

Coordination Aspects in Modern Inorganic Chemistry

A.D. Garnovskii^{*1}, E.V. Sennikova¹ and B.I. Kharisov^{*2}

¹Institute of Physical and Organic Chemistry, Southern Federal University, Rostov-on-Don, Russia

²CIIDIT-Universidad Autónoma de Nuevo León, Monterrey, Mexico

Abstract: Main types of coordination compounds in modern inorganic chemistry are discussed. Principal synthesis techniques for metal complexes and the problem of competitive coordination of ambident hard-soft ligands are discussed. A considerable attention is paid to polyfunctional materials, obtained on the basis of coordination compounds, especially molecular magnetics, organic light-emitting devices, and chemosensors.

Keywords: Coordination chemistry, competitive coordination, synthesis, biomimetics, metal complexes, functional materials.

INTRODUCTION

Generally, coordination chemistry is given as a part of inorganic chemistry courses (for example [1-5]) or as a special course on chemistry of complex compounds [6-11]. A multi-volume edition on general and coordination chemistry [12, 13], a series of monographs (for example [14]) and review articles [15-17], dedicated to the progress of modern chemistry of metal complexes, have been recently published. Results on this area have been published in more than 50 chemistry journals worldwide [10, 14]. Among them, four journals are completely devoted to this area: “*Journal of Coordination Chemistry*”, “*Coordination Chemistry Reviews*”, “*Polyhedron*” and “*Russian Journal of Coordination Chemistry*”. In three leading journals (“*Inorganic Chemistry*”, “*Inorganica Chimica Acta*” and “*Inorganic Chemistry Communications*”), major part of articles corresponds to the field of coordination chemistry.

Coordination chemistry was founded by Swiss scientist A. Werner (1866-1919), who won Nobel Prize in 1913. Great contribution was further made by Russian chemist L.A. Chugaev (1873-1922). Coordination (complex) entities consist of a cationic, anionic, or neutral complex, containing a central atom or ion and molecules or ions, coordinated with it. Those substances, whose molecules contains a central atom, connected with ligands, can be considered as coordination or complex entities [6]. In all these compounds, the cations are surrounded with anions, neutral molecules or radicals. The groups, surrounding directly the cation, are named ligands; the area of inorganic chemistry, studying joint behavior of cations and their ligands, was named as coordination chemistry [10].

The discussions below include, in particular, bioinorganic compounds, mostly copper and vanadium complexes [5, 13(Vol. 8)].

*Address correspondence to these authors at the Institute of Physical and Organic Chemistry, Southern Federal University, Rostov-on-Don, Russia; E-mail: garn@ipoc.rsu.ru

CIIDIT-Universidad Autónoma de Nuevo León, Monterrey, Mexico; E-mail: bkhariss@ccr.dsi.uanl.mx

CLASSIFICATIONS OF COORDINATION COMPOUNDS

Werner’s classification according to ligand nature [6, 17]:

- 1) Amino complexes $M_m A_n (NH_3)_p$, $M_m A_n (NH_2 R)_p$, $M_m A_n (NHR_2)_p$, $M_m A_n (NR_3)_p$.

R = Alk, Ar; m = 1, 2; n, p = 1 – 10; M = d-metals; A = Hal⁻, NO₂⁻, NO₃⁻, SO₄²⁻.

CoCl₃pNH₃ (p = 4-6), PtCl₄pNH₃ (p = 2-6), $M_m A_n L_p$, L = H₂NCH₂CH₂NH₂ (En) – ethylenediamine, Py – pyridine, p = 1-3.

- 2) Aqua complexes – $M_m A_n (H_2O)_p$, CoCl₂·6H₂O, NiCl₂·6H₂O, CuCl₂·4H₂O, CuSO₄·5H₂O.
- 3) Mixed-ligand complexes.

Aminoaqua complexes PtCl₄(NH₃)₆·H₂O, Co(NO₂)₂·(NH₃)₃·2H₂O.

Ethylenediamino aqua complexes CoCl₃(En)₃·3H₂O.

Aminoethylenediamino aqua PtCl₄(NH₃)₄(En)·2H₂O.

Classification of G. Beilar and D. Bush according to the type of ligand donor centers N, P, O, S [18]. This is the most common classification, which is widely used in monographs and systematization of a ligating compounds [14]. Not only classic donor centers are examined (C, N, P, As; O, S, Se, Te; B), but also their various combinations such as C, N; C, O; C, S; N, P; N, As; N, O; N, S; N, Se; N, Te; O, S; O, Se; O, Te; B, N; B, O; B, S [14].

Other approaches to complex classifications are reported in the monograph of K. Day and D. Selbin [3], but their use is limited:

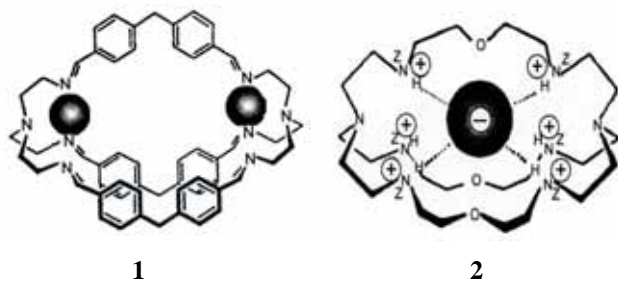
- 1) According to coordination number (CN) 2÷10; however, ~90% of known complexes have CN = 4, 5, 6.
- 2) According to oxidation number of a metal complex-former.
- 3) According to nature of a coordination bond: σ, π, δ or their combinations.

- 4) According to electronic configuration of a complex-former.

Moreover, complexes can be classified according to number of metallic centers in the complexes and the denticity of ligands [3].

An optimal classification is that which examines a complex molecule in whole: donor atoms, CN, bond nature and metal complex-former oxidation number. According to this classification, metal complexes can be divided in five types [17]: molecular complexes, metallocyclic complexes (chelates), complexes with multi-central bonds, di- and polymeric complexes and supramolecular coordination complexes. This classification [14, 17] comprehends all known types of metal complexes and concentrates attention on peculiarities of types of molecules in complexes and not of their separate parts [3, 16, 18].

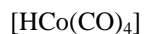
In a book of Nobel laureate J.M. Lehn "Supramolecular chemistry" [19], self-assembling of supramolecular complexes is related with coordinative interactions. It is noted that "chemistry of receptors" (recognizing cations, anions or neutral molecules) represents "generalized coordination chemistry".



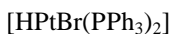
We note that some supramolecular structures may contain, as central atoms, not only cations **1**, but also anions, for instance halides **2** (details in [7-10, 19-21]).

Molecular Complexes $M_m A_n L_p^1 L_q^2$ [6, 14, 17]

Werner's complexes (the basis of coordination chemistry in the end of XIX and beginning of XX century) belongs to this type of complexes [6, 17]. When p or $q=0$, the complexes contain the same ligands (homoleptic complexes); if $q \neq 0$, they contain distinct ligands. Among these complexes, neutral (for instance $[BF_3 \cdot NH_3]$), cationic ($[Al(H_2O)_6]^{3+} Cl_3^-$) and anionic ($K_4^+ [Fe(CN)_6]^{4-}$) are known. The simplest ligand is a hydride anion, which belongs to dielectronic σ -donors [14] and forming a series of complexes, for example **3** and **4**.

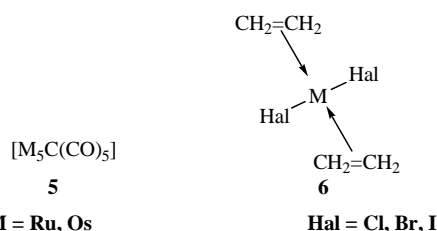


3

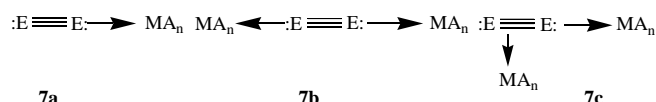


4

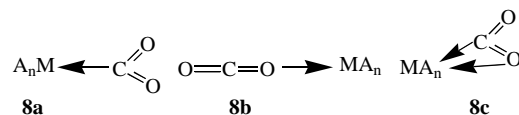
Carbon ligand is a part of clusters **5** or π -complexes **6**.



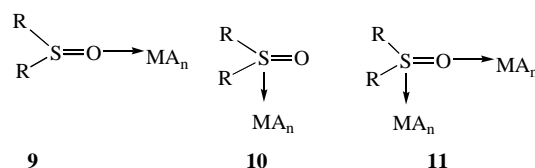
Mono- and dinuclear complexes with diatomic nitrogen, phosphorus, and arsenic (E) molecules **7a-c**, having various coordination modes, are well-known.



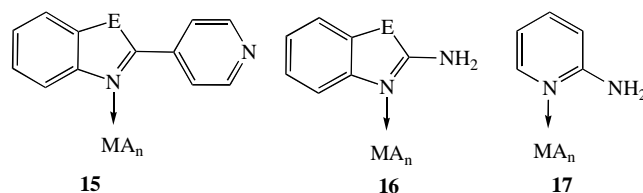
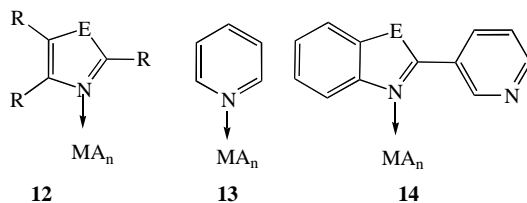
Among triatomic molecular ligands, we note carbon dioxide **8**, according to the importance to resolve the problem of binding CO_2 evolving to the atmosphere.



Dialkyl(aryl)sulfoxide complexes **9-11** have been also reported.



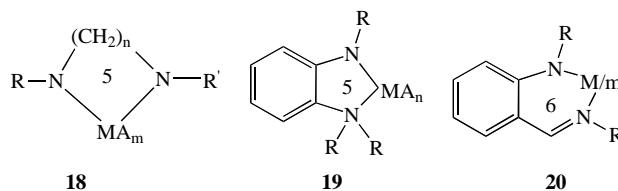
Molecular complexes of azoles **12**, azines **13** and their derivatives **14-17** are of high interest at present [5, 13, 14, 22].



$E = NR, O, S, Se, Te; R = H, Alk, Ar$

Metallocyclic Complexes (Chelates) [5, 14, 15]

In these complexes, metal cycles with distinct number of bonds were observed; among them, 5- or 6-member rings are the most stable, for example **18-22** [10, 15].



$R, R' = H, Alk, Ar;$

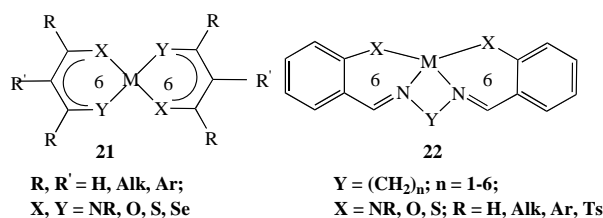
$m = 1-5;$

$n = 1-6;$

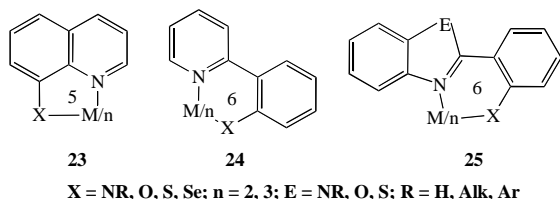
$R = H, Alk, Ar, Ts;$

$Ts = -SO_2R';$

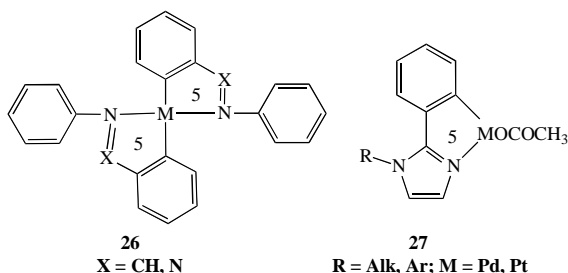
$R' = Me, Ar \quad m = 2,3$



Azine **23**, **24** and azole **25** complexes with 5- and 6-member cycles have been isolated.

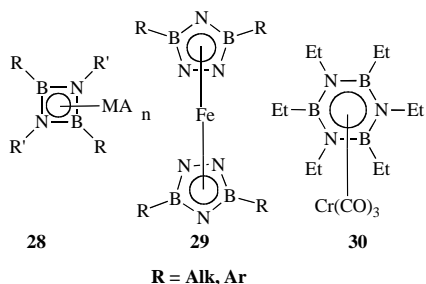


Formation of C,N-cyclometallated 5-member chelate structures **26**, **27** was noted [14, 23].

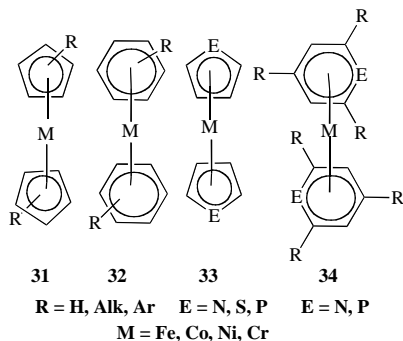


Complexes with Multi-Centered Bonds (CMB) [14]

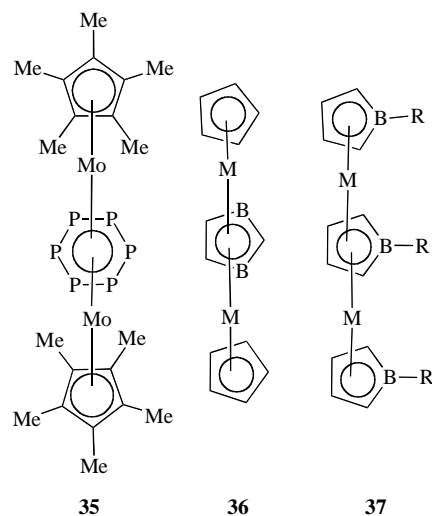
This type of complexes is formed by compounds with delocalized bonds. Examples of less-common coordination compounds are complexes of four- (**28**), five- (**29**) and six- (**30**) member boron-nitrogen systems [14].



