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Review

Coordination properties of didentate N,O heterocyclic alcohols and aldehydes towards Cu(II), Co(II), Zn(II) and Cd(II) ions in the solid state and aqueous solution

Barbara Barszcz *

Institute of Chemistry, Pedagogical University, 5 Chęcińska Str., 25-020 Kielce, Poland

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Contents

Abstract

A critical discussion of the coordination properties of some heterocyclic alcohols and aldehydes derived from imidazole, pyrazole or pyridine are the subject of this review. The versatility of these ligands, which may act as monodentate or didentate, either neutral or deprotonated, and which undergo tautomeric equilibria upon coordination to Cu(II), Zn(II), Co(II) and Cd(II) is discussed and illustrated using relevant examples. Special attention is paid to a comparison of results obtained by the X-ray diffraction method in the solid state with those acquired by the potentiometric, NMR and EPR methods in aqueous solution. A discussion of the crystal structures, as well as a correlation of the stability constants of reported complexes is also provided. Additionally, differences in the geometries of the central ions of these complexes, which extend from tetrahedral (most common for zinc) to the octahedral form for cobalt and dodecahedral for cadmium (and copper) complexes respectively, are extensively discussed.

Keywords: Heterocyclic alcohols; Heterocyclic aldehydes; Chelating ligands; Metal(II) complexes; Stability constants; Crystal structures

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Abbreviations: BIm, benzimidazole; 1-Bz-2-CH_2OHIm, 1-benzyl-2-hydroxmethlimidazole; 1-Bu-2-CH_2OHIm, 1-butyl-2-hydroxmethlimidazole; 1-Bu-2-CH_3Im, 1-butyl-2-methlimidazole; 4-CHO-5-MeIm, 4-carbaldehyde-5-methylimidazole; 1-Et-2-CH_2OHIm, 1-ethyl-2-hydroxymethlimidazole; 1-EtIm, 1-ethylimidazole; 1-C_2H_5OH-3,5-DMePz, 1-(2-hydroxyethyl)-3,5-dimethylpyrazole; 2-CH_2OHBIm, 2-hydroxmethylbenzimidazole; 4(5)-CH_2OHIm, 4(5)-hydroxymethylimidazole; 1-CH_2OH-3,5-DMePz, 1-hydroxymethyl-3,5-dimethylpyrazole; Im, imidazole; OMPA, 6-methoxypyridine-2-carbaldehyde; 1-Me-2-CH_2OHIm, 1-methyl-2-hydroxymethylimidazole; 4-Me-5-CH_2OHIm, 4-methyl-5-hydroxymethlimidazole; MimA, *N*-methylimidazole-2-carbaldehyde; 1-Me-2-CHOIm, 1-methylimidazole-2-carbaldehyde; 4-Me-5-CHOIm, 4-methylimidazole-5-carbaldehyde; 1,2-DMeIm, 1,2-dimethylimidazole; 4(5)-MeIm, 4(5)-methylimidazole; 4,5-DMeIm, 4,5-dimethylimidazole; 3,5-DMePz, 3,5-dimethylpyrazole; MPA, 6-methylpyridine-2-carbaldehyde; 1-Pr-2-CH_2OHIm, 1-propyl-2-hydroxymethlimidazole; 1-Pr-2-CHOIm, 1-propylimidazole-2-carbaldehyde; 1-Pr-2-CH_3Im, 1-propyl-2-methlimidazole; PA, pyridine-2-carbaldehyde; PDA, 2,6-pyridine-dicarbaldehyde; PyMeOH, 2-pyridylmethanol; QuiMeOH, 2-quinolylmethanol

* Tel.: +48 41 361 40 12; fax: +48 41 361 49 42.
E-mail address: basiab@pu.kielce.pl.

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1. Introduction

The aim of this short review is to present a critical look at the coordination chemistry of some hydroxyalkyl and aldehyde derivatives of imidazole, pyrazole or pyridine as ligands. Commonly investigated heterocyclic alcohols and aldehydes are chelating ligands that show many variants in their formation of coordination bonds with a number of inorganic ions. The design of such ligands must take into account the factors influencing the stability and the molecular geometry of the metal complexes. Therefore, this review pays special attention to a comparison of the results describing the coordination ability of ligands, as obtained by potentiometric or NMR methods in aqueous solution with those obtained by X-ray diffraction. Interest in these studies has evolved as a result of a number of different factors:

1. From a bioinorganic point of view, heterocyclic alcohols and aldehydes are of great importance as ligands containing N,O donor atoms which can be adopted to modelling coordination environments of synthetic analogues that mimic both the structure and function of the active sites of metal enzymes [1–6].
2. Model compounds simulating their local coordinating sites, generally employ simple derivatives of imidazole or their isomer, pyrazole because most of metalloproteins contain one or more moieties of the amino acid, histidine [6–8].
3. Studies of such ligands are relevant to medicine as they are linked with the problem of searching for compounds with potential properties as chelators for the removal of toxic metals from the body.
4. The Cu(II), Zn(II) and Co(II) ions as central atoms of complexes with heterocyclic alcohol and aldehydes are examples of the most important trace transition elements essential to all forms of life [9–12]. Therefore, an especially important question in current coordination chemistry is how a protein selects a specific metal from the mixture of ions [13,14].
5. In addition, a study of the compounds covering such chelating ligands can be a promising candidate for the development of coordination chemistry.

Although there has been much interest in the variety of bonding possibilities associated with imidazole, pyrazole- and pyridine-based chelating ligands and the structural data of their coordination complexes [13–20], there is no review available comparing the solid state and aqueous solution chemistry of these complexes. In recent years, many coordination compounds with hydroxymethylimidazoles, carbaldehydeimidazoles, 1-hydroxymethy-3,5-dimethylpyrazoles and their substituted derivatives have been synthesised in our laboratories and their stability constants, structures and spectroscopic properties reported. Therefore, with this review I attempt a comparison of the stability and the molecular geometry of these complexes.

2. Copper(II) complexes

As pointed out in the introduction, the appreciable interest in imidazole derivatives widely used in coordination chemistry results from the presence of the imidazole moiety in a variety of biologically important substances. Much effort has been expended to estimate the parameters modulating the donor–acceptor properties of the imidazole ligands. One of the most important factors is the basicity of the ligands, which is mainly responsible for the σ interaction with metal ions [24,28,30,33]. The protonation constants of hydroxymethyl and aldehydeimidazoles [22,25,33] and some alkylimidazoles as reference compounds [21–23,26,28], determined by pH potentiometric technique at 298 K [$I = 0.5$ (KNO_3)] are given in Table 1. The results indicate that the basicity of imidazoles depends on the electron density on the basic nitrogen atom. Literature data [29,37] show that the stability of the Cu(II) complexes is practically independent of the size of the alkyl substituent at position 1 of the imidazole ring. However, the presence of the alkyl substituent at positions 2 or 4 of the diazole ring increases the basicity due to a positive induction effect. On the contrary, the basicities of hydroxymethyl and aldehyde derivatives are about one to three orders of magnitude smaller due to the strong electron-withdrawing effect of the CH_2OH or CHO groups, respectively. The data given in Table 1 show that the basicity of the imidazoles is only one of the factors determining the stability of Cu(II) complexes in aqueous solution. The high pK_a values of the ligands [23,26,32,33] are not always reflected in high values of the stability constants. Other factors which ought to be considered are: (i) the steric effect of the substituent situated next to the electron-donating nitrogen atom of the imidazole ring, (ii) the contribution not only of σ but also $\pi_{M\rightarrow L}$ back bonding in the coordination bond with the Cu(II) ion, (iii) the chelating effect of the didentate ligands and (iv) the annular tautomerism of some ligands which allow more stable complexes to be formed. Quantitatively, an influence of these factors on the stability of the Cu(II) complexes could be illustrated by the values of the replacement constant, $\log {}^{*}\beta_1$ [38,39] (equations (1a), (1b) and (2):

$$[Cu(H_2O)_6]^{2+} + HL^{+} \leftrightarrows [Cu(H_2O)_5L]^{2+} + H_3O^{+} \tag{1a}$$

$${}^{*}\beta_1 = \frac{[CuL(H_2O)_5]^{2+}[H_3O^{+}]}{[Cu(H_2O)_6]^{2+}[HL^{+}]} \tag{1b}$$

$$\log {}^{*}\beta_1 = \log \beta_1 - pK_a \tag{2}$$

The $\log {}^{*}\beta_1$ reflects the stability of a complex after the influence of ligand basicity has been eliminated and allows properties other than σ donor properties to be identified as responsible for the complexes' stability. In the case of 1,2-DMeIm, 4,5-DMeIm, 4(5)-MeIm, 1-Pr-2-MeIm, 1-Bu-2-MeIm, which in spite of their basicities (higher in comparison to imidazole), form less stable complexes with

Table 1
Stability constants of imidazole and some imidazole derivatives with Cu(II) ion in aqueous solution at 298 K and $I = 0.5\,\text{mol dm}^{-3}$ (KNO_3)

Ligand	pK_a	log β_1	log β_2	log β_3	log β_4	log β_5	log β_6	log $^*\beta_1$	Reference
Im**1**	7.12	4.31	7.84	10.76	12.90	–	–	−2.81	[21,22]
1,2-DMeIm**2**	8.21	3.70	6.80	9.80	10.80	11.72	–	−4.51	[23]
1-Me-2-CH_2OHIm**3**	6.98	4.04	7.48	10.08	11.70	12.38	13.57	−2.94	[24]
1-Me-2-CHOIm**4**	5.16	2.87	5.63	7.62	8.85	11.39	–	−2.29	[25]
4(5)-MeIm**5**	7.80	4.18	7.74	10.70	13.05	13.95	–	−3.62	[36]
	7.69	4.13	7.62	10.49	12.45	–	–	–	[27]
4(5)-CH_2OHIm**6**	6.67	3.60	7.05	9.53	10.90	–	–	−3.07	[24]
4,5-DMeIm**7**	8.19	3.72	6.92	9.55	10.78	–	–	−4.47	[26]
4-CH_2OH-5-MeIm**8**	7.14	3.95	7.26	10.26	11.79	13.00	–	−3.19	[28]
4-CHO-5-MeIm**9**	4.20	3.39	5.80	7.37	8.38	–	–	−0.81	[31]
1-EtIm**10**	7.25	4.40	7.99	10.98	13.22	14.20	–	−2.85	[29]
1-Et-2-CH_2OHIm**11**	7.02	4.12	7.58	10.38	12.13	12.68	14.28	−2.90	[30]
1-Pr-2-MeIm**12**	8.20	3.67	7.23	9.65	11.99	–	–	−4.53	[32]
1-Pr-2-CH_2OHIm**13**	7.04	4.10	7.55	10.31	11.50	12.10	13.42	−2.94	[30]
1-Pr-2-CHOIm**14**	5.15	2.86	5.66	7.88	10.15	–	–	−2.29	[32]
1-Bu-2-MeIm**15**	8.18	3.74	6.98	9.44	11.26	–	–	−4.44	[33]
1-Bu-2-CH_2OHIm**16**	7.00	4.11	7.62	10.39	11.89	13.18	–	−2.89	[33]
1-Bz-2-CH_2OHIm**17**	6.58	3.34	7.54	–	–	–	–	−3.24	[31]
BIm**18**	5.66	3.26	6.02	8.36	10.21	–	–	−2.40	[34]
2-CH_2OHBIm**19**	5.52	2.85	6.26	10.19	–	–	–	−2.67	[35]

$I = 0.16\,\text{mol dm}^{-3}$ (KNO_3) [27]; the potentiometric methods based on simultaneous measurements of [Cu^{2+}] and [H_3O^+] [35].

Cu(II) ions, the parameter log $^*\beta_1$ shows the lowest values (Fig. 1).

This implies that the alkyl substituents situated at the α position to the donating nitrogen atom of the imidazole ring, represent a steric hindrance to complexation. The lowering of log $^*\beta_1$ can also be partially caused by a reduction of π acceptor properties of the ligands due to the inductive effect of the alkyl groups. However, when substituting at the 2 or 4 positions, the CH_2OH or CHO groups do not decrease but rather, on the contrary, increase the stability of the Cu(II) complex. The considerable increase of the log $^*\beta_1$ parameter of the Cu(II) complexes with alcohol and aldehydeimidazoles can be explained by assuming that the stability of the complexes is influenced by additional interactions between the Cu(II) ions and the oxygen atom of the CH_2OH or CHO group. This results in the formation of a five-membered chelate ring involving the exocyclic oxygen atom and the pyridine-like nitrogen atom of the imidazole ring. Formation of chelates by hydroxymethylimidazoles is not accompanied by loss of a proton from the hydroxymethyl group, therefore, quantitative analysis of log (K_1/K_2) does not indicate the existence of typical strong chelates in aqueous solution. The metal–oxygen bond in the complexes is weak and easily broken and it leads to the establishment of the intramolecular equilibrium for Cu(II) complexes (e.g. Scheme 1).

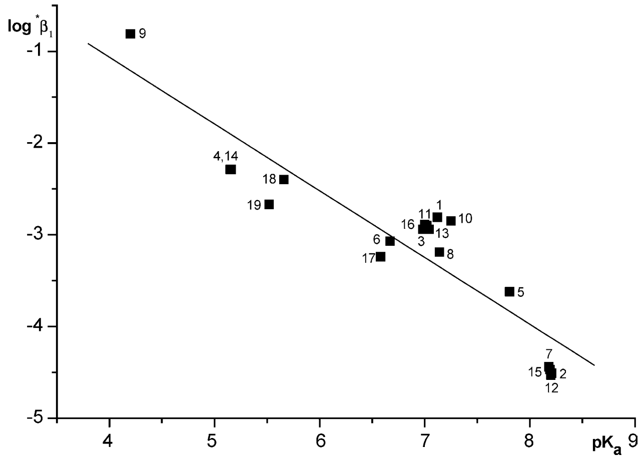


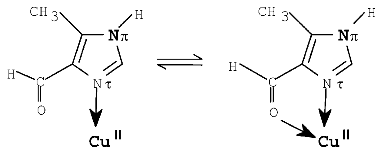
Fig. 1. Dependence log $^*\beta_1 = f(\text{p}K_a)$ of the ligands **1–19** from Table 1 ($R_c = 0.916$).

