STUDIA UBB CHEMIA, LVII, 4, 2012 (p. 33-38)
(RECOMMENDED CITATION)

SYNTHESIS AND CHARACTERIZATION OF Co(II) COMPLEXES WITH TRIDENTATE (ONO) SCHIFF BASES

DIJE DEHARI[a], FETAH PODVORICA[b], SHEFKET DEHARI[a], MUHAMET SHEHABI[a]

ABSTRACT. Complexes of Co(II) with tridentate (ONO) Schiff bases have been prepared in the reaction of Co(II) acetate, ethanolamine and 5-X salicylaldehyde (X= Br, Cl) in nitrogen atmosphere. Bis(2-hydroxyethylimino) methyl)-4-bromo-phenolato)cobalt(II) and bis(2-hydroxyethylimino)methyl)-4-chlorophenolato) cobalt(II) were characterized by elemental analysis, IR spectroscopy and ESI mass spectrometry.

Keywords: *Schiff base, cobalt(II) complexes, IR spectroscopy, mass spectrometry*

INTRODUCTION

Schiff bases are versatile ligands that may be used for different purposes. For exemple Hodnett and Dunn (1970), El-masry et al. (2000), Holla et al. (2006), Jarrahpour et al. (2007) and Hania (2009) investigated antitumoral, antimicrobial, antibacterial, antifugal, antiviral and anticancer properties of Schiff bases as free ligands [1-5]. Schiff bases are also used as ligands in the complexes with transit metals [6-12]. Azomethine group of Schiff bases forms stable complexes in the presence of another atom or group susceptible to act as a ligand [6]. When salicylaldehyde reacts with ethanolamine the resulted Schiff base can act as tridentate, ligand, for example with nickel ions octahedral complexes were obtained [7]. If hydroxyl group of ethanolamine do not take part in the complexation then the previous Schiff base acts as a bidentate ligand [8].

When the reaction of Co(II) ions with Schiff bases is performed in the air presenceoxidiation to Co(III) occurs and anionic complexes are formed due to the deprotonation of OH groups [9]. Schiff bases as ligands form complexes with metal ions of Mn(II), Co(II) and (III), Ni(II), Cd(II), Fe(III), Zn(II) and Cu(II) [10-12]

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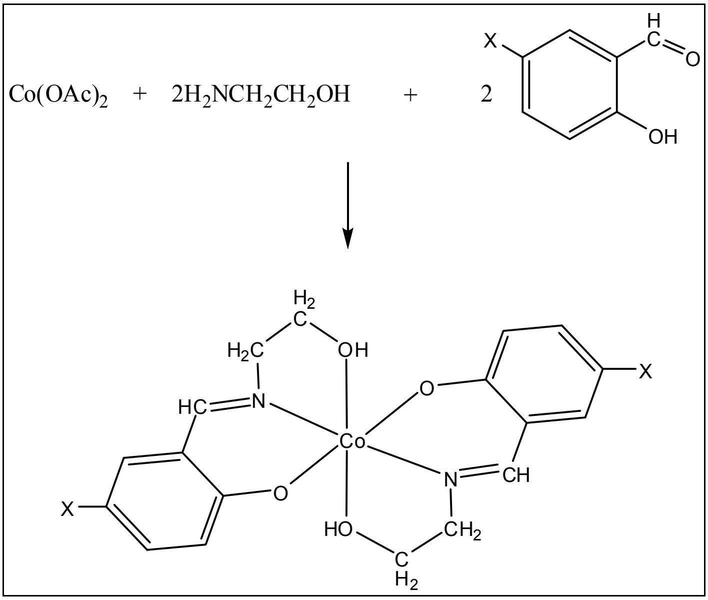
[a] *State University of Tetovo, Faculty of Mathematical and Natural Sciences, Department of Chemistry, 1200 Tetovo, Macedonia*

[b] *University of Prishtina, Faculty of Mathematical and Natural Sciences, Department of Chemistry, "Nëna Terezë" 10000 Prishtinë, Republic of Kosovo*

RESULTS AND DISCUSSION

In this paper we report the ability of cobalt (II) to form stable complexes with ethanolamine and 5-bromo or 5-chloro salicylaldehyde “in situ” under nitrogen atmosphere (Scheme 1).



