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Equilibrium Study of Iminodi(methylenephosphonic) Acid Complexes with Some Metal Ions

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This article discusses coordination preferences of N-substituted iminodi(methylenephosphonic) acids to the different metal ions in an aqueous solution. These ligands exhibit high complexation efficiency towards divalent metal ions. This results from both dinegatively charged phosphonate groups as well as the imino nitrogen present in their structure. A significant preference for an equimolar stoichiometry has been demonstrated in these systems. The only exception is the N-2-methyltetrahydrofuryliminodi(methylenephosphonic) acid with a tetrahydrofuryl moiety, placed in the sterically favoured position that allows its oxygen atom to be an effective metal binding site. Specific interactions between metal ions and furyl oxygen results in higher binding ability of this ligand and a formation of 1:2 species. Coordination properties of iminodi(methylenephosphonic) acids are important factors to understand the role of the ligands and metal ions in biological systems. A summary presented in this review points on the direction of the research for future work in this area, which should be developed.

Key words: iminodiphosphonates, chemistry of complex equilibria, species in solution, stability constants, metal complexes

1. Introduction

Aminophosphonic and aminopolyphosphonic acids – iminodi(methylenephosphonic) acids and bisphosphonates are the phosphonic analogs of compounds, in which carboxylic groups are replaced by phosphonic moieties. Aminoalkylphosphonic acids constitute a unique class of simple mimetics of amino acids [1,2]. In most of their biological effects they compete with their carboxylic acid counterparts for the active sites of enzymes and other cell receptors. Such a competition frequently results in diverse and interesting biological and biochemical properties. Thus, aminophosphonic acids display their activity as antibacterial agents, neuromodulators, anticancer and antihypertensive drugs or plant growth regulators. The aminopolyphosphonic acids are used for industrial purposes, such as scale inhibitors, in paper and textile industry and for the removal of trace amounts of metal ions from bleaching baths [3–5]. These compounds also have different analytical applications based on their remarkable metal binding properties, mainly as solvent extraction reagents in the separation of d- and f-elements [4,6–9], and as a titrant for the direct and indirect methods of titration for the analysis of various metal ions and binary mixtures of metals [10]. Ami-

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nopolyphosphonic acids and their derivatives have received considerable attention, because of their interesting biological activity. Aspects of the biological properties and interesting applications of aminophosphonates have been reviewed [1,2,11].

Bisphosphonates having the P-C-P moiety in the molecule are now established as an important class of drugs for the treatment of many bone diseases [11]. Several bisphosphonates (*e.g.* etidronate, clodronate, pamidronate, alendronate, tiludronate, risedronate and ibandronate) are effective treatments for diseases such as Paget's disease of bone, myeloma and bone metastases, hypercalcemia of malignancy, as well as osteoporosis. They are also used in radiodiagnosis as ligands for ^{99m}Tc. A group of aminomethylenebisphosphonic acids is also found to act as potent herbicides that inhibit biosynthesis of aromatic amino acids [12–17]. However, their targets at cellular level are still poorly understood, but the available biochemical data suggest that they should be considered as a heterogenous group of compounds with various modes of action. It is the most likely that their herbicidal activity derives from their simultaneous action on several enzymes. Since some enzymes inhibited by bisphosphonates are metal-dependent ones, the complexing properties of these compounds may be of vital importance for the exerted inhibition and require realiable data on the stability constants of the corresponding complexes [18]. These data permit modelling and prediction of the technological, environmental and pharmaco-kinetic equilibrium. So, chemical speciations based on numerical chemical equilibrium data are of extreme importance for different applications.

N-Substituted iminodi(methylenephosphonic) acids are very effective and specific ligands for a variety of metal ions. They contain a range of potential donor atoms and the complexes formed demonstrate a variety of coordination modes.

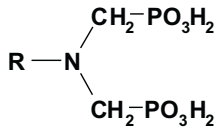
The main aim of this review is collecting information on the stability constants and the presentation of specific interactions in M(II)–iminodi(methylenephosphonic) acid systems, displaying unusual binding modes or very high complex stabilities that involve additional interactions to the direct coordination of a metal ion to a ligand donor system. Some emphasis is laid on spectroscopic methods to understand complex equilibria in solution in the whole range of pH.

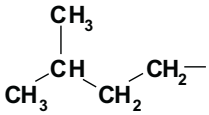
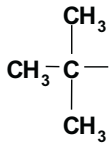
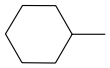
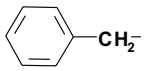
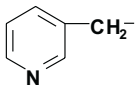
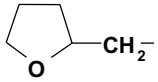
The first part of this review deals with the acid-base properties of the considered ligands, which are consistent with electronic effect of the substituents attached to the imino nitrogen. The second part describes the binding properties of iminodi(methylenephosphonic) acids in copper(II) complexes. A formation of tridentate bonded species has been demonstrated in these systems. The third part of the review reports what is known about zinc(II), cadmium(II) and alkaline-earth metal ion complexes of the same ligands. While the imino nitrogen is mainly bonded in the zinc(II) systems, alkaline-earth metal ions prefer rather pure phosphonate coordination. The interactions of manganese(II), cobalt(II) and nickel(II) ions with N-substituted iminodi(methylenephosphonic) acids are described in the next part of this review. For these complexes the formation of eight-membered rings is reported. In the last two sections the results for oxovanadium(IV) and trivalent metal ions are presented.

2. Coordinative behaviour of N-substituted iminodi(methylenephosphonic) acids towards selected metal ions

Most papers, which have discussed complexes of N-substituted iminodi(methylenephosphonic) acids, involve **Hdmph** [19–25], **Medmph** [19,26–29], **Etdmph** [19,21,28–30], **Ptdmph** [19,28,29], **Budmph** [21], **Hxdmph** [19,21,28,29], **Bzdmph** [19,21,28,29], **Pidmph** [19,28,29] and **Fudmph** [19,28,29].

2.1 Acidity constants. Scheme 1 lists the N-substituted iminodi(methylenephosphonic) acids considered in this review. Crystal structures are known for some, *e.g.* for: **Hdmph**, **Medmph**, **Etdmph** and **Hxdmph** [19,31,32].



R = H-	Iminodi(methylenephosphonic) acid	**Hdmph**
CH_3—	N-methyliminodi(methylenephosphonic) acid	**Medmph**
CH_3–CH_2—	N-ethyliminodi(methylenephosphonic) acid	**Etdmph**
	N-iso-pentyliminodi(methylenephosphonic) acid	**Ptdmph**
	N-tert-butyliminodi(methylenephosphonic) acid	**Budmph**
	N-cyclohexyliminodi(methylenephosphonic) acid	**Hxdmph**
	N-benzyliminodi(methylenephosphonic) acid	**Bzdmph**
	N-3-picolyliminodi(methylenephosphonic) acid	**Pidmph**
	N-2-methyltetrahydrofuryliminodi(methylenephosphonic) acid	**Fudmph**

Scheme 1. The N-substituted iminodi(methylenephosphonic) acids.