According to Sigel [40,41], a positive value of the differences (log $\Delta_{M/L}$) between the experimentally measured stability constants (log $K_{M(L)exp} = \log \beta_{1exp}$) and those calculated on the basis of the acid–base properties of the ligand (Scheme 1: open form of isomers, log $K_{M(L)op} = \log \beta_{1calc}$) reflects the extent of the formation of the chelate complex in equilibrium according to equation (3):

$$\log \Delta_{M/L} = \log \beta_{1\,exp} - \log \beta_{1calc} \qquad (3)$$

The constant describing intramolecular equilibrium between chelating and not chelating forms (Scheme 1) of the complex is defined by equation (4) [42–45]:

$$K_1 = \frac{\beta_{1\,exp}}{\beta_{1calc}} - 1 = 10^{\log \Delta_{M/L}} - 1 \qquad (4)$$



Scheme 1. The configurational equilibrium of Cu(II) complexes (open and chelating forms) with aldehyde- or hydroxymethyimidazoles.

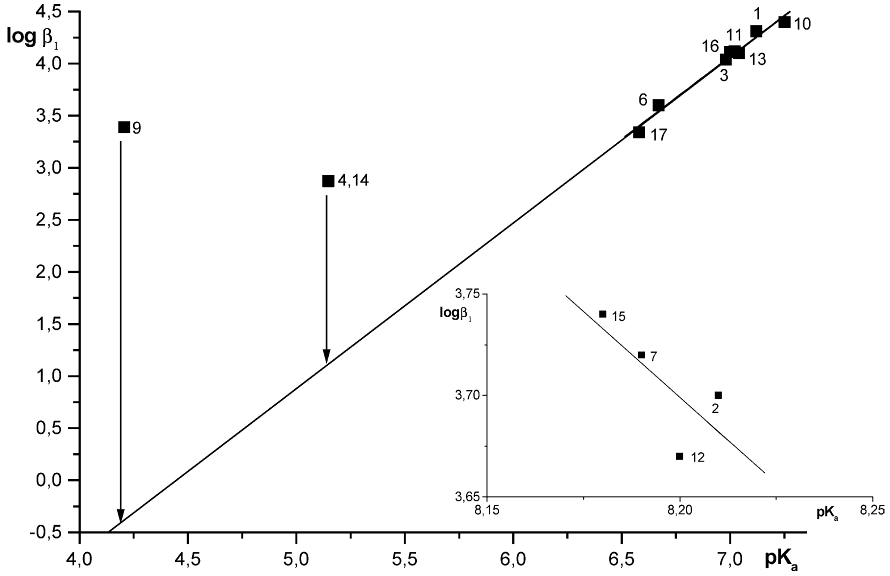


Fig. 2. Plots of log $\beta_1 = f(\mathrm{p}K_\mathrm{a})$ for the Cu(II) complexes with imidazole derivatives (**1–17**) from Table 1 ($R_\mathrm{c} = 0.990$).

Fig. 2 presents an exemplary correlation between the values of the logarithms of the stability of the first Cu(II) complexes and the ligand basicity [21–34]. The points corresponding to the experimentally measured stability constants of Cu(II) complexes for families of related ligands lie about two intersecting lines which were plotted according to linear approximation coefficients, calculated by the least-squares method [42], according to equation (5):

$$\log \beta_1 = m\,\mathrm{p}K_\mathrm{a} + b \tag{5}$$

Those points corresponding to imidazole and its derivatives containing an alkyl substituent in position 1 or to hydroxymethylimidazoles are found on the line with positive slope. The other line shows points corresponding to imidazole derivatives containing alkyl substituent situated at the 2 or 4 positions, which presents steric hindrance to complexation. The points corresponding to the experimentally measured stability constants of Cu(II) complexes with aldehydeimidazoles lie above the line with positive slope, which indicates that the chelating effect of ligands increases the stability constants and leads to establishment of the intramolecular equilibrium mentioned above according to Scheme 1. The positive value for log $\Delta_\mathrm{M/L}$ (log $\Delta_\mathrm{M/L} = 2.65 \pm 0.2$ and 3.75 ± 0.2) for Cu(II) complexes with 1-Pr-2-CHOIm and 4-CHO-5-MeIm, respectively, reflects the extent of formation of the chelating species in equilibrium (Scheme 1).

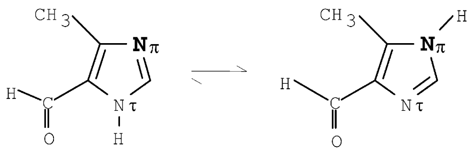
EPR spectra of frozen solutions of Cu(II) hydroxymethylimidazole and aldehydeimidazole complexes are an additional source giving more evidence that complex stability is enhanced due to chelate ring formation. The values of $A_{||}$ and $g_{||}$ parameters [30–32], which are an indication of the change in the coordination sphere around the Cu(II) ion are presented in Table 2. The parameters ($A_{||} = 154 \times 10^{-4}$ cm^{-1} and $g_{||} = 2.356$) of the first complex with 4-CHO-5-MeIm [31] are similar in magnitude to those found for 1-Pr-2-CH$_2$OHIm [30] and can be assigned to the effect of the oxygen atom (of the functional group) on Cu(II) binding. When the pH is increased to 4.1, formation of two equilibrium species is observed for the Cu-4-CHO-5-MeIm system (Table 2). One of them exhibits

Table 2
EPR parameters of dominating species formed between Cu(II) and substituted imidazoles in aqueous solution

l-Pr-2-MeIm [32]			l-Pr-2-CH$_2$OHlm [30]			l-Pr-2-CHOIm [32]			4-Me-5-CHOIm [31]			l-Bz-2-CH$_2$OHIm [31]		
pH	$g_{\|\|}$	$A_{\|\|}$	pH	$g_{\|\|}$	$A_{\|\|}$	pH	$g_{\|\|}$	$A_{\|\|}$	pH	$g_{\|\|}$	$A_{\|\|}$	pH	$g_{\|\|}$	$A_{\|\|}$
5.6	(2.412^a)	(120^a)	5.2	2.356 (2.360^a)	150 (120^a)	3.9	2.412^a (2.360)	120^a (146)	3.2	2.356	154	2.3	2.360	145
5.9	2.360 (2.412^a)	149 (120^a)	5.6	2.294	160	4.3	2.360 (2.412^a)	146 (120^a)	4.1	2.310	166	4.3	2.360	145
6.6	2.312	168	6.2	2.272	180	4.9	2.296 (2.412^a)	157 (120^a)		2.293	165			
7.0	2.280	178	7.5	2.272	184	5.2	2.292	165	4.8	2.293	165			
7.4	2.260	187	8.2	2.261	190	5.6	2.289	171	5.8	2.280	170			
8.5	2.258	188	9.2	2.251	190	7.8	2.270	184	6.1	2.277	175			
						9.2	2.270	180						
						9.9	2.258	187						

$A_{||}$ in 10^{-4} cm^{-1}; parameters of the complexes with smaller contribution are given in parentheses.

[a] Denotes the parameters of Cu-aqua complexes.



(1) **(2)**

Scheme 2. The tautomeric equilibrium between 4-Me-5-CHOIm (1) and 4-CHO-5-MeIm (2).

parameters ($A_{||} = 165 \times 10^{-4}\,\mathrm{cm}^{-1}$, $g_{||} = 2.293$), which can be assigned to the chelate ring formed by the oxygen atom of CHO group in 4-CHO-5-MeIm. Analogous phenomena are observed for Cu(II) complexes with 1-Pr-2CHOIm [32] (pH 5.2, $A_{||} = 165 \times 10^{-4}\,\mathrm{cm}^{-1}$, $g_{||} = 2.292$) and for 1-Pr-2-$\mathrm{CH_2OHIm}$ [30] (pH 5.6, $A_{||} = 160 \times 10^{-4}\,\mathrm{cm}^{-1}$, $g_{||} = 2.294$). Additionally, the EPR data reveal the existence of two species in equilibrium for the Cu-4-Me-5-CHO system, indicating that the two nitrogen atoms present in the five-membered unsaturated imidazole ring, being asymmetrically substituted (4,5-DMeIm, 4(5)-MeIm, 4-Me-5-CHOIm, 4-Me-5-$\mathrm{CH_2OHIm}$), induce imidazole tautomerism at the nitrogen atoms according to Scheme 2.

Theoretical investigations on tautomer equilibria, mainly of the 5-substituted imidazoles, in both geometry and energetics [46–49] as well as those connected with the influence on tautomerism of substituents at C(5) [50–53] have not yielded complete information on stabilization of one of tautomers (Scheme 2) by metal ions on coordination. The donor–acceptor interaction with the metal ion changes the imidazole electronic structure.

This problem was solved by using X-ray diffraction to investigate Cu(II) complexes with 4-Me-5-CHOIm [31] and 4-Me-5-$\mathrm{CH_2OHIm}$ [28] in the solid state. The former complex was obtained in aqueous solution (molar ratio Cu:L was 1:2) and is a good example of how investigations in aqueous solution and in the solid state can complement each other. The molecular structure reveals stabilization of the 4-CHO-5-MeIm tautomer (Scheme 2) as the only isomer able to form a chelate ring with the Cu(II) ion. It is an unusual example of an eight-coordinated Cu(II) complex in which four ligands are bound to the mutual ion in a didentate fashion through the pyridine-like nitrogen atom of the imidazole ring and the oxygen atom of the carbonyl group leading to a $\mathrm{CuN_4O_4}$ local molecular chromophore (see Fig. 3).

The structural data indicated that the Cu(II) ion is involved in a flattened tetrahedron composed by four nitrogen atoms as well as in a more distant elongated tetrahedron of four off-the-*z*-axis oxygen atoms. The coordination polyhedra of this structure were described as a distorted dodecahedral. The form of distortion in the $[\mathrm{Cu(4\text{-}CHO\text{-}5\text{-}MeIm)_4}]^{2+}$ cation involves not only bond length but also apparent bond angle distortions. Selected geometrical parameters for

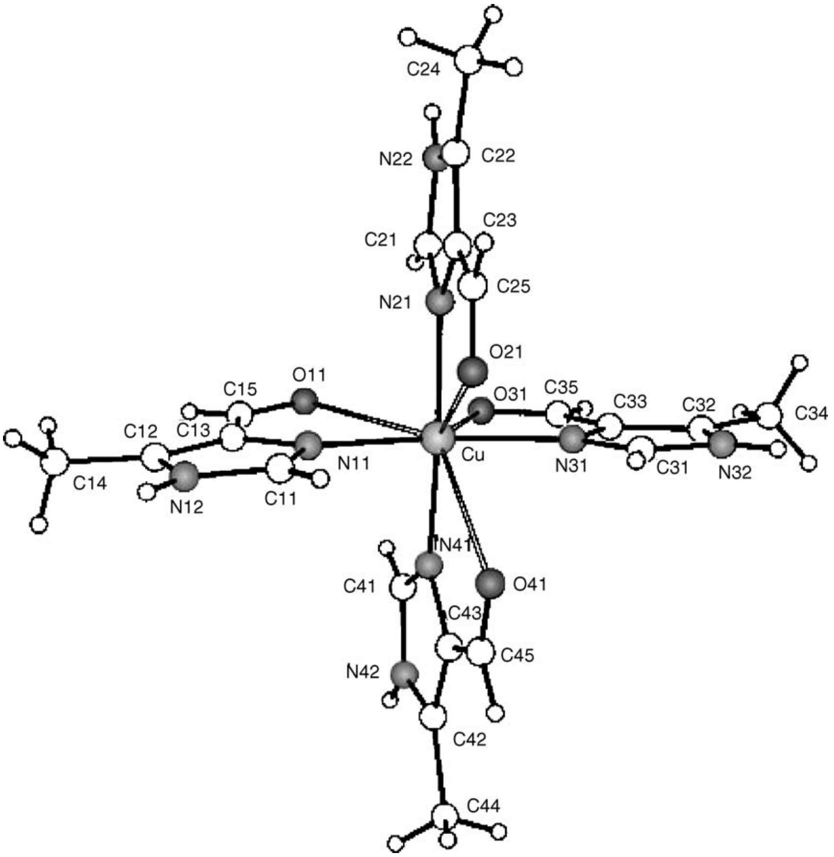


Fig. 3. Atomic numbering scheme and the structure of the $[\mathrm{Cu(4\text{-}CHO\text{-}5\text{-}MeIm)_4}]^{2+}$ cation [31].

