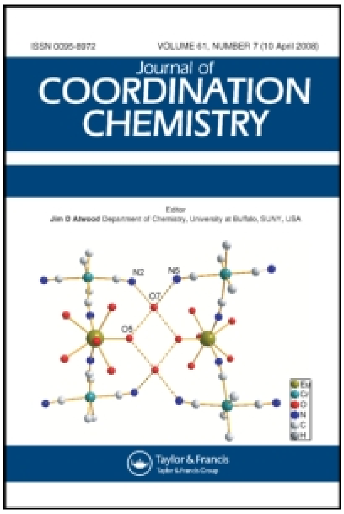

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Direct electrochemical synthesis of metal complexes of phthalocyanines and azomethines as model compounds: advantages and problems of this method <i>versus</i> traditional synthetic techniques

Boris I. Kharisov[a]; Alexander D. Garnovskii[b]; Oxana V. Kharissova[a]; Ubaldo Ortiz Méndez[a]; Aslan Yu. Tsivadze[c]
[a] Universidad Autónoma de Nuevo León, Monterrey, Mexico [b] Rostov State University, Rostov-on-Don, Russia [c] Institute of Physical Chemistry and Electrochemistry, Moscow, Russia

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Direct electrochemical synthesis of metal complexes of phthalocyanines and azomethines as model compounds: advantages and problems of this method *versus* traditional synthetic techniques

BORIS I. KHARISOV*†, ALEXANDER D. GARNOVSKII‡,
OXANA V. KHARISSOVA†, UBALDO ORTIZ MÉNDEZ† and
ASLAN YU. TSIVADZE§

†Universidad Autónoma de Nuevo León, Monterrey, Mexico
‡Rostov State University, Rostov-on-Don, Russia
§Institute of Physical Chemistry and Electrochemistry, Moscow, Russia

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A comparison of traditional and electrochemical synthetic techniques for obtaining metal complexes of azomethine and phthalocyanine is reported. It is shown that the electrochemical method affords azomethinic coordination compounds free of anions of precursors and with higher yields at ambient temperature. Electrolysis in a solid phase of phthalonitrile using a high-surface platinum cathode leads to metal-free phthalocyanine and metal phthalocyaninates at 0–25°C. The typical problems of the electrosynthetic procedures in different conditions are discussed in detail.

Keywords: Phthalocyanines; Ligand synthesis; Electrochemical synthesis; Azomethines

1. Introduction

Electrosynthesis is a readily available one-step method for obtaining coordination compounds [1–9] as described in scheme 1 [8]:

$$M^0 - e \xrightarrow{L} M\cdots\cdots L \tag{1}$$

Scheme 1. Simplest representation for metal oxidation in non-aqueous media.

The same reaction in coordinating solvents can be represented as scheme 2 [9]:

$$M - me \xrightarrow{Solv} [M(Solv)_n]^{m+} \xrightarrow{pL} [ML_p]^{m+} \tag{2}$$

Scheme 2. Metal dissolution in non-aqueous media in coordinating solvents.

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*Corresponding author. Email: bkhariss@mail.ru

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For proton-donor ligands, these processes take place at the cathode (C) and the anode (A) as shown in scheme 3:

$$\begin{gathered}\text{C: LH} + \text{ne} \longrightarrow n\text{L}^- + \frac{n}{2}\text{H}_2 \\ \text{A: M} - \text{ne} \longrightarrow \text{M}^{n+};\ \ \text{M}^{n+} + n\text{L}^- \longrightarrow [\text{ML}_n]\end{gathered} \tag{3}$$

Scheme 3. Electrochemical dissolution of metals in proton-containing solvents.

Electrosyntheses of metal complexes are usually carried out using sacrificial anodes of several metals (Group 11 – Cu, Ag, Au; Group 12 – Mg, Ca, Zn, Cd, Hg; Group 13 – Al, In, Ga, Tl; Group 14 – Sn, Pb; Group 4 – Ti, Zr, Hf; Group 15 – Sb, V, Nb, Ta; Group 6 – Cr, Mo, W; Group 7 – Mn, Re; Group 9 – Co, Ni, Pd; actinides (Th, U) and some lanthanides) and platinum as a cathode in non-aqueous solvents with dielectric constant (ε) from 3.5 to 64 [8, 9]. The most frequently used solvents are CH_3CN ($\varepsilon = 38$) and alcohols ($\varepsilon \sim 30$); usual supporting electrolytes are LiCl, $LiClO_4$, $NaBF_4$, R_4NX (R = Alk, X = Br^-, ClO_4^-, BF_4^-).

In this work, we review our recent results on the electrosynthesis of complexes of two types of nitrogen-containing ligands, namely, azomethines and phthalocyanines. The goal of the present study is: (1) to compare traditional synthetic techniques with electrochemical methods and (2) to propose recommendations for a wider use of direct synthesis in modern coordination chemistry of nitrogen-containing ligands. Detailed physical and chemical studies of the obtained metal complexes are contained in the cited references and are omitted from the present publication.

2. Equipment

The special equipment developed for electrosynthesis is described in detail [3, 10] and shown in (figures 1–4). The electrosyntheses were done in a 100 mL flask with separate cathodic and anodic spaces under an inert atmosphere and at room temperature. The reactions took different times, ranging from minutes to several hours to be completed.

3. Experimental

3.1. *General remarks*

Electrochemical experiments were carried out in the cells shown above, the simplest one an undivided 50–100 mL Pyrex cell. Acetonitrile, low molecular weight alcohols, DMF or DMSO were used as solvents. When the ligands showed low solubility in these solvents, a CH_3CN-benzene (or toluene, up to 30–50 w.%) mixture was used as solvent. Ligands (1–10 g) and the previously dried supporting electrolytes (LiCl, $LiClO_4$, $(n\text{-}Bu_4N)ClO_4$, $(n\text{-}Bu_4N)Br$, 0–0.05 g) were added to the solvent (50–100 mL). Dry nitrogen was bubbled through the cell continuously. Platinum, as wire (5–10 cm) or sheets (2×2 cm), was used as a cathode and the sacrificial metal (Cu, Co, Ni, Zn, etc. as wire or sheet, previously washed with diluted HCl or H_2SO_4) was used as anode. Electrolyses were carried out using a power supply (Sigma-Aldrich) for 1–3 h at

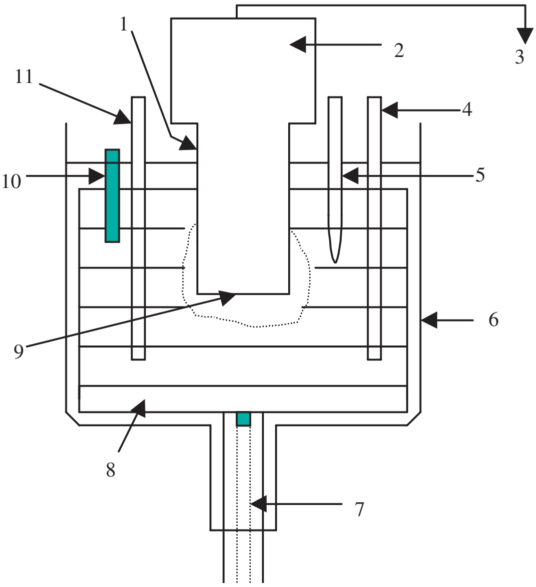


Figure 1. Sonoelectrochemical cell used for electrosynthesis and voltammetric studies [10]. 1–sonic horn, 2–transducer, 3–to control unit of sonic horn, 4–graphite counter electrode, 5–argon inlet for degassing, 6–pyrex reservoir, 7–platinum-disk macro- or micro-electrode, 8–copper cooling coil connected to the thermostatted water-bath, 9–titanium tip, 10–platinum resistance thermocouple, 11–SCE reference.

