum of this compound shows ν : 2872, 2956, 1169, 2239, 1386, 837, 3378, 586 cm⁻¹. UV-Vis (CH₃CN): λ_{\max} (ϵ)= 315(114) nm.

Synthesis of Bis[(2S,3R)-bicyclo[2.2.2]octane-2,3-diamine]copper(II) nitrate:

[Cu(BCODA)₂]²⁺ was prepared as follow:

To a solution of (BCODA) ligand (1.6 gr, 20 mmol) in MeCN the Cu(NO₃)₂.3H₂O (2.41 gr, 10 mmol) was added under stirring at room temperature until a blue precipitate was formed. After 3 hours stirring, the mixture was filtered, washed with ether, and dried at room temperature. The complex is soluble in polar solvents, such as DMSO, DMF, and chloroform but not soluble in hexane, benzene. m.p 195°C. Anal. calc. for C₁₆H₃₂N₆O₆Cu: C, 41.06; H, 6.84; N, 17.96. Found: C, 40.97; H, 6.74; N, 17.87%. The IR spectrum of this compound shows ν : 2935, 1154, 3296, 1627, 1330, 871, 3500, 423 cm⁻¹. UV-Vis (CH₃CN): λ_{\max} (ϵ)= 280(42) nm.

Results and Discussion

Schiff bases are potentially capable of forming stable complexes with metal ions [12,13]. Copper(II) salt react with Schiff base ligands in 2:1(L/M) molar ratio in solvent to afford complexes. The ligands and their complexes are stable at room temperature. In this paper, a direct, simple and one-step method has been used to synthesize these compounds. The advantages of the method are:

a) There is no side product; b) the reaction is quite fast; c) mild conditions and d) the accompanied color change that provides visual means for ascertaining the progress of the reaction.

The infrared spectra of the complexes taken in the region 400–4000 cm^{-1} were compared with those of the free ligands. There are some significant changes between the metal(II) complexes and their free ligands for chelation as expected. The main stretching frequencies of the IR spectra of the complexes are tabulated in Tables 1-2. All of the IR spectra information supports the suggestion of coordination of the nitrogen atoms to the metal ion.

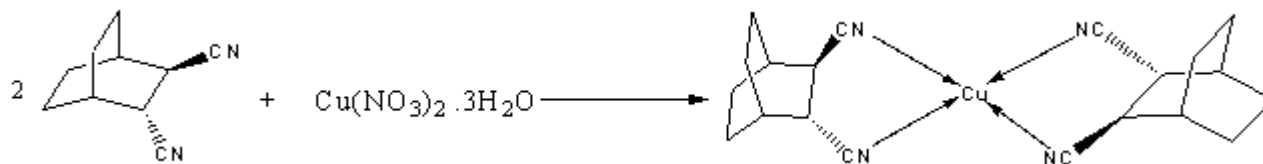
Table 1. The frequencies (cm^{-1}) of $[\text{Cu}(\text{BCODCN})_2]^{2+}$

Vibration	ν (cm^{-1})	Intensity
ν (C-H)	2935	s
ν (C-N)	1154	m
ν (N-H)	3296, 1627	s, s
ν (NO_3)	1330, 871	s, m
ν (O-H) water	3500	m, br
ν (Cu-N)	423	w

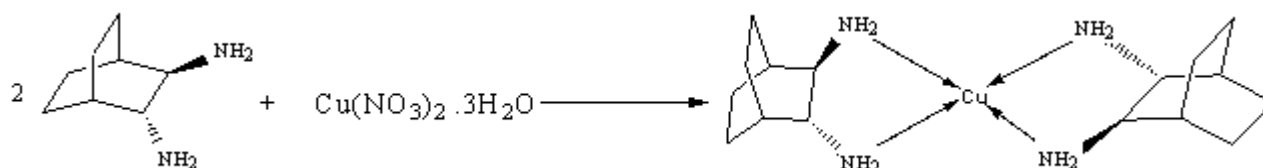
Table 2. The frequencies (cm^{-1}) of $[\text{Cu}(\text{BCODA})_2]^{2+}$

Vibration	ν (cm^{-1})	Intensity
ν (C-H)	872, 2956	s, s
ν (C-N)	169	m
ν ($\text{C}\equiv\text{N}$)	239	m
ν (NO_3)	386, 837	s, m
ν (O-H) water	378	m, br
ν (Cu-N)	86	m

Bis[(2S,3R)-bicyclo[2.2.2]octane-2,3-dicarbonitrile]copper(II)nitrate, $[\text{Cu}(\text{BCODCN})_2]^{2+}$ was prepared by the reaction of (BCODCN) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in a 2:1 ratio in MeCN solvent as follows:



Bis[(2S,3R)-bicyclo[2.2.2]octane-2,3-diamine]copper(II) nitrate, $[\text{Cu}(\text{BCODA})_2]^{2+}$ was prepared by the reaction of (BCODA) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in a 2:1 ratio in MeCN solvent as follows:



CONCLUSION

In summary, the synthesis and characterization of complexes have been described. Two complexes of Copper (II) were synthesized simply. $[\text{Cu}(\text{BCODCN})_2]^{2+}$ was prepared by the reaction of (BCODCN) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in a 2:1 ratio in MeCN solvent and $[\text{Cu}(\text{BCODA})_2]^{2+}$ was prepared by the reaction of (BCODA) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in a 2:1 ratio in MeCN solvent. Electronic and vibrational spectra of these two new complexes were studied. These compounds were characterized by IR, UV/Visible techniques.

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