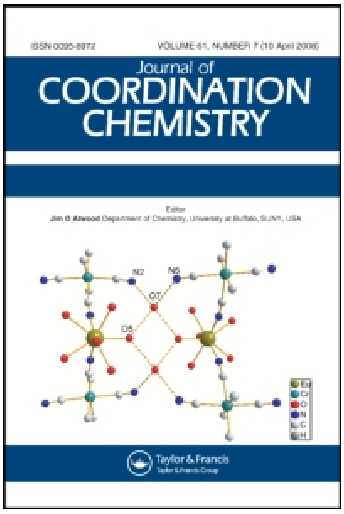

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Review

DIRECT ELECTROSYNTHESIS OF METAL COMPLEXES: STATE OF THE ART

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Recent results on the electrosynthesis of metal complexes are reviewed. The basic principles of such syntheses and the main factors that influence the process quality are covered. The main structural characteristics of each type of coordination compound obtained by this method are discussed. The large number of publications testify to the wide application of direct electrosynthesis to obtain molecular complexes and metal chelates. In addition, this manuscripts shows the necessity of developing this technique to obtain π-complexes, compounds with macrocyclic ligands and lanthanides complexes.

Keywords: Electrochemical synthesis; chelates; adducts; π-complexes; polynuclear structures; review

INTRODUCTION

The "one-step" or so-called "direct" synthesis of metal complexes starting from zero-valent metals[1–3] is an active research field which has undergone rapid progress over the last twenty five years. Contributions to this field are of interest not only to inorganic, organic and organometallic chemists, but also to scientists involved in such diverse areas as electrochemistry,

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cryochemistry, mechanochemistry, sonochemistry, laser applications, matrix isolation, corrosion and catalysis.

Among the different types of "direct syntheses" (electrosynthesis, metal vapor synthesis of coordination and organometallic compounds,[4] oxidative dissolution of metals in non-aqueous media,[5] and mechanosynthesis[1]), electrosynthesis is not only the oldest, but also the best method to obtain complex compounds starting from zero-valent metals. As early as 1882 Gerdes elaborated the electrochemical method for synthesis of platinum(IV) hexa-aminates, based on the anodic dissolution of a platinum electrode in the solution of ammonium carbonate.[6] In 1906, Scillard used this method for obtaining metal alkoxides.[7]

Systematic study on the use of electrosynthesis in coordination chemistry started in 1908[8] with Chugaev, who synthesized the classic series of Werner's complexes ($[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]SO_4$, and $[Co(NH_3)_4(NO_2)_2]NO_3$) by electrolysis with a cobalt anode and a platinum cathode; the chelate compounds (nickel(II) glyoximates) were also obtained using a nickel anode and dimethyl- (or methylethyl) glyoximes. Nine decades after Gerdes's pioneering experiments, Lehmkuhl[9] in Germany and Garnovskii[10–13] in Russia rediscovered "direct electrosynthesis". Soon thereafter, Tuck[14] in Canada and Sousa[15] in Spain gave it additional impulse by developing simple electrochemical methods employing relatively unsophisticated apparatus, non-aqueous solvents, and sacrificial metallic anodes and cathodes. Various coordination and organometallic compounds have been obtained by this route; the materials prepared are summarized in the reviews[2,3,14,16–20] and monographs.[1,21–24]

Electrochemical reactions do not require oxidants or reductants: only electrons (the "universal chemical reagents"[17]) are used. Electrosynthesis can be made highly selective through control of electrode potentials, although in most instances a potentiostat is not required. Other advantages of this method are: high purity of products, high yields and the possibility of synthesis of complexes difficult to obtain by conventional methods.

The published material covered in this paper, reveals that electrosynthesis is highly reliable as a one-step method for obtaining metal complexes starting from zero-valent metals, and should be used more frequently by chemists.

I. GENERAL CONCEPTS ABOUT ELECTROCHEMICAL SYNTHESIS

1. Practical Aspects

Electrosynthesis is the optimal method for carrying out redox reactions because it works at normal temperature and has the following advantages:

- The addition of redox species into the reaction mixture is not necessary.
- Compounds are produced by metal dissolution in soft conditions and with very simple equipment, independent from the metal being an anode or cathode.
- It is possible to produce compounds which are very difficult to obtain by classical procedures, especially those with the lowest metal oxidation state.
- The electrosynthesized compounds are sometimes more reactive than those obtained by conventional methods.
- The working conditions to obtain the electrodic reactions permit minimum contamination as a consequence of the low liberation of gases and avoid the danger by explosion during the electrolytic process.
- At present metal prices are lower than those of their compounds.

Electrosynthesis by metal oxidation as the anode gives the possibility of eliminating anionic contaminant in the product, a characteristic of processes based on metallic salts.

Nevertheless, the electrolytic procedure gives compounds with the higher metal oxidation state whenever a sacrificial anode can be substituted by a platinum electrode.

For practical aspects it is very important to recognize there are different possibilities for carrying out any transformation and different starting materials to a compound. Thus, economics should be taken into account before selecting the synthetic procedure, and the electrolysis should only be applied when economical.

Application of direct electrosynthesis in industry requires the consideration of factors, such as: (1) The availability and price of the starting material, (2) the quantity of obtained product (particularly important when the starting material is very expensive), (3) the type and quantity of secondary products which increase the price of pure product. The presence of impurities can prevent the use of the product, for example, in the pharmaceutical industry, (4) the price of the isolated product from the electrolytic medium, (5) the cell maximum current, which is one of the main factors determining the quantity of the obtained product and thus the number of cells required. At the same time, the cell current depends on the effective area of the electrode and on the current density. The latter parameter will be determined, for those systems having a single phase, by the substrate solubility in the mass transport conditions. For this reason, as a useful practical rule, one must have an electroactive species whose saturated solution will be between 1% and 10% in order to obtain a current density around 100 mA/cm, (6) the chemical and electrochemical stability of the electrolytic medium,

(7) the cell prices (to avoid, if possible, the use of a membrane; it is recommended to use cheaper electrodes and a high current density). The relative importance of these and other factors depends on the process nature and the application level.

In the electrolytic processes it is very important to take into account the following experimental parameters: (1) Electrode potential, (2) electrode material, (3) solvent and supporting electrolyte, (4) concentration of the electroactive species, (5) pH and concentration of all species that can react with the intermediates, (6) temperature and pressure, (7) mass transport regime, which influences the maximum current density, the intermediate product velocities and the magnitude of the mixture between the reaction layer and the solution bulk. The mass transport regime is determined by the electrolytic flow velocity and the electrode movement, (8) geometrical form of the electrodes and the presence or absence of separators or membranes.

2. Solvent and Supporting Electrolyte

The electrosynthesis of organic compounds takes place by dissolution of the solute in an appropriate organic solvent (or mixed solvent) as a consequence of the low solubility of most organic compounds in water and also of the reduced potential range of this solvent.

In order to select the solvent it is necessary to take into account the following aspects: (1) Electroactive species and supporting electrolyte solubility, (2) poor (or no) reactivity to the products, (3) purification facility, (4) stability to the applied potential gradient of approximately $20\,\mathrm{V \cdot cm^{-1}}$, (5) dielectric constant values, (6) low viscosity (especially if fast transport to the electrode is necessary), (7) adequate volatility to facilitate elimination, (8) easy separation by product precipitation from solvent.

The following solvents are widely used in electrosynthesis: alcohols, tetrahydrofuran (THF), dimethylformamide (DMF), dimethylsulfoxide (DMSO), acetonitrile (AN), pyridine (Py). More exotic solvents such as propylene carbonate, sulfolane, diglime and hexamethylphosphortriamide have also been used.[9,14,21] Acetonitrile and dimethylformamide are the most common (Table I). AN has the highest potential ranges and is especially useful because of its resistance to oxidation and its low reactivity with ionic radicals; DMF is easier to oxidize than AN and for this reason is not useful for anodic reactions; it is very resistant to reduction and weakly reactive with anionic radicals.[21]

TABLE I Physicochemical properties of the solvents used in electrosynthesis[21a]

Solvent	m.p. (°C)	b.p. (°C)	ε
THF	−80	66	7,6
DME	−58	82	3,5
$CH_3O(C_2H_4O)_2CH_3$	−68	159	
Py	−42	115	12,3
DMF	−61	153	38
AN	−45	82	38
DMSO	18	189	47
Sulfolane	28	285	44
HMPA	7	235	30

Electrolysis can be carried out in the presence of emulsions or suspensions if adequate agitation or simultaneous ultrasonic treatment[25] is applied. To decrease solution resistance in non-aqueous media with low dielectric constants a high concentration of supporting electrolyte is added to the solute. However, this does not ensure high conductivity, because of the tendency of many electrolytes to produce an ionic pair in organic solvents.

The potential ranges in which several solvent-supporting electrolyte systems are electrochemically inert are reported in the literature. Nevertheless, it is recommended to determine the practical potential ranges in laboratory experiments. In organic media the selection of supporting electrolyte is limited to halides, nitrates and perchlorates from solubililty considerations. The halides are not recommended, because of their ease of oxidation. Nitrates can be used for low anodic potentials, but for extremely high potentials tosylate, tetrafluorborate and hexafluorphosphate are the best selections.

On the other hand, the cations more frequently used are those of aliphatic quaternary ammonium, because of resistance to oxidation in the potential range of either one of the previous solvents. Salts of alkaline metals, which do not oxidize and are soluble in many solvents, are used as well.

3. Types of Cells

Electrolytic cells can be classified as undivided where the electrodes are located in the same compartment and divided which have two compartments, separated by a diaphragm (ceramic, an-ionic exchange membrane, etc.).

The undivided cells have less resistance than the divided ones and are used when the reactant (or the obtained product) in the working electrode reacts to an undesirable substance in the counter electrode, or when the reaction product in this electrode reacts with the former product in the working electrode (the counter electrode can have a significant influence on the reaction and it can even change the nature of the product).

The most common cell for electrosynthesis is a 100 mL tall-form beaker. The experiments can be run in a nitrogen atmosphere (or some inert gas) to study the effect of oxygen on the process. For electrochemical synthesis with simultaneous ultrasonic treatment, it is possible to use the *sonoelectrochemical* cell.[25e]

4. Electrolytic Parameters

Electrosynthesis experiments are normally carried out using a current range of 20–50 mA; the voltage required to obtain this current typically ranges from 10 to 50 V, depending on the electrolyte composition and the cell parameters. The value of voltage is determined not only by the required electrode potential for the reaction, but by the electromotive force required to move the charge through a low dielectric constant medium. The resulting anodic current density is in the approximate range 10–30 $\mathrm{mA\cdot cm^{-2}}$. These values are most commonly found in the literature, although different values are possible. Finally, it is important to point out that the most critical factor is current density. An excessively low value of current density limits the quantity of product to be obtained, whereas a high current density produces an excess of heat in the cell.

Electrosynthesis of coordination compounds is carried out by using a sacrificial anode or cathode (sources of metal ions to form complexes).[17,21,24] The essence of electrosynthesis of complex compounds is described by the simple scheme (**1**):[9]

$$M^+ + \mathrm{Lig} + e^- \rightarrow M\cdots\mathrm{Lig} \qquad (\mathbf{1})$$

For reactions under solvation conditions, the electrosynthesis scheme could be described as (**2**):[26]

$$M \xrightarrow[\mathrm{Ox}]{-me^-} [M(\mathrm{Sol})_n]^{m+} \xrightarrow[+L^0]{+me^-} ML^0_x \qquad (\mathbf{2})$$

where L^0 is a ligand or its precursor.