Table 3
Selected geometrical parameters for monodentate Cu(II) complexes with chosen N,O donor ligands

Compound/stereochemistry	Chromophore	Cu–N/Cu–O (Å)	$g_{\|\|}$	$A_{\|\|}$ (cm^{-1})	Reference
$[Cu(4\text{-}CHO\text{-}5\text{-}MeIm)_4](H_2O)_2(NO_3)_2$/distorted dodecahedron	CuN_4O_4	$2.013(3)_{Cu–N(11)}$ $1.995(3)_{Cu–N(21)}$ $2.028(3)_{Cu–N(31)}$ $2.006(3)_{Cu–N(41)}$ $2.987(3)_{Cu–O(11)}$ $2.997(3)_{Cu–O(21)}$ $2.816(3)_{Cu–N(31)}$ $3.002(3)_{Cu–N(41)}$	2.277	176×10^{-4}	[31]
$[Cu(4\text{-}CH_2OH\text{-}5\text{-}MeIm)_4](NO_3)_2$/distorted tetragonal bipyramid	CuN_4O_2	$1.981(2)_{Cu–N(11,11a)}$ $2.050(2)_{Cu–N(21,21a)}$ $2.496(2)_{Cu–O(11,11a)}$	2.263	185×10^{-4}	[28]
$[Cu(1\text{-}Bz\text{-}2\text{-}CH_2OHIm)_4](NO_3)_2$/distorted tetragonal bipyramid	CuN_4O_2	$2.009(2)_{Cu–N(11,11i)}$ $2.028(2)_{Cu–N(21,21i)}$ $2.472(2)_{Cu–O(11,11i)}$	2.277	176×10^{-4}	[31]
$[Cu(3,5\text{-}DMePz)_3(NO_3)_2$[a]/square pyramidal	CuN_3O_2	$1.966(4)_{Cu–N(11)}$ $2.010(4)_{Cu–N(21)}$ $2.010(4)_{Cu–N(31)}$ $2.015(1)_{Cu–O(1)}$ $2.324(4)_{Cu–O(1)}$	2.270	180×10^{-4}	[58]

[a] The starting ligand is $1\text{-}CH_2OH\text{-}3,5\text{-}DMePz$.

copper complexes are collected in Table 3. Cu(II) complexes with hydroxymethylimidazoles ($4\text{-}CH_2OH\text{-}5\text{-}MeIm$, $1\text{-}Bz\text{-}2\text{-}CH_2OHIm$) [28,31] have been synthesized in a similar manner from an aqueous solution of the corresponding ligand and $Cu(NO_3)_2$ in a 4:1 ratio. The crystal structure of $[Cu(4\text{-}CH_2OH\text{-}5\text{-}CH_3Im)_4](NO_3)_2$ [28] determined by single crystal X-ray diffraction confirmed that similar tautomers to those stated for the related complex with 4-aldehyde-5-methylimidazole are involved in the complexation (Scheme 2). The geometry found in the structural analysis of both $[Cu(4\text{-}CH_2OH\text{-}5\text{-}MeIm)_4](NO_3)_2$ [28] and $[Cu(1\text{-}Bz.\text{-}2\text{-}CH_2OHIm)_4](NO_3)_2$ [31] is the slightly distorted tetragonal bipyramid (e.g. Fig. 4).

The equatorial plane of its base is formed by the four nitrogen atoms of the imidazole rings and two oxygen atoms derived from the CH_2OH substituents located at the axial position. Thus, two of the ligands act as monodentate (N donor) and two as didentate when, in coordination with the Cu(II) ion, not only the nitrogen but also the oxygen atom (N,O donors) the CH_2OH groups are involved. These phenomena are reflected in the IR spectrum which exhibits two OH vibration bands, at 3336 cm^{-1} (the free OH group) and 3112 cm^{-1} (the group being sensitive to metal coordination via the oxygen atom). The X-ray results confirmed the data obtained in aqueous solutions, namely that formation of the chelates by hydroxymethylimidazoles is not accompanied

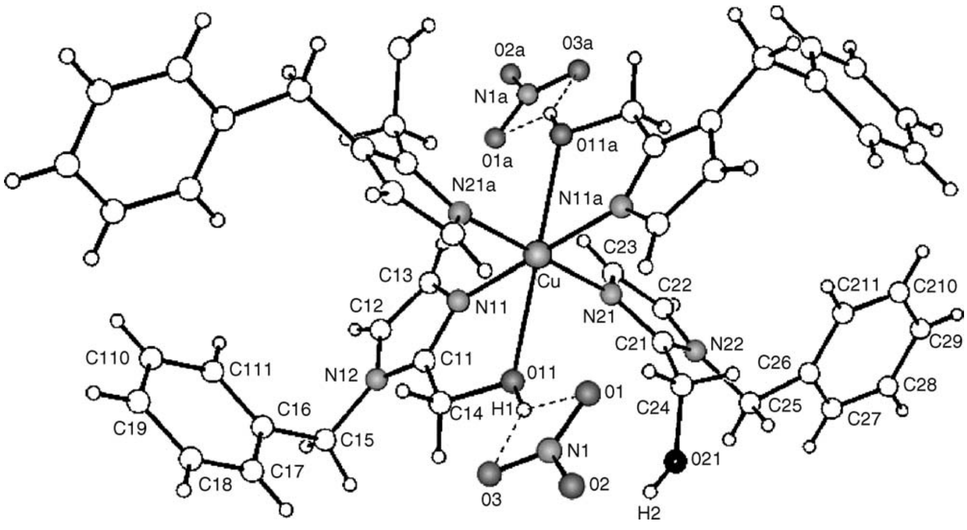


Fig. 4. Atomic numbering scheme and the structure of the complex $[Cu(1\text{-}Bz.\text{-}2\text{-}CH_2OHIm)_4](NO_3)_2$ [31].

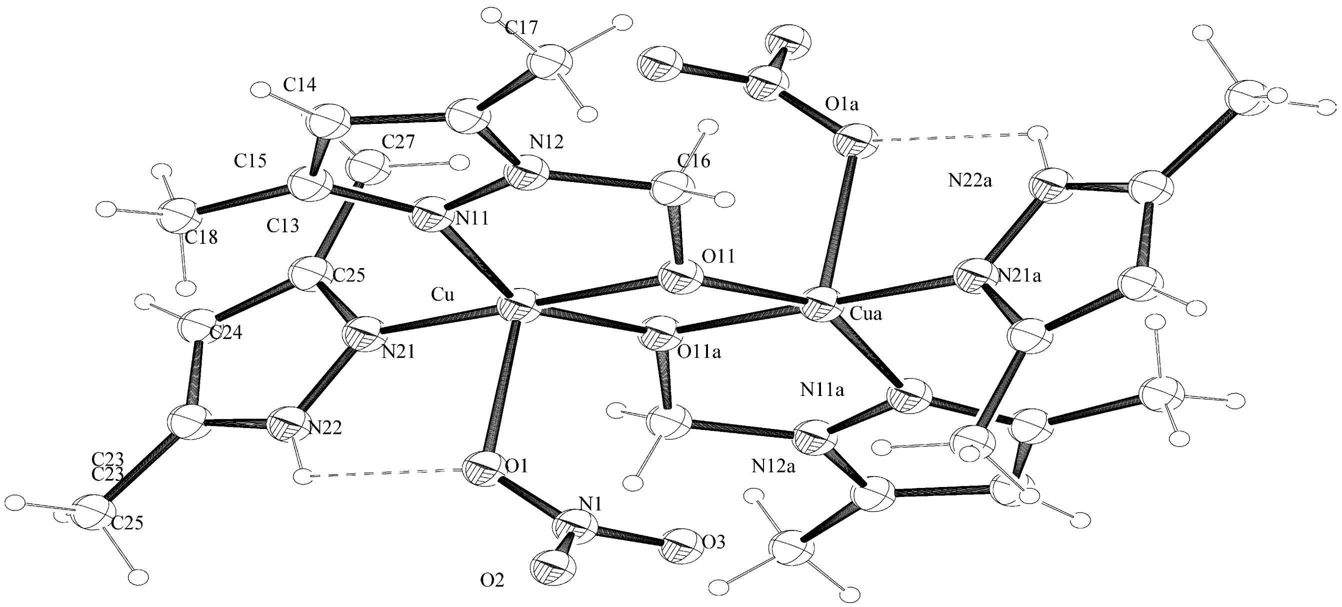


Fig. 5. Molecular structure of dinuclear $[Cu(L)(LO)NO_3]_2$ complex showing the atom numbering scheme. Fifty percent probability amplitude displacement ellipsoids are shown [59].

by loss of a proton from the hydroxymethyl group. Other examples of Cu(II) complexes with heterocyclic alcohols are 1-hydroxymethyl-3,5-dimethylpyrazole (1-CH_2OH-3,5-DMePz) and 1-hydroxyethyl-3,5-dimethylpyrazole (1-C_2H_5OH-3,5-DMePz). The protonation constant of 1-CH_2OH-3,5-DMePz ($pK_a = 3.84$), which is much lower compared to that of hydroxymethylimidazole, shows that the donor properties of the ligand depend on the electron density at the pyridine-like nitrogen atom of the pyrazole ring. The equilibrium stability constants of Cu(II) complexes, determined by the potentiometric technique ($\log \beta_1 = -6.10$, $\log \beta_2 = 2.68$) [25], clearly indicate a competition of H_2O molecules with the weak donor ligand upon coordination to Cu(II) ions in aqueous solution.

Literature data [54–58] show that solid state chemistry of hydroxyalkylpyrazole complexes with Cu(II) ion is more interesting. A number of Cu(II) complexes with 1-CH_2OH-3,5-DMePz [57–58] and 1-C_2H_5OH-3,5-DMePz (N-hed) [54–56] have been prepared and the crystal structure of some of them has been determined by single crystal X-ray diffraction. It is interesting to compare the crystal structures, magnetic and spectroscopic data of Cu(II) complexes with both chelating ligands, which differ from each other only in one CH_2 group of a side substituent of pyrazole ring. Additionally, upon coordination, the ligands exist in neutral or deprotonated forms: 1-C_2H_5O-3,5-DMePz (N-oed), 1-CH_2O-3,5-DMePz (LO). The deprotonated form is more able to form dinuclear complexes. In Table 4, the compounds isolated in the reaction of Cu(II) salts with hydroxyalkylpyrazoles are listed. The table shows that the kind of coordination compound obtained in the reaction of Cu(II) salts with 1-hydroxymethyl-3,5-dimethylpyrazole depends on the type of solvent used during synthesis. Preparation using a solvent mixture of (trimethyl orthoformate, methanol and propan-2-

Table 4
The conditions of synthesis of Cu(II) compounds with hydroxyalkylpyrazoles

Complex	Colour	Solvent	Molar ratio	Reference
$[Cu(N\text{-}hed)_2(NO_3)_2]$	Blue	Ethanol, triethyl orthoformate	1:2 or 1:3	[34]
$[Cu(N\text{-}hed)_2Cl_2]$	Green	Ethanol, triethyl orthoformate	1:2	[55]
$[Cu(N\text{-}oed)Cl]_2$	Dark blue	Ethanol, triethyl orthoformate	1:1	[55]
$[Cu(N\text{-}oed)Br]_2$	Dark green	Ethanol, triethyl orthoformate, triethylamine or KOH	1:1	[55]
$[Cu(N\text{-}oed)(NO_3)]_2$	Blue	Ethanol, triethyl orthoformate, triethylamine or KOH	1:1	[55]
$[Cu_2(N\text{-}hed)_2(N\text{-}oed)_2](ClO_4)_2$	Dark blue	Ethanol, triethyl orthoformate, triethylamine or KOH	1:2	[57]
$[Cu(L)(LO)(ClO_4)]_2$	Dark green	Methanol, 3,5-DMePz, sodium perchlorate, KOH	1:1:1	[56]
$[CuL(LO)(ClO_4)]_2$	Dark green	2-Propanol	1:4	[59]
$[CuL(LO)(BF_4)]_2$	Blue	2-Propanol	1:4	[58]
$[CuL(LO)(NO_3)]_2$	Sea green	2-Propanol	1:4	[59]
$[CuL_3(NO_3)_2]$	Blue	Methanol, 2-propanol, trimethyl orthoformate	1:2 or 1:4	[58]

L: 3,5-DMePz; LO: 1-CH_2O-3,5-DMePz; N-hed: 1-C_2H_5OH-3,5-DMePz; N-oed: 1-C_2H_5O-3,5-DMePz.