All the compounds studied have three common functional groups: imino and two phosphonate moieties. **Pidmph** also possesses the pyridine ring nitrogen. The acid dissociation constants reviewed below were determined by potentiometric measurements [20–28,30], some were confirmed by spectroscopic methods [20,27,30].

The fully protonated forms of **Hdmph**, **Medmph**, **Etdmph**, **Ptdmph**, **Budmph**, **Hxdmph**, **Bzdmph** and **Fudmph** contain five dissociable protons (H_5L^+) (two at each phosphonic function $-PO_3H_2$ and one at the imino nitrogen, $-NH^+_{imino}$), and six protons in the case of **Pidmph** (H_6L^{2+}) (due to additional proton at the pyridine nitrogen atom $-NH^+_{pyr}$). The first protons of the two $-PO_3H_2$ groups are very acidic (pK ≈ 1.0–2.0), and, thus, they are fully deprotonated in the pH range studied by the potentiometric method (2–12.5) and do not take part in metal coordination equilibria. The acid dissociation constants of these protons are not given in Table 1; in some cases, however, they have been determined and can be found in [21–23,27,30].

Table 1. Proton dissociation constants (pK) of N-substituted iminodi(methylenephosphonic) acids at 25°C.

Ligand	$pK_{NH^+_{pyr}}$	$pK_{PO_3H^-}$	$pK_{PO_3H^-}$	$pK_{NH^+_{imino}}$	Medium I [mol dm^{-3}]	Ref.
Hdmph	–	5.28	6.26	9.71	0.1 (KCl)	[20]
	–	4.83	5.82	10.62	1.0 (KNO_3)	[21]
	–	4.90	5.82	10.40	0.5 (KNO_3)	[22]
	–	5.04	6.08	10.79	0.1 (KNO_3)	[23]
	–	4.85	6.12	10.97(3)	0.2 (KCl)	[24]
	–	4.86	5.82	10.60(1)	0.2 (KCl)	[19]
Medmph	–	5.00	6.23	11.93	0.1 ($NaClO_4$)	[26]
	–	4.90	6.04	12.10	0.1 (KNO_3)	[27]
	–	4.79	5.95	11.75(1)	0.2 (KCl)	[28]
Etdmph	–	4.68	5.92	11.98	1.0 (KNO_3)	[21]
	–	4.69	6.04	12.2	0.2 (KCl)	[28]
	–	4.70	5.92	12.42	1.0 (KNO_3)	[30]
Ptdmph	–	4.87	6.21	12.3	0.2 (KCl)	[28]
Budmph	–	4.16	7.62	11.99	1.0 (KNO_3)	[21]
Hxdmph	–	4.57	5.87	11.93	1.0 (KNO_3)	[21]
	–	4.70	6.09	12.5	0.2 (KCl)	[28]
Bzdmph	–	4.59	5.96	11.15	1.0 (KNO_3)	[21]
	–	4.73	6.19	11.32(1)	0.2 (KCl)	[28]
Pidmph	2.94	4.93	6.09	10.40(1)	0.2 (KCl)	[28]
Fudmph	–	4.79	6.13	11.46(1)	0.2 (KCl)	[28]

Proton dissociation constant: $K_{H_nL} = [H_{n-1}L][H]/[H_nL]$; $pK_{H_nL} = -\log K_{H_nL}$. The standard deviations are given in parentheses.

The most basic donor of all ligands is the imino group. The last pK's of the iminodi(methylenephosphonic) acids range from 10.5 to 12.5 and, accordingly, have been assigned to the imino nitrogen. The acid-base properties of the iminodiphosphonic acids differ from those of aminomonophosphonates. The pK values characteristic for the dissociation of $-NH_3^+$ in the aminomonophosphonic acids are ≈ 10–11 [33–37].

The high basicity of this donor of the iminodi(methylenephosphonic) acids stems from the high negative charge of the two deprotonated dinegative phosphonic groups [38]. On the other hand the presence of the imino group in the iminodi(methylenephosphonic) acids increases the acidities of both $–PO_3H^-$ groups as compared with alkyl-1,n-diphosphonic acids [39–45] (the pK values characteristic for the dissociation of $–PO_3H^-$ groups are ≈ 8.4–10.0 and ≈ 7.0–8.0).

The pK value characteristic for the dissociation of pyridine nitrogen ($–NH^+_{pyr}$) of the **Pidmph** ligand is generally lower than those of the simple pyridine ligands [37]. The presence of a positively charged imino group results in the high acidity of the pyridine nitrogen [28].

The change of pK values determined for the iminodi(methylenephosphonic) acids is consistent with electronic effects of the substituents attached to the imino nitrogen (Table 1). The most distinct effect is observed for the imino nitrogen. The basicity of the imino group varies in the sequence: (Table 1)
Pidmph < **Hdmph** < **Bzdmph** < **Fudmph** < **Medmph** < **Etdmph** < **Ptdmph** < **Hxdmph.**

The $pK_{NH^+_{imino}}$ values of the iminodi(methylenephosphonic) acids with alkyl substituents (**Medmph**, **Etdmph** and **Ptdmph**) increase with a growth in the number of carbon atoms in the alkyl group and with the degree of branching of the carbon chain: **Hdmph → Medmph → Etdmph → Ptdmph**. Thus, the substitution of the hydrogen atom by more electrodonating izopentyl group increases the electron density on the nitrogen atom (the difference between the $pK_{NH^+_{imino}}$ values of **Hdmph** and **Ptdmph** is 1.7 log units) [28].

The presence of the acid strengthening aromatic rings decreases $pK_{NH^+_{imino}}$ values for **Pidmph** and **Bzdmph** as compared to **Medmph**; the highest acidity of the $–NH^+_{imino}$ group corresponds to the stronger electron withdrawing effect of pyridine than that manifested by benzene ring [28]. The introduction of the cyclohexyl ring as the substituent increases $pK_{NH^+_{imino}}$ for about 2 log units compared to the corresponding pK value of **Hdmph**.

The difference between the pK values of the corresponding $–PO_3H^-$ groups is not as big as the difference between the pK's of the imino groups. The $pK_{PO_3H^-}$ value derived for **Ptdmph** is about 0.4 log unit greater (Table 1) than the corresponding value derived for **Hdmph**, which suggests that the influence of the substituents attached to the imino nitrogen is less important in the case of the phosphonic groups than in the case of imino nitrogen.

2.2 Metal ion binding to N-substituted iminodi(methylenephosphonic) acids. Most papers on complexes with these ligands relate to divalent transition metal ions and especially to copper(II) [20,21,23,24,26–28], cobalt(II) and nickel(II) [20,21,23,26,27,29]. Zinc(II) and cadmium(II) complexes were investigated too [19,23,26,27]. Very few papers contain results on iron(II) [23,27] and manganese(II) complexes [21,23,27,29]. Complexes of lead(II) and trivalent metal ions such as iron(III), aluminium(III) and lanthanum(III) were considered in [23]. The alkaline-earth metal ions were also studied [19,21,23,26,27,30].

