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# Direct electrochemical synthesis of novel transition metal chelates of tridentate azomethinic ligands

B.I. Kharisov<sup>a,\*</sup>, D.A. Garnovskii<sup>b</sup>, L.M. Blanco<sup>a</sup>, A.S. Burlov<sup>b</sup>, I.S. Vasilchenko<sup>b</sup>, A.D. Garnovskii<sup>b</sup>

<sup>a</sup>Facultad de Ciencias Químicas, Universidad Autónoma de Nuevo León, San Nicolás de los Garza, N.L., A.P.18-F, C.P. 66450, Mexico <sup>b</sup>Institute of Physical and Organic Chemistry, Rostov State University, Rostov-on-Don, 344006, Russia

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#### Abstract

New chelates of the type  $ML(L^1)_n \cdot MeOH$  (n=1, 2) were obtained on the basis of the tridentate azomethinic ligands 2-*N*-tosylamine(2'-hydroxybenzal)aniline (L) and 2-*N*-tosylamine(2'-tosylaminobenzal)aniline (L<sup>1</sup>) and zero-valent transition metals (Co, Ni, Cu, Zn, Cd) under electrosynthesis conditions. The mononuclear character of these products and the participation of N<sub>2</sub>O- or N<sub>3</sub> groups of the azomethinic ligands in the coordination are demonstrated by IR, <sup>1</sup>H NMR spectral and magnetic data (77–293 K). © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Electrosynthesis; Azomethinic ligands; Mononuclear chelates

#### 1. Introduction

Transition metal complexes of the azomethinic ligands are widely studied in modern coordination chemistry. They are generally obtained from the corresponding ligands and metal salts [1–4]. However, the use of metal salts leads not only to those chelates with the composition  $ML_n$  or  $M_mL_n$ , but also to compounds that conserve the anion  $ML_{n-1}X$ (LH, LH<sub>2</sub> are ligands, X is an anion of a salt).

This disadvantage could be eliminated by applying the 'direct electrochemical technique', which, as has been shown recently in reviews [5–8] and other papers [9–12], could be successfully used to produce azomethinic metal complexes in non-aqueous solvents from elemental metals. In this paper, the results of the electrosynthesis of  $M^{II}$  (M=Cu, Ni, Co, Zn, Cd) complexes of tridentate ligands of type **1** are reported.



#### X=NTs; Y=O, NTs; Ts= -SO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub>-p

\*Corresponding author. Fax: +52-8-375-3846; e-mail: bkhariss@ccr.dsi.uanl.mx

# 2. Experimental

#### 2.1. Materials and equipment

Metals and  $Et_4NClO_4$  (Aldrich) were used as supplied. Solvents were purified by standard methods. The electrosyntheses were carried out using a PS 500-1 power supply (Sigma Aldrich). Metal contents were determined by the atomic absorption method. The contents of C, H and N were determined by standard methods of organic analysis on a Carlo-Erba 1108 microanalyzer. IR and <sup>1</sup>H NMR spectra were recorded on a Perkin-Elmer spectrophotometer and on Bruker DPX 400 equipment [125 MHz, 298 K, with Me<sub>4</sub>Si as an internal reference and DMSO-d<sup>6</sup> as a solvent], respectively. Determination of magnetic properties was carried out using Faraday's method at 77–293 K [13].

#### 2.2. Synthesis of the azomethinic ligands

#### 2.2.1. 2-N-Tosylamine(2'-hydroxybenzal)aniline (L)

A hot methanol solution (15 mL) of salicylic aldehyde (1.22 g, 10 mmol) was added to a hot methanol solution (15 mL) of 2-*N*-tosylaminoaniline (2.62 g, 10 mmol), with agitation. In 30 min, a yellow crystal product was precipi-

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tated. It was filtered, washed by methanol and twice recrystallized with ethanol. (Yield, 78%;  $\nu_{N-H}$  = 3275 cm<sup>-1</sup>).

# 2.2.2. 2-N-Tosylamine(2'-tosylaminobenzal)aniline $(L^{1})$

A hot methanol solution (30 mL) of 2-*N*-tosylaminobenzaldehyde (2.75 g, 10 mmol) was added to a hot methanol solution (15 mL) of 2-*N*-tosylaminoaniline (2.62 g, 10 mmol), with agitation. After 20 min, a yellow crystal product was precipitated. It was filtered, washed with methanol and recrystallized using toluene [14]. (Yield, 69%;  $\nu_{N-H}$ =3298 cm<sup>-1</sup>).