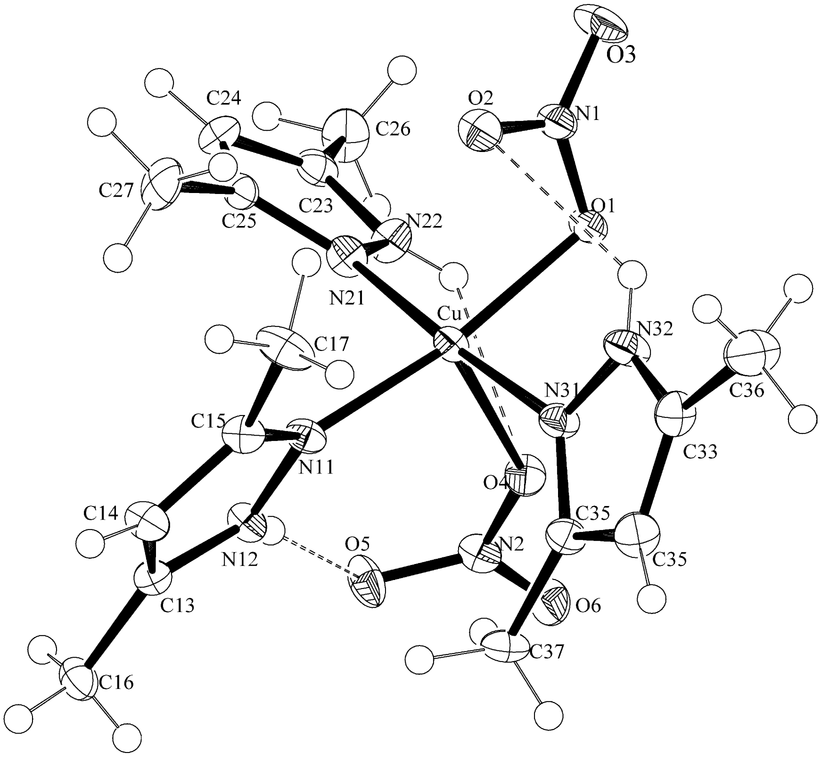
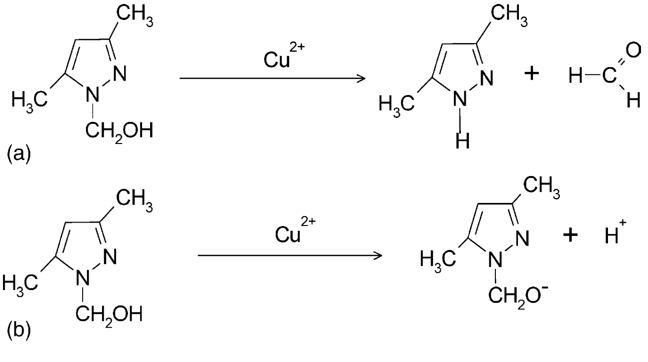


Fig. 6. Molecular structure of mononuclear $[Cu(3,5\text{-}DMePz)_3(NO_3)_2]$ complex [59].

ol), and molar ratio Cu:L, 1:2 or 1:4 results in only one type of the mononuclear Cu(II) complex $[CuL_3(NO_3)_2]$ (Fig. 6, Scheme 3a). Carrying out the reaction using only propan-2-ol as the solvent (Cu:L, 1:4) in the atmosphere results in the formation of dinuclear complexes of the type $[Cu(L)(LO)X]_2$ ($X = NO_3$, BF_4, ClO_4) with mixed ligands (3,5-DMePz (L) and 1-CH_2O-3,5-DMePz (LO)) (Fig. 5). Half of the stoichiometrically used 1-hydroxymethyl-3,5-dimethylpyrazole decomposes to formaldehyde and 3,5-dimethylpyrazole (L) (Scheme 3a).

Another part of the ligand undergoes deprotonation giving 1-methoxy-3,5-dimethylpyrazole (LO) according to Scheme 3b.



Scheme 3. (a) The ligand reaction during the formation of monodentate Cu(II) complex; (b) the process of deprotonation during the formation of dinuclear complexes.

A similar dinuclear complex $[Cu(L)(LO)ClO_4]_2$ was obtained by Oki et al.[56] but in a different way (Table 4), using not only 1-hydroxymethyl-3,5-dimethylpyrazole as a starting ligand but also 3,5-dimethylpyrazole and KOH.

1-(2-Hydroxyethyl)-3,5-dimethylpyrazole (N-hed) with Cu(II) ions forms three types of complexes, mononuclear $[Cu(N\text{-}hed)_2X_2]$ [55] containing neutral ligand and compensating anion X ($X = Cl$, NO_3), dinuclear complexes of the type $[Cu(N\text{-}oed)X]_2$ [55] ($X = Cl, Br, NO_3$) or $[Cu(N\text{-}oed)(N\text{-}hed)]_2(ClO_4)_2$ [57] with deprotonated and with both neutral and deprotonated ligands. From a structural point of view, the dinuclear copper(II) compounds (Table 4) can be divided into two groups. The structures of $[Cu(N\text{-}oed)(NO_3)]_2$ (**1**) and $[Cu(N\text{-}oed)Cl]_2$ (**2**) are the same as described [55] for $[Cu(N\text{-}oed)Br]_2$ (**3**) where the two copper atoms doubly bridged by oxygen atoms of the ethoxy group of the ligands, are at a distance of 3.042 Å. Each copper ion is in a roughly square planar environment (CuO_2NBr). In the structures of $[Cu(N\text{-}hed)(N\text{-}oed)]_2(ClO_4)_2$ (**4**) and $[Cu(L)(LO)X]_2$, the copper(II) ions are in a tetragonal pyramidal environment with X as the monodentate anion (ClO_4, BF_4, NO_3) occupying the axial position except for $[Cu(N\text{-}hed)(N\text{-}oed)]_2(ClO_4)_2$ where the oxygen of C_2H_5OH group is coordinated in this position. All the dinuclear Cu(II) complexes indicate an antiferromagnetic interaction between the individual copper(II) ions. The complexes **1–4** are diamagnetic over the whole temperature range (10–293 K) and EPR silent. The data collected in Table 5 for $[Cu(L)(LO)X]_2$ complexes indicate an

Table 5
Selected structural and magnetic data for dinuclear Cu(II) type $[Cu(L)(LO)X]_2$ complexes

Compound	Cu–Cu (Å)	In plane		Cu–L (Å)	Cu–O–Cu (°)	O–Cu–O (°)	$2J$ (cm^{-1})
		Cu–O (Å)	Cu–N (Å)				
$[CuLL0(C10_4)]_2$ [56]	3.022(1)	1.915(2)	1.965(2)	$2.390(2)_{Cu-O(ClO_4)}$	103.7(1)	76.43(9)	−288 [59]
$[CuLLO(BF_4)]_2$ [58]	3.003(1)	1.914(2) 1.926(2)	1.960(2) 1.964(2)	$2.423(2)_{Cu-F(BF_4)}$	102.9(1)	77.09(9)	−269
$[CuLLO(NO_3)]_2$ [59]	2.958(1)	1.936(2) 1.949(2)	1.973(2) 1.983(3)	$2.256(2)_{Cu-O(NO_3)}$	99.2(1)	80.79(9)	−58, −45

L: 3,5-DMePz, LO: l-CH_2O-3,5-DMePz.

interesting correlation between the X-ray data and the magnetic exchange between the coupled copper centres. The apical anions clearly play a role in determining the $-2J$ value in dinuclear compounds. The value of $-2J$ increases as the axial ligands become stronger electron donors. Thus, the $-2J$ value tends to increase in the series: $NO_3^- < BF_4^- < ClO_4^-$. In the same direction the Cu–Cu distances and Cu–O–Cu angles decrease (see Table 5). This kind of correlation is typical of dinuclear, anti-ferromagnetic Cu(II) dialkoxo-bridged complexes [59,60].

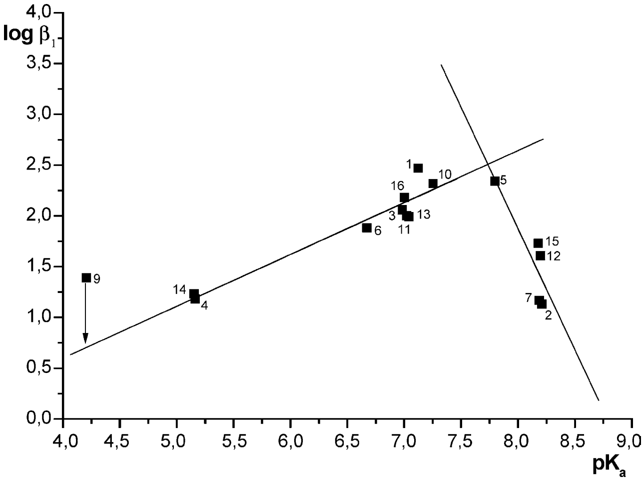


Fig. 7. Plots of $\log \beta_1 = f(pK_a)$ for the Co(II) complexes with imidazole derivatives (**1–7**, **9–16**) from Table 6 ($R_c = 0.954$).

3. Cobalt(II) complexes

The aqueous solution coordination chemistry of Co(II) ions with imidazole derivatives is specially interesting due to the ability of the Co(II) ion to change geometry on reaction with ligands. Some possible reasons for the geometrical flexibility of Co(II) ion can be extracted from the data collected in Table 6 and from the correlation presented in Fig. 7. The ligands containing an alkyl substituent situated at 2 or 4 positions (the points on the line with negative slope (Fig. 7)) decrease the coordination number of the central ion from 6 to 4. This results in configuration equilibrium of the octahedron ↔ tetrahedron type [23,32,33]. The change in the coordination symmetry from octahedral to tetrahedral, due to steric hindrance of the alkyl group positioned at 2 or 4 of imidazole ring, is confirmed not only by a considerable 'red shift' of the UV d–d band ($\lambda_{max} = 580$ mm) but also by the high value of the molar absorption coefficient ($\varepsilon = 430$ or 600 M^{-1} cm^{-1} for 1-Bu-2-MeIm [33] and 1,2-DMeIm [23], respectively).

On the other hand, the visible-range absorption spectra of the Co(II) complexes with aldehydeimidazoles [32] and hydroxymethylimidazoles [24,30,33] in aqueous

Table 6
Stability constants of imidazole and some imidazole derivatives with Co(II) ion in aqueous solution at 298 K and $I = 0.5$ mol dm^{-3} (KNO_3)

Ligand	pK_a	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$	$\log \beta_5$	$\log {}^*\beta_1$	Reference
Im**1**	7.12	2.47	4.40	5.85	6.85	–	−4.65	[21,22]
1,2-DMeIm**2**	8.21	1.13	2.39	3.81	4.32	–	−7.08	[23]
1-Me-2-CH_2OHIm**3**	6.98	2.06	3.65	3.93	5.67	–	−4.92	[24]
1-Me-2-CHOIm**4**	5.16	1.18	1.68	3.22	–	–	−3.95	[25]
4(5)-MeIm**5**	7.80	2.34	4.09	5.33	6.67	–	−5.46	[36]
4(5)-CH_2OHIm**6**	6.67	1.88	3.60	4.62	5.98	–	−4.79	[24]
4,5-DMeIm**7**	8.19	1.17	–	–	–	–	−7.02	[26]
4-CHO-5-MeIm**9**	4.20	1.38	2.45	–	–	–	−2.82	[31]
1-EtIm**10**	7.25	2.32	4.17	5.42	7.02	7.42	−4.93	[29]
1-Et-2-CH_2OHIm**11**	7.02	2.00	3.70	4.60	5.80	–	−5.02	[30]
1-Pr-2-MeIm**12**	8.20	1.61	2.00	3.08	5.40	–	−6.63	[32]
1-Pr-2-CH_2OHIm**13**	7.04	1.99	3.85	4.56	6.23	–	−5.05	[30]
1-Pr-2-CHOIm**14**	5.15	1.23	1.59	3.03	–	–	−3.92	[32]
1-Bu-2-MeIm**15**	8.18	1.73	2.08	2.76	5.65	–	−6.45	[33]
1-Bu-2-CH_2OHIm**16**	7.00	2.18	4.03	4.67	6.65	–	−4.82	[33]

solution suggest that complexation in these systems involves replacing water molecules in the hydration sphere of the central ion by the ligand molecules with retention of the pseudo-octahedral structure. (For example, pH 4.4, $\lambda = 514$ mm, $\varepsilon = 18\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ for Co(II) complexes with 4-CHO-5-MeIm and 1-Pr-2-CHOIm [33] or pH 6.9, $\lambda = 523$ mm, $\varepsilon = 60\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ for 1-Et-2-CH_2OH [30] and 1-Bu-2-CH_2OHIm [33].) The increase in the values of the molar coefficient for hydroxymethyl complexes can be interpreted in terms of an interaction of the oxygen atom with the central ion. It is one more piece of evidence that the hydroxymethyl oxygen is involved in the formation of chelate complexes with Co(II) ion (see equilibrium in Scheme 1 (vide supra)). This kind of interaction of the Co(II) with an O donor atom from the CH_2OH or CHO substituent of imidazoles is reflected in increased complex stability (Table 6) despite the one to three orders of magnitude lower basicity of the ligands compared to alkyl derivatives [24,30,32,35,61]. The increase of log β_1 caused by the chelating effect is especially notable in the case of the first Co(II) complexes with 4-CHO-5MeIm (Fig. 7). A positive value of $\log \Delta_{\mathrm{M/L}} = \log \beta_{1\mathrm{exp}} - \log \beta_{1\mathrm{calc}} = 0.64$ [61] reflects the extent of formation of the chelate complex in equilibrium vide supra (Scheme 1). A large excess of ligand in the solution (pH 6.9) shifts the equilibrium towards complexes with the chelating form of the ligands.