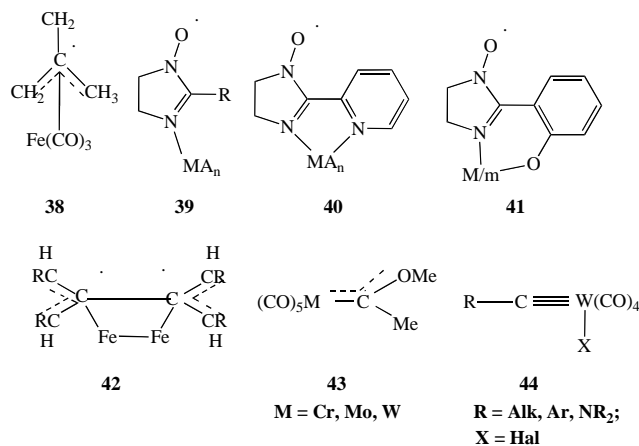
Cene complexes **31** (especially ferrocene **31**, $M = \text{Fe}$) and dibenzene metal sandwich structures **32** (especially dibenzenechromium **32**, $M = \text{Cr}$) are well-known [5, 14].



Heteroaromatic sandwich compounds of types **33** and **34** are also well-known [5, 22], as well as three-decker complexes of phosphorus- (**35**) and boron- (**36**, **37**) containing heterocycles [14].



Numerous CMB are formed by instable organic species: radicals **38-41**, biradicals **42**, carbenes **43** and carbinos **44** [14].

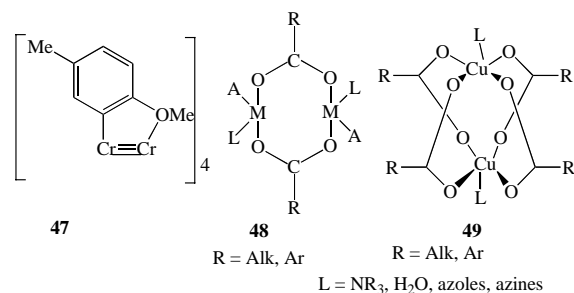


Di- and Polimetalllic Complexes [5, 14]

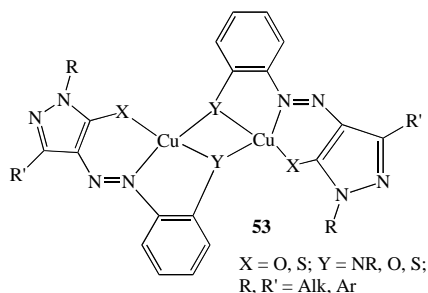
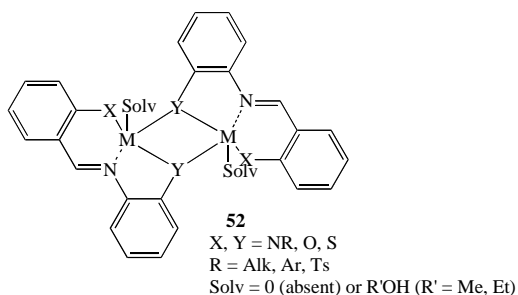
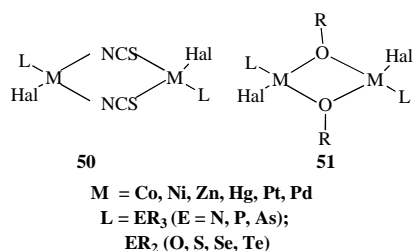
Werner's structures are also known among complexes of this type, for instance complexes **45** and **46** [6, 14].



Di- and polinuclear complexes having multiple bonds are examined in detail, for example **47** [24].

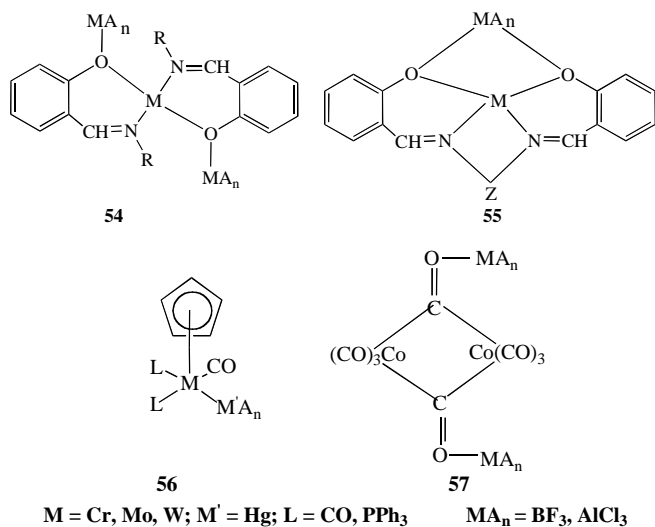


In relation with the problem of synthesis of molecular magnetics, carboxylate complexes **48** and **49** (shape of “Chinese lantern” [5, 7, 8, 10, 14]) are attractive for researchers. Complexes with intramolecular bridges **50-53** [14] are well-known, in particular binuclear complexes with NCS ligands **50** [7, 10, 14].



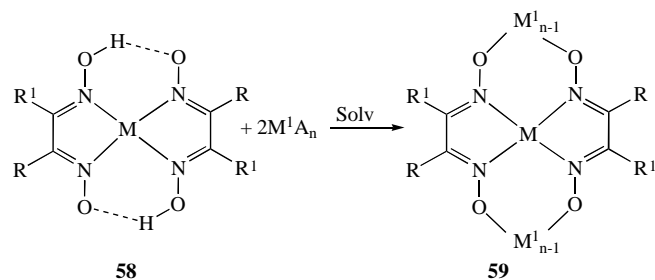
Metalloligand Complexes [14]

Long ago (beginning of 1960th [14]), a possibility of metal complexes to take part as ligands (metalloligands) is known, forming di- and oligonuclear structures in expenses of electron-donor coordinatively unsaturated fragments, for example **54-57**.



Clathrochelates

Metal dioximates **58**, intensively studied by Chugaev, are classic metalloligands; using them as precursors, mostly trinuclear complexes **59**, known as a clathrochelates are obtained [25, 26].



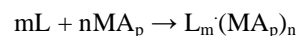
Synthesis of Coordination Compounds [14, 27-46]

Direct Interaction of Precursors [14, 27-29]

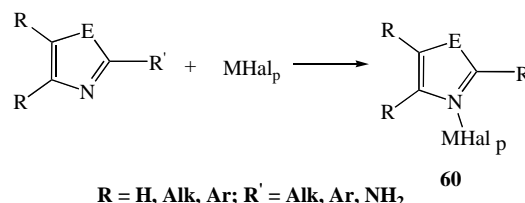
Reactions of Ligating Compounds and Metal Salts

As a result of interaction of these reagents, mostly in non-aqueous organic solvents (alcohols, hydrocarbons and their halide derivatives, etc.), all types of above indicated metal complexes are formed.

Molecular Complexes

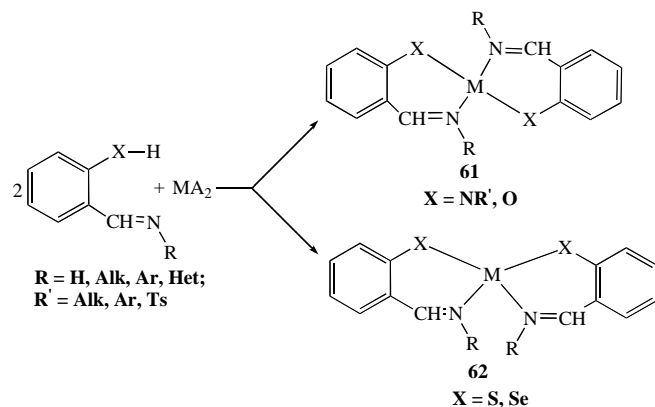


Azole complexes **60** are being intensively studied [22].



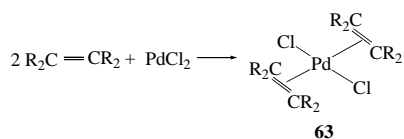
Chelates [14-16, 33-36]

As an example, we selected azomethine chelates, having, depending on donor atom (X), *trans*- (**61**) or *cis*- (**62**) structures [14, 15].

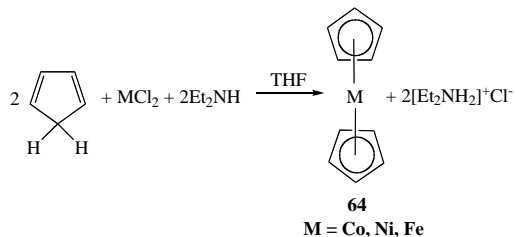


CMB [14, 29]

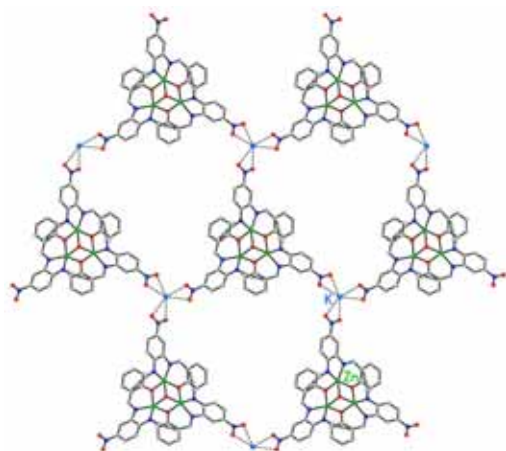
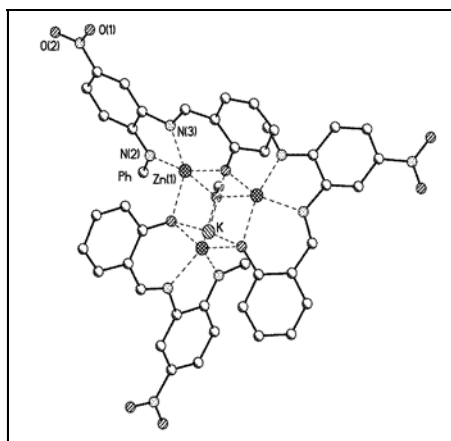
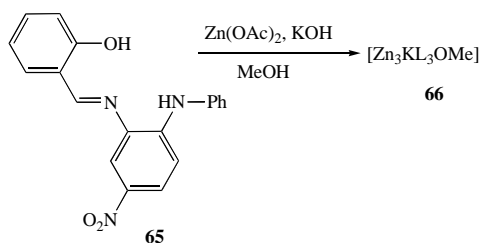
The oldest complexes of this type are π -complexes of ethylene series with dichlorides of platinum metals, for instance **63**.



The syntheses **64** [29] are classic for obtaining sandwich compounds **31**, **32**.

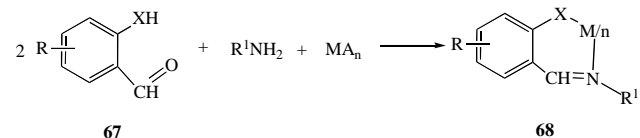


We note that, as a result of a direct interaction **65** of precursors, unpredictable structures were formed, for example tetranuclear complex **66** [37].

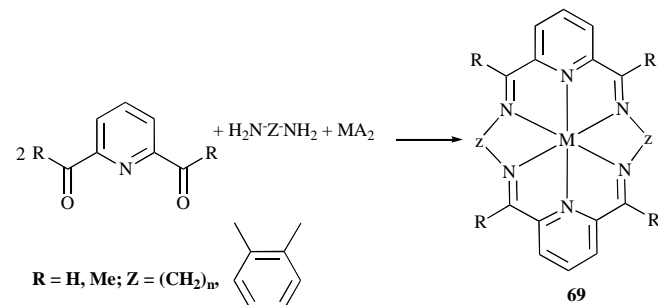


Template Synthesis [5, 14, 15, 30-34]

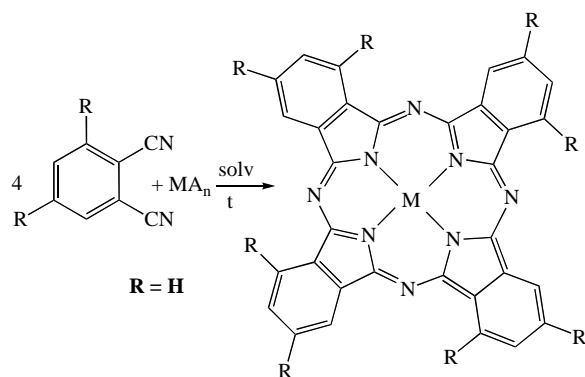
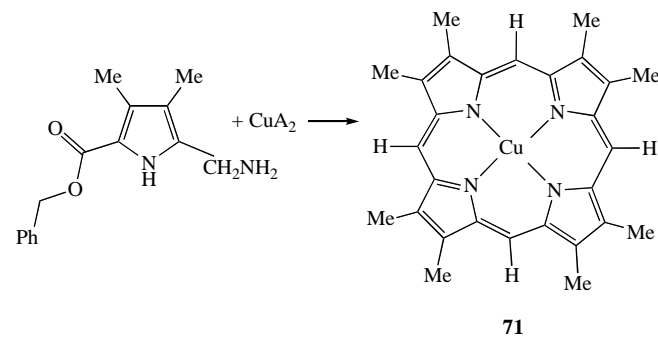
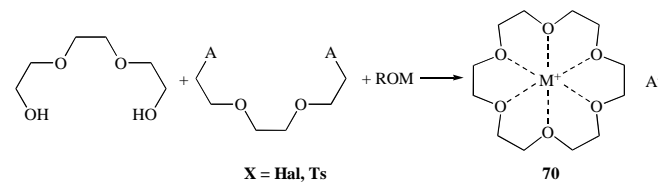
This type of synthesis is based on the formation of ligand on a metal matrix, *e.g.* Schiff bases from aldehydes **67** and primary amines. This route is used for obtaining acyclic **68** and cyclic **69** complexes of azomethines [13(Vol. 2), 14, 33, 36].



