

# COMPLEX COMPOUNDS WITH DIOXYGEN AS LIGAND III<sup>1</sup>. COBALT COMPLEXES WITH THE SCHIFF BASE DERIVED FROM 1-FORMYL-2-NAFTOL AND ETHYLENEDIAMINE

Dana Marinescu \*, Anca Nicolae \*\*, Mihaela Badea Rodica Olar, Emilia Elena Iorgulescu \*\*\*, and Carmencita Ciomaga \*\*\*\*

The new two complexes of Co(II) and Co(III) with the Schiff base derived from 1-formyl-2-naftol and ethylenediamine (H<sub>2</sub>L) were prepared and formulated on the basis of elemental chemical analysis, electronic and infrared spectra. The complexes were formulated as mononuclear species: [CoL(H<sub>2</sub>O)<sub>2</sub>] and its mononuclear adduct with dioxygen [CoLpyO<sub>2</sub>] (where L is the dianion of the Schiff base). An electrochemical study sustains the formulation of the mononuclear superoxo-adduct of Co(III) ion.

## Introduction

Complexes of cobalt (II) involving derivatives of salicylaldehyde and aliphatic amines have received considerable attention because of their similarity to biological dioxygen carriers [2÷10], as well as their potential as catalysts for the insertion of oxygen into organic substrates [11÷13]. In particular, the dioxygen adducts of [Co(salen)] and their ring-substituted analogues have received intensive investigation. Only limited studies have been made on [Co(napen)] (H<sub>2</sub>napen is N, N'-ethylenebis(1-hydroxy-2-naphthylmethyleneimine) and its dioxygen adduct [14÷16].

By continuing our research on complexes with dioxygen [17,18], we have studied the system which contains the N, N'-di(2-hydroxynaftiliden)-ethylenediamine (H<sub>2</sub>L) and Co(II) acetate. The complex resulted from this system is [CoL(H<sub>2</sub>O)<sub>2</sub>], where L is: the dianion of N, N'-di(2-hydroxynaftiliden)-ethylenediamine. By bubbling dioxygen through the solution of this compound in DMF, in the presence of pyridine new mononuclear dioxygenated cobalt complex is obtained.

## Experimental

All reagents used were p.a. grade.

### The synthesis of the Schiff base

1. C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> (H<sub>2</sub>L). To a solution which contains 3.44 g (0.02 moles) 1-formyl-2-naftol in 60 ml anhydrous ethanol it was added 0.8 ml (0.012 moles) ethylenediamine. The mixture was stirred for 1 h at the room temperature and then the sparingly soluble, yellow

---

\* Department of Inorganic Chemistry, University of Bucharest, Dumbrava Rosie, 23, Bucharest, ROMANIA

\*\* Department of Organic Chemistry, University of Bucharest, Panduri, 90, Bucharest, ROMANIA

\*\*\* Department of Analytic Chemistry, University of Bucharest, Panduri, 90, Bucharest, ROMANIA

\*\*\*\* Research Institute of Energy, 8 Energeticienilor Street, Bucharest, ROMANIA

colored product was filtered off and washed with ethanol. The product was recrystallized from a DMF-water mixture. *Chemical analysis. Found:* C 63.21; N 7.96; H 5.46%.  $C_{24}H_{20}N_2O_2$  requires: C 62.49; N 7.29; H 5.24%.

### **The syntheses of the complexes**

1.  $[CoL(H_2O)_2]$  (I). The MeOH/H<sub>2</sub>O (1:1 v/v) solution which contains 0.25 g  $Co(CH_3COO)_2 \cdot 4H_2O$  (1 mmole) and 0.38 g (1 mmole) H<sub>2</sub>A (KOH solution was added stoichiometrically to deprotonate the OH groups) was refluxed on a steam-bath during 30 min. The sparingly soluble, red-brown colored product was filtered off and washed with MeOH/H<sub>2</sub>O (1:1 v/v). *Chemical analysis. Found:* Co 12.71; N 6.26; C 62.66%.  $CoC_{24}H_{22}N_2O_4$  requires: Co 12.77; N 6.07; C 62.48 %.