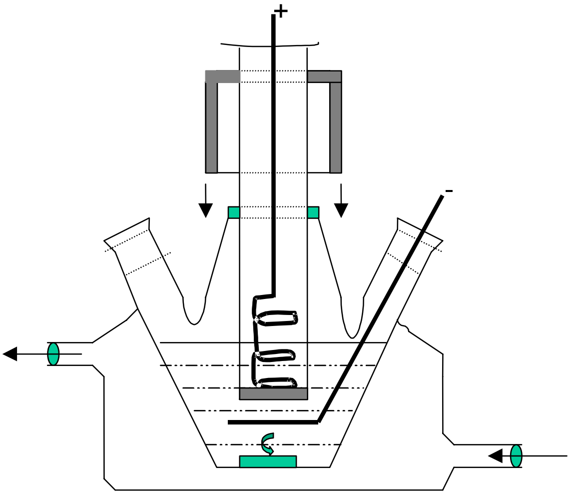


Figure 2. Divided cell for phthalocyanine synthesis [11].

20–30 mA and 10–50 V. In some cases, the cell was thermostated at 0–200°C. When necessary the cell was placed in a glove box for further manipulations, such as decantation and washing. If a solid precipitate was not obtained, the solution was partially evaporated directly in the cell or in another flask at atmospheric or reduced pressure, then filtered and washed. Yields varied from 50–98%. The electrochemical yield, η, was calculated according to equation (4), where Q is the amount of applied

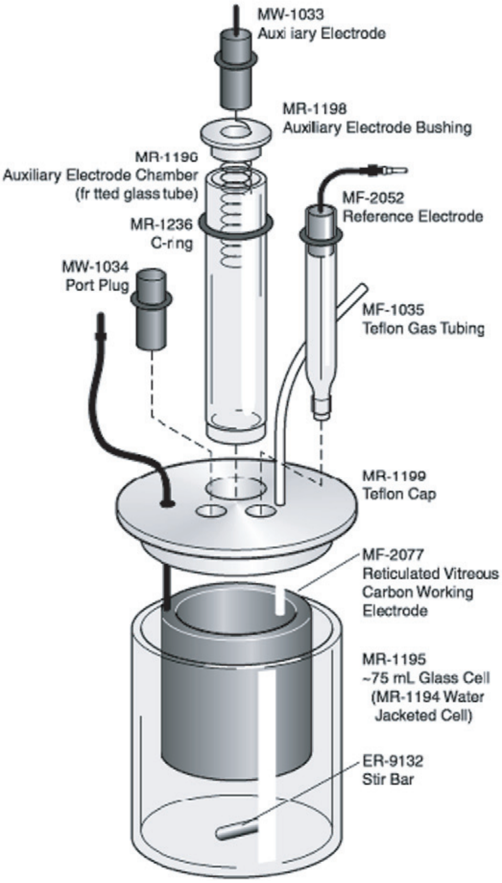


Figure 3. Commercial divided cell ("Bioanalytical systems").

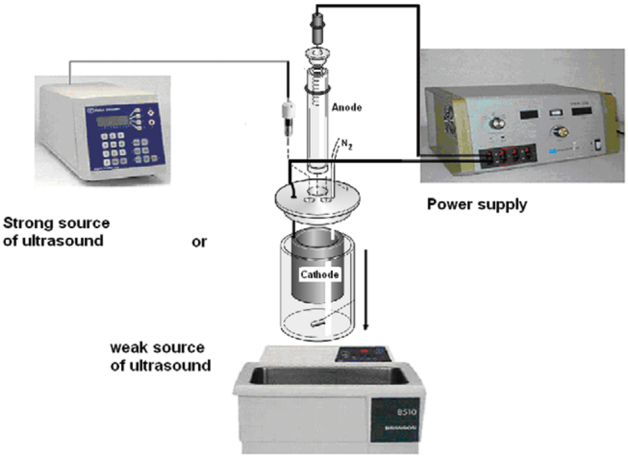


Figure 4. Combined equipment for electrosynthesis under simultaneous ultrasonic treatment.

electricity, χ is the electrochemical equivalent, $\chi = M/nF$ (where M is the metal atomic weight, n is the number of electrons, and $F = 96{,}500\,\mathrm{C\,mol^{-1}}$).

$$\Delta m_{\text{theor.}} = Q \cdot \chi = I(\mathrm{A}) \cdot t(\mathrm{sec}) \cdot \chi\left(\frac{g}{C}\right) \tag{4}$$

3.2. *Non-substituted phthalocyaninates [12]*

Template electrosynthesis in solution was carried out with reflux in the temperature range 50–180°C using phthalonitrile, 1,3-diiminoisoindoline, phthalimide or a mixture of urea and phthalic anhydride for 0.5–3 h in a series of non-aqueous solvents: alcohols, acetonitrile, DMF, DMSO, *N*,*N*-dimethylethanolamine, nitrobenzene, among others. The obtained blue solids were washed with ethanol in a Soxhlet extractor and dried in air at room temperature.

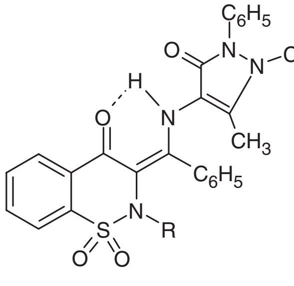
3.3. *Direct low-temperature electrosynthesis of metal-free phthalocyanine and copper phthalocyaninate in the solid phase*

In some experiments, the electrochemical cell did not contain the homogeneous solution mentioned above. Thus, a solid phase of the precursor was electrolysed to obtain phthalocyanine from phthalonitrile (16 g) at 0–25°C in a 200 mL cell. The solid was moistened with a small quantity of *N*,*N*-dimethylethanolamine or methanol (7–10 mL) using CH_3ONA (3 drops of a 25% solution in methanol) as nucleophilic agent and $(n\text{-Bu})_4NClO_4$ (0.02 g). Solid phthalonitrile was in contact with a high-surface cathode (platinum net, ~30 cm^2), which was completely immersed in the solid. The anodic space contained a saturated phthalonitrile solution (platinum or copper anode 2 × 2 cm). During the reaction, the temperature was carefully controlled. Phthalocyanine(ate) yields were 5–30%, depending on temperature and solvent (higher in the case of *N*,*N*-dimethylethanolamine).

Conditions and observations for all phthalocyanine syntheses are presented in table 1.

3.4. β-*Aminovinylketone complexes [13]*

β-Aminovinylketones (**1**) (R = H, Me, Et) were synthesized at Rostov State University and used without additional purification.