Generally, N-substitued iminodi(methylenephosphonic) acids form with metal ions equimolar complexes, but neither 1:2 species nor any polynuclear ones. Only system with **Fudmph** contains protonated and non protonated 1:2 species, which results from the presence of an additional coordination site – furyl oxygen. Specific interactions between metal ions and furyl oxygen result in higher binding ability of this ligand and the formation of 1:2 species.

2.2.1 Copper(II) complexes. The complexing properties of Cu^{2+} ions differ from those of the other ions studied, and, therefore, the discussion will first focus on the systems with copper. As mentioned above, copper(II) complexes were investigated by several authors. However, the first reliable results were obtained by Buglyo *et al*. [24] for **Hdmph**, Sawada *et al*. [27] for **Medmph**, and Kurzak *et al*. [28] for all these ligands presented. In the system with **Hdmph** apart from equimolar complexes (at lower ligand excess [23,24]), 1:2 complexes appear too (at higher ligand excess [24]). For the $[Cu(HL)]^-$ species it was assumed that one of the phosphonate groups is protonated and the central imino group remains coordinated, whereas in species $[Cu(H_2L)]$ protonation takes place on the imino group as reflected in the significant decrease in $A_{||} = 137 \cdot 10^{-4}$ cm^{-1} and increase of $g_{||} = 2.39$ values [24]. The variation of the $g_{||}$ and $A_{||}$ parameters is a widely used criterion for structural identification of the coordination sphere of Cu^{2+} ion, provided by the polyfunctional ligands [46–49,38]. The spectroscopic (UV-Vis, EPR) and pH-metric results indicate the tridentate (1N, 2O) coordination of the ligand in the equatorial plane of the mono fully deprotonated complex $[CuL]^{2-}$ (Table 2). The $[CuL_2]^{6-}$ complex is very likely a 2N species. The ligand molecules occupy five coordination sites around Cu^{2+}: the second ligand molecule occupies an equatorial (–N) and axial ($-PO_3^{2-}$) position to the tridentately bound $[CuL]^{2-}$, which is unambiguously reflected in the significant decrease in $A_{||}$ parameter and also in the occurrence of a characteristic shoulder ~ 10420 cm^{-1} (960 nm) in the visible spectrum (Table 2) [24,50–52]. The tridentate + bidentate binding mode also explains the formation of a mixed hydroxo complex $[CuLH_{-1}]^{3-}$. The displacement of one ligand molecule by OH^- indicates its weaker binding to the metal ion [24]. Such a process is generally not observed for the bidentate aminophosphonate complexes containing two five-membered chelate rings in the equatorial plane around Cu^{2+} [34,35,53,54].

Ligands: **Medmph**, **Etdmph**, **Ptdmph**, **Hxdmph**, **Bzdmph** and **Pidmph** exhibit a similar Cu^{2+}-coordination pattern [28]. The systems with these ligands contain only equimolar complexes in the pH range of 2–11.5. The data presented in [26] describe protonated 1:2 complex, but there is no spectroscopic evidence, which would confirm this finding. The single difference was found for the system with **Pidmph**, which apart from species: protonated $[Cu(H_2L)]$ and $[Cu(HL)]^-$, deprotonated $[CuL]^{2-}$ and hydroxo $[CuLH_{-1}]^{3-}$ and $[CuLH_{-2}]^{4-}$ involves an additional $[Cu(H_3L)]^+$ species (~15% at low pH). In this species the binding mode is $\{PO_3^{2-}, PO_3H^-\}$ with pyridine and imino nitrogens protonated ($-NH^+_{pyr}$, $-NH^+_{imino}$). These observations were additionally proven by electronic absorption and EPR studies [28]. The relatively low energy of the d-d transition at around 12940 cm^{-1} (773 nm) and also the EPR parameters

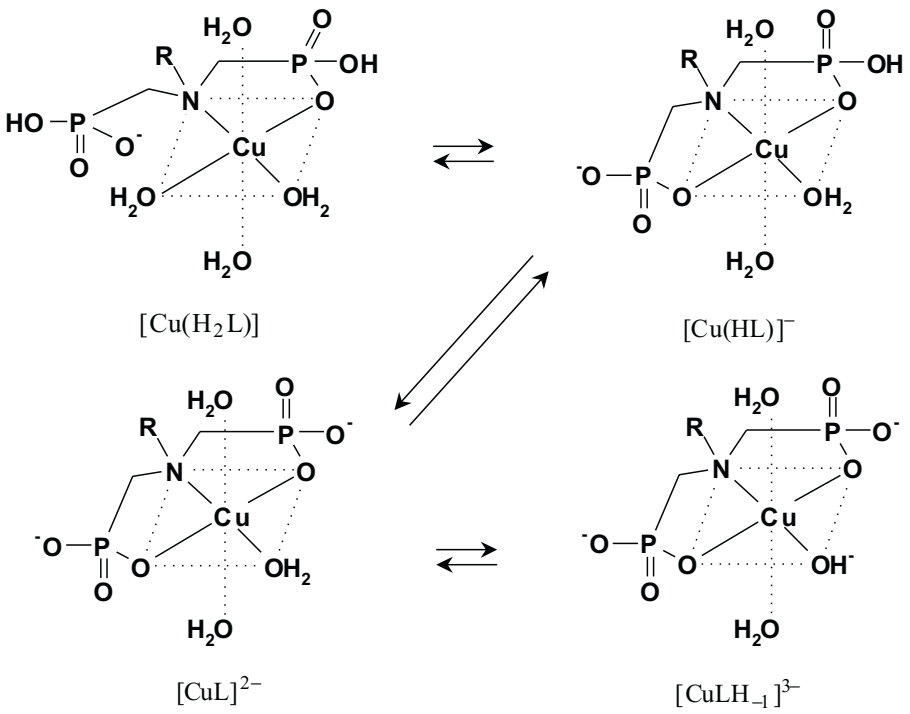
($A_{||} = 145 \cdot 10^{-4}$ cm^{-1} and $g_{||} = 2.355$) imply, that the coordination sphere around the copper(II) in plane consists of oxygen atoms as the only donors. For a species with two monoprotonated phosphonic functions, this transition ranges from 12820 to 12500 cm^{-1} (780–800 nm) [38,55].

Table 2. Spectroscopic parameters (EPR, UV/Vis) for copper(II) complexes of N-substituted iminodi-(methylenephosphonic) acids.