2.  $[CoLpyO_2]$  (II). To a solution of 0.46 g complex (I) (1 mmole) in 50 ml DMF it was added 0.07 ml pyridine (1 mmole). The bubbling of dioxygen through this solution causes a color change to dark brown. The sparingly soluble, brown product obtained by a slow room temperature evaporation of solution was separated and washed with MeOH/H<sub>2</sub>O. *Chemical analysis. Found:* Co 10.47; N 7.95; C 64.81%.  $CoC_{29}H_{23}N_3O_4$  requires: Co 10.99; N 7.83; C 64.93%.

*The elemental chemical analyses* were performed by usual micromethods.

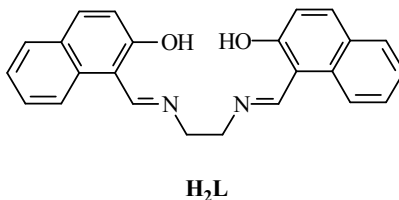
*The diffuse reflectance spectra* were recorded in the 24-14 kK (380-1200 nm) range, on a VSU2-P Zeiss-Jena spectrophotometer, using MgO as standard.

*The IR spectra* were recorded on a Specord M83 Zeiss-Jena spectrophotometer in the 400-4000  $cm^{-1}$  range using KBr pellets.

*The voltammetric measurements* were accomplished with a polarographic and voltammetric ensemble Trace Master 5 and POL 150 Polarographic Analyzer (Radiometer Copenhagen). The electrochemical cell is constituted of three electrodes: a HMDE as working electrode, a coiled Pt electrode and a Ag/AgCl as auxiliary and reference electrode, respectively. A thermostated polarographic cell was used to do all measurements at controlled temperature ( $25.0 \pm 0.1^\circ C$ ). The dissolved oxygen from the analyzed solution was eliminated by bubbling a pure argon stream. In the preconcentration step, the solution was stirred with a PTFE-coated stirring bar.

## **Results and discussion**

In the system  $Co(CH_3COO)_2 - H_2L$  where H<sub>2</sub>L is:



the synthesis has been developed in MeOH/H<sub>2</sub>O (1:1 v/v) using the reactants in the 1:1 molar ratio. There was obtained a sparingly soluble, red-brown colored complex with the formula: [CoL(H<sub>2</sub>O)<sub>2</sub>] (I) where L is the deprotonated Schiff base N, N'-di(2-hydroxynafthiliden)-ethylenediamine.

In the DMF solution of [CoL(H<sub>2</sub>O)<sub>2</sub>] was added pyridine in the molar ratio 1 : 1 and oxygen bubbled for 25 h. The solution color was changed to dark brown. The sparingly soluble, brown product obtained by a slow room temperature evaporation of solution was separated. The complex was formulated according to the chemical analyses as [CoL(py)O<sub>2</sub>].

### **Infrared spectra**

The infrared spectrum of the ligand H<sub>2</sub>L was recorded within the 400-4000 cm<sup>-1</sup> range and compared with that of the new two complexes (Table 1).

The most important remarks are the following:

