Research Journal of Applied Sciences 8 (2): 112-115, 2013
ISSN: 1815-932X

New Complexes of Co(II) and Cd(II) Using 4-Hydroxy-2-Oxo-2H Chromene-3-Carboxamide as Ligand

Dije Dehari, Muhamet Shehabi, Shefket Dehari and Sevdije Govori
Department of Chemistry, Faculty of Mathematical and Natural Sciences,
State University of Tetovo, 1200 Tetovo, Macedonia

Abstract: New complexes of cobalt(II) and cadmium(II) have been synthesized in the reaction mixture of metals(II) acetate and 4-hydroxy-2-oxo-2H-chromene-3-carboxamide. Diaquabis(4-hydroxy-2-oxo-2H-chromene-3-carboxamidato) cobalt(II) and dihidrokso(4-hydroxy-2-oxo-2H-chromene-3-carboxamide) cadmium(II) were characterized by elemental analysis, IR spectroscopy and ESI mass spectrometry. Elemental analysis and mass spectrometry data of the complexes suggests the stoichiometry is 1:2 (metal-ligand). The results are in accordance with an octahedral environment around the Co(II) ion and tetragonal for cadmium ion.

Key words: Coumarin derivative complexes, IR spectroscopy, mass spectrometry, cadmium ion, cobalt(II)

INTRODUCTION

Coumarin is a structural unit of many natural and synthetic compounds which endows them with a wide range of physiological and pharmacological activities as antibacterial (Al-Haiza *et al*., 2003; Dutton *et al*., 1994), antiviral (Parmar *et al*., 1996; Ishikawa *et al*., 1995), bactericidal (El-Sayed *et al*., 2001), fungicidal (El-Agrody *et al*., 2001), anti-inflammatory (Emmanuel-Giota *et al*., 2001) and anticoagulants (Hermodson *et al*., 1971). The interest has grown up when remarkable anticancer (Nofal *et al*., 2000; Raev *et al*., 1990; Shah *et al*., 1998; Valenti *et al*., 1997) and lately anti-HIV activities of some coumarins were confirmed (Skulnick *et al*., 1997; Spino *et al*., 1998).

Especially the coumarin derivative 4-hydroxy-2-oxo-2H-chromene-3carboxamide attracted the attention as potentially very active compound in live cells because of the functional groups connected to each other in the six-member pyranon system. Furthermore, those are very polar groups (keto, hydroxy and amido) which are able to create interactions (as hydrogen bond for example) with the large biomolecules as guest-host systems. Also, the geometric position of those groups is perfect to embrace metal cations.

Many researchers synthesized the complexes of transition metals with coumarin derivatives because these complexes that contain coumarin as a ligand show anticoagulant properties (Deng *et al*., 1992; Jiang *et al*., 1989) and antitumor activity (Kostova *et al*., 1999; Manolov *et al*., 2000). Kostova *et al*. (2005, 2004, 2001) have shown the cytotoxic potential of coumarins complexed with cerium, lanthanum, zirconium and neodymium.

In this research, researchers have shown the synthesis of cobalt and cadmium complexes with 4-hydroxy-2-oxo-2H-chromene-3-carboxamide as ligand using trietylamine for the deprotonation of hydroxyl group in C-4 position, respectively for ionization of water molecules.

MATERIALS AND METHODS

The infrared spectra were determined on a Perkin-Elmer System 2000 FT-IR spectrometer with KBr pellets. The mass spectra were measured on an FT-ICR-MS Bruker-Daltonics ESI spectrometer (APEX II, 7 Tesla). Elemental analyses were performed on a VARIO EL microanalyzer (Heraeus). All the reagents and solvents were obtained from commercial sources and were used without further purification. The ligand have been synthesized by Scarborough and Gould (1961).