X=Br $[Co(HSB^{I})_2]$ **(1)**; X=Cl $[Co(HSB^{II})_2]$ **(2)**

Scheme 1

The elemental analysis data fit very well with those calculated and they show that cobalt is coordinated with Schiff bases in 1:2 ratio. The molecular ions are present in the ESI-MS spectra of the two complexes. The mass spectum of complex **(1)** is shown in the fig. 2. Based on the elemental analysis and mass spectra the formula, $[Co(HSB)_2]$ (HSB = Schiff base), was suggested for the both complexes therefore an octahedral geometry around Co(II) was assumed with three dentate ligands.

IR spectrum of ligand

The reaction of transformation of C=O group of salycylaldehide into azomethine in reaction with the primary amine is quantitative as the carbonyl vibration in the region 1682 cm^{-1} and the bands in the region 3600-3400 cm^{-1} corresponding to the primary amine are not present.

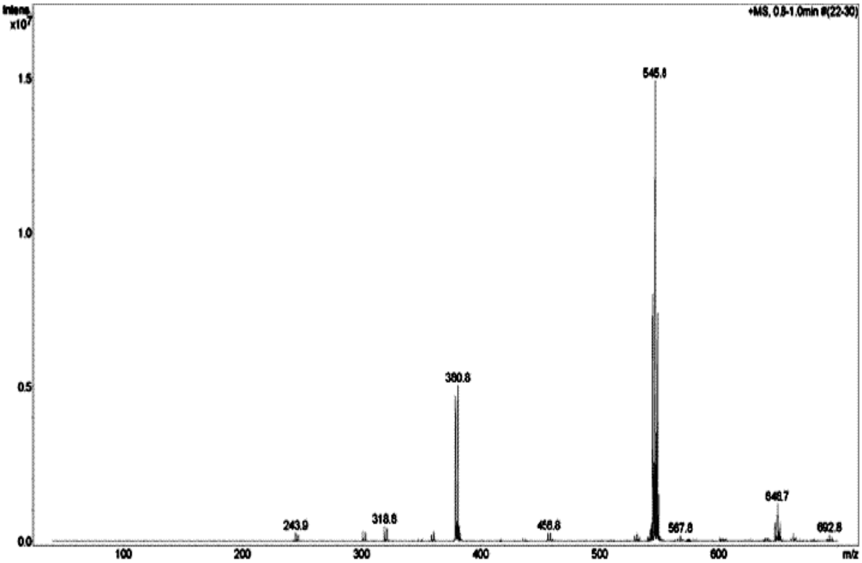


Figure 2. Mass spectrum of $[Co(HSB^I)_2]$ complex

IR spectra of the complexes

The IR spectra of complexes are very clear and the characteristic absorptions of O-H and C=N bands which are present in complexes are easily identified. The broad bands at 3500-3300 cm^{-1} [12,13] with a maximum absorption at 3423 cm^{-1} **(1)** and 3432 cm^{-1} **(2)** suggest the coordination of the hydroxyl groups in the protonated form. The azomethine groups (C=N) in both of complexes appear with as a strong stretching absorption band at 1636 cm^{-1} **(1)** respectively 1634cm^{-1} **(2)** [12,13]. The spectrum of the free ligand shows a band at 1650 cm^{-1} for C=N that means that lower values for complexes are due to the coordination of cobalt ions through the nitrogen of azomethine group. This interaction between Co ion and nitrogen of azomethine group reduces the electron density on nitrogen atom [14]. The strong band at 1306 cm^{-1} was assigned to C-O stretching of the phenolic group, compared to the phenolic C-O stretching of free ligand Schiff base observed at 1240 cm^{-1}. This shift of the band at higher frequency is attributed to the coordination of cobalt ion through the phenolic oxygen atom [15,16]. Finally the existence of two bands at 635 and at 470 cm^{-1} corresponding to Co-N and Co-O stretching vibrations in the case of complex indicates the coordination of the Schiff base to the cobalt ion, as shown previously in the literature. [17]