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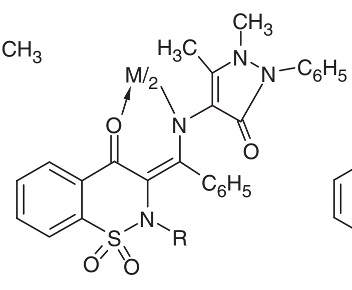

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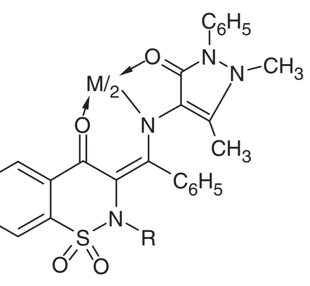

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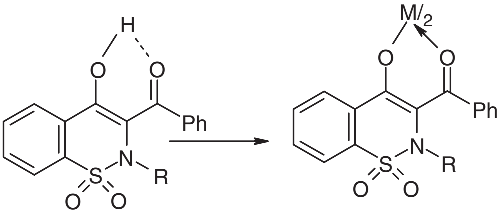
Table 1. Conditions and observations for phthalocyanine syntheses.

System*	Temperature (°C)	Yield (w.%), observations
	0–25	
Direct low-temperature electrosynthesis of a metal-free phthalocyanine and copper phthalocaninate in a solid phase		
200-mL cell, phthalonitrile (16 g), solvent 7–10 mL (*N*,*N*-dimethylethanolamine, methanol).	0–20	5–30 Most of the phthalonitrile was present as a solid, in which the high-surface platinum cathode was immersed.
	70–100	
Electrochemical synthesis of a metal-free phthalocyanine from phthalonitrile		
Solvents (100 mL): EtOH, *n*-BuOH, n-$C_5H_{11}OH$, *N*,*N*-dimethylethanolamine, ethyleneglycol, phthalonitrile (5 g).	75–100	65–98 Interaction of the components of the reaction mixture in *i*-BuOH without electrolysis does not lead to phthalocyanine formation. The product is formed from 52–55°C with yields from 3–97% at 90°C.
Electrochemical synthesis of a metal-free phthalocyanine from 1,3-diiminoisoindline (1,3-D)		
100 mL of solvent, 1,3-D (3 g).	75 (EtOH)	8
	100 (*i*-BuOH)	5
	100–133 (*N*,*N*-dimethylethanolamine)	
	For comparison:	65–92
	189 (DMSO)	98
	145 (DMFA)	94
	190 (nitrobenzene)	44
Electrosynthesis of lanthanide phthalocyaninates		
Phthalonitrile (5 g), Ln, Sm, Nd, Pr (anode, 5–8 g), *i*-BuOH (100 mL), tetra-*n*-butylammonium bromide (0.02 g)	100	92–95 Ultrasonic treatment of the reaction system.
	>100	
Electrosynthesis of copper phthalocyaninate from urea and phthalimide with a copper anode in tetramethylurea (TMU) as a solvent		
Phthalimide (3 g), Cu (1 g), tetramethylurea (100 mL), urea (4 g) and MoO_3 (0.015 g).	170 TMU	17 TMU was used as solvent and promoter simultaneously.
Electrosynthesis of copper phthalocyaninate from urea and phthalic anhydride with copper anode in tetramethylurea (TMU) as a solvent		
Urea (4 g), phthalic anhydride (3 g), TMU (0.12 mL), MoO_3 (0.015 g). Solvent: mixture of nitrobenzene (50 mL) and trichlorobenzene (50 mL).	170 TMU	7 Poorly reproducible. No products were observed with Fe, Sb and Mg anodes.
Chemical and electrochemical interaction of urea and phthalic anhydride with copper in various solvents		
Urea (4 g), phthalic anhydride (3 g), Cu (1 g, powder or sheet-anode), MoO_3 (0.015 g), 1-methyl-2-pyrolidinone (0.5 mL) and solvent (100 mL) (DMEA, ethyleneglycol, glycerine, DMSO, DMF).	120–190	0 In parallel *non-electrochemical* experiments, hysol (mixture of high-weight hydrocarbons), mesitylene, and xylene were used. Only in hysol, the yield of CuPc was 85%, no phthalocyanines were observed in other solvents, except traces of PcCu in mesitylene.

*+0.02 g of tetra-*n*-butylammonium perchlorate or bromide (except in DMSO and DMF) and 3 drops of 25% solution of sodium methoxide in methanol (only in case of phthalonitrile as a precursor). 100–200 mL cell.

No supporting electrolyte was added to avoid the formation of a mixture of products. The sodium salt of the corresponding ligand was generated *in situ* and used as supporting electrolyte [14]. It was obtained by the reaction of 2 mg of metallic sodium and 0.001 mol of ligand **1** in 25 mL of methanol. The electrolysis was carried out at a fixed voltage over 2.5 h (M = Zn) or 1.5 h (M = Cu). The applied voltage, which varied with time, as the *in situ* generated supporting electrolyte was consumed, was optimal at 30 V. The applied current ranged from 10 to 20 mA. After electrolysis, the solid products **2** and **3** were filtered off and washed with hot methanol. Electrosyntheses, but without the *in situ* generation of supporting electrolyte, were also carried out [15] using similar ligands **4** (R = H, Me, reaction (5)) which formed complexe **5**.

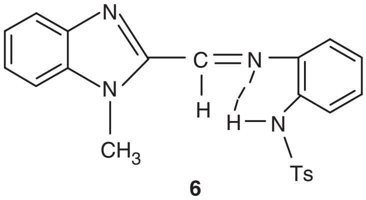


4 **5**

(5)

3.5. *Heteroazomethinic bi- and tridentate ligands LH [16]*

Ligands **6**–**9** were synthesized at Rostov State University and used without additional purification.



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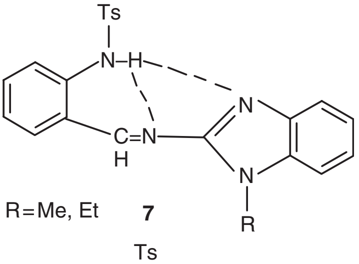
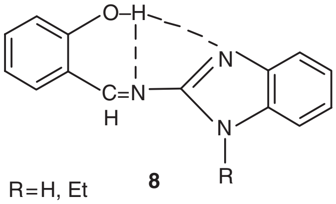


R=Me, Et **7**



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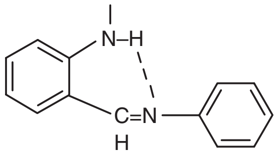
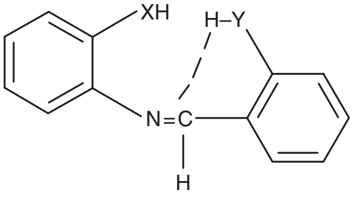


9

Electrosyntheses were carried out with Cu or Ni sacrificial anodes in methanol for 1.2–3 h. The solids formed were filtered off, washed with hot methanol and dried *in vacuo* at 70°C.

3.6. *Tridentate azomethinic ligands of the type LH_2 [17]*

Ligand **10** were synthesized at Rostov State University and used without additional purification.