X = NR², O, S; R = H, Hal, NO₂; R¹ = H, Alk, Ar; R² = Alk, Ts; A = OAc, Hal, NO₃

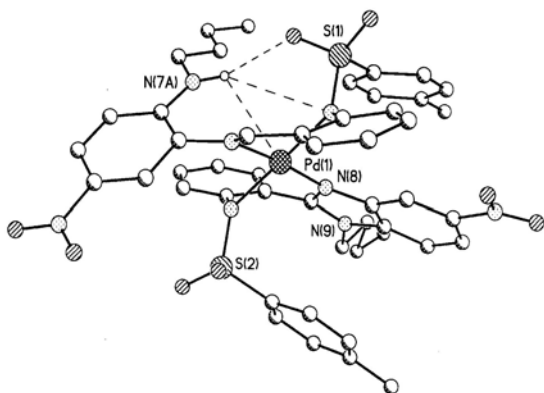
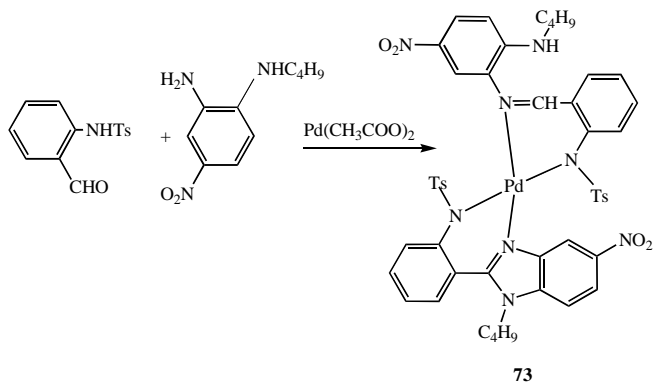


A similar technique is applied for synthesis of coordination compounds of crown-ethers **70** [38], tetrapyrrole derivatives of porphyrins **71** and phthalocyanines **72** [13, 39].



72

Rare structures are sometimes formed in the conditions of template syntheses, for instance **73** [40].



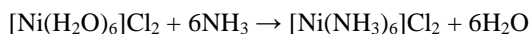
Structure of the chelate **73**

It was established the interaction of *o*-tosylamino-benzaldehyde with aniline derivatives on a palladium matrix leads to formation of the complex **73** with two different form of the same ligand. The structure **73** was proved by X-ray diffraction: one ligand is azomethinic, another one exists in benzimidazole form.

3. Ligand Exchange [14]

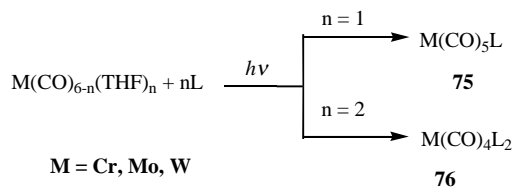
Molecular Complexes

This method is known as far back as from Werner's experiments, for instance for obtaining **74** [6].



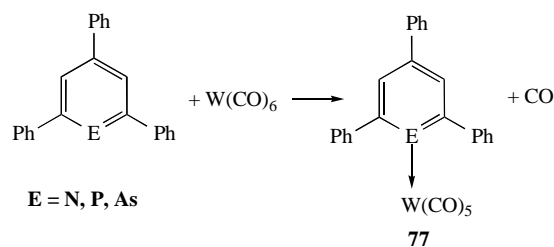
74

Especially widely this technique is applied to synthesize metal carbonyl complexes having distinct compositions **75** and **76** [29].



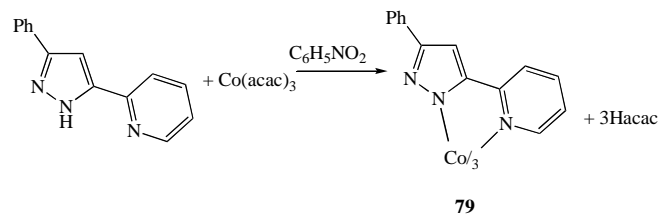
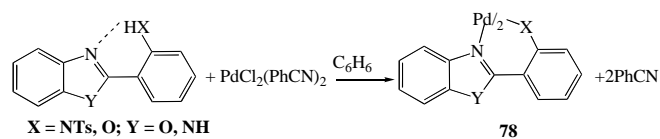
L = amines, azoles, azines;

In this respect, use of this route for syntheses of triphenylpyridine **77** (E = N), phospho- **77** (E = P) and arseno- **77** (E = As) benzene compounds seems attractive [14, 22].



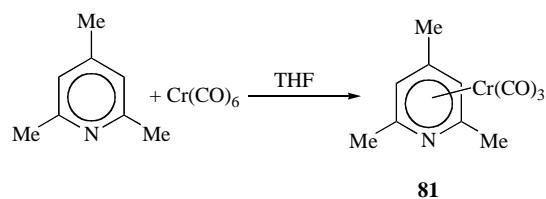
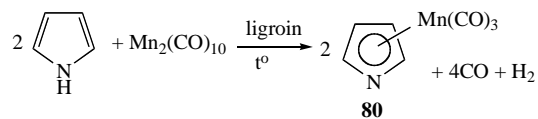
Chelates

The method of ligand exchange is used for obtaining chelates starting from low-soluble salts, for instance palladium chloride **78** or from NH-ligands (acetylacetonate method) **79** [14].



π -Complexes

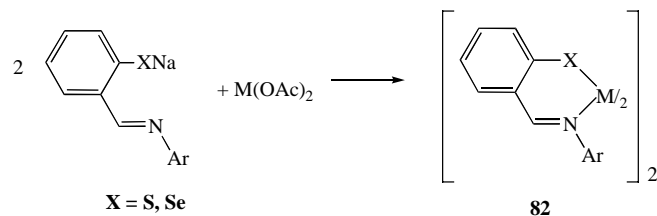
Complexes of classic heterocycles, such as pyrrole **80** or pyridine **81**, were obtained by exchange of the carbonyl ligand [22].

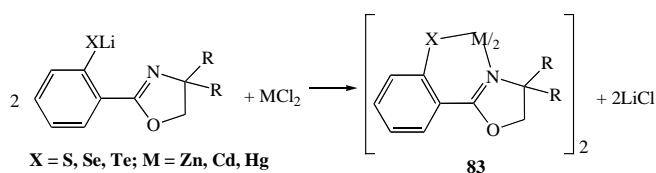


4. Metal Exchange

Chelates

This technique is applied for obtaining chelates of chalcogen-azomethines **82** and **83** from low-stable Schiff bases or 2-phenylazoles [14, 41].





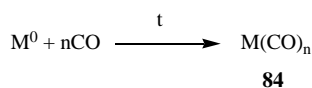
5. Direct Syntheses [14, 42]

Gas-Phase Synthesis (Cryosynthesis)

This technique is a part of the method of a direct interaction of precursors and it is based on the use of elemental (zero-valent) metals as complex-formers.

Molecular Complexes

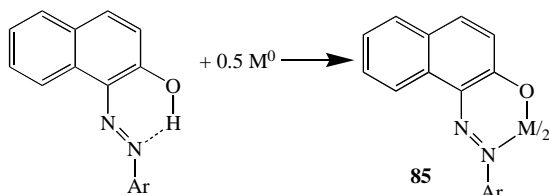
Such syntheses are carried out in vacuum equipment on surfaces cooled with liquid nitrogen or helium. This method is widely applied for obtaining metal carbonyls **84**.



$M = \text{Co, Mn, Cr, Fe, Ni, Pd, Pt, Rh, Cu, Ag, Ir, Eu, Nd}$

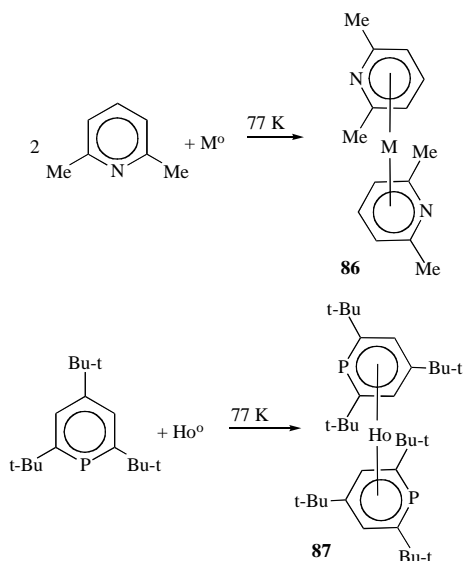
Chelates

At present, only a few examples are known for obtaining chelate structures **85** in gas-phase synthesis conditions [42]. More frequently such structures are formed in the conditions of tribo(mechano)synthesis [42].



π -Complexes

Gas-phase synthesis is widely applied in syntheses of π -complexes of heterocycles, for example pyridine **86** and phosphabenzene **87** sandwiches. Using classic chemical routes, such compounds cannot be obtained [14, 42].

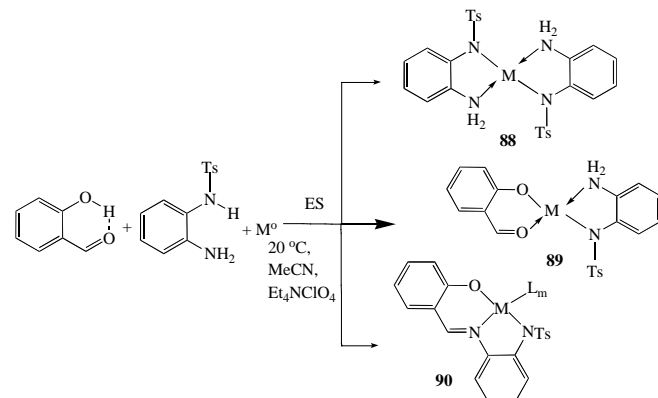


Electrosynthesis (ES) [13(Vol. 1); 14, 42]

This technique of the direct synthesis, which is being developed from 1970, is an important synthetic method in modern coordination chemistry [43-45]. It is based on an anodic dissolution of elemental metals (platinum plate is usually used as a cathode). Reactions are carried out in non-aqueous polar solvents (alcohols, acetonitrile, DMSO, DMF, etc.), generally at 20-50°C, using tertiary ammonium salts as conducting additives. Industrial equipment exists, modified with ultrasound and/or UV-irradiation for activation of electrochemical processes. The advantages [44, 45] of the ES are obtaining only anionless complexes, friendly synthetic conditions and a possibility, in some cases, of isolation of intermediate products.

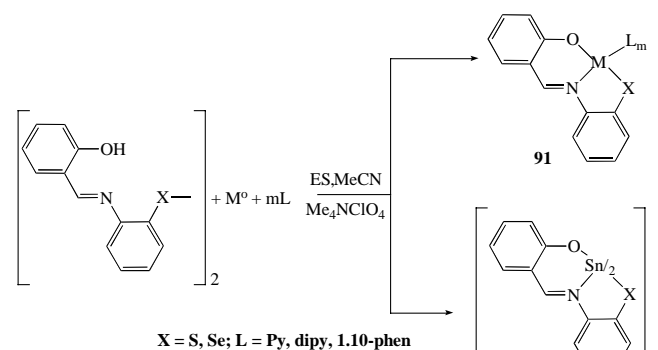
Chelates

Some examples of electrotheses, leading to chelates **88-90**, are represented below [14, 42-45]. A template electro-synthesis route was offered [46], in which, under soft conditions, intermediate products **88** and **89** can be isolated, together with the final compound **90**.

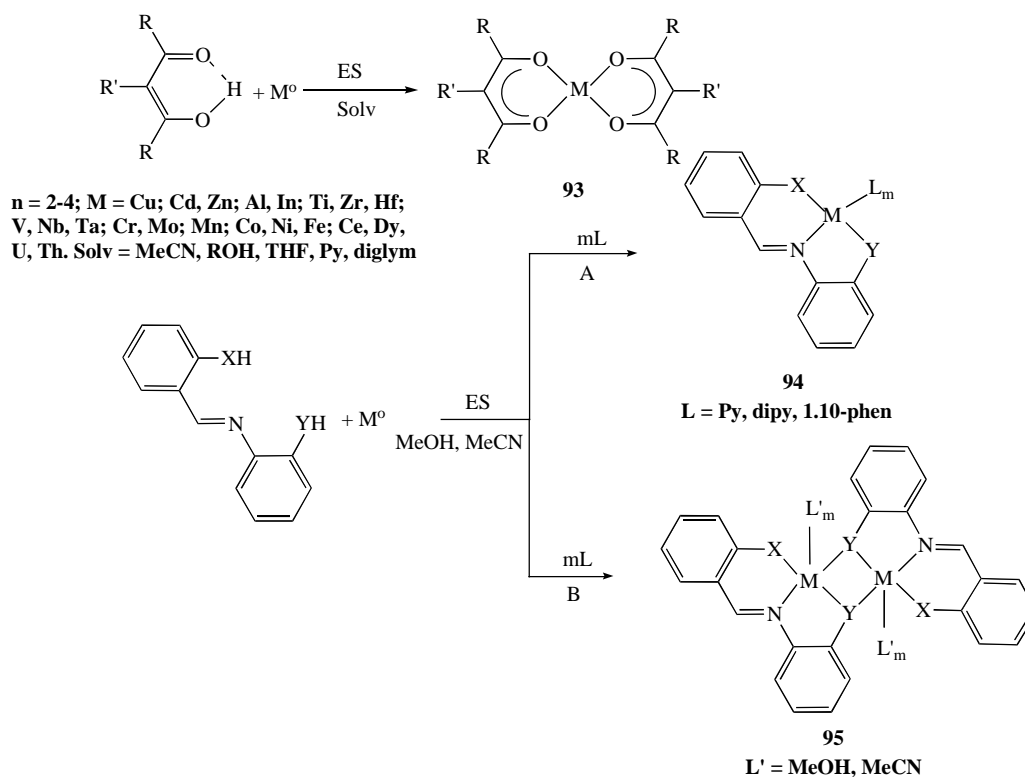


$\text{Ts} = -\text{SO}_2\text{C}_6\text{H}_4\text{Me-p}; L = \text{H}_2\text{O, MeCN}; M = \text{Ni, Cu, Zn}$

The ES had played an important role in obtaining coordination compounds with N,O,S- and N,O,Se-ligand environment. Here, the reaction of electrochemical cleavage of S-S and Se-Se bonds was used, discovered by Tuck [42, 44]. In particular, on the basis of formally tetradentate ligand, the complexes **91** and **92** ($X = \text{S, Se}$) were electrochemically synthesized.



Among other electrochemically obtained chelates, classic β -diketonates **93** ($X, Y = \text{O}$) and salicylaliminates **94** and **95** were reported [14, 42].



Other synthetic techniques (microwave, biphasic, tribochemical, ultrasonic, hydrothermal, and sol-gel) for obtaining coordination compounds also exist and described in [13], but they have still a limited application in coordination chemistry. Thus, MW-heating has been usually applied for obtaining inorganic materials; ultrasonic treatment has been used more widely in synthesis of metal complexes (examples of obtained compounds: carbonyls, diene or Grignard complexes). An example of hydrothermal synthesis is obtaining $[\text{Cu}(2\text{-IC}_7\text{H}_4\text{N}_2)]_n$ from CuI and benzimidazole. Sol-gel processes starting from metal alkoxides can lead to dimeric species such as, for example $(\text{RO})_3\text{TiOSi}(\text{OR})_3$. Biphasic reactions takes place in immiscible phases (solvents) and are widely used in catalysis [13].