The X-ray data (Table 7) for a series of Co(II) complexes provide direct proof of the role of alcohol and aldehyde diazoles as chelates towards the Co(II) ions. All the data collected in Table 7 confirm that N,O-donor ligands form five – (4-CH_2OH-5-MeIm [64],1-V-2-CH_2OHIm [62,63], 1-Bz-2-CH_2OHIm [65], 4-CHO-5-MeIm [61]) – or six – (1-C_2H_5OH-3,5-DMePz [57]) – membered chelate rings with Co(II) ions. In the complexes [62–65], hydroxymethylimidazoles have a dual nature, that is, they can act as monodentate ligands, coordinating only through the pyridine-like nitrogen atom or as didentate ligands where the oxygen atom of the CH_2OH group acts as an additional electron donor. Formation of these chelates is not accompanied by loss of a proton from the hydroxyalkyl substituent. All of the ligands are coordinated in their neutral forms. This fact correlates with the data for Co(II) complexes obtained by the potentiometric method in aqueous solution and it explains the rather low capacity of these ligands to form chelate species. A comparison of the X-ray data (Table 7) clearly emphasizes that cobalt(II) with N,O-donor ligands has a strong preference for distorted octahedral coordination of CoN_4O_2 [64,65] or $CoN_2O_2O_2{}'$ [57] chromophores. The metal–donor distances ranging between 2.072(2) and 2.155(2) Å for Co–N and 2.088(2) and 2.418(3) Å for Co–O bonds, are typical for Co(II) complexes. A further interesting illustration of the geometrical flexibility of the Co(II) ion is provided by Co-1-Bz-2-CH_2OH complexes [65]. Their synthesis, carried out using trimethyl orthoformate as solvent, generates Co:L = 1:6 or 1:4 *trans*- and *cis*-isomers. *Trans*-(*O*)-[Co(1-Bz-2CH_2OHIm)$_4$]$(NO_3)_2$ crystallizes in the triclinic space group $P\bar{1}$ (Fig. 8) and the coordination geometry around the Co atom is approximately octahedral. The hydroxo-oxygen atoms of two ligands occupy axial positions (i.e. are in a *trans* position to each other). The equatorial plane is defined by four nitrogen atoms of the imidazole rings. The stereochemistry of the metal centre of *cis*-(*O*)-[Co(1-B_2-2-CH_2OHIm)$_4$]$(NO_3)_2 \times 1.5H_2O$) [65] is very irregular, and can be considered as a distorted octahedron

Table 7
Selected geometrical parameters for Co(II) complexes with chosen N,O donor ligands

Compound	Chromophore	Co–N (Å)	Co–O (Å)	d–d Spectra (cm^{-1})	FarIR data (cm^{-1})	
					Co–N	Co–O
[Co(4-CH_2OH-5-MeIra)$_4$]$^{2+}$ [64]	CoN_4O_2	$2.079(1)_{\mathrm{Co-N(11)}}$ $2.139(1)_{\mathrm{Co-N(21)}}$	$2.198(1)_{\mathrm{Co-O(11)}}$	10,040 16,600 20,400	282, 266	389
[$CoCl_2$(I-V-2-CH_2OHIm)$_2$] [62]	$CoCl_2N_2O$	$2.036(3)_{\mathrm{Co-N(1)}}$ $2.016(3)_{\mathrm{Co-N(2)}}$	$2.418(3)_{\mathrm{Co-O(2)}}$			
trans-(*O*)-[Co(l-Bz-2-CH_2OHIm)$_4$]$^{2+}$ [65]	CoN_4O_2	$2.091(1)_{\mathrm{Co-N(11)}}$ $2.156(2)_{\mathrm{Co-N(21)}}$	$2.1749(10)_{\mathrm{Co-O(11)}}$	9,340 15,698 20,660	256	461
is-(*O*)-[Co(l-Bz-2-CH_2OHIm)$_4$]$^{2+}$ [65]	CoN_4O_2	$2.096(3)_{\mathrm{Co-N(41)}}$ $2.124(3)_{\mathrm{Co-N(21)}}$ $2.135(3)_{\mathrm{Co-N(31)}}$ $2.143(3)_{\mathrm{Co-N(11)}}$	$2.205(2)_{\mathrm{Co-O(21)}}$ $2.247(2)_{\mathrm{Co-O(11)}}$	8,305 15,674 21,142	298, 269	475, 458
[Co(l-C_2H_5OH-3,5-DMePz)$_2$$(NO_3)$]$NO_3$ [57]	CoN_2O_4	$2.078(2)_{\mathrm{Co-N(12)}}$ $2.072(2)_{\mathrm{Co-N(22)}}$	$2.088(2)_{\mathrm{Co-O(20)}}$ $2.114(2)_{\mathrm{Co-O(30)}}$ $2{,}172(2)_{\mathrm{Co-O(41)}}$ $2.148(2)_{\mathrm{Co-O(42)}}$	8,300 15,900 19,600		
[Co(4-CHO-5-MeIm)$_2$$(H_2O)_2$]$^{2+}$ [61]	CoN_2O_4	2.103(2) (Co1) 2.085(2) (Co2)	$2.0479(2)_{\mathrm{Co1-OW}}$ $2.186(2)_{\mathrm{Co-O(7)}}$ $2.066(2)_{\mathrm{Co2-OW}}$ $2.189(2)_{\mathrm{Co2-O(11)}}$	9,066 16,863 20,325	280	386, 377

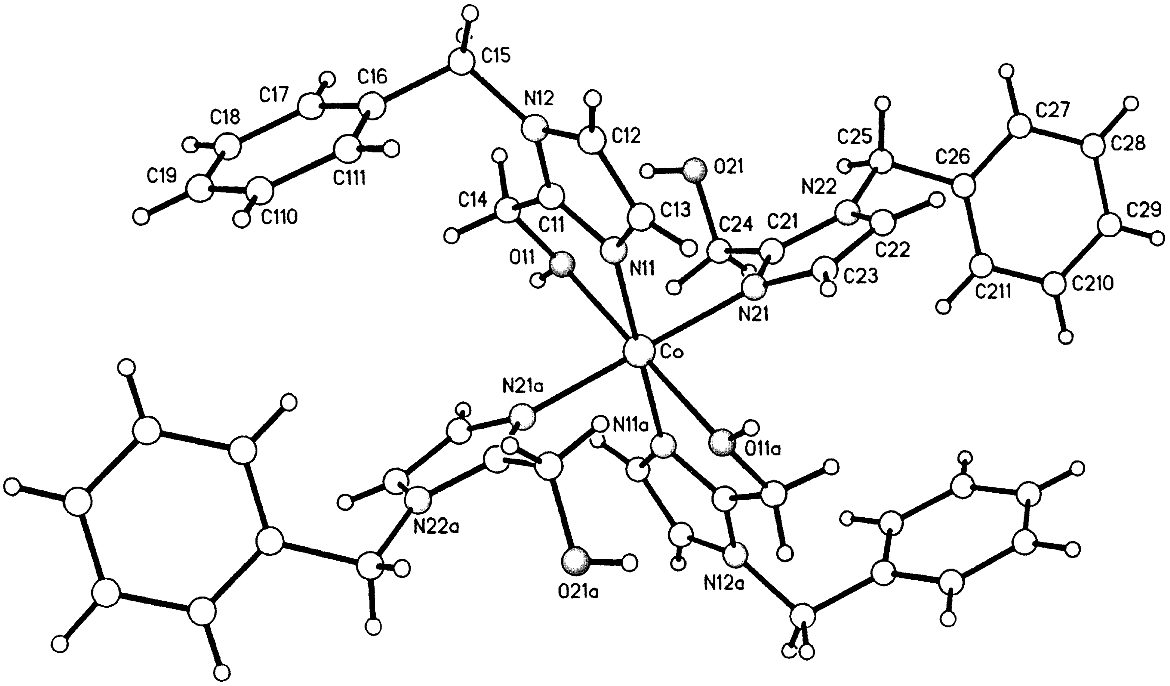


Fig. 8. Atomic numbering scheme and the structure of the complex *trans*-(*O*)-[Co(1-Bz-2-$CH_2OHIm)_4](NO_3)_2$ [65].

(Fig. 9). The cobalt(II) ion is coordinated by two oxygen atoms of the hydroxymethyl groups, which occupy a *cis* position to each other in the equatorial plane, and four nitrogen atoms furnished by the imidazole rings. The complexes, which consist of two kinds of ligands, mono and didentate, exhibit two O–H vibration bands, at 3336 and 3119 cm^{-1} for the *cis*-isomer and at 3336 and 3123 cm^{-1} for the *trans*-Co(II) complex. The first one is assigned to the CH_2OH group of the monodentate ligands and the second to the OH group, which is sensitive to metal coordination via the oxygen atom.

1-(2-Hydroxyethyl)-3,5-dimethylpyrazole, when employed as a neutral ligand, yields two kinds of coordination

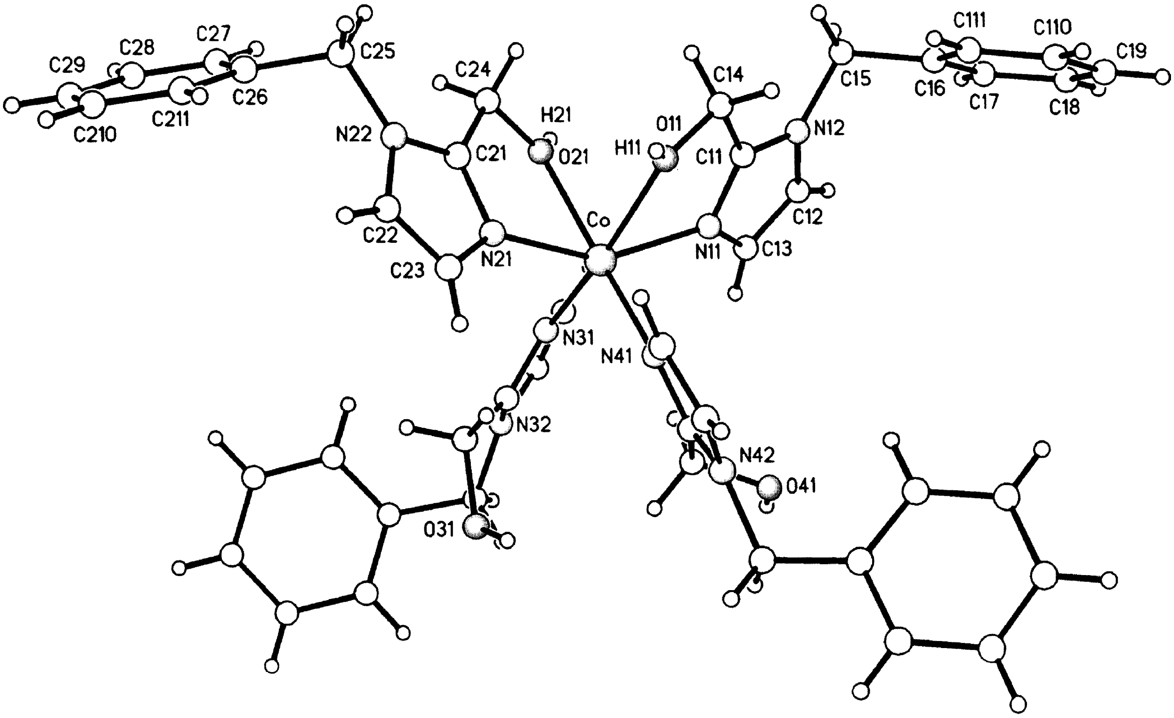


Fig. 9. Atomic numbering scheme and the structure of the complex *cis*-(*O*)-[Co(1-Bz-2-$CH_2OHIm)_4](NO_3)_2 \times 1.5\ H_2O$ [65].

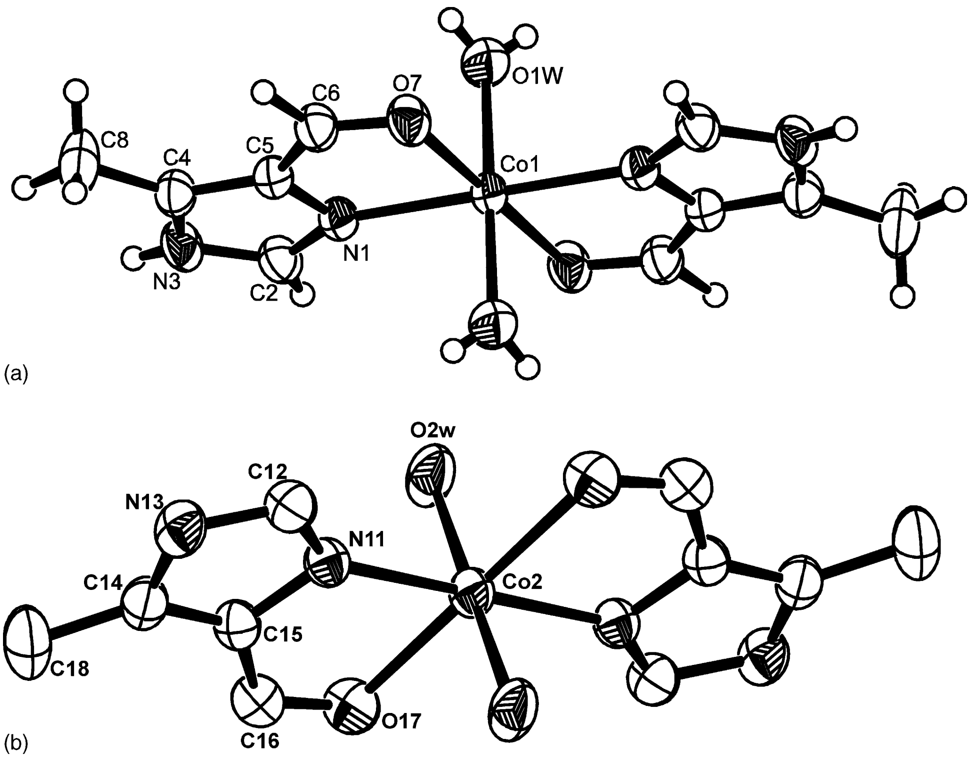


Fig. 10. The structure of the Co(II) complexes with 4-CHO-5-MeIm [61].

compounds, $[Co(1\text{-}C_2H_5OH\text{–}3,5\text{–}DMePz)_2(NO_3)_2]$ [55] and $[Co(1\text{-}C_2H_5OH\text{-}3,5\text{-}DMePz)_2(NO_3)](NO_3)$ [57]. The single crystal X-ray structure analysis, which has been carried out for the other compounds [57], shows that the cobalt(II) ion is in a strongly distorted octahedral $N_2O_2O_2'$ environment due to the didentate coordination of only one of the nitrate ions. Ligand-field spectra of this complex (Table 7) are very much in support of a distorted geometry of the Co(II) environment. An entirely different geometrical complex forms from 1-methoxy-3,5-dimethylpyrazole upon reaction with Co(II) ion [66]. To induce deprotonation of the ligand, the reaction mixture was made alkaline (KOH). The fact that Co(II) complexes [66] of the type $[\{CoX(1\text{-}CH_2O\text{-}3,5\text{-}DMePz)(EtOH)\}_4]$ where X = Cl, Br are isomorphous with $[\{NiX(1\text{-}CH_2O\text{-}3,5\text{-}DMePz)(EtOH)\}_4]$ for which the presence of the cubic core was confirmed by the X-ray data, allow us to predict that the deprotonated ligand coordinates as a N,O-donor ligand. The oxygen atom of the methoxy group acts as a bridge between three metal ions, forming a Co_4O_4 cubane-type cluster. Such compounds show slight anti-ferromagnetic behaviour.