Preparation of Co(II) complex: Measured 0.5 mmol $Co(OAc)_2.4H_2O$ (124.5 mg) and dissolved in 10 mL methanol+5 mL H_2O in room temperature. Also, measured 1 mmol of the ligand and dissolved in 15 mL methanol and

Corresponding Author: Dije Dehari, Department of Chemistry, Faculty of Mathematical and Natural Sciences, State University of Tetovo, 1200 Tetovo, Macedonia

was added 0.2 mL trietylamine in room temperature. The ligand were added in the cobalt solution and the reaction mixture refluxed for 30 min at 40°C. The rose cobalt complex precipitated, filtered and washed with ethanol. Anal. calc. for $C_{20}H_{16}N_2CoO_{10}$: C, 47.73; H, 3.20; N, 5.57; Found: C, 47.06; H, 3.11; N, 5.40. IR KBr, cm^{-1}): 3418, 3306, 3223, 1697, 1620, 1576, 1486, 1433, 1253, 1110, 1035, 907, 764. ESI-MS m/z 501.9 ($M-H^+$).

Preparation of Cd(II) complex: Measured 0.5 mmol $Cd(OAc)_2.2H_2O$ (134 mg) and dissolved in 10 mL methanol+5 mL H_2O in room temperature. Also, measured 1mmol of the ligand and dissolved in 15 mL methanol and was added 1 mL trietylamine in room temperature. The ligand were added in the cadmium solution and the reaction mixture refluxed for 1 h at 40°C. The reaction mixture stayed for 12 h and the white cadmium complex precipitated, filtered and washed with ethanol.

Anal. calc. for $C_{20}H_{16}CdN_2O_{10}$: C, 43.15; H, 2.90; N, 5.03; Found: C, 42.52; H, 2.76; N, 4.68. IR KBr, cm^{-1}): 3400, 1691, 1650, 1608, 1556, 1489, 1435, 1266, 1218, 1039, 905 767, 683. ESI-MS m/z 557.8 ($M-H^+$).

RESULTS AND DISCUSSION

In this study, researchers have shown the forming of Co(II) and Cd(II) complexes using 4-hydroxy-2-oxo-2H chromene-3-carboxamide as ligand. Even though the reaction is carried out in same conditions, the metal complexes have different structures. In case of cadmium complex, the water molecules were ionized from trietylamine and than hydroxid ions were coordinated with Cd ions.

Based on the elemental analysis and mass spectra the formula $[Co(L)_2(H_2O)_2]$ and $[Cd(L)_2(OH)_2]$ (L = ligand) was suggested for the complexes. The general equation for synthesis and suggested structure of complexes is shown in Fig. 1.

Elemental analysis: The elemental analysis data match very well with those calculated and they show that cobalt and cadmium are coordinated with ligand in 1:2 ratio.

IR spectra: The cobalt complex shows a band of amino groups at 3306 cm^{-1}. The C=O bands of amido groups appear at the 1620 cm^{-1} which shows that the ligand is coordinated with cobalt(II) through carbonyl groups and deprotonated phenol groups. The free carbonyl groups of piranon ring appear at 1697 cm^{-1}. The cadmium complex shows a broad band of hydroxyl groups at 3600-3300 cm^{-1} with maximum absorption in the 3400 cm^{-1}. These bands show the coordinated hydroxide groups and amino