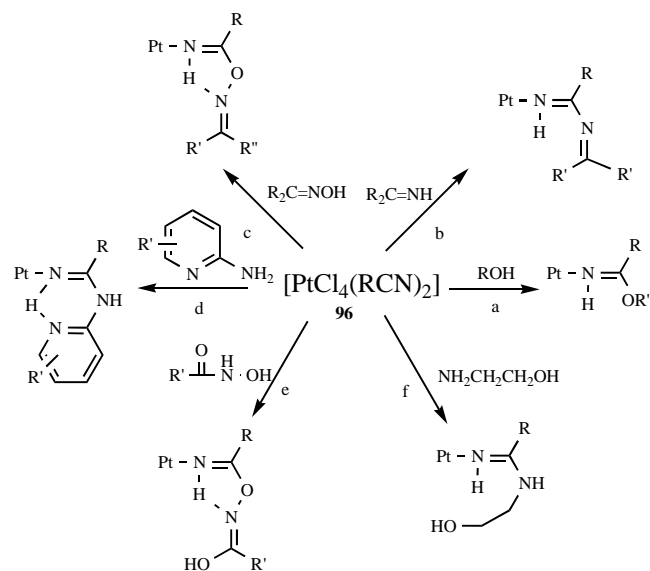
Reactivity of Coordination Compounds [13, 47-50]

Reactivity of metal complexes is an important area of coordination chemistry [47-50], including reactions on coordinatively-unsaturated donor centers **52**, **59** [14, 17, 25, 26] or metals complex-formers **54-57** [14, 41, 42], as well as reactions of self-assembling, leading to various supramolecular structures [19-21]. Reactions of coordinated inorganic and organic ligands are of the high interest. In particular, in 1998-2007 reactivity of such ligands as nitriles (RCN) and oximes, coordinated to the ion Pt(IV) is intensively studied [50-62]. The main attention in these studies is given to the reactions of nucleophilic addition of various nucleophiles on the carbon atom of triple CN-bond of the nitrile fragment, whose electrophilic activation was reached because of its coordination to Pt(IV) **96**. According to Scheme 1, both mono- (route a, b, c, d) and bifunctional (ambidentate) (route e, f) nucleophilic molecules can be used as reagents. Reactions take place in soft conditions and with high grade of selectivity, allowing generate new –

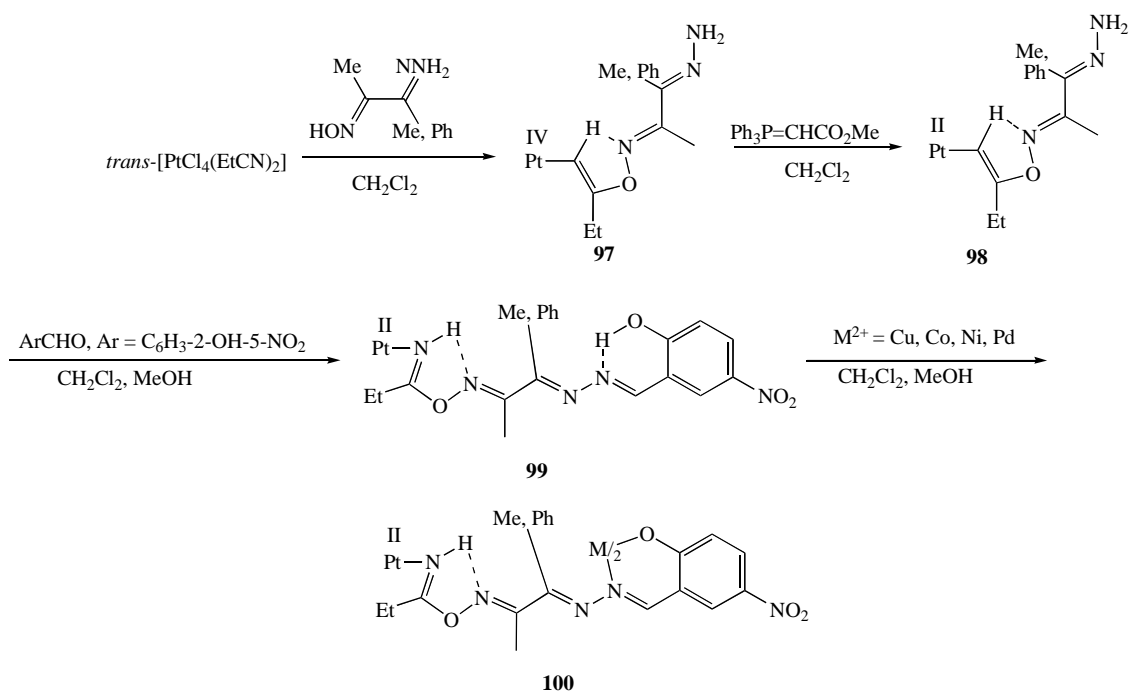
imino (a, b, c, e), amidino (f) and heteroarylamidine (d) ligands, major part of which is unavailable in a classic organic synthesis, in the internal coordination sphere of the Pt(IV) ion.

The most interesting work, on the point of view of the data above on reactions between various metals and Schiff bases, is the study of reactivity of various hydrazoneoximes with propionitrile, coordinated to Pt(IV) **97** (Scheme 2) [58].

This work shows a real possibility of programmed synthesis of a platinum-containing ligand (salicylaldehyde



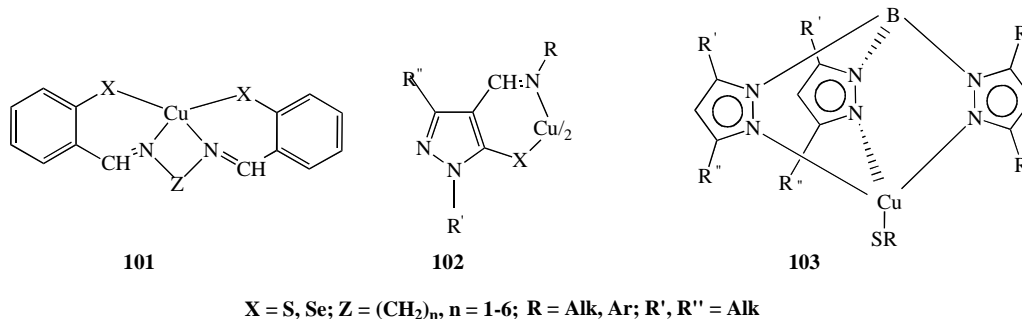
Scheme 1. Reactions of nucleophilic addition of various substrates to the coordinated nitriles.



Scheme 2. Synthesis of Pt-containing metalloligand and its complexes.

derivative) as a result of a series of subsequent transformations. The first step represents a selective nucleophilic addition of the ambidentate base (oximehydrazone **97**) on the oxime group accompanying by conservation of free periph-

copper complexes of bis-thiosalicylidenediethylenediamine and its analogues of the type **101**. Later on ([67] and refs. therein) it became possible to obtain models of pyrazolethioazomethine complexes, showing EPR- and electronic



eral amino group of the hydrazine fragment. In the second stage, a reduction of the product **97** takes place resulting obtaining a soluble isostructural compounds of Pt(II) **98**, which further enters in Schiff condensation reaction with 5-nitrosalicylaldehyde, leading to the salicylaldehyde derivative **99**, which is capable to form metal complexes (Scheme 2, structure **100**). All described compounds are characterized by elemental analysis data, FAB⁺-mass spectra, IR, ¹H, ¹³C{H}, ¹⁹⁵Pt NMR spectroscopies. X-Ray diffraction data are available for the **97-99**.

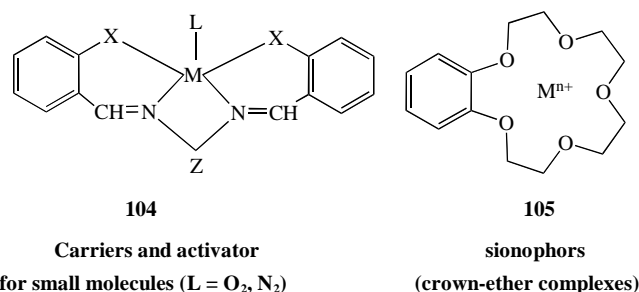
Complexes of Bioligands (Biomimetics [5, 13(Vol. 8); 63-69])

A whole volume of modern coordination chemistry [13(Vol. 8)] is devoted to the complexes of bioligands. Among them, we note copper-chalcogen chelates [63, 64, 66, 67], modeling active centers of blue copper proteins **101-103**. In early studies [63,64], there were cross-linked (Z)

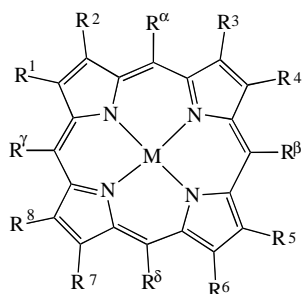
absorption spectral parameters of blue copper proteins **102**. All these parameters, as well as redox-potential, were observed on the model of *tris*(pyrazolyl) borate copper complexes **103** [68].

Active centers of blue copper protein

Complexes **104** и **105** are well-known [13(Vol. 8)]

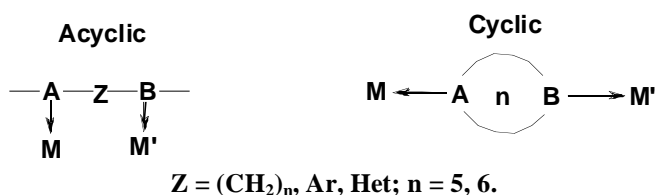


Other models are presented by formulae **104-106**. It is known that **106** ($M = \text{Mg}$) is chlorophyll providing respiration function of plants, **106** ($M = \text{Fe}$). Vanadium coordination compounds are well-known in bioinorganic chemistry [5, 13, 69], whose most important function is nitrogen fixation (vanadium nitrogenase, FeV-protein). A lot of information on the coordination chemistry of biologically important carbohydrates is discussed in reviews [69-71].

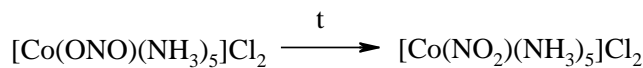
**106** $M = \text{Mg, Fe, Co, Ni, Cu}$

Competitive Coordination [14, 72-76]

Capacity of di- and polidentate ligands to react with metal ion through distinct donor centers was named as *competitive coordination* [72]. Such ligands are ambidentate [74, 75].



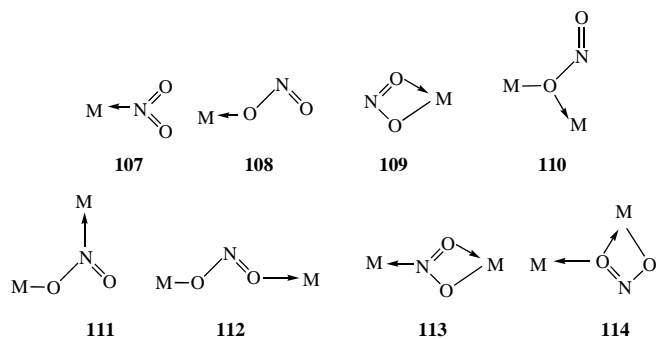
This is an extended variant of bonding ligand isomerism, discovered by Jorgensen as far back as in 1894 on the example of a distinct binding of the NO_2^- anion [11]:



Nitrite, orange

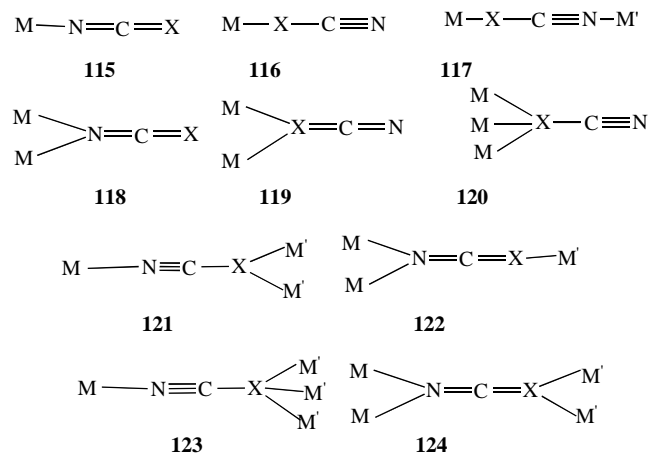
nitro, yellow

Eight coordination modes **107-114** for NO_2^- anion were examined [7]. We note that, according to X-ray diffraction data, **107-110** are the most common modes.

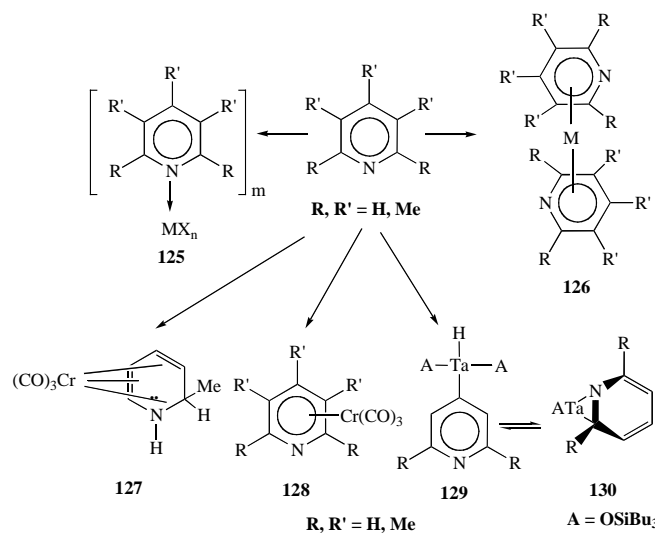


Explanation of competitive coordination was given according to the classic HSAB principle ([72,73] and refs. therein). Ideas about "hard" and "soft" acids and bases were introduced by R. Pearson in 1963 and at present are widely

used in various aspects of coordination chemistry [73]. Competitive coordination has been studied on many ambidentate anions, among which pseudo-halide anions **115-124** should be noted [14, 74, 77]. When $X = \text{O}$, both centers are hard; in case of $X = \text{S, Se}$, a hard-soft ligand system is formed, whose coordination is proved using HSAB principle [14, 72-76].