If ligands (LH) with an acidic EH-group (E = NR, O, S, Se) take part in electrosynthesis, then the following reactions (**3**) take place:[2]

$$M - ne^- \rightarrow M^{n+}, \quad LH \Leftrightarrow L^- + H^+, \quad M^{n+} + nL^- \rightarrow ML_n \qquad (\mathbf{3})$$

In the latter case, the mechanism requires the anodic dissolution of the metal prior to complex formation (**4**):[17,21]

$$\begin{array}{ll} \text{Anode:} & n\mathrm{L}^- + \mathrm{M} \rightarrow \mathrm{ML}_n + n\mathrm{e} \\ \text{Cathode:} & \mathrm{HL} + n\mathrm{e}^- \rightarrow n\mathrm{L}^- + n/2\,\mathrm{H}_2 \end{array} \qquad (\mathbf{4})$$

For this reason, the electrochemical reactions do not require the application of oxidants or reductants making them attractive.[21]

Other important advantages of electrosynthesis of coordination compounds, in comparison to the usual synthetic methods, are control of the reaction, the ease in obtaining difficult to access compounds, and the possibility of conducting processes in high yields under mild conditions.[2,21,24]

II. ELECTROSYNTHESIS AT SACRIFICIAL ANODE

All types of coordinating compounds may be obtained under conditions of electrosynthesis: molecular adducts, metal chelates, π-complexes, di- and trinuclear homo- and heterometallic structures, as well as some σ-organometallic compounds. However, the majority of electrochemically synthesized complexes belong to the first two types.

1. Electrosynthesis of Molecular Complexes (Adducts)

Molecular complexes obtained by electrochemical methods are reported for various adducts of organic N,O,P-donors with metal halides (pseudohalides) and organohalides.[14,17,19,21,24,27-31] The first have the general formula $\mathrm{MX}_n \cdot \mathrm{pL}$, while for the second ones the formula is $\mathrm{R}_m\mathrm{MX}_{n-m} \cdot \mathrm{pL}$, where M are the metals of groups I (Cu, Ag, Au),[14,17,19,21,24,32-37] II (Mg, Zn, Cd, Hg),[14,17,21,24,31,36-41] III (In, Ga, Tl),[14,17,20,21,24,32,36,37,42-46] IV (Sn, Pb, Ti, Zr, Hf),[14,17,21,24,27,35,37,47-49] V (V, Nb, Ta),[14,17,21,44] VI (Cr),[14,28,32,44] VII (Mn),[14,17,21,24,39] VIII (Fe, Co, Ni, Pd),[14,24,30,32,50-52] and the actinides Th[17,21,27,53] and U.[28]

The following ligands were used: N-donors, amines (am),[24,32,33,36,37] acetonitrile (AN),[14,17,21,24,27,35,39,41,43,44,46,47,50,53] pyridine (Py),[14,43] bipyridyl (bipy),[14,24,27,32,35,37,39,45,48,52,54] *o*-phenantroline (phen),[14,24,27,32,35,37,39,45,46,48,52,54] imidazole;[14] P-donors as phosphines,[14,33,34,36,37,43,45,51] and diphosphines;[14,32,36,39] O-donors as methanol,[39] diethyl ether,[34] dioxane,[14,24] DMSO,[14,24,27,32,42,44,53] DMF[28] and triphenylphosphineoxide;[27,54] and

S-donors as carbon disulfide.[36] Compounds used as R-substituents are as follows: Alk, Ar,[14,24] X = OH,[31] Hal,[14,17,21,24,28,33,39,41,43,47,50] CN,[14] NCO[29] and NO_3.[54]

Molecular complexes are usually obtained under electrosynthesis conditions by anodic dissolution of a metal in the presence of ligands (bipy, phen, phosphines, etc.) or donor solvents (AN, Py, DMSO, DMF, etc.). At the same time, in some cases, the electrochemical synthesis could be accompanied by original transformations. Thus, by dissolution of cadmium in an acetonitrile solution containing N-(hydroxyethyl) salicylidenimine and phenanthroline, where an azomethine chelate was expected,[55] the adduct $Cd(OH)_2(phen)_2$ was obtained.[31] The structure of this complex is confirmed by X-ray diffraction: the compound has an octahedral structure with CdN_4O_2 coordination.[31] Cationic[14,17,24,27,29,30,32,42] or anionic[14,17,21,24,27,28,33,41,43,47,51,54] complexes could be prepared. The cationic complexes are present in a sufficiently wide number of compounds,[14,24] synthesized by anodic dissolution of metals in organic solvents containing the mineral acids HBF_4 or $HClO_4$. The ammonium salts of $HClO_4$ also serve as sources of perchlorate ions.[29,30]

The series of cationic complexes with the general formula $[ML_n][BF_4]$, where L = AN or DMSO; $n = 4,6$ and $m = 2,3$ was obtained by electrolytic dissolution of metals (Zn, Cd, In, Ti, V, Cr, Co, Ni, Fe) in acetonitrile solution or DMSO in the presence of HBF_4.[14,24] Electrochemical dissolution of the copper anode in acetonitrile in the presence of 2,2′-bipy, 2(1H)-pyridone, and tetramethylammonium perchlorate, leads to copper(II)*bis*-(2,2-bipy) isocyanatoperchlorate $[Cu(C_{10}H_8N_2)_2(NCO)]ClO_4$.[29] According to the X-ray diffraction data,[29] the cation is a square pyramid with the cyano group apical coordinated through the nitrogen atom. Ambidentate binding of pseudohalide ions[56–58] represents an interesting topic for discussion. Electrosynthesis with a cobalt anode under the same conditions, but in the presence of 1,10-phenanthroline, promotes formation of a complex, which, according to the X-ray diffraction, has an octahedral structure with bidentate binding of the phenanthroline ligand (N,N-coordination) and a carbonate ion (O,O-coordination).[30]

Anionic compounds of the type $[Et_4N]_m[MBr_4]$, obtained by electrosynthesis with participation of zero-valent metals Au, Cd, In, Sn, Ti, Hf, Co, Ni, Fe, bromine and tetraethylammoniumbromide in a benzene–methanol solution are well described in the literature.[14,24]

Adducts of thiolates and selenolates, obtained by electrosynthesis, with N-[35,37,45,46,49,52] and P-[37,45,46,49] donors, formed neutral molecular complexes. The general method for obtaining metal thiolates and selenolates is based on electrochemical cleavage of the X–X (X = S, Se) bond (5):[37,40,45,49]

$$n/2\,\mathrm{Ar-X-X-Ar} \underset{X=S,\,Se}{\overset{M}{\rightarrow}} \underset{\mathbf{I}}{\mathrm{M\,(XAr)}_n} \qquad (5)$$

Adducts of the type $M(XA)_n \cdot L_m$ are formed in the presence of the ligands shown above. Transformation (5), perhaps, should also be characteristic for ditellurides. Metal thiolates and their adducts can also be obtained by starting from thioalcohols[17,21,35,46,49,52,59] (Table II). Similarly, the electrosynthesis of metal alkoxides[7,17,21,60,61] and their use as precursors for sol-gel processes could have practical interest.

Structures of type **I** complexes and their adducts have been studied by various physical methods, in particular X-ray diffraction.[35,49,55] On the basis of these data, it was established that the adduct of the complex of *o*-toluidinsulfide with *o*-phenanthroline and acetonitrile corresponds with the dimer, $[Cu(SC_6H_4CH_3\text{-}o)(C_{12}H_8N_2)]_2$, with sulfide bridges connecting the copper atoms.[35] Its magnetic properties, which unfortunately have not yet been studied, represent especial interest: this complex should be antiferromagnetic.[62] There is an octahedral environment due to the metal in the monomer complex compounds $[Sn(SC_6H_5)_4 \cdot \mathrm{bipy}]$[49] and $[Co(SC_6H_5)_2 \cdot \mathrm{phen}]_2(ClO_4)$.[52]

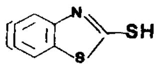
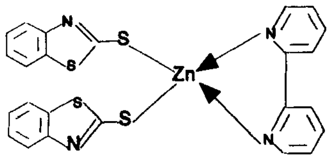
The series of complexes with general formula $M(SR)_2L_2$ (where M = Co, Ni; R = Ph, 2,3,5,6-tetrafluoro-C_6H, C_6H_4Me-*o*, 2-$C_{10}H_7$; L = phen, bipy[52]), has been obtained by galvanostatic electrolysis in acetone or acetonitrile. The magnetic properties (for the cobalt complex $[Co(SPh)_2(phen)_2]$ $\mu_{\mathrm{eff.}} = 2.70$ B.M., and for the nickel analogue 3.30 B.M.) and the composition indicate the octahedral configuration. Adducts with the general formula CuSR · nL, where R = Ph, *o,m,p*-MeC_6H_4, 2,3,5,6-tetrafluor-C_6H; L = $Me_2NCH_2CH_2NMe_2$, PhNCS, *t*-BuNCS, PPh_3; $n = 0.5$; 1.5; 2, were synthesized[49] by electrochemical dissolution of copper in acetonitrile solution of thiols and ligands (L).

Electrosynthesis of molecular complexes gives a number of products and metal chelates (see Part II.2). A summary of the literature data on the electrosynthesis of adducts and related compounds is presented in Table II.