# 2.3. Synthesis of metal complexes by conventional chemical methods

The corresponding ligand (10 mmol) and metal acetate (10 mmol) were dissolved in methanol (20 mL). The resulting hot solutions were combined and boiled for 30 min with reflux. The solids formed were filtered, purified three times with 5 cm<sup>3</sup> of methanol and dried in vacuo at  $110^{\circ}$ C.

#### 2.4. Electrosyntheses of metal complexes

The electrosyntheses of metal complexes were carried out in methanol using Pt as the cathode and the metal as a sacrificial anode according to the technique described by Tuck [5], Duran et al. [9], Labisbal et al. [11] and in our previous works [7,8,10]. The cell consisted of a tall-form beaker, and the solution phase contained the appropriate ligand (1-2 g) dissolved in methanol containing Et<sub>4</sub>NClO<sub>4</sub> as the supporting electrolyte. The electrodes  $(2 \times 2 \text{ cm})$ were treated with diluted HCl, washed and dried before use. A stream of dry Ar was passed through the electrochemical cell before and during the process. All experiments were conducted at room temperature. The voltage was regulated to obtain an initial current of 20 mA. The time of electrolysis ranged between 1.3 and 3 h. After the electrolysis, the anode was washed, dried and weighed in order to calculate the electrochemical efficiency. The

Table 1 Experimental conditions for the electrosynthesis of metal chelates

Compound number	Metal	Initial voltage <sup>a</sup> , V	Time of electrolysis, h	Metal dissolved, g
2	Co	50	2	0.0433
3	Ni	55	1.5	0.0323
4	Cu	76	3	0.1420
5	Zn	65	2	0.0479
6	Cd	70	2	0.0838
8	Co	45	1.3	0.0282
9	Ni	60	2	0.0431
10	Cu	55	1.2	0.0564
11	Zn	62	3	0.0730
12	Cd	73	2	0.0835

<sup>a</sup> To produce an initial current of 20 mA.

resulting complexes were filtered, washed with methanol and dried in air. The yields of the final products were 83–95%. The electrolysis conditions are reported in Table 1. Elemental analysis, and spectral and magnetic data are presented in Tables 2 and 3, respectively.

### 3. Results and discussion

It has been shown [7,9,11,12] that the electrochemical method can be used to obtain metal chelates of the bidentate azomethinic ligands having the composition  $ML_2$ , where LH is salicylidenaniline and its derivatives. In this study, we established the possibility of applying this technique to the production of complexes on the basis of tridentate azomethinic ligands of type **1**.

The electrochemical cell for these systems could be presented as  $Pt(-)/CH_3OH$ ,  $H_2L(H_2L^1)/M(+)$ , where M=Cu, Zn, Ni, Co, Cd. Since  $H_2L$  and  $H_2L^1$  are dissociated in two steps according to the scheme

$$\mathrm{H}_{2}\mathrm{L}(\mathrm{H}_{2}\mathrm{L}^{1}) \Leftrightarrow 2\mathrm{H}^{+} + \mathrm{L}^{2-}(\mathrm{L}^{1(2-)}),$$

the reactions in the electrochemical cell could be described as follows:

Cathode:  $H_2L + 2e^- \rightarrow H_2 + L^{2-}$ 

Anode:  $M + L^{2-} \rightarrow ML + 2e^{-}$ 

Acetonitrile has been used as a solvent in all of the electrosyntheses of similar reported chelates [4,7,9,11,12,15]. Taking into account our previous results [16,17], methanol can also be used in these syntheses. This solvent contributes to a higher solubility of the azomethinic derivatives of type 1 and to the formation of solids with higher crystallinity. Moreover, the use of methanol can bind the electrosynthesis of metal chelates and their conventional chemical synthetic methods. As was shown in a series of publications and generalized in refs. [4,18], the most favorable conditions for metal chelate synthesis are those of a methanol medium. To confirm this fact in the case of tridentate azomethinic ligands, we carried out the synthesis of nickel and cobalt complexes with  $L^1$  by conventional chemical methods (see Table 2).