The chelating nature of aldehydeimidazoles upon reaction with Co(II) ions is reflected in the coordination compounds of 4-CHO-5-MeIm [61]. X-ray investigation shows a specific phenomenon for the crystal structure of the compounds. The unit cell includes two symmetry independent cations: $[Co(1)(4\text{-}CHO\text{-}5\text{-}MeIm)_2(H_2O)_2]^{2+}$ and $[Co(2)(4\text{-}CHO\text{-}5\text{-}MeIm)_2(H_2O)_2]^{2+}$ which differ slightly in bond lengths and valence angles (see Table 7). The position and appearance of the prominent doublet at 1614 and 1586 cm^{-1} in the ν (CO) region of the IR spectrum support the above-mentioned X-ray data. In both six-coordinated Co(II) complexes two molecules of didentate ligands and two water molecules are coordinated to the central ion forming a chromophore of CoN_2O_4 type. The coordination of Co(II) could be considered as a geometric *trans*-isomer due to the water molecules occupying axial positions (i.e. are in a *trans* position to each other) (Fig. 10).

4. Comparison of the zinc and cadmium complexes

Zinc, as one of the most important trace elements, plays a versatile role in biological systems due to its structural and catalytic roles in enzymes [69–73]. Therefore, much effort has been expended on the study of synthetic analogues of zinc enzymes in the hope of clarifying the mechanism of their action [4–6,73]. In studies of how the chemistry of zinc is modulated by its coordination environment, heterocyclic alcohols and aldehydes, as potentially N,O-donor ligands, have been incorporated [4,6]. For this purpose, the Zn(II) complexes with pyridine-2-carbaldehyde (PA), 6-methylpiridine-2-carbaldehyde (MPA) and 2,6-pyridine-dicarbaldehyde (PDA) have been isolated and structurally characterized [4]. Selected X-ray data on some complexes involving coordinating aldehydes are collected in Table 8. Comparison of the structural data of the zinc complexes, $[ZnI_2(MPA)]$, $[ZnX_2(PA)_2]$ (X = Cl, Br, I),

Table 8
The selected X-ray data of the attachment of heterocyclic alcohols, alkoxides and aldehydes to Zn(II) and Cd(II) ions

Compound	Zn–N (Å)	Zn–O (Å)	O–Zn–N/N–Zn–N (°)	Reference
$ZnI_2(MPA)$	2.05(2)/2.06(1)	2.10(1)/2.11(1)	80.3(6)/80.2(6)	[4]
$ZnCl_2(PA)_2$	$2.108(7)_{\text{Zn–N1}}$ $2.108(7)_{\text{Zn–N2}}$	$2.481(6)_{\text{Zn–O1}}$ $2.544(7)_{\text{Zn–O2}}$	$72.2(2)_{\text{N1–Zn–O1}}$ $71.0(2)_{\text{N2–Zn–O2}}$	[4]
$ZnBr_2(PA)_2$	$2.102(15)_{\text{Zn–N1}}$ $2.111(14)_{\text{Zn–N2}}$	$2.498(14)_{\text{Zn–O1}}$ $2.525(14)_{\text{Zn–O2}}$	$71.7(5)_{\text{N1–Zn–O1}}$ $70.9(5)_{\text{N2–Zn–O2}}$	[4]
$ZnI_2(PA)_2$	$2.102(5)_{\text{Zn–N1}}$ $2.117(4)_{\text{Zn–N2}}$	$2.483(4)_{\text{Zn–O1}}$ $2.532(4)_{\text{Zn–O2}}$	$72.1(2)_{\text{N1–Zn–O1}}$ $71.6(2)_{\text{N2–Zn–O2}}$	[4]
$[Zn_2(PA)_2(H_2O)Cl_4]$	$2.087(3)_{\text{Zn–N1}}$ $2.108(3)_{\text{Zn–N2}}$	$2.444(3)_{\text{Zn–O1}}$ $2.267(3)_{\text{Zn–O2}}$	$77.1(1)_{\text{N1–Zn–O1}}$ $75.3(1)_{\text{N2–Zn–O2}}$ $156.7(1)_{\text{N1–Zn–O2}}$	[4]
$[Zn(PA)_2I]^+$	$2.06(1)_{\text{Zn–N1}}$	$2.25(1)_{\text{Zn–O1}}$	$76.8(5)_{\text{N1–Zn–O1}}$ $89.8(5)_{\text{N1–Zn–O1}'}$	[4]
$[(PicA)Zn(SC_6F_5)_2]$	2.07(1)	2.24(1)	73.4(7)	[6]
$[(OpyA)Zn(SC_6F_5)_2]$	2.059(2)	2.165(2)	77.85(6)	[6]
$(MimA)_2Zn(SC_6F_5)_2$	$2.048(3)_{\text{Zn–N1}}$ $2.055(3)_{\text{Zn–N3}}$	$3.061(3)\ _{\text{Zn}\cdots\text{O}}$	$97.2(1)_{\text{N–Zn–N}}$	[6]
$[Zn(4\text{-CHO-5-MeIm})_4](NO_3)_2$	2.022(3)	$3.065\ _{\text{Zn}\cdots\text{O}}$	111.75(8) 105.01(2)	[61]
$(PyMeO)Zn(C_6H_2Pr_3)_4$	2.069(3)	$1.964(3)_{\text{Zn–O}}$ $1.936(3)_{\text{Zn–O}'}$	$81.7(2)_{\text{O}'\text{–Zn–N}}$ 109.0(2)	[6]
$(QuiMeO)Zn(SC_6F_5)_2$	2.048(3)	$1.958(3)_{\text{Zn–O}}$ $1.964(3)_{\text{Zn–O}'}$	$82.5(2)_{\text{O}'\text{–Zn–N}}$ 104.7(2)	[6]
$PicMeOH\cdot Zn(SC_6F_5)_2$	2.048(3)	2.123(3)	80.1(1)	[6]
$[Cd(4\text{-CHO-5-MeIm})_2(NO_3)_2]$	$2.252(1)_{\text{Cd–N1}}$ $2.261(6)_{\text{Cd–N11}}$	$2.340(2)_{\text{Cd–O42}}$ $2.371(2)_{\text{Cd–O21}}$ $2.542(6)_{\text{Cd–O7}}$ $2.756(2)_{\text{Cd–O41}}$ $2.603(2)_{\text{Cd–O22}}$ $2.612(1)_{\text{Cd–O17}}$	$136.13(6)_{\text{N1–Cd–N11}}$ $129.18(6)_{\text{N1–Cd–O42}}$ $83.13(6)_{\text{N11–Cd–O42}}$ $87.93(6)_{\text{N1–Cd–O21}}$	[83]
$[Cd(4\text{-CHO-5-MeIm})_2](NO_3)_2$	$2.298(1)_{\text{Cd–N1}}$ $2.292(1)_{\text{Cd–N11}}$	$2.700(1)_{\text{Cd–O7}}$ $2.745(1)_{\text{Cd–O17}}$	$138.96(5)_{\text{N1–Cd–N11}}$ $67.60(4)_{\text{N1–Cd–O7}}$ $66.66(5)_{\text{N11–Cd–O17}}$ $79.80(5)_{\text{N11–Cd–O7}}$	[61]

$[Zn_2(PA)_2(H_2O)Cl_4]$, $[Zn(PA)_2I]^+$ obtained by the reactions of PA or MPA with zinc halides [4] provides some examples of complexes in which the Zn(II) changes both coordination number and geometry. The complex containing one molecule of MPA is a distorted tetrahedron resulting from the 6-methylpyridine-2-carbaldehyde acting as a symmetrical, N,O ligand with two halides. In the $[ZnX_2(PA)_2]$ complexes with two aldehydes, the central ion changes its coordination number to 6. However, other authors [4], after analysis of the angular distortion and comparatively long Zn–O distances (Table 8), have postulated a distorted tetrahedral (ZnN_2X_2) rather than an octahedral shape of the complex polyhedron. On the other hand, X-ray data of the dinuclear complex $[Zn_2(PA)_2(H_2O)Cl_4]$ and $[Zn(PA)_2I]^+$ cation (Table 8) prepared from $ZnCl_2$, PA and H_2O in the ratio 2:2:1, show that pyridine-2-carbaldehyde should be treated as a didentate N,O-donor ligand. The unique dinuclear complex $[Zn_2(PA)_2(H_2O)Cl_4]$ consists of a cationic unit $[Zn(PA)_2(H_2O)]^{2+}$ (Zn coordination number 6), of octahedral structure and a tetrahedral $[ZnCl_4]^{2-}$, one which is bridged by one of its halides [4]. The X-ray data of the $[Zn(PA)_2I]^+$ cation, likewise, confirm the didentate nature of the PA ligand in forming two of the five coordinating chelate rings with Zn(II) ion. The coordination number of this complex is 5 and the chromophore is $[ZnN_2O_2I]$.

To help assign structural representations to the $ZnNS_2O$ coordination pattern of the enzymatic model ADH, the ligands MPA, 6-methoxypyridine-2-carbaldehyde (OMPA) and *N*-methylimidazole-2-carbaldehyde (MimA) were combined with zinc thiolates [6]. Aldehydes derived from pyridine, on account of their chelating effect, stabilize the above mentioned Zn(II) complexes and provide not only the nitrogen donor atom but also the oxygen atom to the Zn chromophore. However, when the pyridine chelating ligand was exchanged for MimA, the 1:2 complex $[(MimA)_2Zn(SC_6F_5)_2]$ – a ZnN_2S_2 type chromophore – was obtained. This result indicates that *N*-methylimidazole-2-carboaldehyde is bound to zinc in monodentate fashion with its N atom. The Zn–O distance (3.06 Å) is so long and the deformation of the polyhedron too significant to obtain a ZnN_2OS_2 coordination pattern. A similar effect was observed for the $[Zn(4\text{-}Me\text{-}5\text{-}CHOIm)_4]^{2+}$ cation [61]. In the coordination sphere of the central ion there are four 4-CHO-5-MeIm moieties (chromophore ZnN_4). The four identical zinc–nitrogen bond lengths (Table 8) as well as the values of N–Zn–N angles indicate tetrahedral coordination of the Zn(II) ion. The CHO group are oriented in such a way that oxygen atoms are situated 3.065 Å from the central ion. It supports the conclusion that the Zn(II) with aldehyde ligands possessing the imidazole unit of histidine, prefer a tetrahedral geometry; likewise, the geometry of the active site of zinc enzymes (Fig. 11).

In addition, when, in the Zn(II) complexes mentioned above, the aldehyde ligands were changed to heterocyclic alcohols (e.g. 2-pyridylmethanol (PyMeOH); 2-quinolylmethanol (QuiMeOH) the tetranuclear alkoxide complexes $[(PyMeO)Zn(SC_6H_2Pr_3{}^i)]$ and $[(QuiMeO)\text{-}Zn(SC_6F_5)]_4$ were obtained via deprotonation of alcohols. The deprotonation is facilitated by the presence of $Zn[N(SiMe_3)]_2$. The X-ray data revealed their tetrametric nature of the boat-shaped Zn_4O_4 rings and the presence of alkoxide bridging. On the contrary, the neutral alcohol upon coordination forms the mononuclear compound $[PicMeOuZn(SC_6F_5)_2]$ (see Table 8). The same differences between deprotonated and neutral forms of hydroxypyrazoles, leading to polynuclear or mononuclear complexes have been observed upon coordination to Cu(II) and Co(II) ions (vide supra).

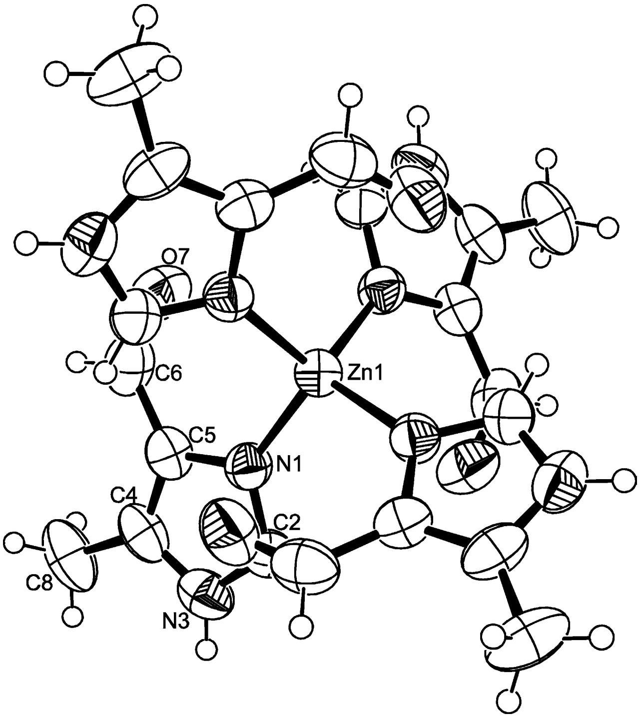


Fig. 11. The structure of Zn(II) complex with 4-CHO-5-MeIm [61].