2. Electrosynthesis of Metal Chelates

Some chelate-forming ligands, such as dimethylglyoxime,[2,7,21,24] *β*-diketones,[2,14,24] azomethines **II**, **III**,[2,17,21,24] oxyphenylazoles and their benzannexed derivatives **IV**,[2,24] 2-acetylpyrrol **V**,[14] and 3-hydroxy-4-pyron

TABLE II Electrosynthesis of metal adducts, alkoxides and related compounds

Metal	*Initial system*	*Products*	*Ref.*
Al	NH_3 (liquid), NH_4Br	$Al(NH_3)_6Br_3 + [Al(NH_2)(NH)]_n$	63a
Pd	HX (X = Cl, Br)	PdX_2	63b
Sb,Fe,Ti, Hg, Re,Ni,Mn	ROH	$M(OR)_n$ or $MO(OR)_n$ $Re_4O_2(OMe)_{16}$	14a,64–66
In,Sn	CH_3CN, $R(OH)_2$ (R = 1,2-dihydroxybenzene, 2,3-hydroxynaphtalene, 2,2′-dihydroxybiphenyl, 1,2-dihydroxytetrabromobenzene)	In[OR(OH)] $Sn(O_2R)$	67,68
Mn,Cd,Fe, Ni,Cu,Mo	EtOH + H_2O, NH_4SCN; Me_4NCl or Me_4SCN	$(Me_4N)_n[M_m(SCN)_l]$, $n = 2,4$; $m = 1,2$; $l = 4,6$	69
Zn	, bipy		70
Cd,Cu,Tl, Sn, Zn	CH_3CN, toluene, Ph_2Se_2	$M(SePh)_2$ (M = Cd,Zn) MSePh(M = Cu,Ag,Tl) $Sn(SePh)_4$	37,45
	In the presence of phen	$Cd(SePh)_2 \cdot 2phen$ $Cu(SePh)_2 \cdot phen$	
	In the presence of PPh_3	$Cu(SePh)_2 \cdot 1.5PPh_3$	
Cd,Co,Fe,In, Ni,V,Zn,Ti,Mn	DMSO, HBF_4	$[M(DMSO)_6(BF_4)_2]$ (M = Cd,Co,Mn,Ni,V,Zn) $[M(DMSO)_6(BF_4)_3]$ (M = In,Fe)	44
CH_3CN, HBF_4		$[M(CH_3CN)_6(BF_4)_3]$ (M = In,Ti)	
Cr	DMSO, HBF_4 CH_3CN, HBF_4	$[Cr(DMSO)_6][BF_4]_3$ $[Cr(CH_3CN)_n][BF_4]_2$, $n = 4,6$	44
In	$HClO_4$, MeOH, DMSO	$[In(DMSO)_6][ClO_4]_3$	42
In	DMSO, benzene, Et_4NX (X = Cl, Br)	$InX_3 \cdot 3DMSO$	42

Mn,Cd,Hg, Co,Tl,Cu,V,Ga	CH_3CN, $(EtO)_2P(S)SH$ (= HL)	ML_2, ML_3, TlL	70
	In the presence of phen	$CoL_3 \cdot$ phen, $MnL_2 \cdot$ phen, $VL_2 \cdot$ phen, GaL · phen	
Pd	HX (X = Cl,Br), further addition of MX {M = NH_4, $(CH_3)_4N$}, LH_2 (phen or bipy hydrates)	$M_2[PdX_4]$ $M_2[PdX_4] \cdot LH_2$	63b
Ti	n-C_3H_7NCl, Cl_2, $SOCl_2$	$(n\text{-}Pr)_4NTiCl_5$	47
	Et_4NBr;		$Et_4NTi^{III}Br_4$
	$Br_2 : C_6H_6 = 1:5$	$[Et_4N]_2Ti^{IV}Br_6$	
	Et_4NBr; $Br_2 : C_6H_6 = 1:3$		
Hf,In,Fe,Ni, Th,Ti,V,Zr	X_2, CH_3CN (X = Cl,Br)	$MX_4 \cdot 2CH_3CN$ (M = Ti,Zr,Hf), $InX_3 \cdot nCH_3CN$ (n = 2,3), $VCl_2 \cdot 2CH_3CN$ $ThX_4 \cdot 4CH_3CN$, $VBr_2 \cdot CH_3CN$ $MX_2 \cdot CH_3CN$ (M = Fe,Ni)	27,39,47,71,39
V,Zr,Hf	I_2, CH_3CN Cl_2, $SOCl_2$, n-Pr_4NCl	VI_2 $(n\text{-}Pr)_4NMCl_5$	
	Br_2, C_6H_6, Et_4NBr Ethylendiamine (en), benzene, methanol	$(Et_4N)_2MBr_6$ $MBr_4 \cdot$ en (M = Zr,Hf)	
U	Cl_2 or Br_2, CH_3CN, N_2	$UCl_4 \cdot 4CH_3CN$ $UBr_4 \cdot 2CH_3CN$	28
	Cl_2 or Br_2, CH_3CN, O_2	UO_2X_2	
	DMF, R_4NX (X = Cl, Br),	$(R_4N)_2UX_6$	
	CH_3CN, N_2 DMF, R_4NX,	$(R_4N)_2UO_2X_4$	
	CH_3CN, O_2 DMF, I_2, CH_3CN	$UI_4 \cdot 4DMF$	
In	X_2 (X = Cl, Br), benzene, CH_3OH or DMSO	$InX_3 \cdot n$Solv, $n = 0;3$	72
In,Fe,Sn	In the presence of R_4NX ($R_4 = Et_4$, Et_3Ph)	$(R_4N)_2InX_5$ Et_4NFeBr_4, $(Et_4N)_2SnBr_6$	42,72,73
	Br_2, CH_3OH, C_6H_6	$MnBr_2 \cdot MeOH$	39
Mn	Br_2,CH_3CN	$MnBr_2 \cdot nCH_3CN$	39
Cd,Ni	Benzene, CH_3OH, Et_4NBr, Br_2	$(Et_4N)CdBr_3$ $(Et_4N)_2NiBr_4$	73
Cu	Br_2, C_6H_6, CH_3OH, Et_2O	$CuBr : CuBr_2 = 0.28 : 0.72$	39
In	C_6H_6, CH_3OH, R_4NCl, Cl_2 ($R_4 = Et_4$ or Et_3Ph)	$(R_4N)_2InCl_5$	42,72

TABLE II (*Continued*)

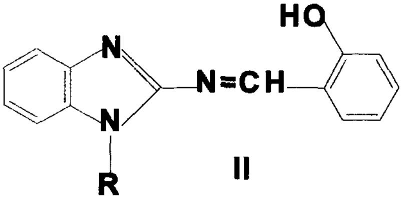
Metal	*Initial system*	*Products*	*Ref.*
	Et_4NI, I_2, CH_3OH	$[Et_4N][InI_2]$	42,74
Cu	CH_3CN, RX, Et_4NX (R = Me,Ar; X = Cl,Br,I)	$[(C_2H_5)_4N]_n[Cu_2X_m]$ ($n = 1-3$; $m = 2-5$)	33
	CH_3CN, PhBr, bipy CH_3CN, CH_3I, bipy	$CuBr \cdot bipy$ $CuI \cdot bipy$	
Tl	Non-aqueous solvent, SiO_3^{2-}, R_4NF, HF	TlF, Tl_2SiF_6, $Tl_3[SiF_6]F$	75
Ga	CH_3CN,HX,PPh_3 (X = Cl,Br,I)	$[Ph_3PH]_2[Ga_2X_6]$	20
Cd,In,Tl	α,ω-alkanedithiols	$Cd[S_2(CH_2)_n]$	76
	$HS(CH_2)_nSH$ ($n = 2-6$), CH_3CN	$In[SR(SH)]$, $Tl_2(S_2R)$ $Zn[S_2(CH_2)_n]$	77
	In the presence of phen or bipy (L) $HS(CH_2)_nSH$ ($n = 3-6$), CH_3CN	$M[S_2(CH_2)_n] \cdot L$ (M = Zn,Cd) M_2S_2R (M = Cu,Ag)	76
Cu,Ag	In the presence of PPh_3 or dppm (L)	$Cu_2S_2R \cdot nL$ (not all combinations)	78
In	CH_3CN, (I_2), RSH (R = Alk,Ar)	$InI_n(SR)_m \cdot CH_3CN$ $In(SR)_n$	46
	In the presence of bipy or phen (L)	$InI_n(SR)_m \cdot L$	
Cd,Co,Au, Ag,Zn,Cd	CH_3CN, PPh_2H	$M(PPh_2)_2$ (M = Cd,Co,Zn) $M(PPh_2)$ (M = Ag,Au)	79
	In the presence of S and toluene	$Cd(S_2PPh_2)_2$	
Cr,Co,Mn, Fe,Ni	RCOOH, CH_3CN (R = Et, n-C_7H_{15}, Ph, Me)	$CrL_3 \cdot 2H_2O$ (R = Et) ML_2(R = Et; M = Co,Ni) FeL_2 (R = Et, n-C_7H_{15}) CrL_3 (R = Ph) MnL_2 (R = Me,Et,Ph,n-C_7H_{15})	80a
Fe,Co,Ni,Cu	Lactic acid (H_2LA), acetone	$M(HLA)_n \cdot mH_2O \cdot k(CH_3)_2CO$	80b
Cu	*H_2O, HL; L = propionic, benzoic, oxalic*, succinic, phthalic, isobutyric, salicylic, acetic acids; glycine, L-alanine, histidine, sodium pyruvate	$CuL_2 \cdot H_2O$	66

Cr,Cu,Fe,Mg,Ni, V,Zr,Mo,W,Sn	DMSO,SO_2	$Cr_2(DMSO)_{20}(S_2O_7)_3$	81,82
		$[M(DMSO)_6][S_2O_7]$	
		$(M = Cu,Mg,Zn)$	
		$Fe_2(DMSO)_{10}(S_2O_7)_3 \cdot SO_2$	
		$Ni_2(DMSO)_7(S_2O_7)$	
		$Zr_2(DMSO)_{10}(S_2O_7)_3$	
		$V_2(DMSO)_{11}(S_2O_7)_3$	
		$(Mo,Sn)\ (DMSO)_4(S_2O_7)$	
		$W_2(DMSO)_6(SO_4)_3$	
Cr,Co	$H_2O + EtOH$; Me_4NCl or Me_4NSCN	$(Me_4N)_3[Cr(SCN)_6]$	69
		$(Me_4N)_2\ [Co(SCN)_2]$	
	In the presence of bipy	$[Co(bipy)_2(SCN)_2]$	
Co,Ni,Hg, Tl,Sn,Pb	$CH_3CN + RSH$ (R = Alk,Ar)	$M(SR)_2$ (M = Co,Ni,Sn,Hg)	46,52,83
	PhSH	TlSR	
	In the presence of phen or bipy (L)	$Pb(SPh)_2$	
		$Ni(SR)_2 \cdot 2L$	
		$Sn(SR)_4 \cdot L$	
Cu	RSH, PPh_3 (R = Ph,*o*,*m*,*p*-MePh,etc.)	$CuSR \cdot nPPh_3$	84
Co	Br_2, CH_3CN	$CoBr_2 \cdot 2CH_3CN$	39
	Br_2, CH_3OH, C_6H_6	$CoBr_2$	
	In the presence of Et_4NBr	$(Et_4N)_2CoBr_4$	73
Au	Benzene, CH_3OH, Et_4NBr, Br_2	$Et_4N \cdot AuBr_4$	73
Au,Ag	PPh_3, CH_3CN, benzyl chloride	$AuCl(PPh_3)_2$	34
	PPh_3, CH_3CN, HCl	$AgCl(PPh_3)$	
		$AuCl(PPh_3)$	
Co	CH_3CN, HCl, PPh_3	$[Ph_3PH]_2[CoCl_4]$	51
Cu	2,2′-dipyridylamine (= HL), CH_3CN/N_2, dppm [*bis*(diphenylphosphino)-methane]	$CuL \cdot 0.5\,dppm$	36
	2,2′-dypridylamine (= HL),CH_3CN/N_2, dppe [*bis*(diphenylphosphino)ethane]	$CuL \cdot 1.5\,dppe$	
Cu	PPh_3, CH_3CN, benzyl chloride	$CuClPPh_3$	34
	PPh_3, CH_3CN, HCl PPh_3,	$CuClPPh_3 + Cu_2Cl_2(PPh_3)_3$	
	CH_3CN, HX X = Br, I	$Cu_2X_2(PPh_3)_3$	

TABLE II (*Continued*)