CONCLUSIONS

The data of elemental analysis, IR spectra and mass spectra show that Schiff bases synthesized “in situ” reaction are coordinated with cobaltI(II) ion and form bis(2-hydroxyethylimino)methyl)-4-bromophenolato) cobalt(II) and bis(2-hydroxyethylimino)methyl)-4-chlorophenolato)cobalt(II). The Schiff bases are coordinated to the Co(II) ion through phenolic oxygen, azomethine nitrogen and alcoholic oxygen.

EXPERIMENTAL SECTION

Material and methods

All reagents and chemicals were used as obtained from Aldrich and Acros organics. The infrared spectra were measured on a Perkin-Elmer System 2000 FT-IR spectrometer with KBr pellets. The mass spectra were obtained on an FT-ICR-MS Bruker-Daltonics ESI spectrometer (APEX II, 7 Tesla). Elemental analyses were performed on a VARIO EL microanalyzer (Heraeus).

Preparation of complex (1)

0.5 mmol of $Co(OAc)_2$ $4H_2O$ are dissolved in a mixture of 10 mL ethanol + 5mL H_2O at 50 ^oC under nitrogen atmosphere. A second solution of 1mmol of 2-aminoethanol and 1mmol of 5-bromosalicyladehyde dissolved in 15 mL of absolute ethanol at 50^{o}C was added and the mixture wasrefluxed for 20 min. The orange precipitate was filtered and washed with acetone and diethyl ether.

IR spectrum (KBr) cm^{-1}): 3423, 1636 (C=N vibrations), 1458 (C=C), 1380 (C=C), 1305 (delta OH), 1174 (ni OH), 824, 684 (C-H aromatic);
IR spectrum of the ligand (KBr, cm^{-1}): 3174, 1650, 1515, 1350, 1240, 1165, 825, 725;
ESI-MS spectrum: *m/z* 545.8 (M+H$^+$);
Elemental analysis: Calc. for $C_{18}H_{18}Br_2CoN_2O_4$: C, 39.66 %; H, 3.33%; N, 5.14%. Found: C, 38.93%; H, 3.19%; N, 4.87%,
Mp: 245^{o}C(decomp).

Preparation of complex (2)

A solution of 1mmol of 2-aminoethanol and 1mmol of 5-chlorosalicyladehyde in 15 ml absolute ethanol prepared at 50^{o}C was added to the solution obtained by solving 0.5mmol $Co(OAc)_2$ $4H_2O$ in a mixture of 10 ml ethanol + 5ml H_2O at 50^{o}C under nitrogen atmosphere. The mixture was refluxed for 20 minute. The orange precipitate was filtered were filtered, washed with acetone and diethyl ether.

IR spectrum (KBr) cm^{-1}): 3432, 1634, 1459, 1381, 1306, 1176, 825, 705;
ESI-MS spectrum: *m/z* 455.9 ($M+H^+$);
Elemental analysis: Anal. Calc. for $C_{18}H_{18}Cl_2CoN_2O_4$: C, 47.39 %; H, 3.98%; N, 6.14%. Found: C, 46.96%; H, 3.89%; N, 5.92%,
Mp: 245°C(decomp).

ACKNOWLEDGMENTS

D.D. and Sh.D. thank the DAAD Programme “Stability Pact for South Eastern Europe” for financial support during their stay at the Faculty of Chemistry and Mineralogy, Universität Leipzig, Germany and at the Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, Cluj-Napoca.

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