10

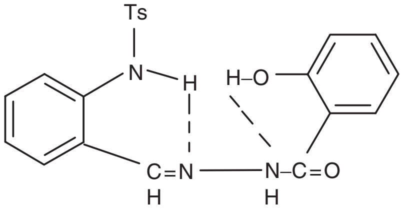
X = NTs; Y = O (LH_2), NTs (L^1H_2)

Ts = $-SO_2C_6H_4-CH_3$-*p*

Electrosyntheses were carried out with Cu, Ni, Co, Cd or Zn sacrificial anodes in methanol for 1.2–3 h. The solids were filtered off, washed with hot methanol and dried *in vacuo* at 70°C.

3.7. *Tridentate azomethinic ligands LH_3 [18]*

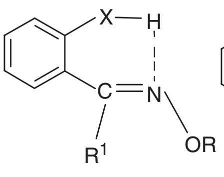
Ligand **11** were synthesized at Rostov State University and used without additional purification. Electrosyntheses were carried out following a similar procedure as before.



11

3.8. *Oximes [19]*

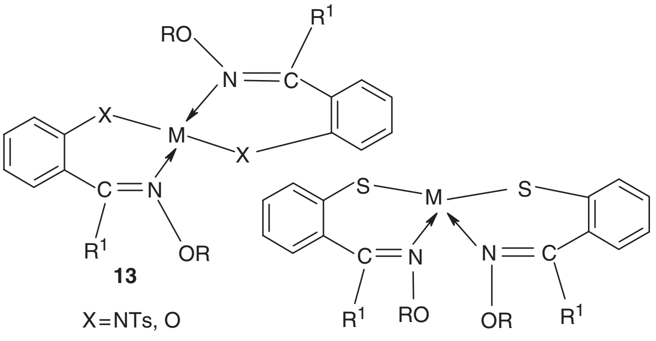
The ligand **12** {2-(*N*-tosylamino)benzaldoxime}(L^1H_2) and {2-(*N*-tosylamino)benzal-*O*-methyloxime (L^2H) were used in the electrosyntheses of complexes **13** and **14**.



12

X = NTs, O, S

R, R^1 = H, Alk, Ar



13

X = NTs, O

14

Conditions and observations for all the syntheses of azomethinic complexes are summarized in table 2.

4. Results and discussion

4.1. *Problems observed during electrosynthesis*

In the electrosynthesis of azomethinic and other metal complexes we often encountered the following problems.

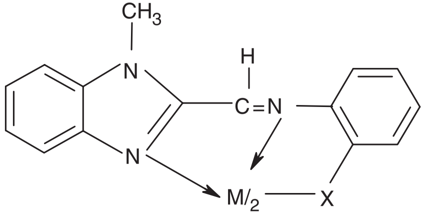
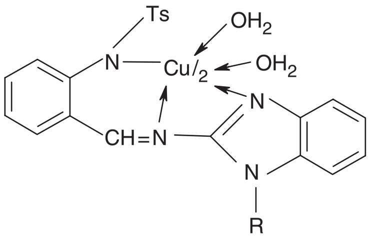
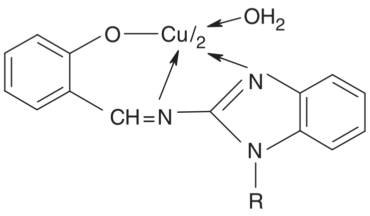
First, when using metals such as copper and nickel (or lanthanides in phthalocyanine synthesis) as the anode, the product deposited on the metal surface resulting in a gradual increase of the voltage and a decrease in the metal dissolution rate. In this case it was necessary to stop the electrolysis (occasionally several times during the process) and open the cell to clean the anode surface with tweezers. In the case of copper anodes, contamination of the product with elemental metal was a reason to eliminate both from the surface, hence, it was impossible to define authentically both product purity and composition by elemental analysis. To avoid this problem we had a combination of direct electrochemical dissolution of metals with simultaneous ultrasonic treatment of the electrochemical cell. Ultrasound promotes metal dissolution, increasing mass transfer to or from a surface of the electrodes, thus reducing duration of reactions, and optimizes chemical and electrochemical output of a product.

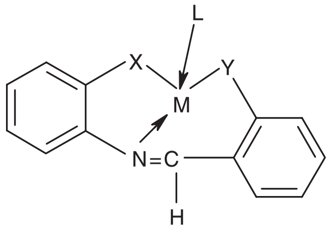
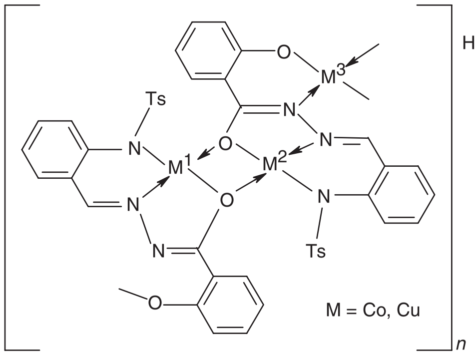
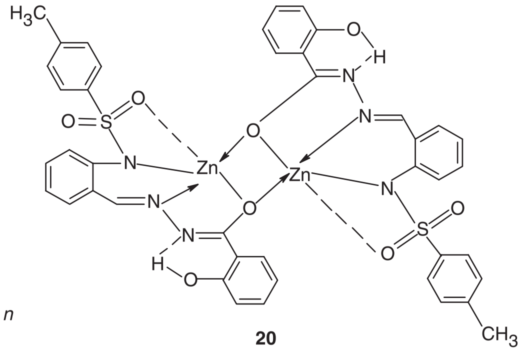
Second, in some systems where copper was used, the desirable dissolution of copper was observed, but also its sedimentation on surfaces of the platinum cathode; metal transfer from the anode on the cathode with a zero or low output of an end-product (copper complex) took place. This happens when electrolysis is carried out using high potentials and the solution has a low electrical conductivity.

Third, in case of high solubility of a product in the solvent used, sometimes there was a problem of separation of a product from the precursor ligand. In this case, partial evaporation of solvent *in vacuo* or air (depending on stability of the coordination compound), or salting out of the complex was used.

Fourth, metals have different ability to electrochemically dissolve and form coordination compounds with ligands in solution. For example, in the case of iron, even when carefully dried solvents were used, formation of appreciable quantities of iron hydroxides instead of the expected product with azomethinic ligands was observed. In case of refractory metals (W, Mo), HF or even an oxidant as strong as hydrogen peroxide [2] or nitrosonium salts [1], needed to be present in the system [2] otherwise electrochemical dissolution of these metals is practically impossible. In those cases, it is not a pure electrochemical process, but a mixture of chemical and electrochemical dissolution of metal and it is not possible to calculate an electrochemical yield. On the other hand, copper itself in an acetonitrile solution of tetramethyltiuram disulfide is rather quickly dissolved, and application of potential sharply accelerates metal dissolution, again leading to a mixture of chemical and electrochemical processes. In general, in any electrochemical anodic dissolution of metal in non-aqueous solutions it is impossible to avoid completely chemical dissolution of the sacrifical metal especially when metals with small lattice energy are used, for example, copper.

Table 2. Conditions and observations for syntheses of azomethinic complexes.