 $X = \text{O, S, Se}$

For azine complexes **125-130**, an N-atom is hard, meanwhile the heteroaromatic π -system is soft [5, 14].

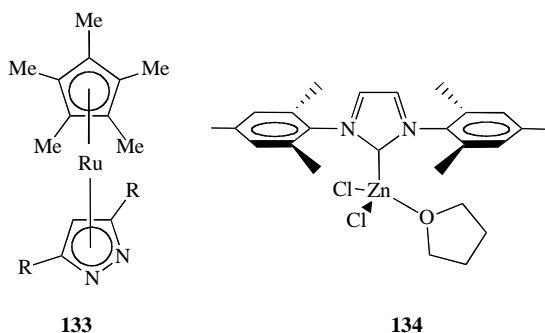
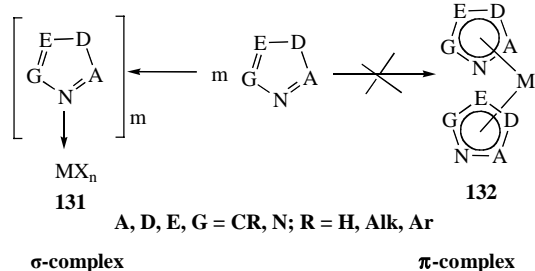


In this case, independently on the hardness or softness of a complex-former, the N-atom could form a coordination bond, but soft acids prefer to be coordinated by a soft π -system of pyridine **126, 128**.

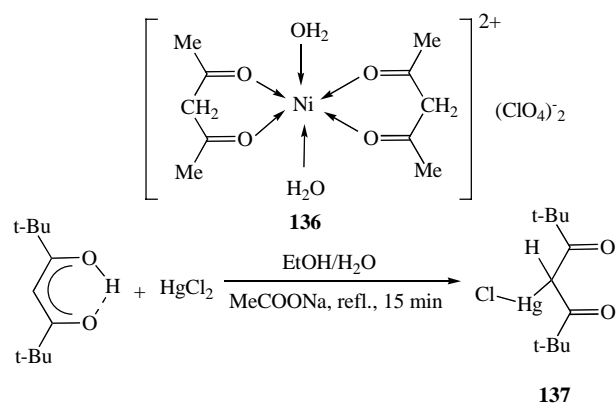
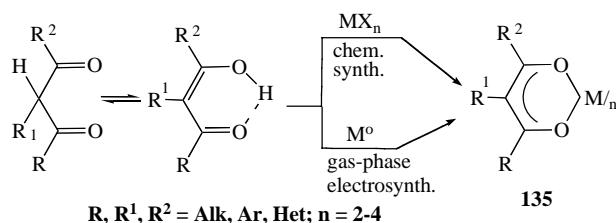
Nobel laureate E.O. Fisher made a first attempt to coordinate heteroaromatic π -system of pyridine. In 1964 he considered that obtained the complex of the type **128** on the basis of *o*-monomethylpyridine. However, later on (in 1967) two additional protons were detected in ^1H NMR spectra, so it had to inscribe the structure of σ, π -complex **127** to this compound. Then (in 1976), D. Lagovskii obtained a pyridine analogue of dibenzenechromium **126** by cryosynthesis technique; Biderman isolated the compound **128** creating additional spatial difficulties for the NB-atom [14]. Highly unexpectedly (in 1991), an equilibrium transformation **129-130**

was discovered, in which a carbene **129** and C,N **130** coordinated complexes take part [5, 78].

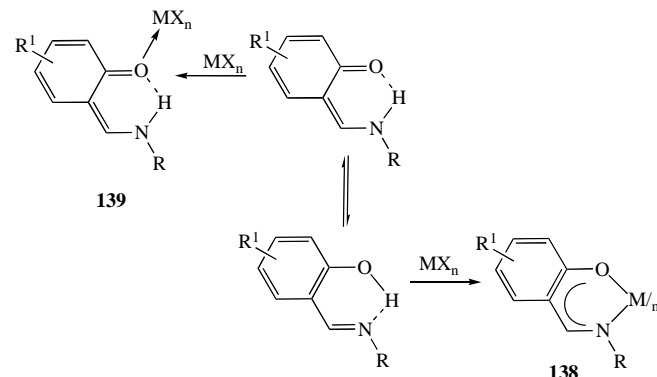
σ -N-Complexes **131** are typical for azoles [14, 22, 79, 80]. *Bis*-azole complexes of the type **132** have not yet been discovered, but a pyrazolocyclopentadienyl ruthenium complex **133** [14, 81] and imidazolecarbene compounds **134** [82] were isolated.



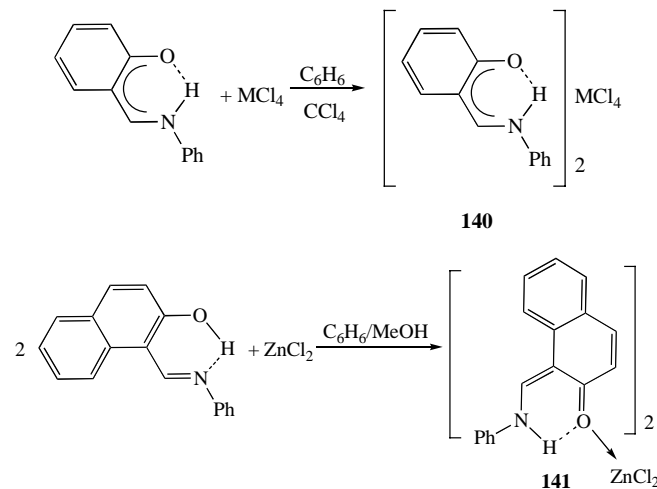
Competitive coordination is clearly observed in chelating ligand complexes. This is well-known that β -diketones form chelate structures of the type **135** with same inner-chelate bonds **136** [14]. At the same time, molecular chelates with completely conserved (non-deprotonated) ligand system are known, in which a diketone form **136** of the ligand is stabilized as a result of metal coordination. Various coordination modes of β -diketones and their analogues are discussed in monographs [14, 83] and reviews [75, 76]. One interesting example is a C-coordinated structure **137** [14].



On the basis of 2-hydroxiazomethine ligands, a host of chelate salicylideneiminates **138** was obtained [14, 15, 34-36, 84]. However, molecular complexes **139** are also known, where usually bidentate Schiff bases behave as monodentate O-donor ligands [14, 34, 84-86].



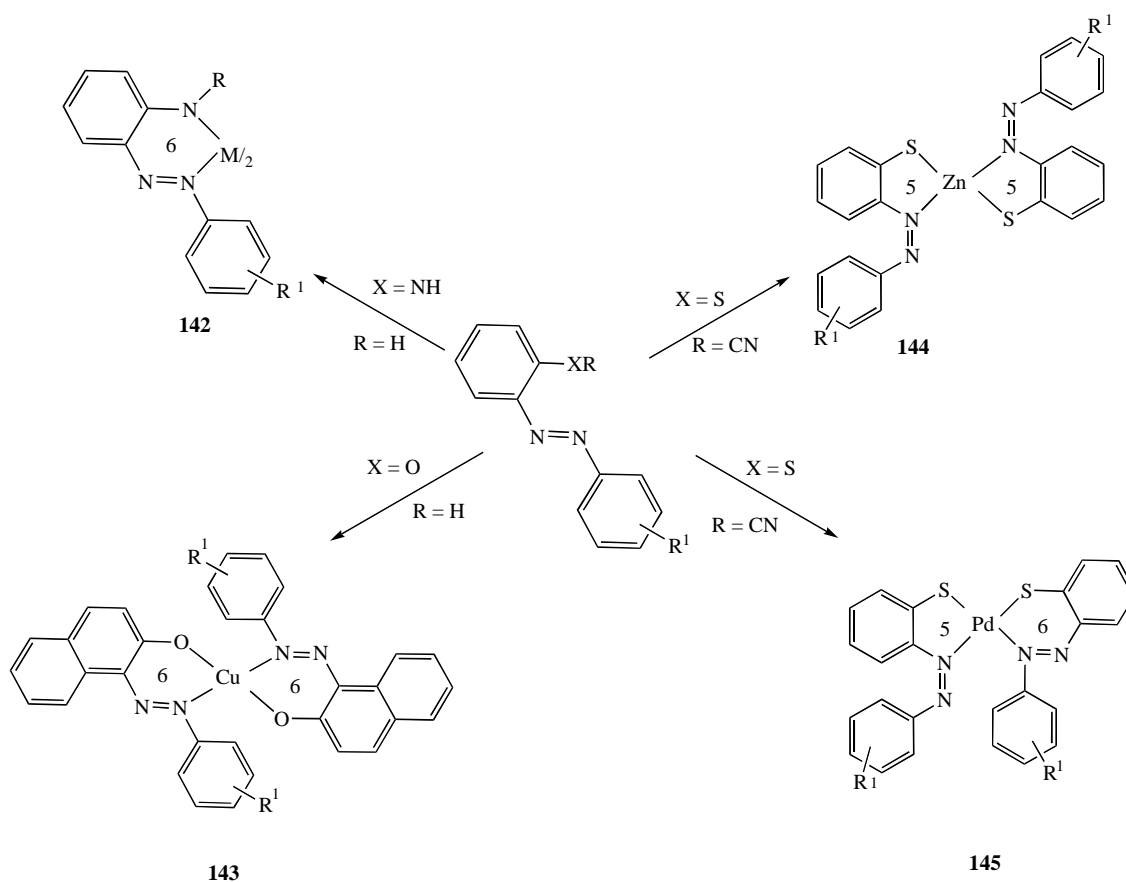
First data on these molecular complexes were reported in 1964, although a coordination mode was not determined **140**. Unusual coordination on the oxygen atom in the *o*-hydroxynaphthalideneaniline complex with ZnCl₂ **141** was proved by X-ray diffraction [85] and keto-amine tautomeric form of the ligand was established. Later on [86], an analogous structural situation was revealed for the complex of zinc dichloride with salicylideneaniline.



Discovery of inner-chelate isomerism in a series of chelates of azo compounds [87-89] was important for coordination chemistry. It is accepted that two six-member metalocycles are present in such complexes. This is really observed for *o*-amine- **142** and hydroxy- **143** azo compounds. However, it was established by X-ray diffraction that an existence of two 5- **144** or 5- and 6- **145** member metalocycles is typical for *o*-mercaptoazo compounds [14, 15, 88, 89]. A similar inner-chelate tautomerism is also observed for other chelates, for example in complexes of aromatic and heteroaromatic formazanes [14, 15].

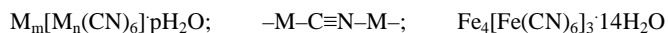
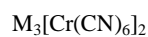
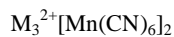
Polyfunctional Materials

A central problem in modern coordination chemistry is application of its results in life, in particular by creation of new polyfunctional materials. This fact is directly emphasized in the second issue of [13], whose two volumes (8 and

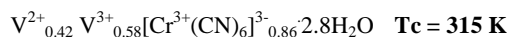


9) are dedicated to biocoordination chemistry and applications of coordination compounds, respectively. A considerable role of metal complexes in creation of new materials is noted in a series of special issues, for instance [90-94]. Here we will describe some important examples of use of coordination compounds.

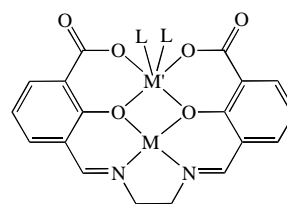
Among magnetoactive complexes, the most interest is caused by those coordination compounds which possess ferromagnetic exchange interactions, in particular metal cyanides **146**. The metal complex of Prussian blue **147**, known from 1704 was one of the first (1967) ferromagnetic [95]. On the basis of cyanides of various metals, a series of high-temperature ferromagnetics **148** [95] were obtained, as well as photoactive magnetic materials (spin-crossover complexes [96]).

**146****147**

M = V, Co, Mn, Cr, Ni, Cu; Tc = 9-20 K

**148**

Famous magnetochemist O. Kahn prepared the compounds with predictable magnetic properties on the basis of azomethine complexes [13(Vol. 2)]. Changing a series of metals, his group has obtained ferro- (positive exchange parameter) and antiferromagnetic complex compounds **149**, **150**. Similar complexes **151** are also ferromagnetic.