On the basis of the tridentate azomethinic ligands of type 1 under the conditions of conventional chemical synthesis starting from metal salts, monomeric (2) [19-24] and dimeric (3) [24-26] complexes could be formed:



L<sup>2</sup>=Solv, Py, o-phen, among others

Table 2 Elemental analysis and related data of the complexes obtained

Number	Compound				m.p.	Color	Formula	Found/calculated, %				
	Lig./ M <sup>2+</sup> (H)	Х	Y	$L^2$	n				С	Н	Ν	S
1	L/H	NTs	0	_	_	139-140	Yellow	C <sub>20</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub> S	65.42	4.80	7.71	8.79
									65.57	4.91	7.65	8.74
2	L/Co	NTs	0	MeOH	1	205 <sup>a</sup>	Brown	$C_{21}H_{20}N_2O_4SCo$	54.92	4.61	6.52	6.89
									55.26	4.38	6.14	7.01
3	L/Ni	NTs	0	MeOH	1	190 <sup>a</sup>	Green	$C_{21}H_{20}N_2O_4SNi$	54.49	4.45	6.43	6.77
									55.26	4.38	6.14	7.01
4	L/Cu	NTs	0	MeOH	1	> 280	Green	$C_{21}H_{20}N_2O_4SCu$	54.59	3.61	6.41	7.26
									54.78	4.34	6.08	6.95
5	L/Zn	NTs	0	MeOH	2	>220	Yellow	$C_{22}H_{24}N_2O_5SZn$	53.71	4.16	6.48	6.61
								~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~	53.76	4.88	5.70	6.51
6	L/Cd	NTs	0	MeOH	1	>280	Yellow	$C_{21}H_{20}N_2O_4SCd$	49.91	3.24	5.82	6.67
7	<b>T</b> <sup>1</sup> / <b>T</b>	NT	NUT			150 160	\$7 11	C H N O S	49.60	3.93	5.51	6.30
/	L/H	NIS	NIS	-	_	159–160	Yellow	$C_{27}H_{25}N_{3}O_{4}S_{2}$	62.21	4.72	7.98	12.50
0	$\mathbf{I}^{1}/\mathbf{C}_{2}$	NT	NTa	MaOU	1	> 250	Decourse	C II N O S Co	02.43 54.80	4.82	8.09	12.33
0	L /C0	1815	1015	меон	1	2250	DIOWII	$C_{28} R_{27} R_3 O_5 S_2 C_0$	55 26	4.00	6.00	9.03
0	$\mathbf{I}^{1}/\mathbf{N}\mathbf{i}$	NTe	NTe	МаОН	1	>250	Green	CHNOSN	55.20	3 80	7.21	10.52
,	L / M	1415	1415	MCOII	1	250	Gitti	$C_{28}I_{27}I_{3}O_{5}O_{2}I_{4}I_{5}$	55.75	3.87 4 44	6.90	10.12
10	$L^1/Cu$	NTs	NTs	MeOH	1	>250	Green	C., H., N.O.S.CI	54.87	3.58	7.00	9.69
10	2,00		1110		•	- 200	oreen	02812713050204	54.81	4.40	6.85	10.44
11	$L^1/Zn$	NTs	NTs	MeOH	1	>250	Yellow	C <sub>20</sub> H <sub>27</sub> N <sub>2</sub> O <sub>5</sub> S <sub>2</sub> Zn	54.42	3.78	6.88	9.88
								28 27 3 5 2	54.72	4.40	6.84	10.42
12	$L^1/Cd$	NTs	NTs	MeOH	1	>250	Yellow	C <sub>28</sub> H <sub>27</sub> N <sub>3</sub> O <sub>5</sub> S <sub>2</sub> Cd	51.67	3.07	6.62	9.32
								20 27 5 5 2	50.83	4.08	6.35	9.68
13 <sup>b</sup>	$L^1/Co$	NTs	NTs	MeOH	2	>250	Brown	C <sub>29</sub> H <sub>31</sub> N <sub>3</sub> O <sub>6</sub> S <sub>2</sub> Co	54.47	4.38	7.18	9.63
									54.37	4.88	6.56	10.01
14 <sup>b</sup>	$L^1/Ni$	NTs	NTs	MeOH	1	>250	Green	C <sub>28</sub> H <sub>27</sub> N <sub>3</sub> O <sub>5</sub> S <sub>2</sub> Ni	55.65	4.94	7.21	10.20
									55.26	4.44	4.60	10.52

<sup>a</sup>Decomposition.