Ligands, conditions	Products, yield (w.%), observations
β-Aminovinylketones (**1**, **4**) (R = H, Me, Et) Cu, Ni, Co or Zn (anode); methanol, metallic sodium (in case of **1**), 23°C.	**2**, **3**, **5**; 28–57% Using the ligand **1**, its sodium salt was generated *in situ* to provide electron conductivity in the cell. The compositions of both chemically and electrochemically generated complexes correspond to ML_2.  **15**
Heteroazomethinic bi- and tridentate ligands LH **6**–**9** Cu, Ni or Zn (anode); methanol, 23°C.	 **16** R=Me, Et  **17** R=H, Et 85–95% *An important difference* between chemical and electrochemical syntheses of these complexes is that in the first case, compounds of the type $ML(OCOCH_3)$ are formed, whereas in the second case, the compounds are isolated free of anions (presence of coordinated water molecules is possible).

Tridentate azomethinic ligands LH_2 **10** Cu, Ni, Co, Cd or Zn (anode); methanol, 23°C.	 **18** L=Solv 87–96% Complexes, obtained chemically and electrochemically, are similar (the difference is due to the number of coordinated water molecules).
Tridentate azomethinic ligands LH_3 **11** Cu, Zn (anode); methanol, 23°C.	 **19**  **20** 90–95% The only difference of chemical and electrochemical routes is the higher yield (90–95%) of the second method in comparison with traditional techniques (75–80%).
Oximes **12** Cu, Ni, Zn (anode); methanol, 23°C.	**13**, **14**; 83–92% Copper complexes, obtained chemically and electrochemically using the ligand L^1H_2, possess compositions $Cu(L^1H)_2$ and CuL^2_2, respectively. For the ligand L^2H, the complexes $ML^2_2(M=Cu, Ni)$ were formed in both cases.

Fifth, for metal alloys as sacrificial anodes, each component of an alloy self-dissolved, as a result, calculation of an electrochemical yield is impossible. Due to the presence of a "higher gradient of concentration of atoms of metal on a surface of an alloy in comparison with metals in the individual form", alloys, especially those containing such chemically active metals as Al, Ca, Sn (these alloys possess intermetallic properties), have higher rates of dissolution [20].

Sixth, electrosynthesis at temperatures above 100°C (to obtain, for example, metal phthalocyaninates from urea and phthalic anhydride) also has several complications. The cell should contain a condenser for high-boiling organic solvents, in particular, solids at room temperature {urea is sometimes used in phthalocyanine synthesis as both a reagent, and solvent M.p. 135°C, or hydrocarbons that are solid at a room temperature and liquid above 100°C; the inert dissolving medium has no influence on the mechanism of macrocycle formation}. The insulation plastic of wires is undesirable due to possible degradation by chemical vapors which often penetrates outside in non-hermetic places of a cell. Sublimation–desublimation processes with participation of precursors are also possible (for example, phthalic anhydride), leading to redistribution of reagents in various parts of the equipment, including the electrodes, and affecting the stirring. In any case, direct electrosynthesis is more suitable in softer conditions, ideal at room temperature. At elevated temperatures (>100°C), preference should be given to classical, pure chemical methods of metal complex synthesis.

Seventh, sometimes it is necessary to carry out electrosynthesis of unstable substances (some organometallic compounds) at temperatures below 0°C. In these conditions, it is necessary to use dehydrated solvents with low melting points, not to apply high current and to strictly supervise temperature to avoid unexpected heating of a cell, as it may be a source of current fluctuations. Techniques of electrosynthesis at low temperatures are insufficiently developed and a promising field for development. Most electrochemical syntheses are carried out at room temperature [3].

Among advantages of the electrochemical dissolution of metals are one-step reactions, higher yields and possibility for obtaining some molecules inaccessible by traditional synthetic routes. When azomethinic ligands were used as precursors, these advantages were observed. Precise chelates are easily formed from ligands containing mobile hydrogen atoms in OH, SH and NH groups. Also, as metals are used in elemental form, the resulting mono- and polynuclear complexes did not contain anions.

Direct electrochemical synthesis with a sacrificial cathode was only applied for obtaining metalloorganic compounds of Pb, Sn and Hg [21]. Attempts to apply this method were unsuccessful for synthesis of phthalocyanine and azomethinic complexes of the metals. Only anodic metal dissolution has some success in all experiments.

4.2. *Electrosynthesis of a metal-free phthalocyanine and metal phthalocyaninates*

According to elemental analysis data, part of the obtained mixture of products corresponds to typical phthalocyanines {metal-free PcH_2 or MPc, M = Cu(II), Fe(II), etc.) [12]. In the synthesis of a *metal-free phthalocyanine*, obtained from phthalonitrile, the use of aprotic solvents (DMSO, Py, dioxane, THF, DMF, acetone, nitrobenzene) both under electrochemical synthesis conditions and without electrolysis did not produce PcH_2. The absence of phthalocyanine may be explained by the difficulty of nucleophilic attack by sodium methoxide to the CN group of the phthalonitrile, in particular, due to the interaction between sodium methoxide and the aprotic solvent. The most reproducible results have been obtained in protic solvents such as *i*-BuOH and dimethylethanolamine with almost quantitative yields. A successful synthesis in protic media is in agreement [11] that "a protic solvent is required for the electrosynthesis of PcH_2". Sodium methoxide as a source of alkoxide favors nucleophilic attack at the cyano group of phthalonitrile to form 1-alkoxy-3-iminoisoindoline as an intermediate subject to further reduction and cyclization.

In contrast to *N*,*N*-dimethylethanolamine, the reaction in *i*-BuOH without electrolysis of the reaction mixture does not produce Pc. This fact could be successfully used to electrosynthesize various metal phthalocyaninates, synchronizing the Pc formation on the cathode and metallic anode dissolution preventing formation of mixtures of metal-free and metal phthalocyaninates. *N*,*N*-dimethylethanolamine can also be used as a solvent for the electrosynthesis in a *solid phase of phthalonitrile* without stirring at low temperatures, where the formation of macrocycle takes place near the cathode surface. Methanol can be also used in this procedure, although yields were smaller (2–8%). No phthalocyanine formation was observed in other alcohols.

Electrosynthesis of a metal-free phthalocyanine from 1,3-diiminoisoindoline (1,3-D), can be carried out [12] (as well as without electrolysis) in *aprotic solvents*, such as DMF or DMSO. It is surprising that the yields of phthalocyanine in ROH are comparatively small (5–8%). Among OH-containing protic solvents, the *N*,*N*-dimethylethanolamine is characterized by the best yields (up to 92%). In our opinion, successful chemical and electrochemical synthesis of Pc from 1,3-D in aprotic solvents in comparison with those with PN shows that the influence of solvent takes place in the first stage of the process (1,3-D formation). For further reactions (cyclization and reduction of 1,3-D), the solvent is not important. The formation of Pc from 1,3-D takes place in all the solvents used; higher yields can be achieved by optimization of the processes (variation of concentration of 1,3-D, use of electrosynthesis and/or selection of the best solvent).