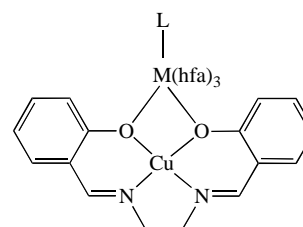
**149**

M, M' = Cu, Fe, VO; L = H₂O, MeOH

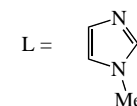
Cu - VO $J = + 118 \text{ cm}^{-1}$

Cu - Cr $J = + 115 \text{ cm}^{-1}$

Cu - Fe $J = - 105 \text{ cm}^{-1}$

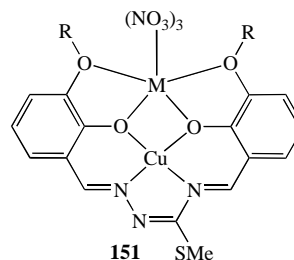
**150**

Hhfa = hexafluoroacetylacetonate



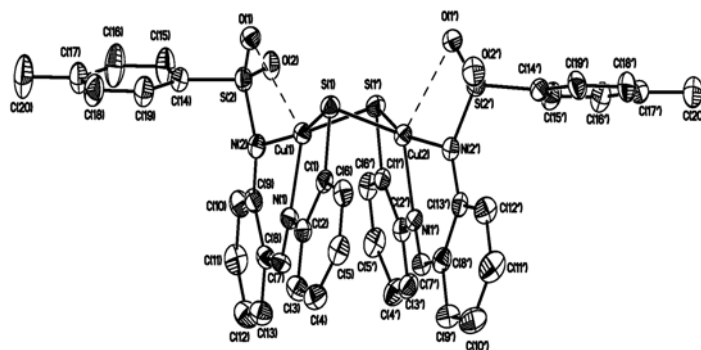
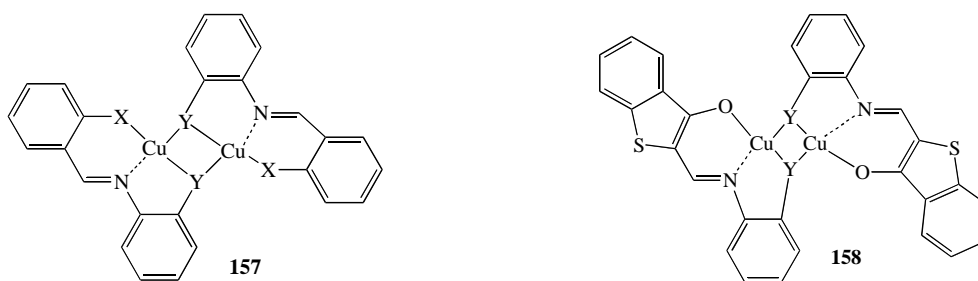
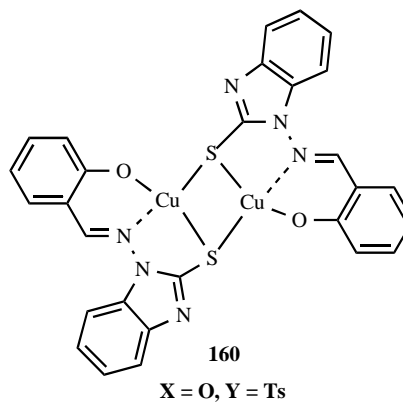
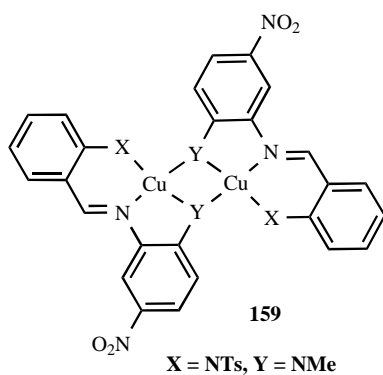
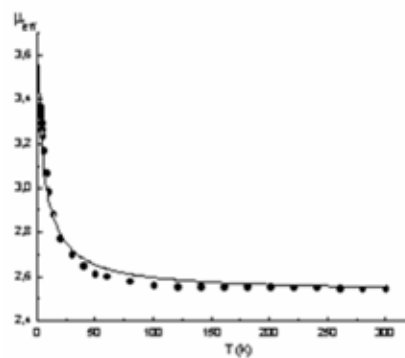
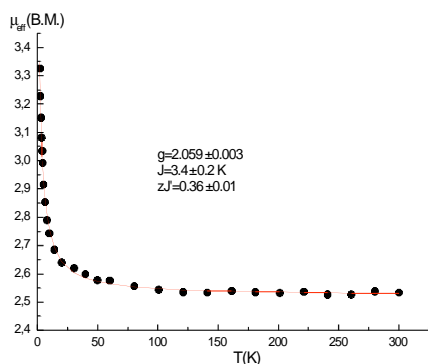
M = Gd, Y, La

L_nCuGd $J = + 5.68 \text{ cm}^{-1}$

**151**

R = Me, Et; M = Ce, Gd

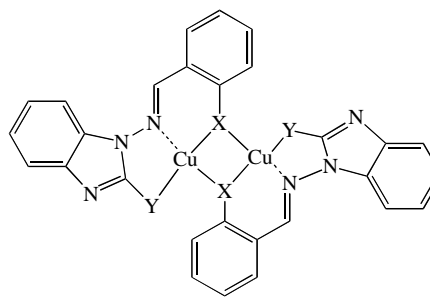
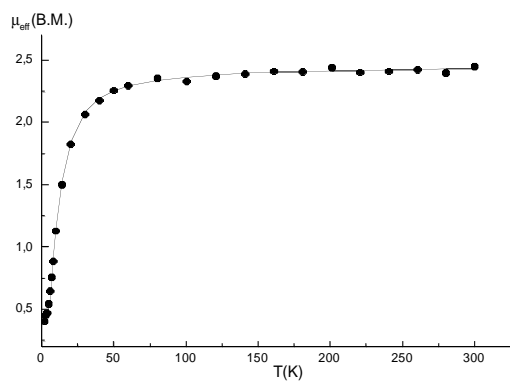
Cu - Gd $J = + 5 \text{ cm}^{-1}$ (R = Me)
 $J = + 5.5 \text{ cm}^{-1}$ (R = Et)

Structure of **157**: Y = S, diamagnetic; Y = O, antiferromagnetic

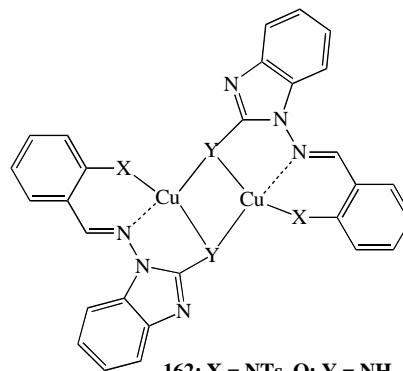
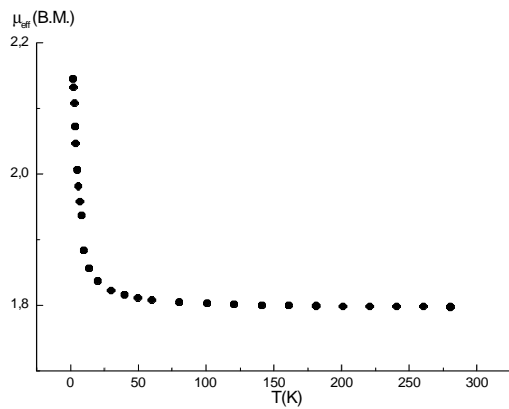
The same situation is observed for the complexes of type **161**, **162** with antiferro- **161** or ferro- **162** magnetic interactions. In this case, it is quite probable (X-Ray data are required) existence of inner-chelate isomers with distinct (X or Y) intermetallic bridges.

Complex compounds of azomethine **163-166**, azine **167-168**, and azole **169-170** series are important among other functional materials [41, 91, 92]. They are luminescent in a

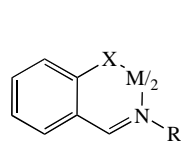
broad spectral range from visible (red, orange, blue, and violet) to IR-region [41, 91]. Thus, complex compounds with blue fluorescence are discovered among mononuclear complexes [91]. In particular, mononuclear complexes of azomethine ligands **165**, **166** and the polyheteronuclear complex compound **171** absorb in red and yellow spectral ranges. Luminescence of heteronuclear lanthanide complexes of type **172** was observed in IR region [91].



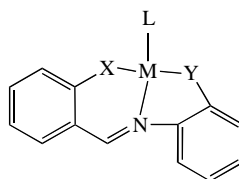
161: X = NTs, O; Y = O.



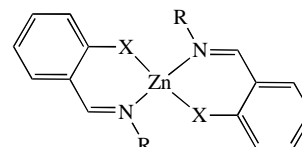
162: X = NTs, O; Y = NH



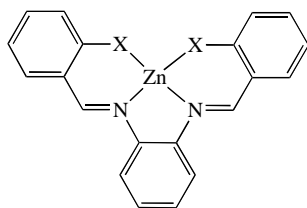
163



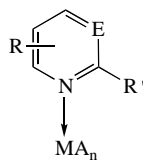
164



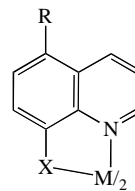
165



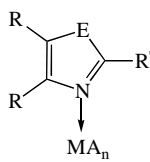
166



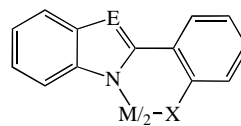
167



168

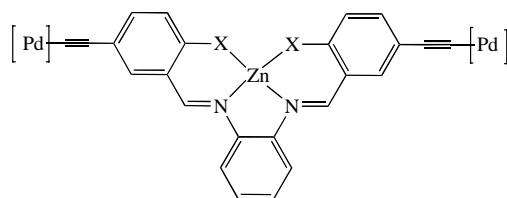


169

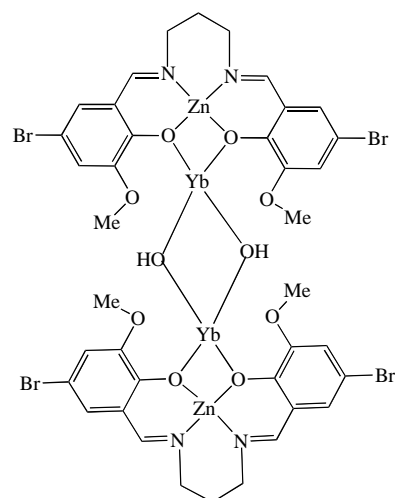


170

X = NTs, O; E = CH, N, NR, O, S; R = H, Alk, Ar



171

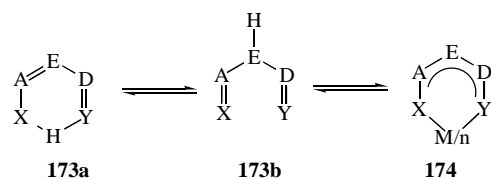


172

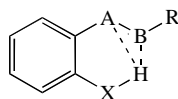
Among other applications of coordination compounds, we would like to mention their use in creation of new metalcomplex additives to lubricants, providing the effect of wear less friction [106-108]. In particular, easily accessible complexes of *o*-azomethines and hydrazones with copper and molybdenum are effective as additive.

Perspectives of Coordination Chemistry

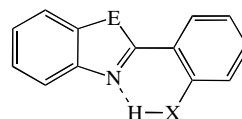
The main direction of metal-complex chemistry in XXI century is emphasized in the title of [13]: “from biology to nanotechnology”. β -Diketones and their analogues **173**, diketonate complexes **174** [109], azomethinic **175** and heterocyc-



A, D, E = CR, N, P, O; X, Y = NR', O, S, Se; R, R' = H, Alk, Ar, Het

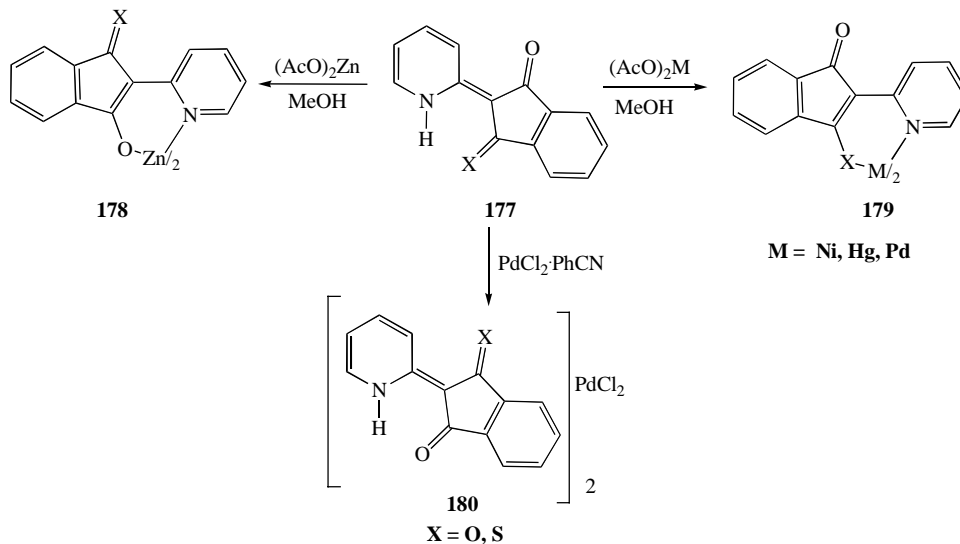


175

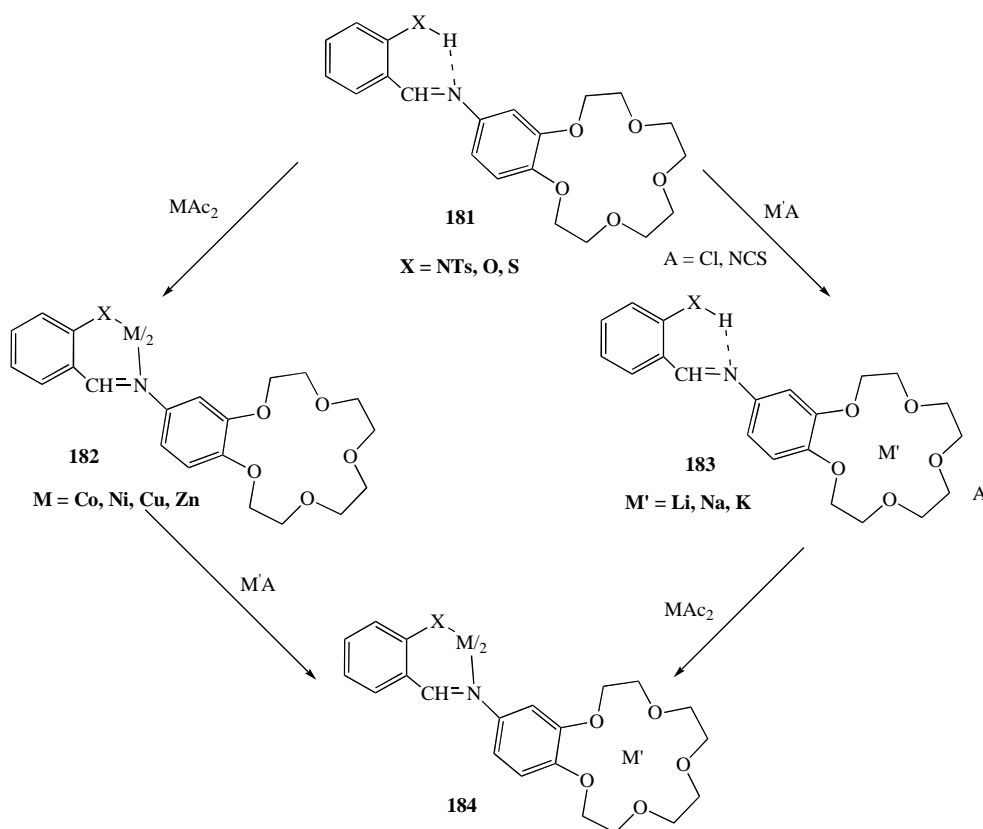


176

A, B = CR', N; E = NR', O, S, Se, Te; X = NR'', O, S; R, R', R'' = H, Alk, Ar, Het



X = O, S



lic **176** ligands remain “eternal”. Thus, the analysis of Cambridge Bank Database shows that about 2500 structures of complexes of the ligands of types **175** and **176** were resolved for 2000-2008.