- the spectra of complexes are alike with that of free Schiff base H<sub>2</sub>L, containing the absorption bands which are assigned to the vibrations:  $\rho(\text{CH}_2)$ ,  $\delta(\text{CH}_2)$ ,  $\delta(\text{CH}_3)$ ,  $\nu(\text{CH}_2)$  and  $\nu(\text{C}=\text{O})$ ;
- the  $\nu(\text{CN})$  band is of particular interest since its energy is diagnostic of the mode of coordination of the ligand H<sub>2</sub>L: when coordinated as the dianionic tetradentate N<sub>2</sub>O<sub>2</sub> specie the  $\nu(\text{CN})$  band is shifted to lower energy by 15-35 cm<sup>-1</sup> from the one corresponding to the free ligand (see table 1), while the coordination of it as neutral bidentate ligand *via* the azomethine nitrogens shifts this band to higher frequencies, the magnitude of this shift being only of the order of 5-10 cm<sup>-1</sup> [16];
- the presence of a broad and intense band at about 3400 cm<sup>-1</sup> in the spectrum of complex (I) is an evidence for the presence of water molecules; in addition, in the spectra of this complex appears a band assigned to the coordinated water molecules ( $\rho_w(\text{H}_2\text{O})$ );
- in the complex (II) spectrum appears a medium intense band at about 1140 cm<sup>-1</sup>, assigned to the  $\nu(\text{O}-\text{O})$  of coordinated dioxygen;
- in the 500-520 cm<sup>-1</sup> range, in all the complexes spectra it appears an absorption band assigned to the stretching vibration  $\nu(\text{Co}-\text{O})$ .

Thus, the infrared spectra suggest the following information about structure of complexes:

- the complex (I) contains the deprotonated Schiff base L<sup>2-</sup> and water molecules as ligands;
- the complex (II) contains as ligands: the deprotonated Schiff base L<sup>2-</sup>, pyridine and dioxygen as ligands.

**Table 1. IR spectra (cm<sup>-1</sup>)**

H <sub>2</sub> L	(I)	(III)	Assignments
-	500 m	515 m	$\nu(\text{Co}-\text{O})$
-	560 m	-	$\rho_w(\text{H}_2\text{O})$
715 m	720 m	725 m	$\rho(\text{CH}_2)$

**Table 1. Continued**

H <sub>2</sub> L	(I)	(III)	Assignments
810 m	810 m	810 m	
970 m	980 m	980 m	δ(CH)
1010 m	1020 m	1025 m	
-	-	1140 m	ν(O <sub>2</sub> )
1180s	1170 m	1175 m	ν(C–O)
1330 m	1340 m	1340 m	δ(CH <sub>2</sub> )
1510 s	1510 s	1515 s	ν <sub>s</sub> (C=C)
1580 vs	1580 vs	1585 vs	ν <sub>as</sub> (C=C)
1690 s	1660 s	1660 s	ν(C=N)
2870 m	2860 m	2875 m	ν(CH <sub>2</sub> )
-	3430 m	-	ν(OH)

**(I)** [CoL(H<sub>2</sub>O)<sub>2</sub>]**(II)** [CoL(py)O)<sub>2</sub>]**Electronic spectra**

The examination of the diffuse reflectance spectra of complexes and of the ligand H<sub>2</sub>L, recorded within the 380÷1200 nm range (Table 2) offers the following information about stereochemistry of the complexes, according to the literature [19].

- for the complex (I) the electronic spectrum is characteristic for Co(II) ions in an octahedral stereochemistry;
- the electronic spectrum of the complex (II) is characteristic for Co(III) low spin in a distorted octahedral stereochemistry (see Table 2).

**Table 2. Electronic spectra**

Compound	λ(nm)	Assignments
H <sub>2</sub> L	436	π → π*
	404	π → π*
	566	<sup>4</sup> T <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub>
	680	<sup>4</sup> T <sub>1g</sub> → <sup>4</sup> A <sub>2g</sub>
	1215	<sup>4</sup> T <sub>1g</sub> → <sup>4</sup> T <sub>2g</sub>
[CoL(H <sub>2</sub> O) <sub>2</sub> ] (I)	408	π → π*
	460	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>2g</sub>
	788	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1g</sub>

Oxygenation of Co(II) complexes invariably leads to products which strongly absorb in the near UV. Their absorption spectrum is characterized by broad and intense CT bands reaching into the visible and thus, giving rise to yellow and brown solution colors.