For *metal phthalocyaninates*, the electrochemical method has been used before for the synthesis of PcCu, using a copper anode [11, 22] or $CuSO_4$ [22] and for some other metal (Ni, Co, Mg, Pb) phthalocyanines using metal salts dissolved in a reaction system containing phthalonitrile [22]. Electrochemical processes in these reactions can be represented as follows (6, 7): Anodic dissolution in phthalonitrile solutions (6):

$$\begin{aligned}&\mathit{Cathode}: 4\mathrm{PN} + 2\mathrm{e}^- + 2\mathrm{ROH} \rightarrow \mathrm{PcH_2} + 2\mathrm{RO}^-\\&\mathit{Anode}: \mathrm{M}^0 - 2\mathrm{e}^- \rightarrow \mathrm{M}^{2+}\\&\mathit{Then}: \mathrm{M}^{2+} + \mathrm{PcH_2} \rightarrow \mathrm{PcM} + 2\mathrm{H}^+\\&\mathrm{H}^+ + \mathrm{RO}^- \rightarrow \mathrm{ROH}\end{aligned} \tag{6}$$

Formation of phthalocyaninates by electrolysis of metal salts (7):

$$\begin{aligned}&\mathit{Cathode}: 4\mathrm{PN} + 2\mathrm{e}^- + 2\mathrm{ROH} \rightarrow \mathrm{PcH_2} + 2\mathrm{RO}^-\\&\mathit{Anode}: 2\mathrm{Cl}^- - 2\mathrm{e}^- \rightarrow \mathrm{Cl}_2^*\\&\mathit{Then}: \mathrm{M}^{2+} + \mathrm{PcH_2} \rightarrow \mathrm{PcM} + 2\mathrm{H}^+\\&\mathrm{H}^+ + \mathrm{RO}^- \rightarrow \mathrm{ROH}\end{aligned} \tag{7}$$

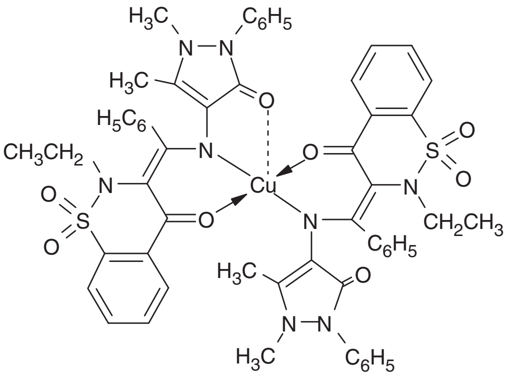
*Chlorination of the formed macrocycle is possible.

Attempts to use phthalimide or a mixture of urea and phthalic anhydride for one-step electrochemical preparation of a metal-free phthalocyanine were unsuccessful [12]. However, use of a copper anode, give PcCu with small yields (7%) in tetramethylurea (used as solvent and promoter simultaneously, "inert" in relation to urea and phthalic anhydride) using these precursors (table 1) [12]. Other metals (Fe, Mg, Sb) did not produce PcM electrochemically, although copper and iron phthalocyanines are formed from metal powders and these precursors without electrolysis in yields of 69–77%. Using these precursors, electrosynthesis affects reaction route instead of increasing yields.

The *main conclusion* on usefulness of direct electrosynthesis for template synthesis of metal-free phthalocyanines and metal phthalocyaninates is that it is possible to obtain PcH_2 or PcM from different precursors in wide temperature ranges, 0–190°C with different yields. The preferred solvents are low-weight alcohols for phthalonitrile, aprotic solvents for 1,3-diiminoisoindoline and tetramethylurea in case of industrial precursors (urea and phthalic anhydride). In the last case electrosynthesis is not desirable since it affects reaction course.

4.3. β-*Aminovinylketones [13, 15]*

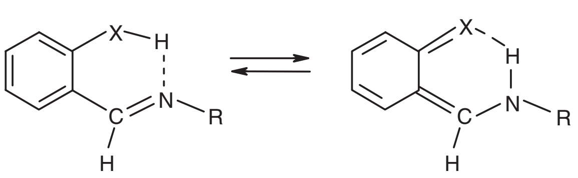
A series of ligands, derived from the β-aminovinylketones (**1**) and (**4**), was used for electrosynthesis. These ligands can be considered as mono (*O*)-, bi- (*N*,*O*)- or tri (*N*,*O*,*O*)-dentate ligands, depending on the number of donor atoms connected with the metal atom. As mentioned above, the electrochemical synthesis of metal complexes of ligand **1** was carried out by generation of supporting electrolyte *in situ*. The composition of electrochemically synthesized compounds **2**, **3**, and **5** corresponds to ML_2 (where LH is a protonated ligand **1** and L is the corresponding deprotonated ligand. Such a composition is typical for chemically synthesized metal chelates of aliphatic and aromatic β-aminovinylketonates [23–25], β-diketonates of 1,2-benzothiazine-1,1-dioxide [26] and 3-carboxamide-4-hydroxy-1,2-benzothiazine-1,2-dioxide [27]. Chelate structures of the synthesized complexes are confirmed by disappearance of typical bands for the secondary amino group in IR spectra of the complexes (for the ligand LH **1**, vibrational oscillations of the NH-group are observed at 3300–3450 cm^{-1}) and other data (see details in [13]), in particular X-ray structural data for a copper complex **21** of ligand **1**:



The electrochemical synthesis of new β-aminovinylketonates with 1,2-benzothiazine-1, 1-dioxide fragments and the coordinatively-active antipyrine fragment generates products with the same ML_2 basic formula and with coordination core Mo_4, as the complexes obtained by traditional techniques.

4.4. *Schiff bases [16]*

Azomethinic ligands **6**–**9** can produce distinct metal complexes in different synthetic conditions due to the presence of intra-molecular hydrogen bonds, tautomeric equilibrium (8) between keto–enol (thion–thiol) and imino–amine forms with molecular configurations **22** and **23**:

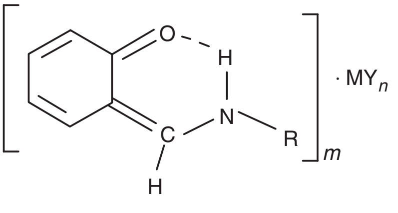


(8)

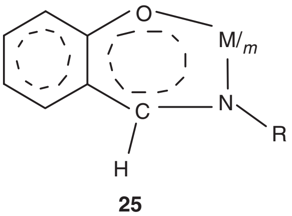
22 **23**

X = NR′, O, S; R′ = H, Alk, Ar, Ts

These structures lead to the formation of two types of coordination compounds – adduct **24** and chelate **25** with deprotonated azomethine molecule having inner-chelate bonds:

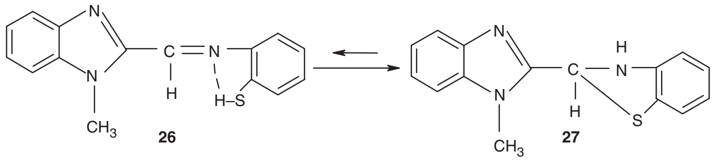


24

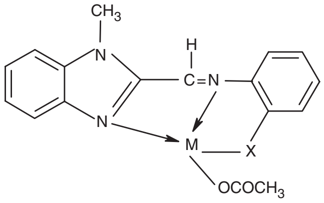


25

Comparison of electrochemically obtained complexes of the ligands **6**–**9** with analogous complexes, synthesized by pure chemical routes, shows the *following important differences*. Co, Zn and Cd complexes with **6** have composition $ML_2 \cdot nH_2O$ (**15**) ($n = 0, 1, 2, 5$) forming five-membered cycles, while chemically obtained Cu, Ni and Pd complexes with similar ligands **26**–**27** (existing in two tautomeric forms) correspond to the general formula $MLAc \cdot nH_2O$ (**28**) ($n = 0, 1, 2$); they also contain an acetate-anion, which is absent in the electrochemically synthesized product.