Metal	*Initial system*	*Products*	*Ref.*
Ni	CH_3CN, PPh_2H CH_3CN, PPh_2H, PhNCS	$Ni(PPh)_2 \cdot (PPh_2H)$ $[Ni(PPh_2)(PhNCS)]_2$	79
Cu	CH_3CN, dppm, $Cl_4C_6(1,2\text{-}OH)_2$	$Cu_2[OC_6Cl_4(OH)]_2(dppm)_2$	78
Mn	CH_3CN, pyrimidine-2-thione (pymtH) or 4,6-dimethylpyrimidine-2-thione (4,6-Me_2pymtH), bipy or phen	[Mn(pymt)$_2$phen] [Mn(4,6-Me_2pymt)$_2$phen] Mn(4,6-Me_2pymt)$_2$bipy]	85
Th	Acetone, Hoxine (8-hydroxyquinoline)	Th(oxine)$_4$	27
Sn	$AgClO_4$, CH_3CN	$Sn(ClO_4)_2 \cdot 2CH_3CN$	18
V	H_2O_2	After raising the pH with KOH: $K[VO(O_2)_2(H_2O)]$ $K_3[VO(O_2)_3] \cdot 3H_2O$	18
Mo,W,Nb, Ta,Ti,V	H_2O_2, HF	$[MO(O_2)F_4]^{2-}$ $[M(O_2)F_5]^{2-}$ $[VO(O_2)_2F]^{2-}$	18,86
Fe	Indene, 1-methylindene, 1,3-dimethylindene, 3-phenylindene (HL)	FeL_2	87

VI,[14] were earlier used for the reactions of electrosynthesis of metal chelates:



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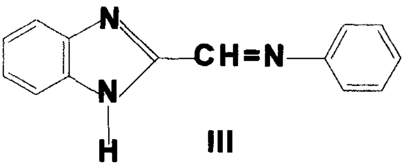
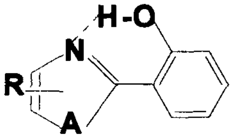
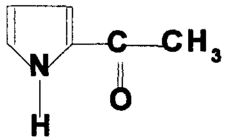


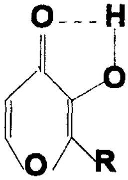
III



IV



V



VI

Electrosynthesis of chelates with an N,O,S-ligand system† containing various metal cycles has been carried out. Most electrochemically obtained chelate complexes with a six-member metallacycle, are reported β-diketones[14,17,21,24,27,90–97] and azomethinic ligands.[10,17,21,24,55,98–116] Thus, electrochemical synthesis was used to prepare β-diketonates of the following metals: copper,[14,24,91] cadmium and zinc,[14,24,92] aluminum and indium,[91,94] titanium, zirconium and hafnium,[14,91,94] vanadium, niobium and tantalum,[14,94] chromium and molybdenum,[91,94] manganese,[14,24,91] iron, cobalt and nickel,[14,24,91,97] cerium,[24] dysprosium,[96] uranium,[93,95] and thorium.[27] The structure of the adduct $Cd(acac)_2 \cdot phen$ has been determined by X-ray diffraction.[92]

A systematic study[94] showed that β-diketonates with the following compositions: ML_2 (M = Ni), ML_3 (M = Al, In, Co, Fe, Ti, Zr) ML_4 (M = Zr, Hf), $ML_2 \cdot solv$ (M = Ni, Fe), ML_3Cl (M = Ti, Zr), $TiL_2(OMe)$, ZrL_3OMe, where L is a diketone anion, are obtained from various β-diketones and their fluor-substituted derivatives in good yields by electrosynthesis. The syntheses of these chelates were carried out using liquid β-diketones or their solutions (15–20%) in methanol, ethanol, AN, and DMF, with LiCl, LiBr, NH_4Cl or Bu_4NBF_4 as supporting electrolytes (Table III).

The electrochemical oxidation of uranium leads to chelates of the type UL_4 and UO_2L_2 (LH - diketone).[93,95] In addition to these complexes, a

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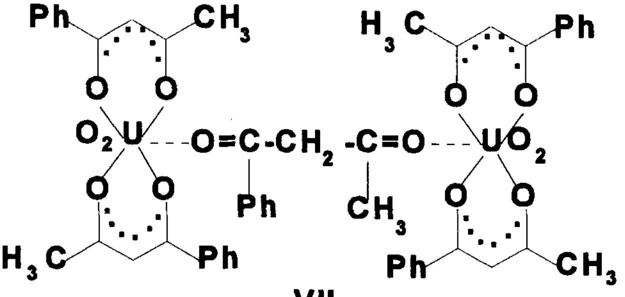
† The electrosynthesis of chelates, obtained on the basis of chelate-forming ligands with an acidic XH-group, where X = NR, OR, S, will be discussed below; their usual synthesis is reported in.[88,89]

TABLE III Conditions for the preparation of some metal acetylacetonates[94]

Compound	*Solvent* (mL)	*Electrolyte* (g)	*Water* (g)	*Hacac* (g)	E_F*	*Decrease of anode weight* (g)	*Yield* (%)
$Ni(acac)_2$	MeOH (50)	NaCl (2)	60	40	0.44	3.18	93
$Co(acac)_2$	EtOH (50)	KCl (2)	60	40	0.51	6.54	63
$Co(acac)_2$	DME (100)	$LiClO_4$ (1.75) LiBr (2.5)	—	75.4	0.51	5.80	67
$Co(acac)_2$	Diglyme (100)	$LiClO_4$ (1.25) LiBr (2.5)	—	75.4	—	—	89
$Ni(acac)_2$	DME (100)	$LiClO_4$ (1.25) LiBr (2.5)	—	75.4	0.41	6.30	87
$Ni(acac)_2$	PDC (100)	$LiClO_4$ (1.25) LiBr (2.5)	—	75.4	—	—	80
$Ni(acac)_2$	Py (100)	$LiClO_4$ (1.25) LiBr (2.5)	—	75.4	—	—	68
$Mn(acac)_2$	THF (39,4)	$LiClO_4$ (0.95) LiCl (0.04)	—	43.3	0.58	5.88	86

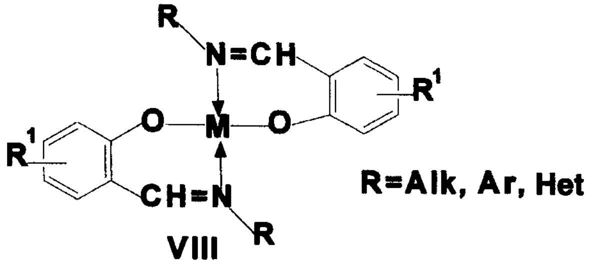
*E_F is the electrochemical efficiency (amount of metal dissolved per unit of charge (in F)).

compound of composition $UO_2L_2(HL)_{0.5}$ was also isolated;[95] structure **VII** was proposed from IR-spectroscopy data but requires proof.



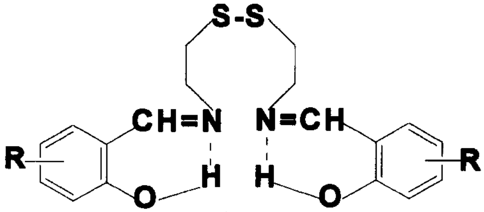
VII

The chelates of Schiff bases have been obtained by electrosynthesis of acetonitrile solutions of ligands using a platinum cathode and an anode made from the corresponding metal. The chelates **VIII**, obtained on the basis of ligand systems with various substituents (R) in the amine fragment,[55] and as well as by the complexes of heterocyclic amines and azomethines[10,17,21,24,98] provides examples.

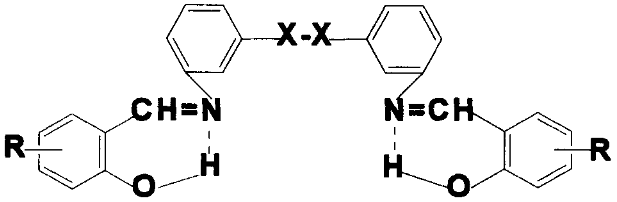


VIII

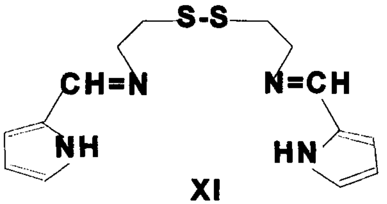
Complexes containing alkyl or aryl substituents[55] (R = *i*-Pr, Bu, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-$NO_2C_6H_4$) on the azomethinic nitrogen atom and the majority of the *o*-hydroxyazomethines are synthesized by electrochemical methods[99–115] giving the fragments **VIII** (R = 2-Py;[99,101] R = CH_2CH_2-Py-2;[100,102] R = $CH_2CH_2NMe_2$[100]), **IX**,[105] **X** (X = S;[106,108,111] X = Se[110]); **XI**;[104] **XII**.[104]



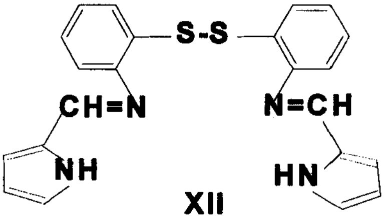
IX



X=S, Se **X**



XI

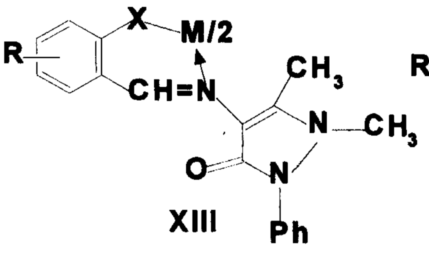


XII

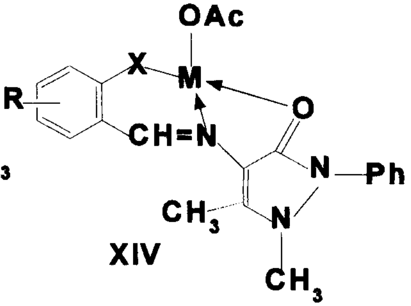
X-ray diffraction data indicates[101] that the N-atom in the pyridine does not take part in coordination to copper in **VIII** (R = 2-Py-3-Me, R′ = 5-OMe), *i.e.*, this is formally a tridentate ligand system behaving as bidentate; metallacycles, MN_2O_2, are found in the described complex compounds with participation of a phenolic oxygen atom and an azomethine's nitrogen atom. Other copper complexes **VIII** (R = CH_2CH_2Py, R = 4,6-OMe) have a square-planar structure with a non-coordinated nitrogen atom of pyridine.[100] At the same time, X-ray diffraction data indicate participation of the pyridine in the nickel complex of N-2-pyridilethylsalicylidenimine **VIII**

($R = CH_2CH_2Py$), which leads to the octahedral polyhedra $Ni_2N_4O_2$.[102] The results are important in understanding competitive coordination in a number of formally tridentate ligand systems; the binding depends on the electronic configuration of the metal, and the structures of the complexes.[89,116–119]

Azomethines containing the antipyrine fragment[107] could have the same ambidentate ligand systems. On the basis of this fragment, chelates of type **XIII** ($X = O$), of composition ML_2, where LH is the ligand, were obtained[73] by the electrochemical method. These compounds are suggested to have both participation and non-participation of the O-atom from the carbonyl group in the coordination sphere,[107,110] in addition to participation of an oxygen atom from the phenolic group and a nitrogen atom from the azomethinic group. In this case, the electrochemical method has an important advantage in that complexes having the composition ML_2 (**XIII**) are specifically formed. Under the usual synthetic conditions, two types of coordination compounds {ML_2 (**XIII**) and MLAcO (**XIV**)[120]} are isolated by the use of metal acetates.