The electronic spectrum of (II) in CH<sub>3</sub>CN solution (Fig. 1) is characterized by absorption maxima at 424 and 320 nm. This type of spectrum has been observed before for the mononuclear superoxo complexes [16] with the same type of ligand.

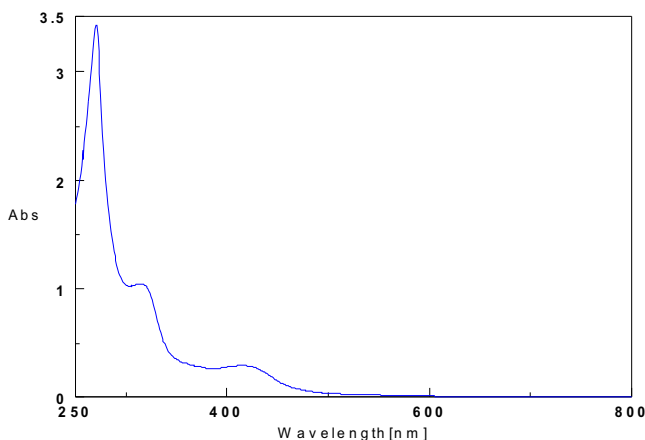


Fig. 1: Electronic spectrum in solution of complex [CoL(py)O<sub>2</sub>] (II)

### Redox behavior

Cyclic voltammogram (Fig. 2) was run in CH<sub>3</sub>CN containing 0.1M NaClO<sub>4</sub> as the supporting electrolyte; the scan rate was 50 mV/s.

Figure 2 shows a redox couple Co(III) - Co(II) at -0.442 V. The ratio between the anodic and cathodic peak currents,  $i_{pa} : i_{pc}$ , is almost unity and the separation between the anodic and cathodic peaks ( $\Delta E_p$ ) is 60 mV. The present electrochemical redox reaction in CH<sub>3</sub>CN is consistent with reversible one-electron transfer process.

A secondary peak appears at a more cathodic potential for the O<sub>2</sub><sup>-</sup> - O<sub>2</sub><sup>2-</sup> reduction reaction. This is an irreversible one-electron redox process ( $i_{pa} : i_{pc} = 1.5$ , and the anodic and cathodic peak potential difference,  $\Delta E_p$ , is slightly larger than 60 mV) similar with other complexes containing superoxo specie as ligand [20].

The reduction peak corresponding to  $E_{pc} = -0.16$  V could be assigned to a charge transfer process that appears between the metallic ion and the Schiff base.

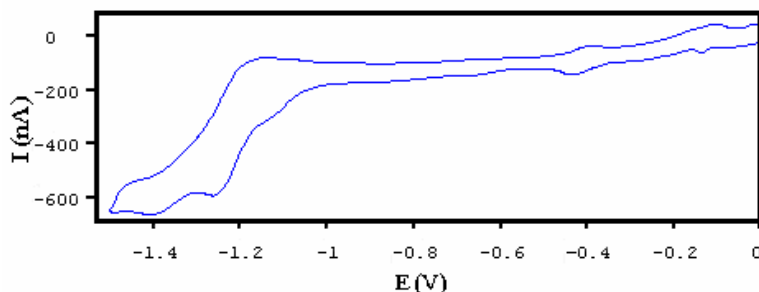
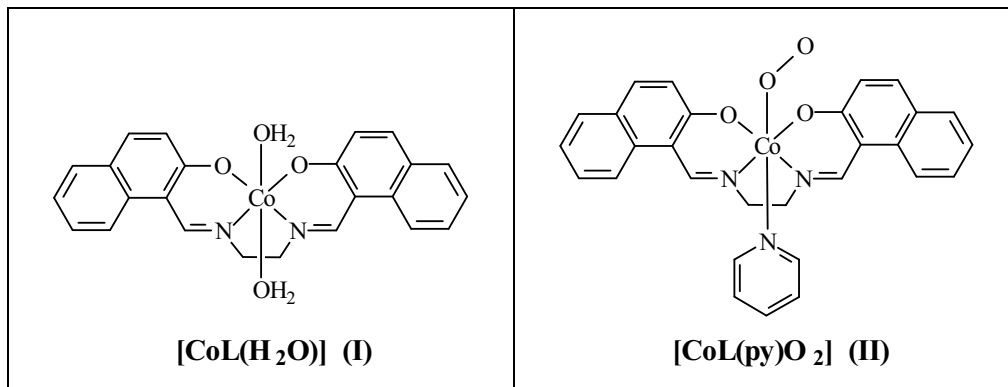