26 **27**



28

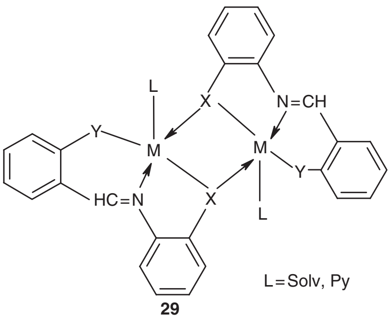
Ligands **7** and **8** were used as six-membered chelate rings. The ligand **7** chemically forms copper chelate $CuLAc \cdot H_2O$. Electrosynthesis using **7** and **8** allows formation of chelates $CuL_2 \cdot 2H_2O$ (**16**), NiL_2 and $CuL_2 \cdot H_2O$ (**17**). The coordination sphere of the copper atom is saturated by deprotonation of *O*-tosylamino- or *O*-hydroxo groups and preservation of the acetate-anions (chemical synthesis) or OH-groups (electrosynthesis). Ligand **9** with a *O*-tosylamino group, but no heterocyclic fragment, chemically and electrochemically forms the same products ML_2 [16]. Thus, the nature of metal and ligand, as well as the synthetic method, influences composition of the final products of the studied heteroazomethinic ligands LH.

4.5. *Tridentate azomethinic ligands LH_2 [17]*

Tridentate ligand **10** (H_2L {2-*N*-tosylamino(2′-hydroxybenzal)aniline} and H_2L^1 {2-*N*-tosylamino(2′-tosylaminobenzal)aniline} dissociate in two steps according to the scheme $H_2L(H_2L^1) \leftrightarrow 2H^+ + L^{2-}(L^{1(2-)})$, and reactions (9) in the cell can be described as follows [17a]:

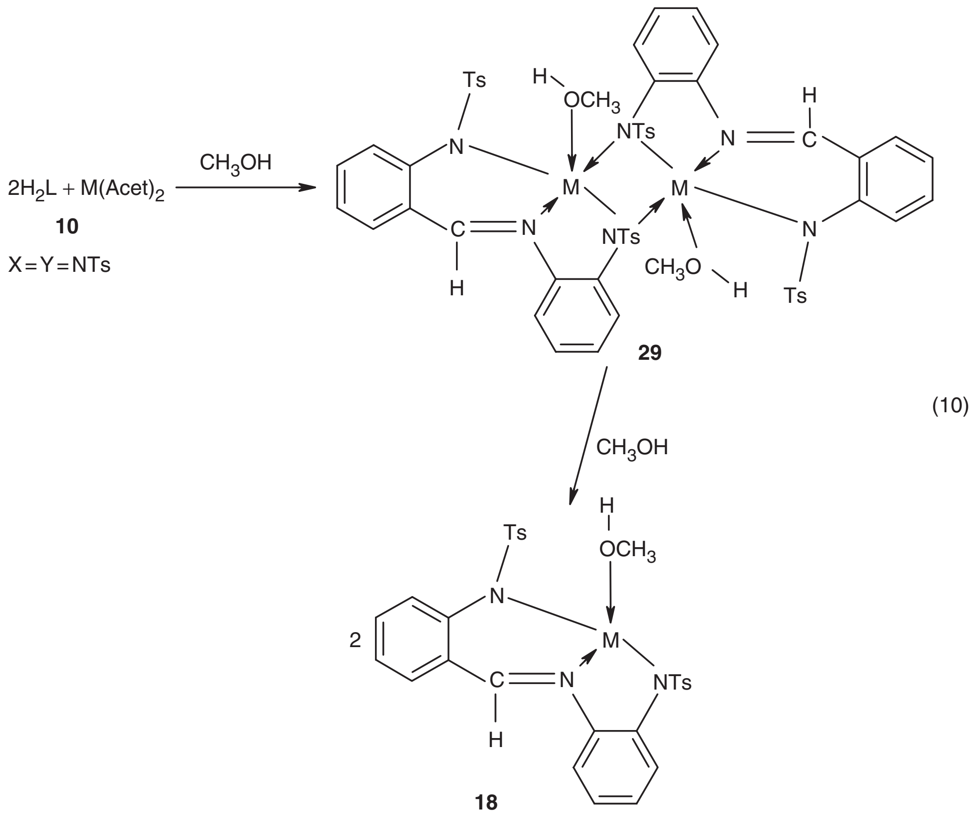
$$\begin{aligned} &\mathit{Cathode}\colon H_2L + 2e \rightarrow H_2 + L^{2-} \\ &\mathit{Anode}\colon M + L^{2-} \rightarrow ML + 2e \end{aligned} \tag{9}$$

On the basis of this ligand, traditional syntheses give monomeric **18** [28, 29] and dimeric **29** [30] complexes:



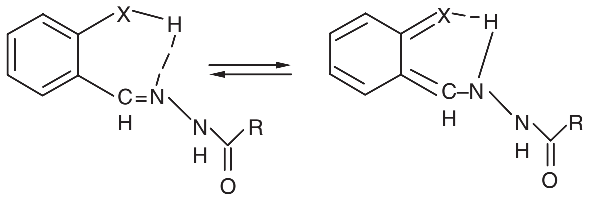
29

Electrochemically obtained complexes, $ML(L^1) \cdot nCH_3OH$ or $M_2L_2(L^1_2) \cdot nCH_3OH$ ($n = 1, 2$), have a structure such as **18** ($L = CH_3OH$) on the basis of physical and chemical studies [17a]. Complexes of the same metals, obtained chemically and electrochemically, are similar (differences can be related to the number of solvated methanol molecules) [17b]. Formation of complexes ML CH_3OH is related to instability of dimeric molecules **29**, caused by a steric influence of NTs-fragments and methanol (reaction (10)):



4.6. *Tridentate azomethinic ligands LH_3 [18]*

Salicylhydrazone of 2-(*N*-tosylamino)benzaldehyde **11** exists in two tautomeric forms **30** ⇄ **31**, typical for other azomethinic ligands, where the left form **30** prevails.



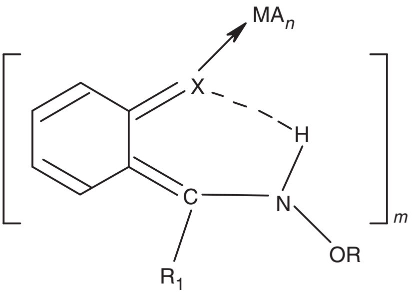
30 **31**

X=NTs, O; R=H, Alk, Ar

Ligand **11** forms various types of complexes, including bi- and trinuclear structures [31]. In our experiments, the coordination compounds $[Cu_3L_2]_n$ **19** (M = Cu) and $[Zn(LH)]_2$ **20** (LH_3 = **11**) were isolated both by chemical and electrochemical methods. For copper complex **19**, a full deprotonation of the ligand system LH_3 takes place (all 3 hydrogen atoms are displaced by metal), while for zinc complex **20**, one hydrogen remains in the molecule. For this ligand system, the difference between chemical and electrochemical techniques is only a higher yield of formed coordination compounds in case of electrosynthesis (90–95%) in comparison with traditional methods (75–80%).