It is evident that the importance of zinc derives from its role in enzymes, with functions that are both structural and catalytic. Therefore, a comparison of the zinc and cadmium complexes ought to provide a solidly based example of how metal ion substitution may perturb the structure of the active site of zinc enzyme. Moreover, cadmium has been designated as a human carcinogen by the International Agency for Research on Cancer and the US National Toxicology Program [67,68] For such a comparison, two Cd(II) complexes with aldehydeimidazole have been synthesized from ethanolic solutions of 4-CHO-5-MeIm and $Cd(NO_3)_2$ in 2:1 and 4:1 molar ratio for $[Cd(4\text{-}CHO\text{-}5\text{-}MeIm)_2(NO_3)_2]$ [83] (**1**) and $[Cd(4\text{-}CHO\text{-}5\text{-}MeIm)_4](NO_3)_2$ [61] (**2**), respectively. The complexes obtained are rare examples of distorted dodecahedron geometry brought about by the presence of N,O donors in small-molecule ligands. It is noteworthy that coordination number of 8 is the stable one because in the case of species **1**, in which the cadmium can bond only for donor atoms from two molecules of aldehydeimidazole, it completes the eight-coordination environment by additionally bonding two nitrate anions in didentate fashion (See Fig. 12). The structural data for $[Cd(4\text{-}CHO\text{-}5\text{-}MeIm)_2(NO_3)_2]$ indicate that cadmium ions coordinate eight atoms in double coordination sphere. The internal coordination sphere consists of two nitrogen atoms of imidazoles and two oxygen atoms from nitrate anions (one oxygen atom from each coordinating nitrate anion) with the bond length Cd—donor atoms ranging from 2.252(2) to 2.371(2) Å. The second coordination sphere is composed of four oxygen donors with the Cd–O distances of 2.543(2)–2.756(2) Å. The observed Cd–O bond distances (Table 8) are in good agreement with the values previously reported for eight-coordinated cadmium(II) complexes [74–79].

In the $[Cd(4\text{-}CHO\text{-}5\text{-}MeIm)_4](NO_3)_2$ [61] complex, the four 4-CHO-5-MeIm molecules act as N,O didentate lig-

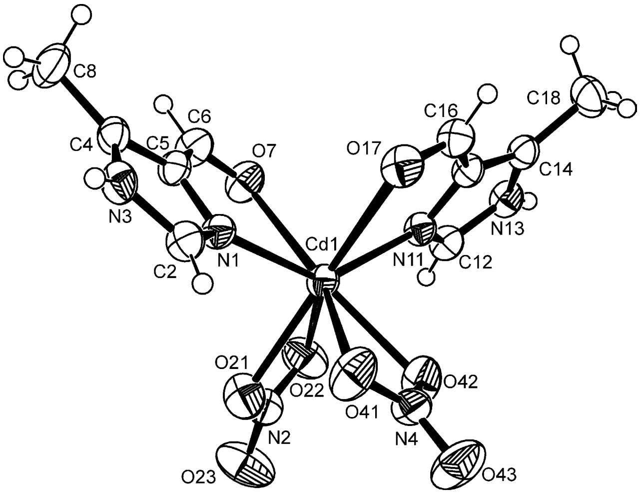


Fig. 12. The structure of Cd(II) complex with the 4-CHO-5-MeIm (M:L, 1:2) [83].

ands, in contrast to the same ligand in [Zn(4-CHO-5-MeIm)$_4$](NO$_3$)$_2$ compound (vide supra) where ligands bind to zinc only by the N pyridine-like nitrogen atom of imidazole ring indicating a preference for tetrahedral ZnN$_4$ coordination. The shape of eight-coordinating polyhedron of Cd complex can be described as a distorted dodecahedron with four oxygen atoms occupying the vertices with four neighbours and the four nitrogen atoms, which are in the vertices with five neighbours (see Fig. 13).

Cadmium–nitrogen and cadmium–oxygen distances (Table 8) are similar to those observed for other N,O-eight-coordinated complexes [74–79]. The possibility that an alternative coordination mode of 4-CHO-5-MeIm to Cd(II) and Zn(II) ions (didentate or monodentate, respectively) exists, can be explored by NMR spectra recorded in D$_2$O solution [61]. The ^{1}H resonance of the aldehyde proton is shifted by 0.15 ppm or by 0.08 ppm to lower fields compared to the free aldehyde, for Cd(4-CHO-5-MeIm)$_4{}^{2+}$ and Zn(4-CHO-5-MeIm)$_4{}^{2+}$, respectively. The same mode of coordination is confirmed, too, by NMR data for 1-Pr-2-CHOIm with Zn(II) ion in aqueous solution (D$_2$O). The most important conclusion derived from potentiometric investigations on Zn(II) and Cd(II) complexes with alcohol and aldehydeimidazoles (Table 9; Fig. 14) is that complexation in aqueous solution occurs in a different way for each metal cation. The plot of the

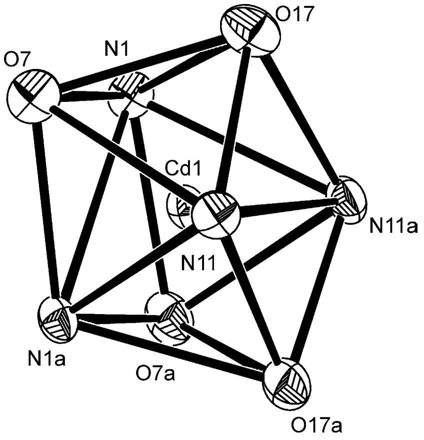


Fig. 13. Scheme of the coordination polyhedron of [Cd(5-Me-4-CHOIm)$_4$]$^{2+}$ cation [61].

Table 9
Stability constants of imidazole and some imidazole derivatives with Zn(II) and Cd(II) ions in aqueous solution at 298 K and $I = 0.5$ mol dm^{-3} (KNO$_3$)

Ligand	pK_a	Central ion	log β_1	log β_2	log β_3	log β_4	log β_5	log $^*\beta_1$	Reference
Im$^{\mathbf{1}}$	7.12	Zn(II)	2.56	4.89	7.16	9.19	–	−4.56	[21]
		Cd(II)	2.67	4.87	6.01	7.14	–	−4.45	[21]
1-MeIm$^{\mathbf{2}}$	7.19	Zn(II)	2.70	4.80	–	–	–	−4.49	[80]
		Cd(II)	2.73	4.64	6.30	6.80	–	−4.46	[61]
2-MeIm$^{\mathbf{3}}$	8.05	Zn(II)	1.88	3.99	7.49	9.32	–	−6.17	[81]
		Cd(II)	2.78	4.74	5.84	–	–	−5.27	[61]
1,2-DMeIm$^{\mathbf{4}}$	8.21	Zn(II)	1.92	4.32	7.11	9.00	9.62	−6.29	[23]
1-Me-2-CHOIm$^{\mathbf{5}}$	5.16	Zn(II)	1.41	2.24	3.88	–	–	−3.75	[25]
		Cd(II)	1.38	2.20	3.85	–	–	−3.78	[61]
4(5)-MeIm$^{\mathbf{6}}$	7.80	Zn(II)	2.44	4.97	7.61	9.99	–	−5.36	[27]
		Zn(II)	2.48	5.06	4.74	10.52	12.62	−5.32	[36]
		Cd(II)	2.65	4.65	6.30	6.70	–	−5.15	[36]
4(5)-CH$_2$OHIm$^{\mathbf{7}}$	6.67	Zn(II)	2.04	4.48	6.10	8.12	–	−4.63	[24]
		Cd(II)	2.01	4.06	4.93	6.37	–	−4.66	[24]
4,5-DMeIm$^{\mathbf{8}}$	8.19	Zn(II)	2.48	–	–	–	–	−5.71	[26]
		Cd(II)	2.48	4.30	–	–	–	−5.71	[26]
4-Me-5-CHOIm$^{\mathbf{9}}$	4.20	Zn(II)	1.59	3.18	3.96	–	–	−2.61	[61]
1-Ex-2-MeIm$^{\mathbf{11}}$	6.83	Zn(II)	1.88	3.33	5.67	7.13	–	−4.95	[82]
		Cd(II)	2.20	3.80	4.70	–	–	−4.63	[82]
1-Et-2-CH$_2$OHIm$^{\mathbf{12}}$	7.02	Zn(II)	2.19	4.94	6.37	7.67	–	−4.83	[30]
		Cd(II)	2.27	4.25	5.48	6.60	–	−4.75	[30]
1-PrIm$^{\mathbf{13}}$	7.22	Zn(II)	2.62	4.68	7.25	9.19	9.99	−4.60	[29]
		Cd(II)	2.60	4.92	6.96	8.74	10.20	−4.62	[61]
1-Pr-2-MeIm$^{\mathbf{14}}$	8.24	Zn(II)	1.35	4.40	7.45	9.41	10.45	−6.89	[32]
		Cd(II)	2.56	4.06	5.57	–	–	−5.68	[61]
1-Pr-2-CH$_2$OHIm$^{\mathbf{15}}$	7.04	Zn(II)	2.07	4.92	6.11	7.42	–	−4.97	[30]
		Cd(II)	1.99	4.19	5.03	6.25	–	−5.05	[30]
1-Pr-2-CHOIm$^{\mathbf{16}}$	5.15	Zn(II)	1.65	2.11	4.19	–	–	−3.50	[32]
		Cd(II)	1.45	2.45	3.76	–	–	−3.70	[61]

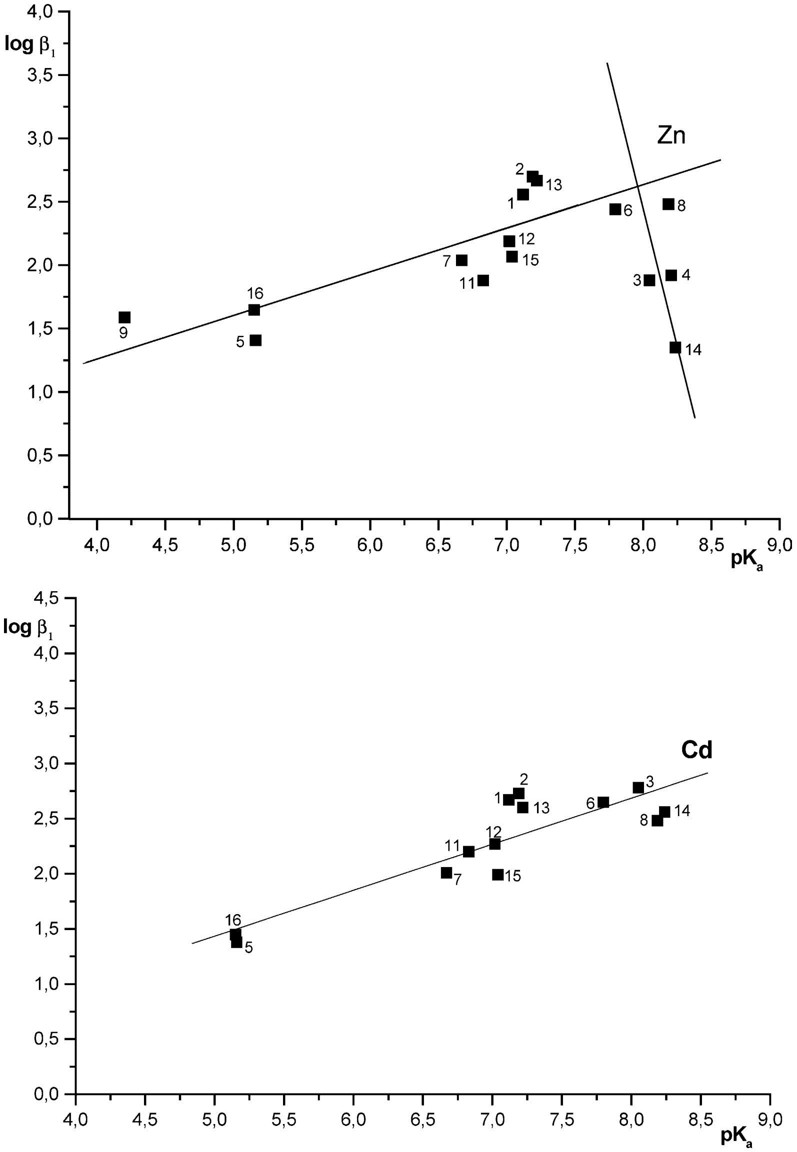


Fig. 14. Plots of log $\beta_1 = f(\mathrm{p}K_a)$ for the Zn(II) and Cd(II) complexes with imidazole derivatives (**1–9**, **11–16**) from Table 9 (R_c = 0.783 and 0.881).

correlation between the values of log β_1 of Zn(II) complexes and the ligand basicity is similar to that obtained for Co(II) complexes with the same ligands (see Figs. 7 and 14) and intimates the possibility of establishment of a configurational equilibrium, occurring as early as the first complex (equation (6)):

$$\begin{gathered}[\mathrm{Zn(H_2O)_5L}]^{2+} \leftrightarrows [\mathrm{Zn(H_2O)_3L}]^{2+} + 2\mathrm{H_2O} \\ \text{octahedral} \leftrightarrow \text{tetrahedral}\end{gathered} \qquad (6)$$

On the other hand, based on the stability constants (Table 9) and on the same correlation for Cd(II) complexes, it can be concluded that the stability of cadmium compounds, contrary to those of zinc, is practically independent of the steric hindrance to complexation presented by some ligands. All of the experimentally obtained points are found on one line (Fig. 14). The coordination process in the case of cadmium complexes, suggests successive displacement of water molecules from the coordination sphere of the central ion by the ligands, the basic structure being retained:

$$[\mathrm{Cd(H_2O)_6}]^{2+} + n\mathrm{L} \leftrightarrows [\mathrm{Cd(H_2O)}_{6-n}\mathrm{L}_n]^{2+} + n\mathrm{H_2O} \qquad (7)$$

Moreover, NMR data [61] have shown that for heterocyclic aldehydes, an additional equilibrium takes place during the coordination process (Scheme 1). The preference for coordination number 6 or 8 by cadmium and 4 by zinc ions in aldehydeimidazole complexes cannot be explained by the ligand-field stabilization energy gain, which is not open to closed shell d^{10} ions. Therefore, it is suggested that differences in the radii of these ions might be a reason why cadmium prefers dodecahedral coordination, whereas the zinc ion in complexes prefers tetrahedral structure in its aldehyde complexes.