Fig. 2: Cyclic voltammogram of complex [CoL(py)O<sub>2</sub>] (II).

By correlating the data of the chemical analysis, IR and electronic spectra and cyclic voltammetry the proposed formula for the new complexes are the following:



## REFERENCES

1. Marinescu, D., Nicolae, A., Badea, M., Olar, R., Paraschiva (2002) *C. Bull. I.P.B.* (in press).
2. Floriani, C., Calderazzo, F. (1969) *J. Chem. Soc. A* 946.
3. Yamada, S. (1966) *Coord. Chem. Rev.* **1**, 415.
4. Chen, L. S., Koehler, M. E., Bestel, B. C., Cummings, S. C. (1978) *J. Am. Chem. Soc.* **100**, 7243.
5. Lancashire, R. L., Smith, T. D., Pilbrow, J. R. (1979) *J. Chem. Soc., Dalton Trans.* 66.
6. Kanda, W., Okawa, H., Kida, S. (1983) *J. Chem. Soc., Chem. Commun.* 973.
7. Machida, R., Kimura, E. Kodama, H. (1983) *Inorg. Chem.* **22**, 2055.
8. Kasuga, R., Nagahara, T., Tsuge, A., Sobage, K., Yamamoto, Y. (1983) *Bull. Chem. Soc. Jpn.* **56**, 95.
9. Trzebiatowska, B. J., Chmielewski, Vogt, A. (1984) *Inorg. Chim. Acta* **83**, 129.
10. Motekaitis, R. J., Martell, A. E., Nelson, D. A. (1984) *Inorg. Chem.* **23**, 275.
11. Tomaja, D. L., Vogt, L. H., Wirth, J. G. (1970) *J. Org. Chem.* **35**, 2029.
12. Nishinaga, A., Tojo, T., Matsuura, T. (1974) *J. Chem. Soc., Chem. Commun.* 896.
13. Nishinaga, A., Tomita, H., Nishizawa, K., Matsuura, T. (1981) *J. Chem. Soc., Dalton Trans.* 1504.
14. Abel, E. W., Pratt, J. M., Whelan, R. (1971) *Inorg. Nucl. Chem. Lett.* **7**, 901.
15. Abel, E. W., Pratt, J. M., Whelan, R. (1973) *Inorg. Nucl. Chem. Lett.* **9**, 151.
16. Ashmawy, F., Issa, R., Amer, S., McAuliffe, C., Parish, R. V. (1986) *J. Chem. Soc., Dalton Trans.* 421.
17. Marinescu, D., Ivan, L., Olar, R. (1991) *Bul. I. P. B. - Seria Chimie - Metalurgie*, **LIII (1-2)** 63-68.
18. Badea, M., Segal, E., Marinescu, D. (1989) *Thermochim. Acta* **149**, 251.
19. Lever, A. B. P., **Inorganic Electronic Spectroscopy**, Elsevier Publ. Comp., Amsterdam, London, New York, 1984, p. 473, 480.
20. Rodriguez, M. C., Morgenstern-Badarau, I., Cesario, M., Guilhem, J., Keita, B., Nadjo, L. (1996) *Inorg. Chem.* **35**, 7804.