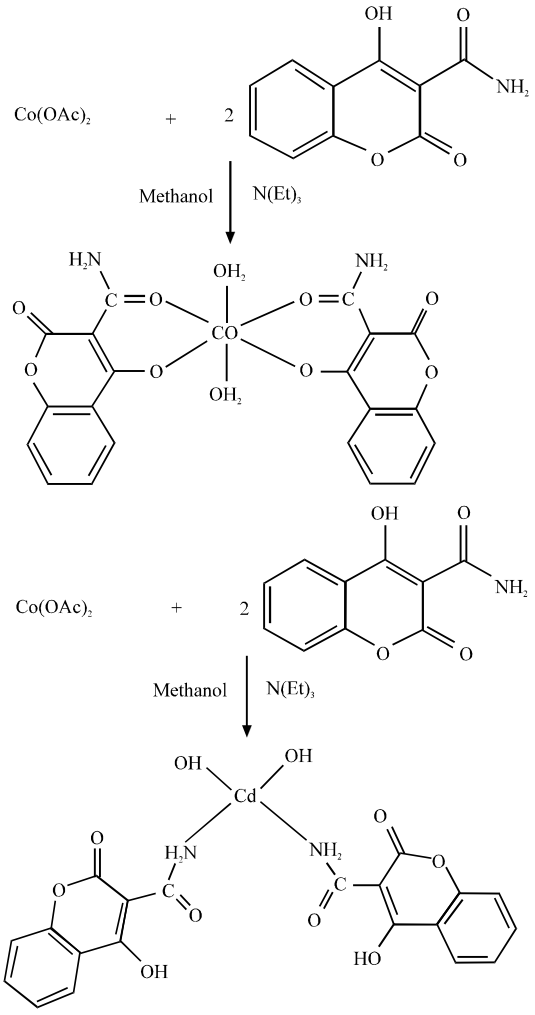

Fig. 1: Synthesis and suggested structure for Co(II) and Cd(II) complexes

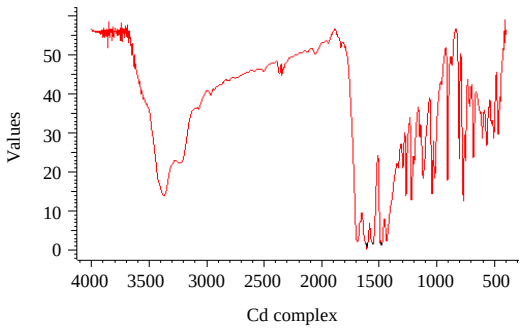

Fig. 2: IR specter of Cd complex

groups to the Cd(II) ion in the complex. The free carbonyl groups of amido groups and piranon ring appear at 1650 and 1694 cm^{-1} (Pretsch *et al*., 2009). The IR specter of cadmium complex is shown in the Fig. 2.

Table 1: Mass specters data of cobalt and cadmium complexes

Compounds	m/z Calc.	m/z found
$C_{20}H_{16}CoN_2O_{10}$	503.01	501.9
$C_{20}H_{16}CdN_2O_{10}$	557.98	557.8

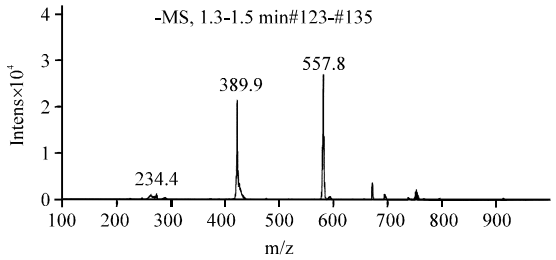

Fig. 3: Mass specter of Cd complex

Mass spectra: The m/z values of complexes prove that complexes were formed in the above mentioned ratio. The experimental values of ESI-MS are almost the same with theoretically calculated (Table 1). The mass specter of cadmium complex are shown in Fig. 3.

CONCLUSION

New complexes of Co(II) and Cd(II) complexes with 4-hydroxy-2-oxo-2H chromene-3-carboxamide as ligand have been synthesized. On the basis of elemental analysis, IR spectra and mass spectroscopic data the complexes hava been formulated as $[Co(L)_2(H_2O)_2]$ and $[Cd(L)_2(OH)_2]$ (L = ligand).

REFERENCES

Al-Haiza, M.A., M.S. Mostafa and M.Y. El-Kady, 2003. Synthesis and biological evaluation of some new coumarin derivatives. Molecules, 8: 275-286.

Deng, R., J. Wu and L. Long, 1992. Lanthanide complexes of bis (4-hydroxy-3-coumarinyl) acetic acid and their anticoagulant action. Bull. Soc. Chim. Belg., 101: 439-443.

Dutton, C.J., J. Sutcliffe and B. Yang, 1994. 4-Hydroxy coumarin derivatives with antibacterial activity. PCT International Application US1993/006308.

El-Agrody, A.M., M.S. Abd El-Latif, N.A. El-Hady, A.H. Fakery and A.H. Bedair, 2001. Heteroaromatization with 4-Hydroxycoumarin. Part II: Synthesis of Some New Pyrano[2,3-d]pyrimidines,[1,2,4]triazolo[1,5-c] pyrimidines and Pyrimido[1,6-b]-[1,2,4]triazineDerivatives.Molecules, 6: 519-527.

El-Sayed, A.M. and O.A. Abd-Allah, 2001. Synthetic and biological studies on coumarinhydrazone derivatives. Phosphorus Sulfur Silicon Related Elements, 170: 75-86.