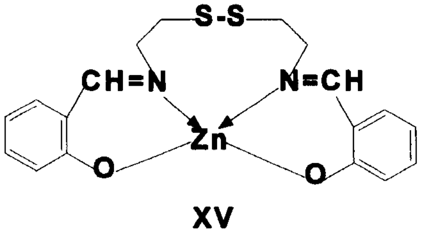


XIII

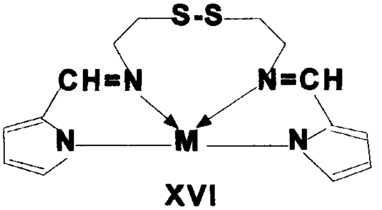


XIV

Formally hexa-dentate ligand systems **IX–XII** are unique under conditions of electrosynthesis. For the ligand **IX**, the disulfide structure remains unchanged[105] in complex formation. The complex could be represented by **XV** with a tetrahedral polyhedrun, formed by the phenolic oxygen and the azomethinic nitrogen atoms.[105]

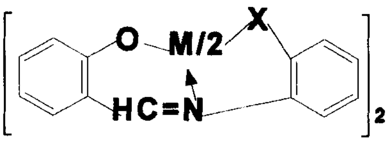


XV

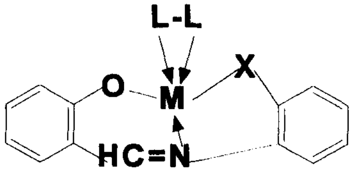


XVI

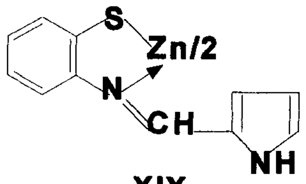
Complexes of composition ML, obtained from ligands **XI** and **XII**,[104] for example the complex **XVI**, evidently have similar structures without sulfur coordination. In the remaining cases, cleavage of X–X bonds (X = S, Se) and formation of complexes with comparatively rare N,S- or N,O,S-ligand environments,[89,116] are observed. X-ray diffraction confirmed that two types of complexes; **XVII** (M = Cu, Ni, X = O;[113] M = Sn, X = S,[106] Se[110]) and **XVIII** (M = Cu, Ni, L-L = *o*-phen; M = Zn, L-L = 2,2-bipy;[108] M = Co, L-L = *o*-phen[111]) are formed on the basis of compound **X**.



XVII



XVIII

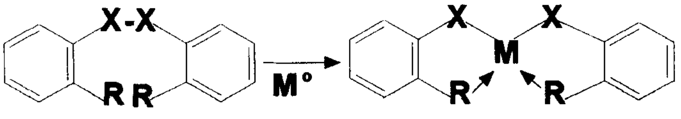


XIX

Complex **XIX** has the composition $Zn(LH)_2$ and is a compound of pyrrol-*o*-aminothiophenol, in which the pyrrol fragments do not take part in the coordination,[104] it is formed by cleavage of the disulfide bond of ligand **XII** (LH_2).

Thus synthesis of complexes containing N- and halcogen S(Se) donor atoms.[89,116–119] Complexes of the type **XIX**, containing coordination MN_2X_2 (X = S, Se) and aryl (hetaryl) substituents in the aldehyde fragment, were synthesized many years ago from metal salts or as a result of template synthesis.[89,116]

The transformations discussed above suggest that electrochemical cleavage of a bond X–X (X = S, Se)[37,45,49,103,104,110] could open the way to synthesis of complexes with chelate five- and six-member metallacycles, containing a donor atom of tellurium (**XX** and **XXI**) (**6**):



XX X=S,Se **XXI**

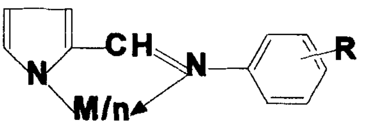
R = -NH$_2$, -N=CH-Ar(Het), —CH=O, -CH=N-R^1 (Alk, Ar, Het)

(6)

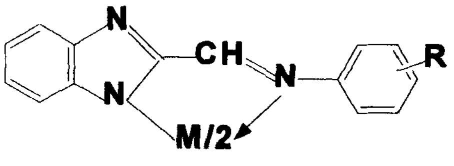
These studies, which take into consideration the synthetic methods for the ligands **XX**:[121,122] R = $-NH_2$, $-N=CHR$, CH=O, $-CH=N-Ar$, have been started by A. Sousa and co-workers (University of Santiago de Compostela, Spain) simultaneously with I.D. Sadekov and A.D. Garnovskii (State University of Rostov-on-Don, Russia). The possibility of obtaining complexes of the type **XXI** (X = Te) is confirmed by successful synthesis in the usual conditions (starting from ligands and metal salts, template transformation) of chelates **XXI** (X = S, Se).[89,116]

Electrochemical synthesis of chelates with tridentante Schiff bases, obtained on the basis of 2-[(2-aminoethyl)-thiomethyl]benzimidazole, with a substituted acetophenone and acetylacetone, has been carried out.[115] A template electrosynthesis of transition metal chelates containing azomethinic ligands and benzimidazoles is presented in a recent paper;[123] a comparison of conventional chemical and direct electrochemical methods using the azomethinic ligands was reported.[124]

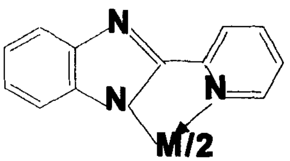
Coordination compounds **XXII–XXIV** with five-member metal cycles MN_n have been obtained by an electrochemical method from azomethines derived from aldehydes with five-member nitrogen heterocycles: pyrrol-2-aldehyde **XXII**,[15,125–133] benzimidazole-2-aldehyde **XXIII**,[17,21,98] as well as 2(2′-pyridil)benzimidazole **XXIV**.[10,17,21,24,98] Although **XXII** are classic coordination complexes,[89,134,135] application of electrosynthesis not only allows extension to similar compounds, but also helps to specify their structures and the problems of competitive reactions of azole ligand systems with zero-valent metals.



XXII



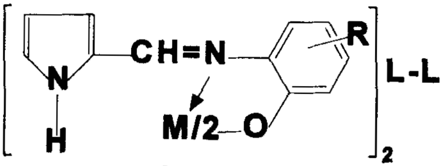
XXIII



XXIV

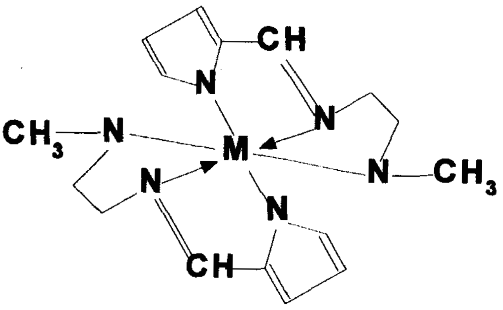
The X-ray diffraction data for pyrroaldiminates **XXII**, obtained from electrosynthesis (AN solution), indicate that the copper complex **XXII** ($M = Cu^{2+}$, R = *p*-Me, $n = 2$)[126] contains a tetrahedrally distorted metallacycle CuN_4, but the chelate of Co(III) **XXII** ($M = Co^{3+}$, R = *o*-Me, $n = 3$)[127]

has octahedral coordination, CoN_6. The analogous ligand environment N_6, shown by X-ray diffraction is characteristic for nickel chelates **XXII** ($M = Ni^{2+}$, $R = H$, $n = 2$) and cadmium **XXII** ($M = Cd^{2+}$, $R = 2\text{-OMe}$, $n = 2$)[128] with α,α'-bipy. For the ambidentate ligand systems of the pyrrolaldimine type, competitive coordination is characteristic, with formation of three types of structures: (1) with participation of the phenolimine fragment as in **XXV**,[15,129,133] (2) of all donor atoms as in **XXVI**,[130] and (3) imino-amine group as in **XXVII**.[132]

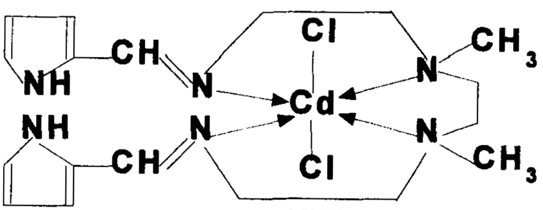


XXV

R = H, 4-Me, 5-Me, 5-Cl, 3,5-dimethyl
M = Cd, Ni, Zn; L-L = bipy, o-phen



XXVI

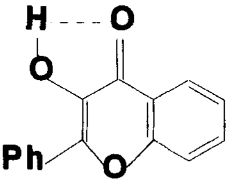


XXVII

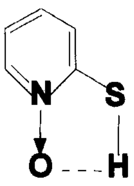
We emphasize that the pyrrol fragment does not coordinate in complexes **XXV** and **XXVII**. Perhaps, this is because the electrosynthesis occurs in acetonitrile solution in the presence of such strong chelating N-donors as

2,2′-bipy, 1,10-phen (the complexes **XXV**) or a macrocyclic fragment (the complex **XXVII**). Electrochemical synthesis for ligands of the azole series with less NH-acidity than pyrrol,[136] in alcohol solution, leads to the N-metal-substituted derivatives **XXIII** and **XXIV**.[10,17,21,24,98] It is very characteristic that N-metal-substitution is also observed under electrochemical synthesis in methanol or ethanol for azoles themselves.[10,17,21,24,98]

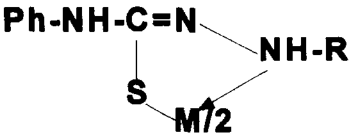
Other chelates with a five-member metallacycle, are synthesized electrochemically from bidentante oxygen-containing donors **VI** (R = Me),[137a] **XXVIII**[137b] and N-oxide-pyridine-2-thiol **XXIX**.[138a]



XXVIII



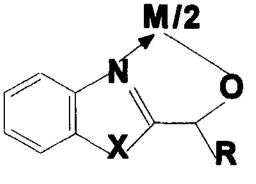
XXIX



XXX

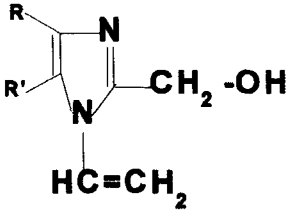
The existence of five-member metallacycles, MO_4, MO_2S_2 and MS_2N_2, in chelates of the ligands **VI** and **XXVIII, XXIX, XXX** respectively, is confirmed by X-ray diffraction.[137,138]

Five-member metallacycles having the composition ML_2, in chelates of hetaryl substituted monosugars as in **XXXI**, were prepared with a yield of 80–90% by electrolysis in methanol solution of the ligands with an anode made from the corresponding metal (cobalt, nickel, copper) and a platinum cathode, (Ref. [2], p. 1026). The electrochemical route, is preferred since the usual conditions of synthesis, starting from LH and M(Acet)$_2$ (Acet = acetate anion), give complexes of compositions ML_2 and MLAcet in 30% yield.[2]



XXXI

X = NCH_3, O; R = glycozide

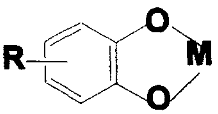


XXXII

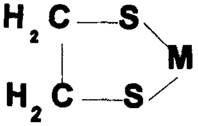
Highly unexpected results were obtained under electrochemical synthesis for coordination compounds of 1-vinyl-2-hydroxymethyl(benz)imidazoles

(LH) **XXXII.**[139] For reactions conducted in acetonitrile solutions with electrodes made from 3*d*-metals (Ti, Cr, Fe, Cu) in the presence of Bu_4NClO_4, instead of complexes with composition ML_n, chelates retaining the perchlorate anion $LM(ClO_4)_n$ were produced. For titanium and copper the mixed-ligand chelates $(LH)LM(ClO_4)_n$ were also formed; for copper the binuclear compounds $LCu_2(ClO_4)_3$ were also obtained.[139]

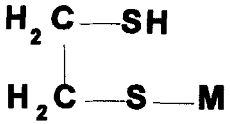
Chelate complexes with four-member chelates obtained electrochemically are represented by the complexes of orthodiphenols **XXXIII**,[67,68,140–141] alkanedithiols **XXXIV**[76,77] and their adducts with N- and O-bases. Thus, complexes having compositions ML,



XXXIII



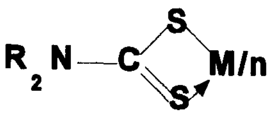
XXXIV



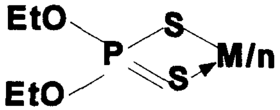
XXXV

(LH_2 = ligand) **XXXIV**[76] or InLH, $InI_2 \cdot LH$ (with mono-H-substituted ligand; in the latter-last case in the presence of iodine) **XXXV**, as well as the anionic complexes $[NR_4][InL]$ and $[NR_4][InI_2L]$, have been synthesized[77] (see Table II).