4.7. *Oximes [19]*

Among oximes, we selected metal chelates of 2-(*N*-tosylamino)benzaldoxime L^1H_2 (**12**, X = NTs, R = R^1 = H) and its *O*-methylderivative L^2H (**12**, X = NTs, R = Me, R^1 = H), which have not been electrochemically obtained. Among other types of complexes [32, 33], the most typical complexes of ligands **12** are monomeric *trans*-planar complexe **13** (X = O) [34] and *cis*-planar complexes **14** (X = S) [35]. In addition to *trans*-planar structures (M = Pd) [36], a distorted octahedral structure is formed in complexe **13** at the expense of inter-molecular coordination M–O (M = Cu) [37, 38]. Also, molecular adduct **32** can be isolated using metal halides $MHal_n$ in non-aqueous media [39].



32

X = MNTs, O, S; R, R^1 = H, Alk, Ar;
A = Hal, NO_2, NCY (Y = O, S, Se);
m,*n* = 1–5

According to our data, complexes ML^1 (M = Cu) are chemically formed from the ligand L^1H_2 and copper chloride or acetate, while direct electrosynthesis leads to $M(L^1H)_2$. However, using L^2H, the complexes ML^2_2(M = Cu, Ni) were obtained both chemically and electrochemically. Copper complexes $Cu(L^1H)_2$ and CuL^2_2(N = NTs) possess tetrahedral structures, according to the results of physical and chemical studies.

The *main conclusion* on comparison of traditional and electrochemical methods for this series of ligands is that the replacement of the first techniques by the second allows obtaining azomethinic complexes having distinct composition. Thus, in case of oximes, copper complexes of the ligand **12** (X = NTs, R = R^1 = H; X = NTs, R = Me, R^1 = H), obtained chemically and electrochemically, have compositions $Cu(L^1H)_2$ and

CuL_2^2, respectively, and different properties. Depending on the metal, ligand systems can behave as ambidentate ligands, forming, in case of β-aminovinylketones (**1**), metal chelates with tetrahedral (Cu^{+2} and Zn^{+2}) or octahedral (Co^{+2} and Ni^{+2}) environments. At the same time, both techniques also give identical or similar products, for instance complexes of the ligands **1**, **4** and **9**. Main advantages of the direct electrochemical methods are high yields (80–96%) and absence of salt anions in complexes (anions are frequently present in chelates of tridentate heteroarene ligands [4].

4.8. *Optimization of the electrosynthesis using ultrasonic treatment*

In addition to advantages, direct electrosynthesis possesses have disadvantages, as, for example, formation of a solid insoluble product on anode surface, especially using a copper anode and azomethine ligands in non-aqueous solvents or lanthanides (anode) and phthalonitrile [40]. Observing behavior of various metals, it was noted that metal nature (particularly determining solubility of their complexes) has a primordial role in adhesion of reaction product to a metal anode. For instance, at equal other conditions (the same azomethinic ligands, solvents, temperature, reaction time, voltage and current, electrode surface and distance between them, volume of solution, etc.), nickel complexes, which are slightly more soluble in comparison with analogous copper complexes, do not form a stable product layer on the anode surface and accumulate in the bottom of the cell. A small quantity of the product, which is still kept on anode surface, is easy deleted mechanically; moreover, nickel particles are not deleted from the anode together with the product, in a difference with copper.

To resolve these problems, we used a combination of the direct electrochemical dissolution of metals and simultaneous ultrasound treatment of the electrochemical cell (figure 4). It is well known that ultrasound is an additional factor, accelerating metal dissolution in non-aqueous solutions [41–43]. In case of *phthalonitrile* as precursor in template formation of phthalocyanine and lanthanides (La, Nd, Pr and Sm) as anodes, use of ultrasound was not only desirable, but necessary because of difficulty in electrolysis with these metals as anodes [40]. In a difference of copper, nickel, cobalt and other transition metals as anodes in phthalocyanine synthesis, use of lanthanides, even in well-polished form, led to a stable product layer on the anode surface, sharply increasing voltage in the system.

Electrosyntheses with lanthanides were carried out at 100°C in *i*-BuOH for 2 h under weak ultrasonic treatment (electrodic reactions (11)).

$$\begin{aligned} &\mathit{Cathode}: 4C_6H_4(CN)_2 + 2e \rightarrow PcH_2 \\ &\mathit{Anode}: Ln \rightarrow 3e \rightarrow Ln^{3+} \\ &\mathit{Then}: 2Ln^{3+} + 3PcH_2 \rightarrow Ln_2Pc_3 + 6H^+ \end{aligned} \tag{11}$$

According to [44], maximum yield (80–90%) of three-decker super-complexes Ln_2Pc_3 (in comparison with compounds XLnPc and $LnPc_2X$) takes place (by chemical synthesis) at molar ratio "phthalonitrile : metal salt" ($LnCl_3$, M = La, Sm, Gd, Tm and Lu) of 6 : 1. In our experiments, yields were about 95% (at ultrasonic treatment) or 35–50% (without it). No phthalocyanine formation takes place in the system "*i*-BuOH-CH_3ONa-(*n*-Bu)$_4$NBr-phthalonitrile" without electrolysis at 100°C [12], although in other alcohols such a process can take place forming (in case of presence of a metal-anode) a mixture of a metal-free phthalocyanine and metal phthalocyaninate. So, precisely this solvent was chosen to synchronize anodic dissolution of a metal and formation of free phthalocyanine on the cathode surface and avoid formation of mixture "PcH_2-Ln_2Pc_3". Showing a clear difference with traditional synthetic methods for synthesis of rare-earth phthalocyaninates at 170–290°C [44, 45], electrosynthesis allowed reduction to 100°C.

Using *heteroazomethinic ligands* **6–9** in various non-aqueous solvents, the problem of removal of insoluble precipitate from anode was, in general, solved. Applying ultrasound (weak source), the major part of a solid was cleaned from the anode. It is clear that the voltage was gradually increasing in the cell, but not as fast, as in case of pure electrochemical dissolution of metal. Yields with ultrasonic treatment were 2–5% higher. In control experiments under ultrasonic treatment with the same metallic anode and the same experimental conditions, but without electrolysis, for some azomethinic ligand systems partial copper dissolution (2–4% of anode weight) and lesser nickel weight loss (0.5–0.8%) forming the same metal complexes, as from electrosynthesis, but due to pure chemical metal dissolution.

On the basis of these and numerous other experiments with various metals and nitrogen(sulphur)-containing ligands with and without application of ultrasonic treatment together with electrosynthesis, it can be concluded that aggravation of electrosynthesis conditions (instability of voltage in the electrochemical cell) depends on the metal and ligand (and, respectively, on the properties of formed products) and to a lesser extent on solvent (acetonitrile, alcohols or their mixtures with toluene). Comparing the metals Cu and Ni, electrochemical dissolution of nickel is carried out much more easily, evidently due to higher solubility of its complexes in non-aqueous solvents in comparison with analogous copper complexes. Use of ultrasound levels this difference, carrying out electrochemical processes without the problems above; sometimes (use of lanthanides) application of ultrasound is absolutely necessary.

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