Emmanuel-Giota, A.A., K.C. Fylaktakidou, D.J. Hadjipavlou-Litina, K.E. Litinas and D.N. Nicolaides, 2001. Synthesis and biological evaluation of several 3-(coumarin-4-yl)tetrahydroisoxazole and 3-(coumarin-4-yl) dihydropyrazole derivatives. J. Heterocycl. Chem., 38: 717-722.

Hermodson, M.A., W.M. Barker and K.P. Link, 1971. Studies on the 4-hydroxycoumarins. Synthesis of the metabolites and some other derivatives of warfarin. J. Med. Chem., 14: 167-169.

Ishikawa, T., K.I. Kotake and H. Ishii, 1995. Synthesis of toddacoumaquinone, a coumarin-naphthoquinone dimer and its antiviral activities. Chem. Pharma. Bull., 43: 1039-1041.

Jiang, D., R. Deng and J. Wu, 1989. Synthesis and properties of lanthanide compounds of 3-sulfo-4-hydroxycoumarin. Wuji Huaxue, 5: 21-28.

Kostova, I., G. Momekov, M. Zaharieva and M. Karaivanova, 2005. Cytotoxic activity of new lanthanum complexes of bis-coumarins. Eur. J. Med. Chem., 40: 542-551.

Kostova, I., I. Manolov and G. Momekov, 2004. Cytotoxic activity of new neodymium (III) complexes of bis-coumarins. Eur. J. Med. Chem., 39: 765-775.

Kostova, I., I. Manolov and M. Karaivanova, 2001. Synthesis, physicochemical characterization, and cytotoxic screening of new zirconium complexes with coumarin derivatives. Arch Pharm., 334: 157-162.

Kostova, I., I. Manolov, S. Konstantinov and M. Karaivanova, 1999. Synthesis, physicochemical characterisation and cytotoxic screening of new complexes of cerium, lanthanum and neodymium with warfarin and coumachlor sodium salts. Eur. J. Med. Chem., 34: 63-68.

Manolov, I., I. Kostova, T. Netzeva, S. Konstantinov and M. Karaivanova, 2000. Cytotoxic activity of cerium complexes with coumarin derivatives. Molecular modeling of the ligands. Arch. Pharm., 333: 93-98.

Nofal, Z.M., M.I. El-Zahar and S.S. Abd El-Karim 2000. Novel coumarin derivatives with expected biological activity. Molecules, 5: 99-113.

Parmar, V.S., K.S. Bisht, R. Jain, S. Singh and S.K. Sharma *et al*., 1996. Synthesis, antimicrobial and antiviral activities of novel polyphenolic compounds. Ind. J. Chem. Sec. B, 35: 220-232.

Pretsch, E., P. Buhlmann and M. Badertscher, 2009. Structure Determination of Organic Compounds. 4th Edn., Springer-Verlag, Berlin, Heidelberg, Pages: 317.

Raev, L., E. Voinov, I. Ivanov and D. Popov, 1990. Antitumor activity of some coumarin derivatives. Pharmazie, 45: 696-698.

Scarborough, H.C. and W.A. Gould, 1961. The reaction of urea with cyclic 1,3-dicarbonyl and other active hydrogen compounds. J. Org. Chem., 26: 3720-3723.

Shah, A., Y. Naliapara, D. Sureja, N. Motohashi and M. Kawase *et al*., 1998. 6,12-dihydro-1-benzopyrano[3,4-b][1,4]benzothiazin-6-ones synthesis and MDR reversal in tumor cells. Anticancer Res., 18: 3001-3004.

Skulnick, H.I., P.D. Johnson, P.A. Aristoff, J.K. Morris and K.D. Lovasz *et al*., 1997. Structure-based design of nonpeptidic HIV protease inhibitors: The sulfonamide substituted cyclooctylpyranones. J. Med. Chem., 40: 1149-1164.

Spino, C., M. Dodier and S. Sotheeswaren, 1998. Anti-HIV coumarins from calophyllum seed oil. Bioinorg. Med. Chem. Lett., 8: 3475-3478.

Valenti, P., A. Rampa, M. Recanatini, A. Bisi and F. Belluti *et al*., 1997. Synthesis, cytotoxicity and SAR of simple geiparvarin analogues. Anticancer Drug Des., 12: 443-451.