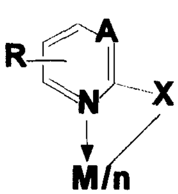
Electrochemical synthesis has been used to obtain the carboxylates,[80] diethyldithiocarbamates **XXXVI**,[142] diethyldithiophosphates **XXXVII**,[142] chelates of 2-pyridone **XXXVIII** (X = O, A = CH),[143] 2-pyrimidinthiol **XXXVIII** (X = S, A = N[144,145]) and their molecular adducts with azines and *bis*-azines.[144b,145]



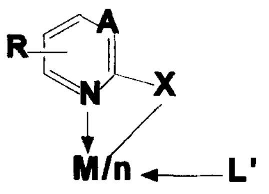
XXXVI



XXXVII



XXXVIII



XXXIX

Electrosynthesis of dialkyldithiocarbamates **XXXVI** (R = Me, Et) and diethyldithiophosphates **XXXVII** was carried out[142] in acetonitrile solution with anodes made of copper, silver, zinc, cadmium, indium, thallium, cobalt, nickel, and iron. The adducts $ML_n \cdot$phen (M = Ga, V, Mn, Co, Fe) were obtained by addition of 1,10-phen to the reaction mixture. The complexes were characterized by analytical data,[142] showing compositions ML_2 (**XXXVI**, **XXXVII**; $n = 2$) and ML: **XXXVI** (M = Ag, Tl; $n = 1$), **XXXVII** (M = Cu,Tl,Ga; $n = 1$), as well as ML_3: **XXXVI** (M = Fe, In, Tl; $n = 3$), **XXXVII** (M = Co; $n = 3$). The ^{31}P NMR-spectra of **XXXVII** were discussed.[142] For copper-tetramethylthiuram disulfide (TMU),[146] the interaction of metallic copper with non-aqueous solutions of TMU in the presence of Cl_4 and bipy was studied in detail without use of the electrosynthesis. Compounds of general formula $[Cu_nI_m(Me_2NSC_2)_l] \cdot A$, where $n = 1$–3, $m = 0, 1, 2, 4$, $l = 1$–$3, 5$, A = H_2O, Cu_2S and CH_3I, containing Cu(I), Cu(II), or rare Cu(III), are formed according to the magnetic data.

Metal chelates of divalent iron, copper, zinc, cadmium, cobalt and nickel[147,148] were isolated from electrosynthesis of pyridinone-2 **XXXVIII** (A = CH, X = O). Magnetic properties of complexes **XXXVIII** and **XXXIX** (X = O, A = CH) are of interest. The magnitudes of μ_{eff} for the copper complexes $CuL_2 \cdot 3H_2O$ and $[CuL_2 \cdot \text{phen}] \cdot 3H_2O$, are 1.5 and 2.4 B.M., respectively,[147a] perhaps from an exchange interaction of antiferromagnetic and ferromagnetic types.

It is well-known that the ligands of hetaryl-2-ones and hetaryl-2-thiones form several types of complexes.[70,143a,144a,145b] Diffraction data indicate that structures of adducts of 2-pyridinthiol **XXXIX** (A = CH, X = S, M = Ni,[143a] L^1 = bipy, R = H, $n = 2$; M = Zn;[143b] L^1 = phen, R = H, $n = 2$) and 2-pyrimidinthiol **XXXIX** (A = N, X = S; M = Ni,[144a] L^1 = bipy, $n = 2$; M = Cd,[144b] L^1 = phen, R = H, $n = 2$; m = Zn,[145a] L^1 = Py, R = 4,6-dimethyl, $n = 2$; M = Ni, Cd,[145b] L^1 = bipy, phen, $n = 1$), have a four-member metallacycle MN_2S_2. This cycle is formed by an endocyclic nitrogen atom of the pyridine and a thiol sulfur atom. The ligands (L^1) complete the octahedral (bipy, phen)[143,144,145b] or trigonal-bipyramidal (Py)[145a] configurations.

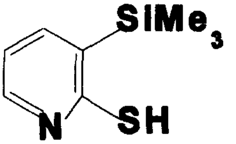
Electrosynthesis could be used to obtain macrocyclic chelates, in particular, porphyrin or phthalocyanine complexes.[24] The feasibility of such a process has been reported by C.H. Yang and B.P. Straughan, who electrochemically obtained some metal phthalocyanines from metal salts (Cu, Pb, Mg, Co, Ni) and elemental Fe and Cu.[149] Furthermore, Petit *et al.*[150] prepared copper phthalocyanine from electroreduction of phthalocyanine using a copper sheet or an electrodeposited layer of copper on platinum as the anode. The effect of some electrolytic parameters on the yield and a mechanism involving several steps were reported iso. The electrosynthesis of lithium phthalocyanine radical which is an intrinsic molecular semiconductors has been reported.[151,152] In our opinion, the electrosynthesis of phthalocyanines and related macrocycles is a promising field that should be developed.

A summary of the data on electrosynthesis of metal chelates is presented in Table IV.

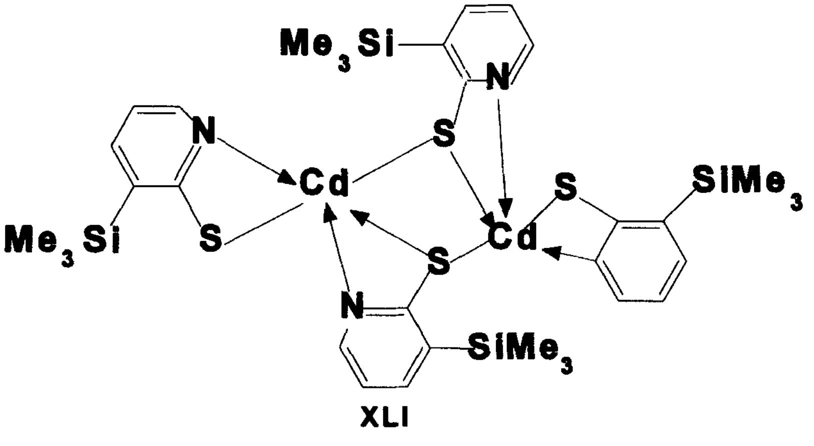
3. Electrosynthesis of di- and Polymetallic Complexes

Electrosynthesis has been used to obtain di- and polymetallic complexes.

The cadmium complex CdL_2[162] was obtained as a dimer from pyridine-2-thioles containing a trimethylsilyl substituent, XL (LH), by electrosynthesis (AN, Et_4NClO_4). The dimer $(CdL_2)_2$ XLI,



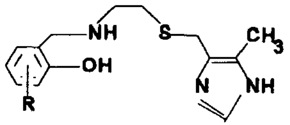
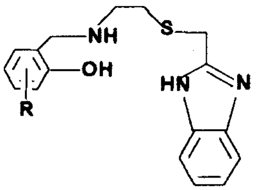
XL



XLI

consists of two cadmium atoms in a trigonal-bipyramidal configuration,[162] connected through a sulfide bridge. It is possible that a nickel complex and, especially, a zinc complex with the ligand XL,[162] have similar structures. A series of binuclear complexes has been obtained by electrochemical

TABLE IV Electrosynthesis of metal chelates

Metal	*Initial system*	*Products*	*Ref.*
Co,Dy,U	EtOH, benzoylacetone (Hba) or dibenzoylmethane (HDBM)	$[Co(EtOH)(ba)_2]$	95,96,97
		$Co(DBM)_2 \cdot 3EtOH$	
		$[Dy(HDBM)(DBM)_3]$	
	In N_2 atmosphere	$U(ba)_4$	
	In the presence O_2	$UO_2(ba)_2(Hba)_{0.5}$	
In,Fe,Ni,Ti,Zn, Zr,Cu,Mn,Co, V,Hg,Th,U	Hacac, CH_3OH, N_2	$M(acac)_n$	27,64,66,72, 91,93,95
	Hacac, O_2	$UO_2(acac)_2$	
		$UO_2(acac)_2 \cdot$ Hacac	
		$VO(acac)_2$	
Th	Acetone, tfha (1,1,1-trifluoromethylheptane-2,5-dione)	$Th(tfha)_4$	27
Cd,Co,Ni,Zn	 R = H; 3-OEt; 5-Br, CH_3CN	$ML \cdot nH_2O$	153
Cd,Co,Ni,Zn	 R = H; 3-OEt; 5-OMe, CH_3CN	$ML \cdot nH_2O$	153

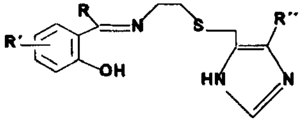
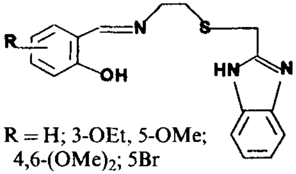
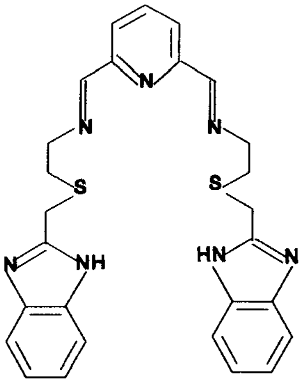
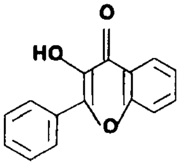
Cd,Cu,Ni,Zn	 R = H; Me R′ = H; 5-OMe; 4,6-(OMe)$_2$; 5Br; 3,5-Br$_2$; R″ = H, Me CH$_3$CN	ML · nH$_2$O	154
Cd,Ni,Zn	 R = H; 3-OEt, 5-OMe; 4,6-(OMe)$_2$; 5Br CH$_3$CN	ML · nH$_2$O	154