Ligand	Species	Ligand binding mode	EPR		UV/Vis	Ref.
			$A_{\|\|}$ [10^{-4} cm^{-1}]	$g_{\|\|}$	$\bar{\nu}_{max}$ 10^{-3} [cm^{-1}]	
Hdmph	$[CuL]^{2-}$	$\{1N_{imino}, 2PO_3^{2-}\}_{eq}$	150	2.33	13.51	[24]
	$[CuL_2]^{6-}$	$\{2N_{imino}, 2PO_3^{2-}\}_{eq}$ + $\{1PO_3^{2-}\}_{ax}$	128	2.33	13.53 10.42^{sh}	
Medmph	$[CuL]^{2-}$	$\{1N_{imino}, 2PO_3^{2-}\}_{eq}$	158	2.328	13.76	[28]
Etdmph	$[CuL]^{2-}$	$\{1N_{imino}, 2PO_3^{2-}\}_{eq}$	156	2.327	13.77	[28]
Ptdmph	$[CuL]^{2-}$	$\{1N_{imino}, 2PO_3^{2-}\}_{eq}$	157	2.325	14.00	[28]
Hxdmph	$[CuL]^{2-}$	$\{1N_{imino}, 2PO_3^{2-}\}_{eq}$	157	2.315	14.68	[28]
Bzdmph	$[CuL]^{2-}$	$\{1N_{imino}, 2PO_3^{2-}\}_{eq}$	157	2.325	13.97	[28]
Pidmph	$[CuL]^{2-}$	$\{1N_{imino}, 2PO_3^{2-}\}_{eq}$	157	2.328	14.16	[28]
Fudmph	$[CuL]^{2-}$	$\{1N_{imino}, 2PO_3^{2-}\}_{eq}$ + $\{1O_{furyl}\}_{ax}$	152	2.313	13.11	[28]
	$[CuL_2]^{6-}$	$\{2N_{imino}, 2PO_3^{2-}\}_{eq}$ + $\{2O_{furyl}\}_{ax}$	160	2.279	13.25	

The coordination in the $[Cu(H_2L)]$ species is realized by the $\{PO_3H^-, N_{imino}\}$ donor set [28]. EPR parameters of the protonated species, $g_{||} \sim 2.34$ and $A_{||} \sim 147 \cdot 10^{-4}$ cm^{-1}, formed with **Medmph**, **Etdmph**, **Ptdmph**, **Hxdmph**, **Bzdmph** and **Pidmph** at pH 3.6 are apparently different from those found for Cu^{2+} ions, coordinated by oxygen donors of phosphonic groups as the only ligands [56,57] (in which $g_{||} = 2.400$ and $A_{||} = 143 \cdot 10^{-4}$ cm^{-1}). This fact confirms the participation of the imino nitrogen and phosphonic group in the chelate ring of $[Cu(H_2L)]$ (Scheme 2).

The formation of the $[Cu(HL)]^-$ species has only a small effect on d-d transition. Thus, for this species the proposed binding mode is $\{PO_3^{2-}, N_{imino}, PO_3H^-\}$ (Scheme 2). However, the tridentate character of the donor set results in a small but detectable increase $A_{||} \sim 153 \cdot 10^{-4}$ cm^{-1} and decrease $g_{||} \sim 2.333$ [28]. The formation of $[CuL]^{2-}$ follows the liberation of the proton from the weakly coordinated $-PO_3H^-$ group, which consequently becomes more strongly bound to Cu^{2+}. This process is accompanied by a significant shift of the d-d transition to higher energies, for example: from 13250 cm^{-1} (755 nm) for $[CuHL]^{-1}$ to 14010 cm^{-1} (714 nm) for $[CuL]^{2-}$ (L = Ptdmph) [28]. The $[CuL]^{2-}$ complexes are predominant species in solution in the pH range about 6–9. An evident increase in $A_{||}$ and decrease in $g_{||}$ values (Table 2) can be treated as a



Scheme 2. Tentative structures of the copper(II) complexes formed by **Medmph**, **Etdmph**, **Ptdmph**, **Hxdmph**, **Bzdmph** and **Pidmph**.

further indication that Cu^{2+} coordination is involving the $\{PO_3^{2-}, N_{imino}, PO_3^{2-}\}$ donor set [28]. Furthermore, two bands are observed corresponding to the CT transitions in the UV region [28]. A number of respective bands indicate clearly the diversity of the metal-bind donor set. The CT band at 36100–33110 cm^{-1} (277–302 nm) observed for the copper(II)–L systems (L = **Medmph**, **Etdmph**, **Ptdmph**, **Hxdmph**, **Bzdmph**, **Pidmph** and **Fudmph**) was interpreted as the $N_{imino} \rightarrow Cu^{2+}$ LMCT transition [58]. A similar range of energy was found for the copper(II)–aminobisphosphonic acid system [38]. The second band observed for these seven systems at 44440–43290 cm^{-1} (225–231 nm) is reasonably assigned to the $O^{2-} \rightarrow Cu^{2+}$ LMCT transition.

The energy order of the $N_{imino} \rightarrow Cu^{2+}$ LMCT transition in the $[CuL]^{2-}$ species displays hipsochromic effect (*i.e.* increasing energy) [28]:

Hxdmph < **Bzdmph** < **Ptdmph** < **Pidmph** < **Fudmph** < **Etdmph** < **Medmph**

A similar energy relation is observed for the second LMCT transition $O^{2-} \rightarrow Cu^{2+}$ [28].

The proposed binding mode for $[Cu(HL)]^-$ and $[CuL]^{2-}$ should be favoured by the stability increase, due to the simultaneous presence of two five-membered chelate rings in the molecule. The sterically possible simultaneous binding of the phosphonate oxygen of both phosphonic groups and imino nitrogen (Scheme 2) of these tridentate ligands to Cu^{2+} is reflected in a high stability constant for $[Cu(HL)]^-$ and $[CuL]^{2-}$ [27,28]. The X-ray structure of the copper(II) complex with **Etdmph** supports the

O,N,O-tridentate binding mode of the ligands with two fused chelate rings in the $[CuL]^{2-}$ complex [59].

Two further deprotonation processes of $[CuL]^{2-}$, leading to the formation of $[CuLH_{-1}]^{3-}$ [27,28] and $[CuLH_{-2}]^{4-}$ [28], were detected in potentiometry and correspond to the subsequent dissociation of the protons from coordinated water molecules. The first $[CuLH_{-1}]^{3-}$ complex exhibits slightly blue-shifted d-d band (from ~13740–14160 cm^{-1} (727–706 nm) to 13990–14510 cm^{-1} (715–689 nm) as the pH value is increased from ~7 to ~11) and is observed in the EPR spectrum ($g_{||} \sim 2.290$ and $A_{||} \sim 166 \cdot 10^{-4}$ cm^{-1}) [28]. Its geometry is similar to that of $[CuL]^{2-}$ with an OH^- group in place of a water molecule (Scheme 2). The characteristic change of the EPR parameters is consistent with replacement of a water molecule by an OH^- group in the metal plane, which has the much higher electron-donating ability of OH^- relative to that of H_2O [28,60].