Creation of new hard-soft ligand systems is also attractive. One of them **177** was just synthesized [41, 110-112] and then a series of transformations was carried out allowing obtaining complexes with hard-hard **178**, hard-soft **179** and soft **180** coordination.

Creation of hybrid biologically perspective ligating systems, for example **181** [113-117], is also interesting. A cycle of transformations **181-184** was carried out, including such ligand **181** and its mononuclear azomethinic **182** and crown-ether **183** complexes, as well as binuclear structure **184** (confirmed by X-Ray diffraction). The principal goal is to work not only for theoretical, but also for practically useful coordination chemistry (competitive coordination), taking into account an operated creation of polyfunctional materials (for instance, selective electrodes). Other crown-containing azomethines are of a considerable interest as optically active chemosensors [118-121].

Modern achievements in coordination chemistry are presented in the Proceedings of the 38th International Conference on Coordination Chemistry (ICCC38, Jerusalem, Israel, July 2008) [122].

Nobel Prizes on Coordination Chemistry [123, 124]

1912 Victor Grignard, Grignard's reagents.

1913 Alfred Werner, the area on the nature of bonds of atoms in molecules in inorganic chemistry.

1915 Rihard Vilshetter, the area of pigments in plant world, especially chlorophyll.

1930 Hans Fisher, investigation of construction of heme and chlorophyll.

1963 Karl Ziegler u Giulio Natta, discovery of isotactic polypropylene.

1964 Doroti Meri Kroufut Hodžkin, determination of structures of biologically active substances by X-Rays.

1973 Ernst Otto Fischer and Geoffrey Wilkinson, organometallic chemistry.

1987 Donald James Cram, Jean-Marie Lehn and Charles J. Pedersen, elaboration and applications of molecules having structurally-specified interactions of high selectivity.

2001 William S. Knowles, Ryoji Noyori and K. Barry Sharpless, research in pharmaceutical industry: creation of chiral catalysts for redox-reactions.

2005 Yves Chauvin, Robert H. Grubbs, Richard R. Schrock, the development of the metathesis method in organic synthesis.

ACKNOWLEDGEMENTS

The authors are grateful to numerous researchers of the Institute of Physical and Organic Chemistry (Southern Federal University, Rostov-na-Donu, Russia) for their help, the Russian President grant IIII-363.2008.3, and to Paicyt-UANL (Monterrey, Mexico, project 2008) for the financial support.

REFERENCES

- [1] Shriver, D.F.; Atkins, P.W. *Inorganic Chemistry*, University Press: Oxford, **1999**.
- [2] Tretyakov, Yu.D.; Martynenko, Yu.D.; Grigoriev, A.N.; Tsivadze, A.Yu. *Inorganic Chemistry*, Khimiya: Moscow, **2001**.
- [3] Day, M.C.; Selbin, D. *Theoretical Inorganic Chemistry*, Reinhold Book Corporation: New-York-Amsterdam-London, **1973**.
- [4] Cotton, F.A.; Wilkinson, G. *Basic Inorganic Chemistry*, Wiley: New-York, 1976.
- [5] Cotton, F.A.; Wilkinson, G.; Murillo, C.A.; Bochman, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, **1999**.
- [6] Grinberg, A.A. *Introduction in Chemistry of Complex Compounds*; Khimiya: Leningrad, **1971**.
- [7] Kukushkin, Yu.N. *Chemistry of Coordination Compounds*; Vysshaya Shkola: Moscow, **1985**.
- [8] Kostromina, N.A.; Kumok, V.N.; Skorik, N.A. *Coordination Chemistry*. Moscow: Vysshaya Shkola, **1990**.
- [9] Minkin, V.I.; Simkin, B.Ya.; Minyaev, R.M. *Theory of Molecule Structure (Chapter 11)*. Fénix: Rostov-na-Donu, **1997**.
- [10] Skopenko, V.V.; Tsivadze, A.Yu.; Savranskii, L.I.; Garnovskii, A.D. *Coordination Chemistry*. Akademkniga: Moscow, **2007**.
- [11] Gade, L.H. *Koordinationschemie*, VCH: Weinheim-New York-Toronto, **1998**.
- [12] In *Comprehensive Coordination Chemistry I*, Wilkinson, G.; Gillard, R.D.; Mc Cleverty, J.A. Eds.; Elsevier: Oxford-New-York, **1987**, V. 1-7.
- [13] In *Comprehensive Coordination Chemistry II*, McCleverty, J.A.; Meyer, T.J. Ed. Elsevier-Pergamon Press; Oxford-New York, **2003**, V. 1-10.
- [14] In *Synthetic Coordination and Organometallic Chemistry*, Garnovskii, A.D.; Kharisov, B.I. Eds.; Marcel-Dekker: New York-Basel, **2003**.
- [15] Metal chelates. *Russ. Khim. J.* **1996**, 40(4-5), 3 (all issue); *Mendeleev Chem. J.* (Zhurn. Ross. Khim. Ob-va im. D.I. Mendeleeva. **1996**, 40(4-5), part I-II.
- [16] Progress in Coordination Chemistry. *Russ. Khim. J.*, **2004**, 48(1), 3 (all issue).
- [17] Garnovskii, A.D.; Sennikova, E.V.; Kharisov, B.I. *Chem. Educator*, **2008**, 13, 67.
- [18] *The Chemistry of Coordination Compounds*, Bailar, J.; Busch, D.H. Ed.; Capman-Hall: New York-London, **1956**.
- [19] Lehn, J.-M. *Supramolecular Chemistry Concept in Perspectives*, VCH: Weinheim-New York-Basel-Cambridge-Tokio, **1995**.
- [20] Steed, J.W.; Atwood, J.L. *Supramolecular Chem.*, Willey: Chichester, **2002**.
- [21] *Encyclopedia of Supramolecular Chemistry*, Atwood, J.L.; Steed, J.W. Marsel Dekker: New-York, **2004**.
- [22] Garnovskii, A.D.; Sadimenko, A.P. *Adv. Heterocycl. Chem.*, **1998**, 72, 1.
- [23] Omae, I. *Organometallic Intramolecular-Coordination Compounds*, Elsevier: Amsterdam-New York, **1986**.
- [24] Cotton, F.A.; Walton, R.A. *Multiple Metal-Metal Bonds*, Wiley: New York-Chichester, **1982**.
- [25] Kostromina, N.A.; Voloshin, Ya.Z.; Nazarenko, A.Yu. *Clatrocchelates: Synthesis, Structure, Properties*, Naukova Dumka: Kiev, **1992**.
- [26] Voloshin, Ya.Z.; Kostromina, N.A.; Kramer, J. *Chlatrocchelates: Synthesis, Structure and Properties*, Elsevier: Amsterdam, **2002**.
- [27] Kukushkin, V.Yu.; Kukushkin, Yu.N. *Theory and Practice of Synthesis of Coordination Compounds*, Nauka: Leningrad, **1990**.
- [28] Davies, J.A.; Hokensmith, C.M.; Kukusnkin, V.Yu.; Kukusnkin, Yu.N. 1996. *Synthetic Coordination Chemistry. Principle and Practice*, World Scientific: Singapore, **1998**.
- [29] *Handbuch der Preparativen Anorganischen Chemie*, Herausgeben von G. Brauer., Bd. 3. Ferdinand-Enke Verlag: Stuttgart, **1981**.
- [30] Hoss, R.; Fogle, F. *Templatsynthesen. Angew. Chem.*, **1994**, 106(4), 389.
- [31] Yatsimirskii, K.B.; Kolchinskii, A.G.; Pavlischuk, V.V.; Salanova, G.G. *Synthesis of Macrocyclic Compounds*, Naukova Dumka: Kiev, **1987**.
- [32] Gerbeleu, N.V.; Arion, V.B. *Template Synthesis of Macrocyclic Compounds*, Shtiintsa: Kishinev, **1990**.
- [33] Gerbeleu, N.V.; Arion, V.B.; Bargess, J. *Synthesis of Macrocyclic Compounds*, Wiley-VCH: Weinheim, **1999**.
- [34] Garnovskii, A.D.; Vasilchenko, I.S. *Usp. Khim.*, **2002**, 71(11), 1064; *Russ. Chem. Rev.* **2002**, 71(11), 943.
- [35] Garnovskii, A.D. *Russ. J. Coord. Chem.*, **1993**, 19(5), 368.
- [36] (a) Vigato, P.A.; Tamburini, S. *Coord. Chem. Rev.*, **2004**, 248, 1717. (b) Vigato, P.A.; Tamburini, S.; Bertolo L. *Coord. Chem. Rev.*, **2007**, 251, 1311. (c) Vigato, P.A.; Tamburini, S. *Coord. Chem. Rev.*, **2008**, 252, 1871.
- [37] Burlov, A.S.; Koshchienko, Yu.V.; Lyssenko K.A.; Vasilchenko, I.S.; Alexeev, Yu.E.; Borodkina, I.G.; Antipin M.Yu.; Garnovskii, A.D. *J. Coord. Chem.*, **2008**, 61(1), 85.
- [38] Hiraoka, M. *Crown Compounds*, Elsevier: New York, **1982**.
- [39] Lenzhoff, C.C.; Lever, A.B.P. Eds.; In *Phthalocyanines. Properties and Application*, Verlag Chemie: New York, **1990-1996**, V. 1-4.
- [40] Burlov, A.S.; Lyssenko K.A.; Koshchienko, Yu.V.; Vasilchenko, I.S.; Garnovskii, D.A.; Uraev, A.I.; Garnovskii, A.D. *Mendeleev Commun.*, **2008**, 18(4), 198.
- [41] Garnovskii, A.D.; Sennikova, E.V. *Chem. Heterocycl. Comp.*, **2007**, 43(11), 1359.
- [42] In *Direct Synthesis of Coordination and Organometallic Compounds*, Garnovskii, A.D.; Kharisov, B.I. Eds.; Elsevier: Amsterdam, **1999**.
- [43] Cassoux, P.; Valade, L. In: *Comprehensive Coordination Chemistry*, McCleverty, J.A.; Meyer, T.J. Eds.; Elsevier-Pergamon Press: Oxford-New York, **2003**, J, p. 761.
- [44] Tuck, D.G. In: *Molecular Electrochemistry of Inorganic, Bioinorganic, and Organometallic Compounds*. Kluwer Acad. Publishers: Dordrecht, **1993**, 15.
- [45] Kharisov, B.I.; Garnovskii, A.D.; Tsivadze, A.Yu.; Kharisova, O.V.; Mendez, U.O. *J. Coord. Chem.*, **2007**, 60(12-14), 1435.
- [46] Garnovskii, D.A.; Burlov, A.S.; Garnovskii, A.D.; Vasilchenko, I.S. *Zhurn. Obsch. Khim.*, **1996**, 66(9), 1546.
- [47] Kukushkin, Yu.N. *Reactive Capacity of Coordination Compounds*. Khimiya: Leningrad, **1987**.
- [48] Constable, E.C. *Metals and Ligand Reactivity*. VCH: Weinheim, **1995**.
- [49] Pombeiro, A.J.L.; Kukushkin, V.Yu. In: *Comprehensive Coordination Chemistry II*, McCleverty, J.A.; Meyer, T.J. Eds.; Elsevier-Pergamon Press: Oxford-New York, **2003**, 1, 585.
- [50] Kukushkin, V.Yu.; Pombeiro, A.J.L. *Chem. Rev.*, **2002**, 102, 1771.
- [51] Garnovskii, D.A.; Silva, M.F.C.G.; Pachomova, T.B.; Wagner, G.; Silva, J.J.R.F. *Inorg. Chim. Acta*, **2000**, 300, 499.
- [52] Garnovskii, D.A.; Kukushkin, V.Yu.; Haukka, M.; Wagner, G.; Pombeiro, A.J.L. *Dalton Trans.*, **2001**, 5, 560.
- [53] Bokach, N.A.; Kukushkin, V.Yu.; Kuznetsov, M.L.; Garnovskii, D.A.; Natile, G.; Pombeiro, A.J.L. *Inorg. Chem.*, **2002**, 41(8), 2041.
- [54] Makarycheva-Mikhaylova, A.V.; Kukushkin, V.Yu.; Nazarov, A.A.; Garnovskii, D.A.; Pombeiro, A.J.L.; Haukka, M.; Keppler, B.K.; Galansky, M. *Inorg. Chem.*, **2003**, 42(8), 2805.
- [55] Luzyanin, K.V.; Kukushkin, V.Yu.; Kuznetsov, M.L.; Garnovskii, D.A.; Haukka, M.; Pombeiro, A.J.L. *Inorg. Chem.*, **2002**, 41(11), 2981.
- [56] Makarycheva-Mikhaylova, A.V.; Haukka, M.; Bokach, N.A.; Garnovskii, D.A.; Galanski, M.; Keppler, B.K.; Pombeiro, A.J.L.; Kukushkin, V.Yu. *New J. Chem.*, **2002**, 26(8), 1085.
- [57] Makarycheva-Mikhaylova, A.V.; Nazarov, A.A.; Haukka, M.; Garnovskii, D.A.; Keppler, B.K.; Galansky, M.; Pombeiro, A.J.L.; Kukushkin, V.Yu. *Inorg. Chem.*, **2003**, 42(8), 2805.
- [58] Garnovskii, D.A.; Pombeiro, A.J.L.; Haukka, M.; Sobota, P.; Kukushkin, V.Yu. *Dalton Trans.*, **2004**, 7, 1097.