TABLE IV (*Continued*)

Metal	*Initial system*	*Products*	*Ref.*
Cu,Ni	 (bH-pyrathH$_2$), EtOH	[M(bHpyratb)]$\cdot n$H$_2$O	115
Cd,In,Hg,Sn	 CH$_3$CN, toluene	M(C$_{15}$H$_9$O$_3$)$_n$	137a
	In the presence of bipy	Cd(C$_{15}$H$_9$O$_3$)$_2$bipy	
In,Zn,Cd	Toluene, CH$_3$CN, 3-hydroxy-2-methyl-4-pyrone (= HL)	ML$_n$	137b

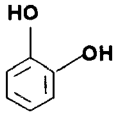
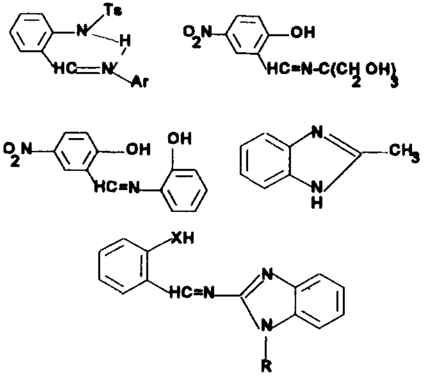
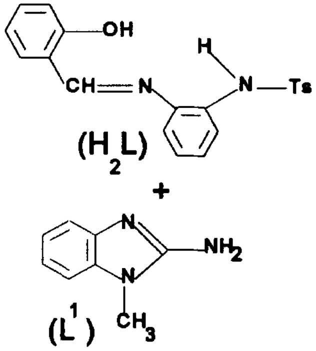
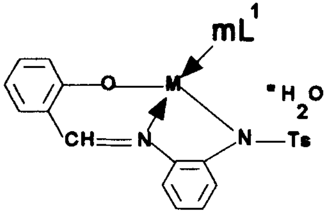
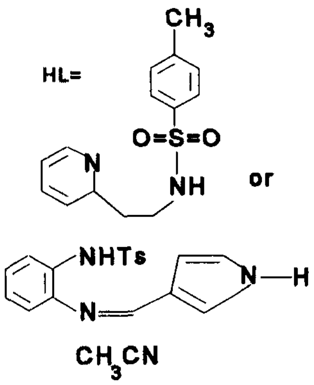
Cd	 CH_3CN, toluene	$Cd(C_8H_9O_2)_2$	137a
Cd,Zn,Cu	Acetone, 4-phenylthiosemicarbazide (HPTS)	$[Cd(PTS)_22H_2O] \cdot H_2O$ $Zn(PTS)_2(HPTS)$ $[Cu(PTS)H_2O](HPTS)$	138b
	In the presence of phen	$[Cd(PTS)_2phen] \cdot 2H_2O$	
Zn	H_2L = 1,7-bis(2-benzimidazolyl)-2,6-dithiaheptane, CH_3CN or 1,6-bis(2-benzimidazolyl)-2,5-dithiahexane, EtOH	$[Zn(bbdhp)] \cdot 3.5H_2O$ $[Zn(bbdhx)] \cdot 3.25H_2O$	155
Cd	2,2-dipyridylamine (= HL), CH_3CN	CdL_2	36
Cd,Zn	C_6H_6, CH_3OH, HL(L = oxine, 8-hydroxyquinoline), Hsal (salicylaldehyde)	ML_2	91
Co	Non-aqueous solvent, 4-aminoantipyrine Schiff base of salicylaldehyde (SAAP) and 2-hydroxy-1-naphthaldehyde (NAAP) [= R(OH)]	*ROH = SAAP* $Co(OR)_2(H_2O)_2$	107
	In the presence of phen	$Co(OR)_2phen \cdot 3H_2O$	
	In the presence of Ph_3P	$Co(OR)_2Ph_3PH_2O \cdot 5H_2O$ *ROH = NAAP* $Co(OR)_22H_2O$	
	In the presence of phen	$Co(OR)_2phen \cdot 2H_2O$	
	In the presence of Ph_3P	$Co(OR)_2Ph_3PH_2O \cdot 4H_2O$	
Co,Cu,Ni	CH_3OH, azoles or their derivatives (HL)	CoL	10–13

TABLE IV (*Continued*)

Metal	*Initial system*	*Products*	*Ref.*
Cu,Ni		CuL$_n$ or CuL$_n$ · Solv	124,156–158
Ni,Cu,Co,Zn,Cd	CH$_3$CN or EtOH 	 MLmL$_1$ · nH$_2$O $m = 1$ (M = Ni,Cu) $m = 2$ (M = Co,Zn,Cd) $n = 0$–2	123

Zn,Cd		ML_2	159,160
Cu	Schiff bases, derived from 2-(2-aminoethyl)pyridine and substituted salicylaldehydes (HL), CH_3CN	CuL_2	100
Cu	EtOH, CH_3ONa, phthalonitrile	CuPc (copper phthalocyanyne)	150
Fe,Cu	CH_3OH, 1,2-dichlorobenzene	CuPc, FePc	149c
La,Sm,Nd,Pr	*i*-BuOH, CH_3ONa, phthalonitrile	M_2Pc_3	161
Cd,Co,Cu, Fe,Ni,Zn	CH_3CN or acetone, $(S_2CNR_2)_2$, R = Me, Et	$M(S_2CNR_2)_2$	142
Tl	CH_3CN, $(S_2CNEt_2)_2$	$Tl(S_2CNR_2)_3 + Tl(S_2CNR_2)$	
Au		$Au(S_2CNEt_2)$	
In		$In(S_2CNR_2)_3$	
Cd	R_2NH (R = Me, Et, *i*-Pr, piperidine); CS_2	*$Cd(S_2CNR_2)_2$*	142

dissolution of metals in the presence of dioles[78] and thioles.[77,163] Thus, under electrochemical oxidation of copper in an acetonitrile solution of aromatic dioles (dihydroxybenzene), tetrachloro-1,2-dihydroxybenzene and 2,2′-dihydroxybiphenyl) in the presence of N-(bipy) and P-(triphenylphosphine, *bis*-diphenylphosphinomethane)-donors, binuclear complexes of copper(I) were obtained.[78] The structure of one ($Cu_2[OC_6Cl_4(OH)_2]_2$-$[(C_6H_5)_2PCH_2P(C_6H_5)_2]_2$) was determined by X-ray diffraction. The main feature of this structure is its eight-member metallacycle, containing two copper(I) atoms with two P–Cu–P bridges.[78]

Anodic dissolution of alkanethiols $R(SH)_2$ produced dimers with the general formula M_2S_2R (where M = Tl,[77] Cu and Ag[163]), with a doubly deprotonated ligand. The dimers with P-bases were also obtained with acetonitrile. A structural study of one indicate tetramers formation of and octanuclear clusters with sulfide bridges, having the formula $[Cu_2S_2C_3H_7$-$1,2(C_6H_5)_2PCH_2P(C_6H_5)_2]_4 \cdot CH_3CN$.[163]

A series of di-, tri- and tetranuclear, heteronuclear, complexes $M[M'(CO)_n]_m$ (where M = Zn, Cd, In; M′ = Co, Mn; $m = 2, 3$; $n = 4, 5$) and their adducts with bipyridyl and with N,N,N′,N′-tetramethylendiamine were obtained by electrosynthesis starting from zero-valent metals and carbonyls $Co_2(CO)_8$ or $Mn_2(CO)_{10}$ in methanol[164] (see also Tables V and VI). The tetranuclear complex $[Cu_4(\mu\text{-}C_5H_{11})_4 \cdot (Ph_2PCH_2PPh_2)_2]$ was synthesized from copper, allylsulfide and *bis*(diphenylphosphino)methane under conditions of electrosynthesis (AN, Et_4NClO_4)[165] with a new type of eight-membered cyclic structure Cu_4S_4 with the copper atoms connected through sulfide bridges.[165]

Complexes with tetranuclear cations $[Et_3NH][M_4(SPh)_{10}]$ (M = Zn and Cd),[166] are prepared by direct electrosynthesis with the participation of zinc or cadmium, thiophenol and triethylamine in acetonitrile (the supporting electrolyte is Et_4NClO_4). A bicyclic structure with terminal coordination of zinc and bridging SPh-fragments[166] is present in this anion (M = Zn). X-ray data showed that electrochemical synthesis generates two types of hexanuclear clusters with 4,6-dimethylpyrimidin-2-thione: an octahedral cluster with six Cu–Cu bonds and facet pyrimidinthionic fragments is obtained for Cu_6L_6[164,167] and a circular caliharene-like system with six cadmium atoms, bound by sulfide bridges, was found for Cd_6L_6.[145b] Since electrosynthesis of both examined structures was carried out under similar conditions (AN, Et_4NClO_4), the main factor in formation of the different structures is the nature of the central metal atoms Cu^+, Cd^{2+}.

Obtaining clusters from electrochemically synthesized complexes is very attractive. Thus, the eight-member cluster $[Cu_8(SC_5H_{11})_4(S_2CSC_5H_{11})_{11}]$[168]

TABLE V Electrosynthesis of σ and π organometallic and polynuclear complexes

Metal	*Initial system*	*Products*	*Ref.*
Cd	RX, CH_3OH, benzene $(n\text{-Pr})_4NX$; $R = Me, Et, n\text{-}Bu, CF_3, Ph$; $X = Cl, Br, I$	$[(n\text{-Pr})_4N][RCdX_2]$	38,170,171
	CH_3OH, RX, L (L = bipy,DMSO,phen,diox)	$RCdX \cdot nL$	
Tl	RX, acetone	RTlX	14a
Sn	Et_2SO_4, EtI	$SnEt_4$	172
Sn	Benzene, methanol, RX (R = Me, Et; X = Cl,Br,I)	R_2SnX_2	173
	RX (R = Me, Et, *n*-Bu, Ph), DMSO, CH_3CN, diphos(1,2-*bis*-(diphenylphosphino)-ethane), bipy (L)	$R_2SnX_2 \cdot L$	
Cd,Hg,Sn	Non-aqueous solvents, R_3SnCl	$Ph_3SnCdCl$ R_3SnSnR_3	174,175
Mg	CH_3CN, ArX bipy	$ArMgX \cdot bipy$ $MgX(CH_2)_nMgX \cdot 2bipy$	82
	CH_3CN, $X(CH_2)nX$	$R_4N[RMgX_2] \cdot CH_3CN$	
	CH_3CN, R_4NX, ArX		
Ti,Zr,Hf	CH_3CN or CH_3OH, RX (X = Cl,Br,I; R = Me,Et,Ph,$PhCH_2$)	$R_2MX_2 \cdot n\text{Solv}$	176
	In the presence of bipy	$R_2MX_2 \cdot bipy$	
Ni,Pd	CH_3CN, RX ($R = C_6F_5$, $C_6H_5CH_2$; X = Cl, Br)	RMX	177
	C_6F_5Br, PEt_3	$C_6F_5PdBr \cdot 2PEt_3$	
	RCN (R = Me, Et, Ph, C_6F_5), PEt_3	$RNiCN \cdot 2PEt_3$	
	$C_6H_5CH_2CN$, PEt_3	$C_6H_5CH_2NiCN \cdot Et_3P$	
In	CH_2X_2/CH_3CN (X = Cl, Br, I)	X_2InCH_2X	71
Zn,Cd,In	Bipy, CH_3OH, C_6H_6, $Co_2(CO)_8$	$Zn[Co(CO)_4]_2 \cdot bipy$ $Cd[Co(CO)_4]_2$	164
	Bipy, CH_3OH, C_6H_6, $Mn_2(CO)_{10}$	$Zn[Mn(CO)_4]_2 \cdot bipy$ $Cd[Mn(CO)_5]_2 \cdot bipy$ $In[Mn(CO)_5]_3 \cdot bipy$	
Cd	CH_3OH, benzene, $Co_2(CO)_8$, L L = tmed, bipy	$Cd[Co(CO_4)]_2 \cdot nL$	164