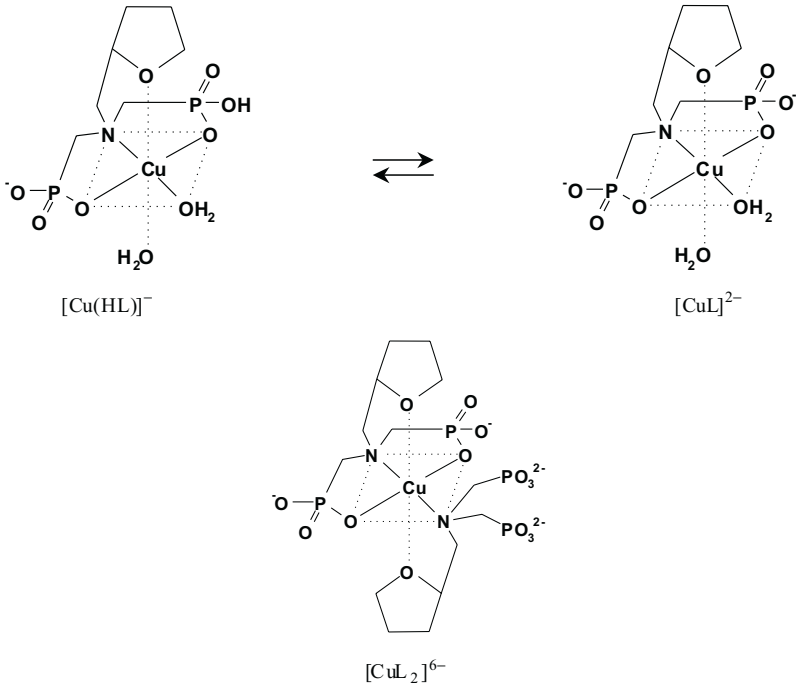
Fudmph is a more effective chelating agent than the others studied here, because of the strong interaction between Cu^{2+} and the furyl oxygen atom, which is placed in the sterically favoured position that allows it to occupy an axial position of the metal site. This is reflected in the higher basicity-adjusted stability constant (in order to normalize the basicity of the ligands), $\log K_{[CuL]} - \Sigma pK$ (Table 3) and also in the pH value of complexation of 20% of Cu^{2+}, which is ~ 5% for other ligands [28].

Table 3. Stability data for copper(II) complexes of N-substituted iminodi(methylenephosphonic) acids at 25℃ in 0.2 M KCl.

Ligand	$\log\beta_{[CuL]^{2-}}$	$\log K_{[CuL]^{2-}} - \Sigma pK$	Ref.
Hdmph	12.90(1)	–9.04	[24]
Medmph	13.82(1)	–8.67	[28]
Etdmph	13.26(1)	–9.67	[28]
Ptdmph	13.49(1)	–9.89	[28]
Hxdmph	12.69(1)	–10.60	[28]
Bzdmph	13.06(1)	–9.18	[28]
Pidmph	12.41(1)	–9.01	[28]
Fudmph	14.81(1)	–7.57	[28]

Overall formation constant: $\beta_{pqr} = [M_pL_qH_r]/[M]^p[L]^q[H]^r$; $\beta_{110} = K_{ML} = [ML]/[M][L]$.

The system with **Fudmph** contains not only 1:1 complexes but also protonated $[Cu(HL)_2]^{4-}$ and $[Cu(HL)L]^{5-}$ and non protonated $[CuL_2]^{6-}$ species. The most possible binding mode in some species, which is proposed by Kurzak *et al.* [28], is shown in Scheme 3. This type of interaction is observed in all the systems studied with this ligand (see below). The introduction of the tetrahydrofuryl ring as the substituent allows for the simultaneous participation of phosphonate O^- of both phosphonic groups, imino nitrogen and furyl oxygen in the binding to Cu^{2+}. This causes a growth in stabilities of about 1.6 log units compared to the other ligands considered (Table 3).



Scheme 3. Tentative structures of the copper(II) complexes formed by **Fudmph**.

The absorbance in the lower energy region is greatly enhanced for the $[CuL]^{2-}$ complex compared to those for corresponding species in the system with above mentioned ligands (Table 2). Such a spectral change, that is the red shift of the d-d absorption band, indicates the structural change around the copper(II) ion suggesting that the furyl oxygen atom occupies an axial position of the metal ion [61]. The relatively high energy of the d-d transition in the $[CuL_2]^{6-}$ species (13245 cm^{-1}) is probably the result of the two opposite effects. Occupying the axial position of the Cu^{2+} site by the furyl oxygen atom of the second ligand should cause a red shift relative to ν_{max} for $[CuL]^{2-}$, but coordination of the second N_{imino} donor in the equatorial position of the metal site should cause a blue shift relative to this complex. As a result of these two opposite effects, a 140 cm^{-1} (8 nm) shift to higher energies occurs in ν_{max} compared to that for $[CuL]^{2-}$ (Table 2). The EPR parameters (Table 2) also suggest that in the $[CuL_2]^{6-}$ complex of **Fudmph**, the ligand molecules occupy six coordination sites around Cu^{2+}. Thus, the second ligand molecule occupies an equatorial – (N_{imino}) and axial – (the furyl oxygen atom) sites to the tetradentate bound $[CuL]^{2-}$. The $[CuL_2]^{6-}$ complex has the same geometry as $[CuL]^{2-}$, *i.e*. tetragonal bipyramid (Scheme 3).

Because the spectroscopic parameters of $[CuL_2]^{6-}$ in the systems with **Hdmph** (no N-substituent) or **Fudmph** differ – the significant decrease in $A_{||}$ parameter and also in the occurrence of a characteristic shoulder ~10420 cm^{-1} (960 nm) in the visible spectrum of this complex (see above), which is evidence of axial coordination (ligand molecules occupy five coordination sites around Cu^{2+}), the assumption that in the

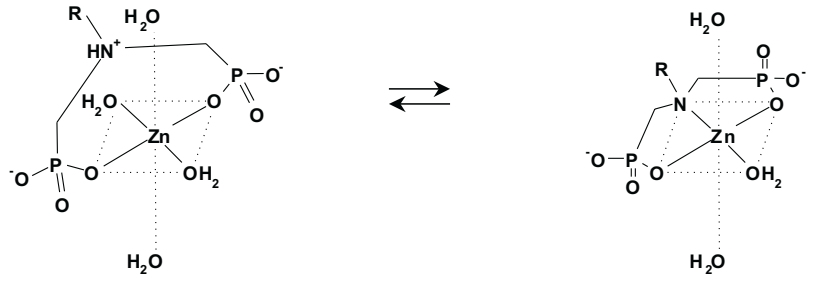
systems with **Fudmph** ligand molecules occupy six coordination sites around Cu^{2+} is supported (Table 2).

Bzdmph and **Pidmph** are also very effective ligands. Although the values of the overall stability constants of their $[CuL]^{2-}$ complexes ($\log\beta_{[CuL]^{2-}}$ in Table 3) are lower than the corresponding values of the complexes formed in the systems with aliphatic ligands, the presence of an aromatic ring results in a slight increase in the basicity-adjusted stability constant of the $[CuL]^{2-}$ species (Table 3). Such an effect with aromatic ligands was observed by other authors [34,35] and was explained by an interaction between the empty d orbital of the metal(II) ion and the 6π electron system of the aromatic rings.