5. Conclusions

This review shows that the X-ray data of heterocyclic alcohols and aldehydes chelated with Cu(II), Co(II), Zn(II) and Cd(II) ions correlate well with potentiometric and NMR studies of those compounds in aqueous solution. Moreover, it shows the versatility of hydroxyalkyl and aldehyde derivatives of imidazole, pyrazole or pyridine as ligands to bind metal ions. The existence of a tautomeric equilibrium of the asymmetrically substituted hydroxymethyl (4-CH$_2$OH-5-MeIm) or aldehydeimidazole (4-CHO-5-MeIm) allows these ligands to be not only monodentate (N donors) but also didentate (N,O donors). In addition, upon coordination with metal ions, pyrazole and pyridine alcohols exist in their neutral or deprotonated forms, which are more likely to form dinuclear or polynuclear complexes. The data extracted from a comparison of Zn(II) and Co(II) model complexes with N,O-donor ligands shows that zinc exhibits a different structure (tetrahedral) from those of the cobalt complexes (octahedral). This observation should not be ignored when using these metals as spectroscopic probes for studying zinc enzymes. The differences in the structure of the Cd(II) (coordination number 8) and Zn(II) (coordination number 4) complexes with aldehydeimidazoles, recognized by X-ray, IR, NMR and potentiometric methods confirm that the geometries of the cadmium active sites may not be similar to those of the native zinc enzymes. This may be a pointer to the reason for the differences in activity of the substituted enzymes. On the other hand, the identical structure of Cu(II) and Cd(II) complexes with 4-CHO-5-MeIm (distorted dodecahedral) can lead to replacing the natural cofactor, e.g. Cu, by a heavier metal. This may constitute one of the possible pathways for heavy-metal intoxication of redox process in living organisms.

References

[1] D.J. Creighton, J. Hajdu, D.S. Sigman, J. Am. Chem. Soc. 98 (1976) 4619.
[2] C. Sudbrake, B. Műller, H. Vahrenkamp, Eur. J. Inorg. Chem. (1999) 2009.
[3] B. Műller, H. Vahrenkamp, Eur. J. Inorg. Chem. (1999) 117.
[4] B. Műller, H. Vahrenkamp, Eur. J. Inorg. Chem. (1999) 137.
[5] M. Tesmer, B. Műller, H. Vahrenkamp, J. Chem. Soc. Chem. Commun. (1997) 721.
[6] B. Műller, A. Schneider, M. Tesmer, H. Vahrenkamp, Inorg. Chem. 38 (1999) 1900.
[7] X.M. Chen, B.H. Ye, X.C. Huang, Z.T. Xu, J. Chem. Soc. Dalton Trans. (1996) 3465.
[8] R. Mukherjee, Coord. Chem. Rev. 203 (2000) 151.
[9] J.E. Weder, C.T. Willon, W. Hambley, B.J. Kennedy, P.A. Lay, J.R. Biffin, H.L. Regtop, N.M. Davies, Coord. Chem. Rev. 232 (2002) 95.
[10] E. Kim, E.E. Chufan, K. Kamaraj, K.D. Karlin, Chem. Rev. 104 (2004) 1077.
[11] B.L. Vallee, D.S. Auld, Biochemistry 29 (1990) 5647.
[12] W. Kaim, J. Chem. Soc. Dalton Trans. (2003) 761.
[13] R.J.P. Williams, J.J.R. Fraústo da Silva, Coord. Chem. Rev. 200–202 (2000) 247.
[14] T. Dudev, C. Lim, Chem. Rev. 103 (2003) 773.
[15] J. Reedijk, in: G. Wilkinson, R.D. Gillard, J.A. Mc Cleverty (Eds.), Comprehensive Coordination Chemistry, vol. 2, Pergamon, Oxford, 1987, p. 73.
[16] E.C. Constable, P.J. Steel, Coord. Chem. Rev. 93 (1989) 205.
[17] E. Bouwman, W.L. Driessen, J. Reedijk, Coord. Chem. Rev. 104 (1990) 143.
[18] F. Mani, Coord. Chem. Rev. 120 (1992) 325.
[19] R. Carballo, A. Castiñeiras, B. Covelo, E. García-Martínez, J. Niclós, E.M. Vázquez-López, Polyhedron 23 (2004) 1505.
[20] C. Pettinari, F. Marchetti, A. Cingolani, S.I. Troyanov, A. Drozdov, Polyhedron 17 (1998) 1677.
[21] G. Berton, C. Luca, Anal. Chim. Acta 51 (1970) 239.
[22] E.K. Sklenskaya, M.Kh. Karapet'yants, Russ. J. Inorg. Chem. 11 (1961) 1102.
[23] B. Lenarcik, B. Barszcz, J. Chem. Soc. Dalton Trans. (1980) 24.
[24] J. Kulig, J. Kurdziel, B. Barszcz, B. Lenarcik, Pol. J. Chem. 65 (1991) 2159.
[25] J. Kulig, unpublished data.
[26] B. Lenarcik, K. Kurdziel, Pol. J. Chem. 55 (1981) 737.
[27] Y. Nozaki, F.R.N. Gurd, J. Am. Chem. Soc. 79 (1957) 2123.
[28] K. Kurdziel, T. Głowiak, J. Jezierska, Polyhedron 21 (2002) 1857.
[29] B. Lenarcik, B. Barszcz, Pol. J. Chem. 53 (1979) 963.
[30] J. Kulig, B. Barszcz, B. Lenarcik, Pol. J. Chem. 66 (1992) 79.
[31] B. Barszcz, T. Głowiak, J. Jezierska, Polyhedron 18 (1999) 3713.
[32] B. Barszcz, J. Kulig, J. Jezierska, J. Lisowski, Pol. J. Chem. 73 (1999) 447.
[33] B. Barszcz, J. Kulig, J. Chem. Soc. Dalton Trans. (1993) 1559.
[34] B. Lenarcik, J. Głowacki, M. Gabryszewski, R. Czopek, Pol. J. Chem. 64 (1990) 43.
[35] M. Rzepka, J. Kulig, Chem. Anal. 37 (1992) 659.
[36] B. Lenarcik, K. Obłąk, Ann. Soc. Chim. Polonorum (Roczniki Chem.) 51 (1977) 2079.
[37] B. Lenarcik, B. Barszcz, J. Kulig, Ann. Soc. Chim. Polonorum (Roczniki Chem.) 51 (1977) 1315.
[38] J. Lewis, R.G. Wilkins, Modern Coordination Chemistry, Interscience Publishers, New York, 1960.
[39] B. Barszcz, M. Gabryszewski, J. Kulig, B. Lenarcik, J. Chem. Soc. Dalton Trans. (1986) 2025.
[40] H. Sigel, Chem. Soc. Rev. 33 (2004) 191.
[41] M.J. Sánchez-Moreno, A. Fernández-Bottello, R.B. Gómez-Coca, R. Griesser, J. Ochocki, A. Kotynski, J. Niclós-Gutiérrez, V. Moreno, H. Sigel, Inorg. Chem. 43 (2004) 1311.
[42] R.B. Martin, H. Sigel, Comments Inorg. Chem. 6 (1988) 285.
[43] H. Sigel, S.S. Massoud, R. Tribolet, J. Am. Chem. Soc. 110 (1988) 6857.
[44] H. Sigel, S.S. Massoud, N.A. Corfii, J. Am. Chem. Soc. 116 (1994) 2958.
[45] H. Sigel, L.E. Kapinos, Coord. Chem. Rev. 200–202 (2000) 563.
[46] J. Sadlej, A. Jaworski, K. Miaskiewicz, J. Mol. Struct. 274 (1992) 247.
[47] C. Őğretir, S. Yaligan, J. Mol. Struct. (Theochem.) 366 (1996) 227.
[48] S.-G. Cho, Y.-G. Chevn, B.-S. Park, J. Mol. Struct. (Theochem.) 432 (1998) 41.
[49] G.-S. Li, M.F. Ruiz-López, M.-S. Zhang, B. Maigret, J. Mol. Struct. (Theochem.) 442 (1998) 197.
[50] M. Charton, J. Org. Chem. 30 (1965) 3346.
[51] M.R. Grimmett, Adv. Heterocycl. Chem. 27 (1980) 241.
[52] A.R. Katritzky, C.W. Rees, M.R. Grimett, Comprehensive Heterocyclic Chemistry, vol. 5, Pergamon Press, 1984, p. 363.
[53] M. Kurzepa, J.C. Dobrowolski, A.P. Mazurek, J. Mol. Struct. 565–566 (2001) 107.
[54] W.L. Driessen, Recl. J. The Royal Netherlands Chem. Soc. 12 (1982) 441.
[55] W.L. Driessen, S. Gorter, W.G. Haanstra, L.J.J. Laarhoven, J. Reedijk, K. Goubitz, F.R. Seljée, Recl. Trav. Chim. Pays-Bas 112 (1993) 309.

[56] A.R. Oki, J. Sanchez, R.J. Morgan, J. Coord. Chem. 36 (1995) 167.

[57] W.L. Driessen, B. Maase, J. Redijk, H. Kooijman, M.T. Lakin, A.L. Spek, Inorg. Chim. Acta 300–302 (2000) 1099.

[58] B. Barszcz, T. Głowiak, J. Jezierska, K. Kurdziel, Inorg. Chem. Commun. 5 (2002) 1056.

[59] B. Barszcz, T. Głowiak, J. Jezierska, A. Tomkiewicz, Polyhedron 23 (2004) 1309.

[60] M. Melnik, Coord. Chem. Rev. 42 (1982) 259.

[61] B. Barszcz, S. Hodorowicz, K. Stadnicka, A. Jabłońska-Wawrzycka, Polyhedron 24 (2005) 627.

[62] V.I. Sokol, M.A. Porai-Koshic, V.P. Nikolaev, E.S. Domnina, L.V. Baikalova, G.G. Skvorcova, L.A. Butman, Koord. Khim. 5 (1979) 1725.

[63] E.S. Domnina, J.A. Teterin, L.V. Baikalova, G.G. Skvorcova, Koord. Khim. 12 (1986) 175.

[64] K. Kurdziel, T. Głowiak, J. Jezierska, Inorg. Chem. Commun. 6 (2003) 459.

[65] B. Barszcz, T. Głowiak, K. Detka, Polyhedron 22 (2003) 1329.

[66] F. Paap, E. Bouwman, W.L. Driessen, R.A.G. de-Graaff, J. Reedijk, J. Chem. Soc. Dalton Trans. (1985) 737.

[67] International Agency for Research on Cancer Monographs, Cadmium, vol. 58, IARC Press, Lyon, 1993, p. 119.

[68] M.P. Waalkes, J. Inorg. Biochem. 79 (2000) 241.

[69] B.L. Valee, D.S. Auld, Biochemistry 29 (1990) 5647.

[70] J.E. Coleman, Annu. Rev. Biochem. 61 (1992) 897.

[71] J.M. Berg, H.A. Godwin, Annu. Rev. Biophys. Biomol. Struct. 26 (1997) 357.

[72] D.W. Christianson, J.D. Cox, Annu. Rev. Biochem. 68 (1999) 33.

[73] G. Parkin, Chem. Rev. 104 (2004) 699.

[74] A.A. Naiini, V. Young, J. Verkade, Polyhedron 3 (1995) 393.

[75] N. Niklas, F. Hampel, G. Liehr, A. Zahl, R. Alsfasser, Chem. Eur. J. 23 (2001) 5135.

[76] J.M. Grevy, F. Tellez, S. Bernès, H. Nöth, R. Contreras, N. Barba-Behrens, Inorg. Chim. Acta 339 (2002) 532.

[77] F. Hueso-Ureña, S.B. Jiménez-Pulido, M.N. Moreno-Carretero, M. Quirós-Olozábal, J.M. Salas-Peregrín, Inorg. Chim. Acta 227 (1998) 103.

[78] E.R. Acuña-Cueva, R. Faure, N.A. Illan-Cabeza, S.B. Jimènez-Pulido, M.N. Moreno-Carretero, M. Quirós-Olozábal, Inorg. Chim. Acta 342 (2003) 209.

[79] M.A. Romero, M.N. Moreno, J. Ruiz, M.P. Sánchez, F. Nieto, Inorg. Chem. 25 (1986) 1498.

[80] B. Lenarcik, B. Barszcz, Ann. Soc. Chim. Polonorum (Roczniki Chem.) 51 (1977) 1849.

[81] B. Lenarcik, J. Kulig, P. Laidler, Ann. Soc. Chim. Polonorum (Roczniki Chem.) 48 (1974) 1151.

[82] B. Barszcz, T. Głowiak, A. Jabłońska-Wawrzycka, Transition Met. Chem., in press.

[83] B. Barszcz, S. Hodorowicz, K. Stadnicka, A. Jabłońska-Wawrzycka, J. Coord Chem. 58 (2005) 203.