TABLE V (*Continued*)

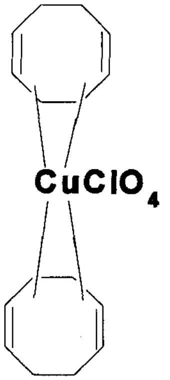
Metal	*Initial system*	*Products*	*Ref.*
Ni,Co,Fe,Zn	CH_3CN, CpH (cyclopentadiene) or Me_5C_5H	$M(Cp)_2$	178
		$M(Me_5C_5)_2$	
	CH_3CN, CpH, HX (X = Cl, Br), Bu_4NBr	$[Co(Cp)_2]_2CoX_4$	
Co,Cu,Au,Ag Zn	CH_3CN, Me_5C_5H, THF, KPF_6	$[Co(Me_5C_5)_2]_2(PF_6)$	178,179
	CH_3CN, Me_5C_5H, Bu_4NBr	$[Co(Me_5C_5)_2]Br$	
	CH_3CN, $PhC{\equiv}CH$	$M(PhC{\equiv}C)_n$	
	CH_3CN, CpH, THF, L (L = PPh_3, phen)	$M(Cp) \cdot L$	
Pb anode	EtCl, EtMgCl	$PbEt_4$	21,45
Pb cathode	EtBr	$PbEt_4$	

was prepared from copper(I) amilsulfide, obtained under electrosynthetic conditions in AN with a copper anode.[25] Interaction between the electrochemically obtained adduct of the cadmium complex of pyrimidin-2-thione with 1,10-phen ($R = H$, $A = N$, $M = Co$, $L^1 = phen$, $n = 2$) and copper(I) hexafluoracetylacetonate in AN leads to formation of the tetraheteronuclear complex $[Cu_2(phen)(\mu_3 - L)_2Cd_2(nFacac)_2] \cdot 2AN$,[169] where L is the trianion of 1,3,5-*tris*-(trifluormethyl)-1,3,5-trioxyhexane.

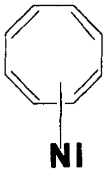
Additional bimetallic complexes obtained electrochemically are presented in Table V.

4. Electrosynthesis of σ- and π-Organometallic Complexes

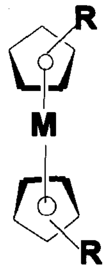
Electrochemical syntheses of π-complexes involving transition metals[9,17,21,24] include the electrosynthesis of metal complexes of cycloolefins, for example, copper complex of cyclooctadiene)[24] $Cu(COD)_2ClO_4$ **XLII**, a nickel derivative of cyclooctatetraene[9] Ni(COT) **XLIII**, and *bis*-(η^5-cyclopentadienyl) derivatives of the type **XLIV** ($M = Fe, Mn, Ni$).[9,21,24]



XLII



XLIII



XLIV

Ferrocene **XLIV** ($M = Fe$, $R = H$) was obtained by electrochemical dissolution of an iron anode in a solution of cyclopentadienylthallium in DMF (Ref. [21a], p. 135). The analogous manganese and nickel complexes have been synthesized by electrolysis of lithium, sodium or cadmium complexes of cyclopentadiene in a solution of THF (Ref. [21a], and references therein). However, the possibility to produce cyclopentadienides[180] and cyclopentadieniles[181-183] (see also Table V) starting directly from cyclopentadiene itself, was shown later. Thus, the cyclopentadienides of Mg, Zn and Al are formed by electrolysis of cyclopentadiene solutions in DMSO, DMF or AN with anodes of the metals.

The metallocenes of type **XLIV** ($M = Fe, Co$; $R = H$) have been obtained in THF or pyridine solutions in the presence of $[Bu_4N]Br$ (see Table V). The yields are 15–60% and depend on the nature of the metal, the solvent and the temperature.[178,183] It was impossible to isolate nickelocene in these conditions. Cobaltocene and its derivatives were obtained as cobaltocene salts in DMF solution with a yield of 20–30%.[182]

Electrosynthesis of metallocene complexes of the type **XLIV** starting from CH-acids RH (where $R =$ *cyclo*-C_5H_5, MeC_5H_4, 2,4-dimethyl C_5H_3, C_5Me_5, indenyl and fluorenyl) have special interest.[178] It was shown that π-complexes R_2M ($R = C_5H_5$, 2,4-dimethyl-C_5H_3, $M = Fe, Ni, Co, Zn$; $R = MeC_5H_4$, fluorenyl, $M = Fe, Ni$; $R =$ indelyl, $M = Fe$) could be obtained by electrosynthesis with anodes of ligands in AN, AN/1,2-dimetoxyethane, and AN/THF.[178] Moreover, the following mixed-ligand π-complexes have been synthesized: $(C_5H_5)CuPPh_3$, $[Co(C_5H_5)_2]Br$, $\{Co(C_5H_5)_2[CoCl_4]\}$, and $\{Co(C_5H_5)_2[CoBF_4]\}$.[178] The mixed-ligand complexes of the types $(\pi\text{-}C_p)_nM(CO)_m$, and $(\pi\text{-}C_p)_nM(CO)_mPR_3$, together with several metal carbonyls ($M = Fe, Co, Ni, Ti, V$) were synthesized from the same ligand system and CO electrochemically.[168] For metal carbonyls, two aspects are important: (a) metal carbonyls could also be obtained from reactions at a sacrificial cathode (Part III);[14a] (b) the mixed-ligand complexes $L_nM_m(CO)_{l-k}L'_k$ have been prepared from $L_nM_m(CO)_l$ by ligand substitution of CO under conditions of *electrocatalysis*.[21,184–186]

The σ-organometallic compounds obtained as a result of *oxidative insertion* of metals into C–H or C–X bonds (where $X = Cl, Br, I$) are generalized in Tables V and VI. They also can be obtained by electrochemical reduction of ketones using a sacrificial cathode (Part III, Table VI). Detailed description of their syntheses is presented in the papers.[14a,18]

The examples above testify to a limited application of the electrochemical method for the synthesis of metal π-complexes.

III. ELECTROSYNTHESIS AT SACRIFICIAL CATHODE

In some cases the electrolysis of ketones, organic halides or non-saturated compounds can lead to formation of organometallic compounds from metallic cathode dissolution. Only Hg, Pb, and Sn[14a] can dissolve by this method. Metal cathode dissolution is paradoxal;[17] organic radicals are formed on the cathode surface and then react with the metal. The reactions of cathode dissolution are summarized in Table VI.[14a,17,187,188] It should be noted that at present this method has limited applicability (the majority of the synthesized complexes have been obtained by anodic dissolution of metals).

TABLE VI Data on the electrosynthesis of metal complexes at sacrificial cathode

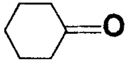
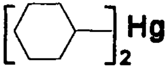
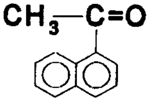
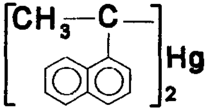
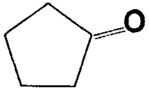
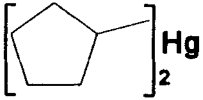
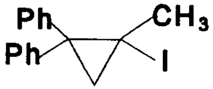
Metal	*Initial system*	*Products*	*Ref.*
Sn,Bi,Sb	$CH_2=CHCN$	$(NCCH_2CH_2)_nM$, $n=2-4$	17
Hg	 H_2SO_4 (5%)		187
Hg	 H_2SO_4 (45%)		14a,187
Hg	 $HCl+CH_3COOH$		187
Pb	$(C_2H_5)_2CO$, H_2SO_4	$[(C_2H_5)_2CH-]_4Pb$	187
Hg	$RC_6H_4CH_2Br$, LiBr, CH_3OH	$Hg(CH_2C_6H_4R)_2$	14a,17
Hg	HL =  CH_3CN, $(CH_3)_4NBr$	HgL_2	14a,17

TABLE VI (*Continued*)

Metal	*Initial system*	*Products*	*Ref.*
Sn	C_2H_5Br, CH_3CN, $(C_2H_5)_4NBr$	$Sn(C_2H_5)_4$	14a, 17
Pb	CH_3X ($X = Cl,Br,I$), C_2H_5X ($X = Cl,Br$), CH_3CN, $(C_2H_5)_4NBr$	PbR_4	14a, 188
Hg	$RHgBr$	$R_2Hg + HgBr_2$	14a
Hg	$Ph_2Pb(OAc)_2$	$R_2Hg + Pb + 2OAc$	14a
Hg	$(CH_3)_2CO$	$Hg[CH(CH_3)_2]$	14a
Hg	$Re_2(CO)_{10}$	$Hg[Re(CO)_5]_2$	14a
Hg	$Mn_2(CO)_{10}$	$Hg[Mn(CO)_5]_2$	14a

CONCLUSIONS

Electrosynthesis has wide application to synthesis of molecular complexes and metal chelates. Various metals (almost of all groups of the periodic table) and ligands, including both inorganic and organic compounds have been used for electrochemical synthesis.

However, elements of a secondary subgroup of groups IV–VII and acthinides are little represented. Using lanthanides (except cerium) in the electrosynthesis of metal complexes is almost absent from the literature. Successful development of this area would lead to new adducts of lanthanide salts with N-, P-, O-, S-bases and also to metal chelates of rare-earth elements, a branch of synthetic chemistry for which little has been done

Using electrosynthesis to obtain π-complexes and chelates with macrocyclic ligands are not as general, although successful electrosyntheses of some metal complexes of these types (see Parts II.2 and II.4 of the paper) are very promising. Undoubtedly, the lanthanides should be more used in future electrosynthetic procedures. The electrosynthesis of peroxocomplexes (Ref. 18 and references therein) seems very interesting as an approach to metals in unusually high oxidation numbers and should also be developed. Moreover, the combination of the electrochemical dissolution of metals with simultaneous ultrasonic treatment of the reaction system[25e,124,156,189,190] could help to avoid typical problems of the electrochemical procedures and to increase the yields. The sonoelectrochemical cell reported by Compton *et al.*,[25e] is the first attempt of such a combination.

Several electrochemical reactions of metal complexes obtained on a sacrificial cathode are described in the literature.[14a,17,21,24] However, except for these references, there is no information about sacrificial cathodes as a source of metal.

The material included in this review indicates the importance of electrochemical dissolution of metals to synthesize coordination compounds. The recent papers in this area[1,3,14b,18,21b,29–31,70,104–115,124,144,145,156–160,189–194] strongly support this idea.

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