2.2.2 Zinc(II), cadmium(II), magnesium(II), calcium(II), strontium(II) and barium(II) complexes. N-substituted iminodi(methylenediphosphonic) acids exhibited different complexation efficiency towards discussed metal ions. A significant preference for an equimolar stoichiometry is a common feature of these systems too (except for **Fudmph**). However, for **Medmph** the presence of 1:2 species was reported by Lukes and Dominak [26]. The amount of the tridentate species, as well as the pH region where they appear, strongly depend upon the cation binding ability towards the nitrogen donor. Thus, the tridentate complexes with two joined five-membered chelate rings predominate in solutions at pH of about 7–11 for the majority of the zinc and cadmium(II) systems. On the contrary, Ca(II) and Mg(II) prefer a pure phosphonate coordination.

According to the results presented in [19,27], the $[M(H_2L)]$ species is formed as a minor one. Deprotonation of this species leads to the formation of the [MHL] species. This species is dominant in the Mg(II)/Ca(II)–L systems in the pH range 6–10, whereas in the Zn(II)/Cd(II)–L systems the [ML] complex is dominant one in this pH range. In the systems with magnesium(II) or calcium(II), the [ML] complex starts to form just above pH 10. On the basis of comparative analysis of the stability and the spectroscopic (NMR) data [19,27], it has been established that in these two protonated forms $[M(H_2L)]$ and [MHL] ligand L coordinates to metal(II) ions only by the oxygen atom of the phosphonate group(s) and the imino nitrogen does not participate in coordination and an eight-membered chelate ring can be assumed [19] (Scheme 4). Such a type of chelate ring was postulated earlier in the literature, especially for the zinc(II) polyphosphonate complexes [30,62–66] and for the magnesium(II) and calcium(II) complexes with **Hdmph** [23], **Medmph** [27] and **Etdmph** [30]. The same binding mode, with an eight-membered chelate ring, was postulated by Sawada *et al*. [27] for the strontium(II) and barium(II) monoprotonated complexes.

However, for the $[ML]^{2-}$ complexes with zinc(II) and cadmium(II) the ligands coordinate to the metal(II) ions in a tridentate manner $\{PO_3^{2-}, N_{imino}, PO_3^{2-}\}$ forming two joined five-membered chelate rings (Scheme 4) [19,27], whereas for magnesium(II) or calcium(II) complexes Carter and Carroll [30] have suggested that binding Ca(II) and Mg(II) in **Etdmph** complexes is principally by the phosphonate group with little or no interaction by the imino nitrogen. On the other hand Sawada *et al*. [27] have postulated that both Ca(II) and Mg(II) form rather weak ionic $M–N_{imino}$ binds in com-



Scheme 4. Tentative structures of the zinc(II) complexes formed by **Medmph**, **Etdmph**, **Ptdmph**, **Hxdmph**, **Bzdmph** and **Pidmph**.

plexes with the unprotonated **Medmph**. Furthermore, the same team has assumed an identical binding mode for the strontium(II) and barium(II) complexes. The results presented in [19] (dealing with all the current ligands) seem to indicate that Ca(II) is not complexed through the imino nitrogen in $[CaL]^{2-}$, except for the case of **Fudmph**, see below.

The equilibrium model for the systems of **Fudmph** with zinc(II), magnesium(II) and calcium(II) is different, if compared with the systems mentioned above, due to the presence of an additional coordination site – a tetrahydrofuryl moiety. The potentiometry and the NMR titration data presented in [19] revealed, that the imino nitrogen is quite tightly binded to Zn(II) also in $[Zn(HL)]^-$ and ligand protonation occurs on the phosphonate moiety. The ^{31}P NMR chemical shifts for the system with **Fudmph** differ considerably from those for the systems with mentioned above ligands depending on pH. The pH region indicating a steep change in δ_P values moves by about 3 log units towards the acidic side, compared to the respective curves obtained for the other systems [19]. Finally, complexation of zinc(II) by the tetrahydrofuryl oxygen, resulted in tetradentate coordination of the ligand in both $[Zn(HL)]^-$ and $[ZnL]^{2-}$ (two positions are occupied by water molecules). This should play a significant role as a metal-nitrogen binding stabilization factor (Scheme 3). The coordination ability of the tetrahydrofuryl oxygen to Zn^{2+} has been well documented [67–69]. It was reported that Zn is tetrahedrally coordinated by a C_4H_8O ligand (Zn–O = 1.981(3) Å) [69].

Although the ligand coordination in the Ca(II)–**Fudmph** and Mg(II)–**Fudmph** complexes is the same, crystallographic studies confirm the coordination ability of Mg^{2+} and Ca^{2+} towards the tetrahydrofuryl oxygen [67–73], the metal-ligand interaction is much stronger for the former. The considerable affinity of Ca(II) for the tetrahydrofuryl oxygen seems to facilitate Ca(II)–N bond formation. Such binding, although weak (usually distances 2.5–2.7 Å) and rather seldom, has been proved by the crystal structures of several calcium complexes [74–79]. The $Mg–N_{imino}$ binding in the $[MgL]^{2-}$ complexes with **Hdmph**, **Medmph**, **Etdmph**, **Ptdmph**, **Hxdmph**, **Bzdmph** appears to be weaker than that with **Fudmph** and easily ruptured by protonation.

The data presented in [19] have shown that about pH 10.5, coordinated water molecules lose protons and $[ZnLH_{-1}]^{3-}$ and $[ZnLH_{-2}]^{4-}$ are formed. The $[ZnLOH]^{3-}$ species, which corresponds to $[ZnLH_{-1}]^{3-}$, was considered to be a mixed-hydroxo complex with L as a primary ligand and OH^- as a secondary one. In order to characterize the stabilities of the mixed-ligand complexes ΔlogK parameter was given (Table 4). $\Delta\log K = \log K^{ML}_{MLOH} - \log K^{M}_{MOH} = \log K^{MOH}_{MOHL} - \log K^{M}_{ML}$ expresses the effect of the binded primary ligand (L) towards the incoming secondary ligand (OH^-) in the $[ZnL]^{2-}$ species. The binding strength of OH^- in mixed-hydroxo complexes depends on the stability of $[ZnL]^{2-}$ which, in this case, does not mean that it depends on the basicity of the ligand. The tendency for the formation of mixed form decreases with increasing stability of the $[ZnL]^{2-}$ complex (Table 4). In systems with **Etdmph**, **Ptdmph** and **Bzdmph** the stability constants of the $[ZnL]^{2-}$ complexes are very close and this leads, as it was expected, to the almost identical ΔlogK parameters. The other observation is that **Hxdmph** shows the highest tendency to the formation of the mixed-hydroxo complex (the values of the ΔlogK parameter is the highest). From the above discussion, it can be concluded that in a case of bulky L binded in the zinc(II) equimolar complex, the coordination of small OH^- group is more favoured than that of the second ligand of the same kind.