- [59] Garnovskii, D.A.; Kukushkin, V.Yu. *Vestnik RFFI*, **2005**, 43(5), 13.
- [60] Garnovskii, D.A.; Bokach, N.A.; Pombeiro, A.J.L.; Haukka, M.; da Silva, J.J.R.; Kukushkin, V.Yu. *Eur. J. Inorg. Chem.*, **2005**, 11, 3467.
- [61] Garnovskii, D.A.; Kukushkin, V.Yu. *Usp. Khim.*, **2006**, 75(2), 125; (*Russ. Chem. Rev.*, **2006**, 75(2), 125).
- [62] Garnovskii, D.A.; Garnovskaya, E.D.; Uraev, E.D.; Uraev, A.I.; Xaukka, M.; Eremenko, I.L.; Kukushkin, V.Yu. *Izv. Akad. Nauk, Ser. Khim.*, **2006**, 55(9), 1572; (*Russ. Chem. Bull.*, **2006**, 55(9), 1631).
- [63] Nivorozhkin, A.L.; Uraev, A.I.; Burlov, A.S.; Garnovskii, A.D. *Mendeleev Chem. J. (Zhurn. Ross. Khim. Ob-va im D.I. Mendeleeva)*, **1996**, 40(4-5), 255.
- [64] Madal, S.; Das, G.; Singh, R. *Coord. Chem. Rev.*, **1997**, 160, 191.
- [65] Bioinorganic Chemistry. *Mendeleev Ross. Khim. J.* **2004**, 4, 3 (all issue).
- [66] Holm, R.H.; Solomon, E.I. Eds. *Biomimetic Inorganic Chemistry*, *Chem. Rev.*, **2004**, 104(2), 347.
- [67] Uraev, A.I.; Nivorozhkin, A.L.; Bondarenko, G.I.; Lyssenko, K.A.; Korshunov, O.Yu.; Vlasenko, V.G.; Shuvaeva, A.T.; Kurbatov, V.P.; Antipin, M.Yu.; Garnovskii, A.D. *Izv. Akad. Nauk, Ser. Khim.*, **2000**, 11, 1891.
- [68] Kitajima, N.; Fujisawa, K.; Tanaka, M.; Moro-oka, Y. *J. Am. Chem. Soc.*, **1992**, 114, 9232.
- [69] Chasteen, N.D. Ed.; *Vanadium in Biological Systems*, Kluwer: Dordrecht, **1990**.
- [70] Zhdanov, Yu.A.; Alexeev, Yu.E. *Usp. Khim.*, **2002**, 71(11), 1090.
- [71] Alexeev, Yu. E.; Vasilchenko, I.S.; Kharisov, B.I.; Blanko, L.M.; Garnovskii, A.D.; Zhdanov, Yu.A. *J. Coord. Chem.*, **2004**, 57(17-18), 1447.
- [72] Garnovskii, A.D.; Osipov, O.A.; Bulgarevich, S.B. *Russ. Chem. Rev.*, **1972**, 41, 341.
- [73] Pearson, R.G. *J. Am. Chem. Soc.*, **1963**, 85, 3533.
- [74] Burmeister, J.L. *Coord. Chem. Rev.*, **1990**, 105, 77.
- [75] Garnovskii, A.D.; Garnovskii, D.A.; Vasilchenko, A.P.; Burlov, A.S.; Sadimenko, A.P.; Sadekov, I.D. *Russ. Chem. Rev.*, **1997**, 66(5), 389.
- [76] Garnovskii, A.D.; Sadimenko, A.P.; Sadimenko, M.I.; Garnovskii, D.A. *Coord. Chem. Rev.*, **1998**, 173, 31.
- [77] *The Chemistry of Pseudohalides*, Golub, A.M.; Keler, H.; Skopenko, V.V. Ed.; Elsevier Science: Lausanne-Amsterdam-New York -Tokyo, **1986**.
- [78] Covert, K.J.; Neithamer, D.R.; Zonnevylle, M.C.; LaPointe, R.E.; Schaller, C.P.; Wolczanski, P.T. *Inorg. Chem.*, **1991**, 30, 2494.
- [79] Sadimenko, A.P. *Adv. Heterocycl. Chem.*, **2001**, 81, 167.
- [80] Garnovskii, A.D.; Osipov, O.A.; Kuznetsova, L.I.; Bogdashev, N.N. *Usp. Khim.*, **1973**, 42(2), 177; (*Russ. Chem. Rev.*, **1973**, 43(2), 89).
- [81] Perera, J.R.; Heeg, M.J.; Schlegel, H.D.; Winter, C.H. *J. Am. Chem. Soc.*, **1999**, 121, 4536.
- [82] Wang, D.; Wurst, K.; Buchmeiser, M.R. *J. Organomet. Chem.*, **2004**, 689, 2123.
- [83] Kawaguchi, S. *Variety in Coordination Modes of Ligands in Metal Complexes*. Springer Verlag Chemie: Berlin, **1988**.
- [84] Garnovskii, A.D.; Vasilchenko, I.S. *Russ. Chem. Rev.*, **2005**, 74(3), 193.
- [85] Sergienko, V.S.; Mistryukov, A.E.; Litvinov, V.V.; Knyazhanskii, M.I.; Garnovskii, A.D.; Porai-Koshits, M.A. *Koord. Khim.*, **1990**, 16(2), 168.
- [86] Torzilli, M.A.; Colquhoun, S.; Doucet, D.; Beer, R.H. *Polyhedron*, **2002**, 21, 697.
- [87] Kogan, V.A.; Antsyshkina, A.S.; Sadikov, G.G.; Sergienko, V.S.; Scherbakov, I.N.; Kochin, S.G.; Garnovskii, A.D. *Zhurn. Neorg. Khim.*, **2004**, 49(12), 1988.
- [88] Kogan, V.A.; Scherbakov, I.N. *Ross. Khim. J. (Zhurn. Ros. Khim. ob-va im D.I. Mendeleeva)*, **2004**, 48(1), 69.
- [89] Garnovskii, A.D.; Uraev, A.I.; Minkin, V.I. *Arkivoc* (iii), **2004**, 3, 29.
- [90] Tompson, K.L. *Magnetism: Molecular and Supramolecular Perspective*, Ed.; *Coord. Chem. Rev.*, **2005**, 249, 2549.
- [91] Metelitsa, A.V.; Burlov, A.S.; Bezuglyi, S.O.; Borodkina, I.G.; Bren, V.A.; Garnovskii, A.D.; Minkin, V.I. *Russ. J. Coord. Chem.*, **2006**, 32(12), 858.
- [92] Kuzmina, N.P.; Eliseeva, S.V. *Zhurnal. Neorg. Khim.*, **2006**, 51(1), 80.
- [93] *Organic Light-Emitting Devices*, Mueller, K.; Schert, U. Eds.; Wiley-VCH: Weinheim-New York, **2006**.
- [94] *Single-Molecule Magnets and Related Phenomena*, Winpenny, R. Ed.; *Structure and Bonding*, **2006**, Vol. 122.
- [95] Ovcharenko, V.I.; Sagdeev, R.Z. *Russ. Chem. Rev.*, **1999**, 68(5), 345.
- [96] Sato, O. *Acc. Chem. Res.*, **2003**, 36, 692.
- [97] Kiskin, M.A.; Eremenko, I.A. *Russ. Chem. Rev.*, **2006**, 75(7), 559.
- [98] Foguet-Albiol, D.; O'Brien, T.A.; Wernsdorfer, W.; Moulton, B.; Zaworotko, M.J.; Abboud, K.A.; Christou, G. *Angew. Chem. Int. Ed. Engl.*, **2005**, 44, 897.
- [99] Murugesu, M.; Habrych, M.; Wernsdorfer, W.; Abboud, K.A.; Christou, G. *J. Am. Chem. Soc.*, **2004**, 126, 4766.
- [100] Kogan, V.A.; Lukov, V.V. *Koord. Khim.*, **1997**, 23(1), 18.
- [101] Lukov, V.V.; Levchenko, S.I.; Scherbakov, I.N.; Kogan, V.A. *Koord. Khim.*, **1997**, 23(7), 544.
- [102] Uraev, A.I.; Ikorskii, V.N.; Lyssenko, K.A.; Vlasenko, K.A.; Borodkina, I.G.; Borodkin, G.S.; Garnovskii, D.A.; Garnovskii, A.D. *Koord. Chem.*, **2006**, 32(4), 299.
- [103] Burlov, A.S.; Koschienko, Yu.V.; Ikorskii, V.N.; Vlasenko, V.G.; Zarubin, I.A.; Uraev, A.I.; Vasilchenko, I.S.; Garnovskii, D.A.; Borodkin, G.S.; Nikolaevskii, S.A.; Garnovskii, A.D. *Zhurn. Neorg. Khim.*, **2006**, 51(7), 1143.
- [104] Burlov, A.S.; Ikorskii, V.N.; Uraev, A.I.; Koschienko, Yu.V.; Vasilchenko, I.S.; Garnovskii, D.A.; Borodkin, G.S.; Nikolaevskii, S.A.; Garnovskii, A.D. *Zhurn. Obsch. Khim.*, **2006**, 76(8), 1337.
- [105] Garnovskii, A.D.; Ikorskii, V.N.; Uraev, A.I.; Vasilchenko, I.S.; Burlov, A.S.; Garnovskii, D.A.; Lyssenko, K.A.; Vlasenko, V.G.; Shestakova, T.E.; Koshchichko, Yu.V.; Kuz'menko, T.A.; Divaeva, L.N.; Bubnov, M.P.; Rybalkin, V.P.; Korshunov, O.Yu.; Pirog, I.V.; Borodkin, G.S.; Bren, V.A.; Uflyand, I.E.; Antipin, M.Yu.; Minkin, V.I. *J. Coord. Chem.*, **2007**, 60(12-14), 1493.
- [106] Chigarev, G.G.; Ponomarenko, A.G.; Bolotnikov, V.S.; Alexeev, V.A.; Burlov, A.S.; Garnovskii, A.D.; Barchan, G.P. *Koord. Khim.*, **1989**, 10(6), 1051.
- [107] Garkunov, D.N. *Tribotechnique (Deterioration and non-deterioration)*, MSHA Editoria: Moscow, **2001**, p. 614.
- [108] Burlov, A.S.; Uraev, A.I.; Lyssenko, K.A.; Chigarev, G.G.; Ponomarenko, A.G.; Matuev, P.V.; Nikolaevskii, S.A.; Garnovskaya, E.D.; Borodkin, G.S.; Garnovski, A.D. *Russ. J. Coord. Chem.*, **2006**, 32(8), 686.
- [109] Skopenko, V.V.; Amirkhanov, B.M.; Sliva T.Yu.; Vasilchenko, I.S.; Anpilova, E.L.; Garnovskii, A.D. *Usp. Khim.*, **2004**, 73(8), 797; (*Russ. Chem. Rev.*, **2004**, 74, 737).
- [110] Sennikova, E.V.; Borodkina, I.G.; Antsyshkina, A.S. Sadikov, G.G.; Bicherov, A.V.; Korshunov, O.Yu.; Borodkin, G.S.; Korobov, M.S.; Sergienko, Kharabaev, N.N.; Garnovskii, A.D. *Russ. J. Inorg. Chem.*, **2006**, 51(10), 1548.
- [111] Sennikova, E.V.; Korshunov, O.Yu.; Borodkin, G.S.; Korobov, M.S.; Vlasenko, V.G.; Kharabaev, N.N.; Garnovskii, A.D. *Russ. J. Gener. Chem.*, **2007**, 77(10), 1738.
- [112] Sennikova, E.V.; Antsyshkina, A.S. Sadikov, G.G.; Bicherov, A.V.; Korshunov, O.Yu.; Borodkin, G.S.; Korobov, M.S.; Sergienko, V.S.; Kharabaev, N.N.; Garnovskii, A.D. *Russ. J. Coord. Chem.*, **2008**, 34(5), 315.
- [113] Minacheva, L.H.; Ivanova, I.S.; Dorokhov, A.V.; Bicherov, A.V.; Burlov, A.S.; Garnovskii, A.D.; Sergienko, V.S.; Tsivadze A.Yu. *Dokl. Akad. Nauk., Ser. Khim.*, **2004**, 398(1), 62.

- [114] Ivanova, I.S.; Dorokhov, A.V.; Pyatova, E.N.; Bicherov, A.V.; Burlov, A.S.; Garnovskii, A.D.; Sergienko, V.S.; Tsivadze, A.Yu. *Koord. Khim.*, **2005**, 31(7), 512.
- [115] Minacheva, L.H.; Ivanova, I.S.; Dorokhov, A.V.; Burlov, A.S.; Garnovskii, A.D.; Sergienko, V.S.; Tsivadze, A.Yu. *Koord. Khim.*, **2006**, 32(3), 174.
- [116] Burlov, A.S.; Tsukanov, A.V.; Borodkin, G.S.; Revinskii, Yu.V.; Dubonosov, A.D.; Bren, V.A.; Garnovskii, A.D.; Tsivadze, A.Yu.; Minkin, V.I. *Zhurn. Obshch. Khim.*, **2006**, 76(6), 1037.
- [117] Dorokhov, A.V.; Chernyshov, D.Yu.; Burlov, A.S.; Ganovskii, A.D.; Ivanova, I.S.; Pyatova, E.N.; Tsivadze, A.Yu.; Aslanov, L.A.; Chernyshev, V.V. *Acta Crystallogr. B*, **2007**, B. 63, 402.
- [118] Dubonosov, A.D.; Minkin, V.I.; Popova, L.L.; Shepelenko, E.N.; Tkalina, N.N.; Tsukanov, A.V. Bren, V.A. *Arcivoc*, **2003**, 13, 12.
- [119] Bren, V.A.; Dubonosov, A.D.; Popova, L.L.; Rybalkin, V.P.; Sadekov, I.D.; Shepelenko, E.N.; Tsukanov, A.V. *Arcivoc*, **2005**, 7, 60.
- [120] Bren, V.A.; Dubonosov, A.D.; Minkin V.I.; Gribanova, N.N.; Rybalkin, V.P.; Shepelenko, E.N.; Tsukanov, A.V.; Borisenko, R.N. *Mol. Cryst. Liq. Cryst.*, **2005**, 431, 417.
- [121] Bren, V.A.; Dubonosov, A.D.; Minkin V.I.; Tsukanov, A.V.; Gribanova, N.N.; Shepelenko, E.N.; Revinsky, Y.V.; Rybalkin, V.P. *J. Phys. Org. Chem.*, **2007**, 20(11), 917.
- [122] 38th International Conference on Coordination Chemistry (ICCC38). Jerusalem, Israel, July 20-25, 2008. <http://www.kenes.com/iccc38>. Accessed August 6, 2008.
- [123] Volkov, V.A.; Vonskii, E.V.; Kuznetsova, G.I. *Outstanding chemists worldwide*. Vysshaya Shkola: Moscow, **1991**.
- [124] http://nobelprize.org/nobel_prizes/chemistry/laureates/index.html.

Received: July 25, 2008

Revised: October 04, 2008

Accepted: December 02, 2008

© Garnovskii et al.; Licensee Bentham Open.

This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.