<sup>b</sup>Obtained by chemical synthesis.

According to the elemental analysis data (Table 2), the composition of the formed complexes corresponds to the formulae  $ML(L^1) \cdot nCH_3OH$  or  $M_2L_2(L_2^1) \cdot nCH_3OH$  (n = 1, 2). Physico-chemical data indicate that structure **2** ( $L^2 = CH_3OH$ ) applies to them. The participation of the N atom

Table 3 Spectral and magnetic data of the complexes obtained

Number	IR data	<sup>1</sup> H NMR da	$\mu_{\rm eff.}$ , B.M.			
	$\frac{\nu_{\mathrm{C=N}}}{\mathrm{cm}^{-1}}$	$\delta_{_{ m OH}}$ or $\delta_{_{ m NH}}$ (aldehyde)	$\delta_{_{ m NH}}$ (amine)	$\delta_{\rm HC=N}$	293 K	77 K
1	1612	11.80	9.80	8.20	_	_
2	1605	_	_	_	4.12	4.11
3	1608	_	_	_	3.39	3.38
4	1607	_	-	_	1.83	1.82
5	1606	_	_	8.80	_	_
6	1608	_	_	8.50	_	_
7	1616	11.4	9.6	8.3	_	_
8	1610	_	_	_	4.17	4.14
9	1609	_	-	_	3.26	3.19
10	1606	_	-	_	1.87	1.84
11	1607	_	-	9.0	_	_
12	1609	_	-	8.9	_	_
13	1610	_	_	_	4.15	4.12
14	1609	-	_	_	3.47	3.22

of the azomethinic group decreases the frequency of the valent oscillations of the C=N group in the complexes in comparison to those of the ligands L and L<sup>1</sup> (Table 3) [27]. A comparative analysis of <sup>1</sup>H NMR (DMSO-d<sup>6</sup>) spectra of ligand **1** and its Zn and Cd complexes, **2** (Table 3), leads to the same conclusion, i.e. a weak-field shift of the HC=N group protons is observed which testifies about the HC=N $\rightarrow$ M coordination [28].

A wide band of valent oscillations of the coordinated methanol molecules at  $3000-3500 \text{ cm}^{-1}$  is observed in the IR spectra of the complexes. It makes it difficult to use the absorption frequencies of NH and OH groups to characterize the type of complex formation (substitution of the protons of these groups to metal ion). The <sup>1</sup>H NMR (DMSO-d<sup>6</sup>) data give more detailed information: the peaks of the protons of the NH (9.8 ppm for L and 9.6 ppm for L<sup>1</sup>) and OH (11.8 ppm for L and 11.4 ppm for L<sup>1</sup>) groups disappear in the spectra of the complex-es.

Magnetochemical data of Co, Ni and Cu complexes over a wide temperature range testify about the absence of a change in  $\mu_{eff.}$  (Table 3). This fact, especially in the case of copper complexes (the data about the antiferromagnetism of the compounds of type **3** (M=Cu) are presented in refs. [11,19,21]), also confirms the monomeric character of the chelates described.

Use of the above-mentioned tridentate ligands in conventional chemical methods (see Tables 2 and 3) allows one to produce cobalt and nickel complexes 13 and 14, which are close to those obtained by the electrochemical method. According to the reported data on the X-ray study of the similar complex, **3** (X=O, Y=NTs, M=Ni, Solv= CH<sub>3</sub>OH, n=4) [26], there are reasons to propose that they have dimeric structure **3**. However, the magnetochemical data (Table 3) testify about their monomeric character.

#### 4. Conclusions

The above data allow one to assign a structure of type 2 to the synthesized complexes. This result, in addition to the data published previously [7,11,12,29], indicates that electrochemical synthesis usually leads to mononuclear chelates of type 2; meanwhile, conventional chemical methods, with the participation of tridentate azomethinic ligands and metal salts, could also produce binuclear chelates of type 3 [24]. Moreover, the main advantages of the electrochemical methods of synthesis are the higher yields (83-95%) and the absence of anions that are frequently present in the chelates of tridentate ligands [30,31].

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