Table 4. Stability data for magnesium(II), calcium(II) and zinc(II) complexes of N-substituted iminodi(methylenephosphonic) acids at 25°C in 0.2 M KCl [19].

Ligand	$\log\beta_{[ML]^{2-}}$			$\log K_{[ML]^{2-}} - \Sigma pK$			ΔlogK**/ for Zn^{2+}
	Mg^{2+}	Ca^{2+}	Zn^{2+}	Mg^{2+}	Ca^{2+}	Zn^{2+}	
Hdmph	3.47	3.11	*/ 9.03	–17.81	–18.17	*/–12.88	–
Medmph	4.74	4.11	9.68	–17.75	–18.38	–12.81	–0.54
Etdmph	4.25	3.71	9.33	–18.68	–19.22	–13.60	–0.16
Ptdmph	4.36	3.77	9.37	–19.02	–19.61	–14.01	–0.18
Hxdmph	4.04	3.39	8.67	–19.25	–19.90	–14.62	0.18
Bzdmph	4.34	3.88	9.39	–17.90	–18.36	–12.85	–0.20
Pidmph	4.25	3.69	9.21	–17.17	–17.73	–12.21	–0.29
Fudmph	5.06	6.03	10.85	–17.32	–16.35	–11.53	–1.38

*/ from ref. [23], at 25°C in 0.1 M KNO_3
**/$\Delta\log K = \log K^{ML}_{MLOH} - \log K^{M}_{MOH} = \log K^{MOH}_{MOHL} - \log K^{M}_{ML}$

Intriguing results were obtained for the zinc(II)–**Hdmph** and –**Medmph** systems. According to [19], new species are formed in these solutions. The NMR spectra revealed a slow (on the NMR timescale) exchange that was considered to result from the formation of polymeric species. The chelated Zn(II)–**Medmph** and Zn(II)–**Hdmph** units form one-dimensional chains *via* coordination binds from one phosphonate group. These chains further cross-link *via* coordination of the second phosphonate group towards Zn(II) of adjacent chains, thus forming a two-dimensional layer. It was established that the formation of these species is strongly dependent upon the metal to ligand stoichiometry and the solution concentration. The dilution of the systems

Zn(II)–**Hdmph** and Zn(II)–**Medmph** leads to disintegration of the layered organization and the formation of well characterized mononuclear complexes.

For the metal(II) complexes, as was observed in systems with copper(II) (see section 2.2.1), the decrease in the stability of the $[ML]^{2-}$ complexes with increasing the substituent size attached to the imino nitrogen (all the complexes in the systems with the same metal ion have a similar geometry) is noted with increasing the basicity of the coordinating donor groups: **Medmph** (CH_3) > **Etdmph** (C_2H_5) > **Hxdmph** (C_6H_{11}). The higher basicity of the coordinating ligands results in their lower effective binding ability. The contrary relation between the stability of the complexes and the basicity of the ligands (Table 4) indicate, that steric and electrostatic effects of the substituents are the distinct factors influencing the binding properties. In spite of the highest basicity, **Hxdmph** exhibits the lowest binding ability to zinc(II), magnesium(II) and calcium(II) metal ions. Steric hindrance associated with the presence of the cyclohexyl ring directly attached to the imino nitrogen seems to be the distinct factor influencing the complex-forming properties.

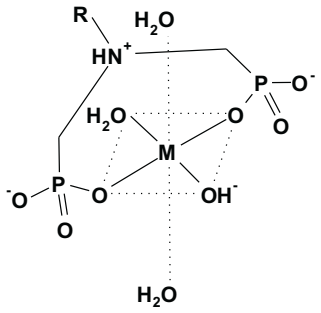
2.2.3 Manganese(II), iron(II), cobalt(II) and nickel(II) complexes. The interactions among N-substituted iminodi(methylenephosphonic) acids and manganese(II), iron(II), cobalt(II) and nickel(II) ions have been the subject of some papers [20,21,23,26,27,29], but most of these studies have been less systematic than those for copper(II) ions. The complexes were usually characterized by potentiometric measurement, except [20] and [29], in which a combined potentiometric and spectroscopic study was published. These results are often different and are not comparable.

The interaction of the manganese(II), cobalt(II) and nickel(II) ions and iminodi(methylenephosphonic) acid derivatives (**Hdmph**, **Medmph**, **Etdmph**, **Ptdmph**, **Hxdmph**, **Bzdmph** and **Pidmph**) led generally to the formation of equimolar protonated, deprotonated and hydroxo complexes $[M(H_2L)]$, $[M(HL)]^-$, $[ML]^{2-}$ and $[MLH_{-1}]^{3-}$ [23,27,29]. Iron(II) complexes were included in two papers only, in the systems with **Hdmph** [23] and **Medmph** [27], but bonding modes were not considered or author's suggestions were not confirmed by other methods. The overall stability constants of the manganese(II) complexes are distinctly lower if compared with those obtained for the cobalt(II) and nickel(II) complexes [23,27,29]. In systems of **Medmph** with cobalt(II) and nickel(II) the stability constants of the 1:2 complexes were determined by potentiometric method [26], but the formation of bis-complexes was not confirmed later. Chemical models in systems with some of these ligands proposed by Bel'skii *et al*. [21] are poor and the bonding modes were not considered. In addition $[M(H_3L)]^+$ species was also found in systems with **Pidmph** at low pH [29]. In this species the pyridine nitrogen is involved in the coordination and both PO_3^{2-} and N_{imino} groups remain protonated. In this case the phosphonate O^- is unable to coordinate the metal ion issued from steric reasons [29].

In present systems, only one species, $[M(H_2L)]$, is formed as a minor one. The protonated ligands coordinate to these metal ions by the phosphonate group(s) in a monodentate(bidentate) manner [27,29]. Deprotonation of $[M(H_2L)]$ leads to the formation of $[M(HL)]^-$ complex. In this species the protonated ligand coordinates to me-

tal ion by the phosphonate groups in a bidentate manner, without participation of the nitrogen atom [29].

The $[ML]^{2-}$ complex was found to be the dominant species in solution in the pH range 7–10 [20,21,23,27,29]. The formation of the $[ML]^{2-}$ species from $[M(HL)]^{-}$ does not generate considerable changes in the spectra of the cobalt(II) and nickel(II) systems, so the binding mode in both species might be the same. Thus, it was assumed that the real structure of the $[ML]^{2-}$ species is rather that of $[M(HL)OH]^{2-}$, in which the OH^{-} group is the result of the dissociation of a proton from a water molecule bound in the coordination sphere of the metal ion and N_{imino} remains protonated (Scheme 5). So, it was concluded that the coordination in the $[ML]^{2-}$ species is realized by both phosphonic groups $\{PO_3^{2-}, PO_3^{2-}\}$ with an eight-membered chelate ring and the N-atom is not coordinated [65]. The coordination of oxygen atoms to nickel(II) observed for the $[Ni(H_2O)_6](ClO_4)_2$ complex is beyond doubt (the CT band at 50510 cm^{-1} (198 nm)). Thus, the CT band at 47390–45050 cm^{-1} (211–222 nm) observed for the $[NiL]^{2-}$ species (L = **Medmph**, **Etdmph**, **Ptdmph**, **Bzdmph** and **Pidmph**) was reasonably assigned to the transition from PO_3^{2-} oxygen to Ni^{2+}, *i.e.* the $O^{2-} \rightarrow Ni^{2+}$ LMCT transition [29].



$[ML]^{2-}$ (M = Mn^{2+}, Co^{2+} and Ni^{2+})

Scheme 5. Tentative structures of the manganese(II), cobalt(II) and nickel(II) complexes formed by **Medmph**, **Etdmph**, **Ptdmph**, **Hxdmph**, **Bzdmph** and **Pidmph**.

Sawada *et al.* [27] have suggested that Mn^{2+}, Co^{2+} and Ni^{2+} form $M–N_{imino}$ bonds in the complexes with these ligands. On the other hand in the results presented by Zhadanov *et al*. [20] nitrogen complexation was not assumed. However, it should be noticed here that both authors have considered the bonding modes in the complexes basing only on the potentiometric results.

As the pH is raised, the deprotonation of $[ML]^{2-}$ leads to the formation of $[MLH_{-1}]^{3-}$. Because $[ML]^{2-} = [M(HL)OH]^{2-}$ (see above) it corresponds to the subsequent dissociation of the proton from the imino nitrogen atom. Since the $pK_{[ML]^{2-}}$ value is considerably lower than the corresponding dissociation constant of the free ligand (see Table 1), the coordination of the imino nitrogen atom with formation of two five-membered chelate rings in the molecule may be assumed. It was observed,

that in the case of the system with cobalt(II), the formation of this species is associated with preorganization at Co^{2+} binding site and changing geometry [29].

Similarly as it was observed in the systems with metal ions mentioned in the previous sections, specific interaction between metal ion and the furyl oxygen atom occurs in the presented systems too, the strongest in the system with cobalt(II) [29].

2.2.4 Oxovanadium(IV) complexes. According to our knowledge, there exists only one paper on equilibrium studies of oxovanadium(IV)-iminodi(methylenephosphonic) acid derivatives [25]. It relates to **Hdmph**. The system involves two equimolar complexes $[VOLH]^-$ and $[VOL]^{2-}$, one protonated 1:2 species – $[VOL_2H]^{5-}$, and different hydroxo species with polynuclear structure. At acidic pH (up to pH ≈ 6) the coordination of the phosphonate groups dominates to yield $[VOLH]^-$ composition ($A_{||} = 180 \cdot 10^{-4}$ cm^{-1}, $g_{||} = 1.93$, and $\nu^{i}_{max} = 15500$, 11500 cm^{-1} (645, 870 nm)). In the $[VOL]^{2-}$ complex, the ligand is tridentate and the nitrogen atom as well as a phosphonate group occupy two equatorial positions, while the second phosphonate moiety occupies an axial position of the metal site $\{1N_{imino}, 2PO_3^{2-}\}$. This complex exhibits $A_{||} = 171 \cdot 10^{-4}$ cm^{-1}, $g_{||} = 1.942$, which indicates the presence of the imino nitrogen atom coordinated in the equatorial plane. It was also supported by a significant shift of the d-d transition to higher energies. It was reported that the coordination of the second ligand molecule to the metal ion and the rise of the $[VOL_2H]^{5-}$ species is accompanied by a change in the EPR parameters ($A_{||} = 161 \cdot 10^{-4}$ cm^{-1}, $g_{||} = 1.942$). So, it could be assumed that, the coordination mode in this species is $\{1N_{imino}, 2PO_3^{2-}\}$, $\{1N_{imino}, PO_3^{2-}\}$ and protonation occurs on the phosphonate group in the non-coordinating arm of the second ligand. The coordination of the second ligand is hindered. The unavailability of a sixth coordination position and charge effects do not promote the full deprotonation of the second ligand, therefore, the $[VOL_2]^{6-}$ species is lacking in this system.

To gather information on the factors influencing the composition and structures of the complexes and to draw general conclusions, further studies with different derivatives of iminodi(methylenephosphonic) acids should be undertaken.

2.2.5 Iron(III), aluminium(III) and lanthanum(III) complexes. The solution chemistry of these metal ions has been the subject of a single paper [23]. According to the potentiometric results presented, the system with **Hdmph** and trivalent metal ions contains equimolar and bis complexes. However, because of lack structural studies, the coordination mode must be considered as inconclusive.

3. Concluding remarks

This review has confirmed that N-substituted iminodi(methylenephosphonic) acids exhibit a high complexation efficiency towards different metal ions. This results from the presence of the dinegatively charged phosphonate groups and the strong metal binder, which is the imino nitrogen.

The significant preference for an equimolar stoichiometry is a common feature of these systems. The formation of the bis complexes seems to be generally hindered, because of the electrostatic repulsion of the negatively charged phosphonate groups. However, the systems with N-2-methyltetrahydrofuryliminodi(methylenephospho-

nic) acid and different metal(II) ions contain protonated and non protonated 1:2 species, which results from the presence of the additional coordination site.

These ligands are very effective chelating agents towards copper(II). The coordination is realized by the phosphonate oxygen(s) and the imino nitrogen in the protonated and non protonated complexes as well. The cooperation of all three donor groups of these ligands in metal binding is made possible by the formation of two fused five-membered chelate rings.

The binding mode in the protonated zinc(II) and cadmium(II) complexes seems to be through the oxygen atoms. The imino nitrogen does not participate in coordination to the metal(II) ion and an eight-membered chelate ring may be assumed. However, in non protonated complexes ligands coordinate to the metal(II) ions in tridentate manner, forming two joined five-membered chelate rings. The only exception is N-2-methyltetrahydrofuryliminodi(methylenephosphonic) acid, in which the tetrahydrofuryl oxygen atom is sterically accessible for an additional effective binding to the metal ion. The involvement of the tetrahydrofuryl oxygen in the zinc(II) complexation strongly promotes nitrogen binding, which results in a tetradentate coordination not only in $[ZnL]^{2-}$, but also in the protonated complex.

In protonated complexes of magnesium(II), calcium(II), strontium(II) and barium(II) metal ions protonation occurs on the imino nitrogen atom and the ligand coordinate only by the phosphonate group(s) in a monodentate or bidentate manner. In the $[ML]^{2-}$ complexes the binding of metal(II) ion is principally by the phosphonate group with little or no interaction by the imino nitrogen, except for the case of N-2-methyltetrahydrofuryliminodi(methylenephosphonic) acid, where the ligand coordination in calcium(II) and magnesium(II) complexes is through the imino nitrogen.

The coordination in all the manganese(II), cobalt(II) and nickel(II) complexes seems to be by the phosphonic groups without the participation of the imino nitrogen.

In spite of the quite detailed studies of the complexes with iminodi(methylenephosphonic) acids, still a large part of experimental work, particularly on metal(III) complexes should be performed.

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