New complexanes. XXXVII. Acid-base properties of N-(carbamoylmethyl)iminodiacetic and N-(2-carbamoylethyl)iminodiacetic acid and the formation of their complexes with alkaline earth cations and bivalent cations of heavy metals

I. BENEDIKOVIČ, P. BALGAVÝ, J. MAJER, E. FÜLEOVÁ, and I. VALÁŠKOVÁ

Department of Analytical Chemistry, Faculty of Pharmacy, Komenský University, 880 34 Bratislava

Received 13 February 1979

Accepted for publication 11 April 1979

The preparation of N-(carbamoylmethyl)iminodiacetic and N-(2-carbamoylethyl)iminodiacetic acid is described. The results of study of the acid-base properties of these acids obtained by means of 'H-n.m.r. spectroscopy and potentiometric neutralization titration as well as the data about formation of complexes of these substances with Ca(II), Mg(II), Sr(II), Ba(II), Cu(II), Co(II), Cd(II), Ni(II), Pb(II), and Zn(II) obtained by means of direct potentiometric neutralization titration and paper electrophoresis are presented. The values of protonation constants K_{H2L} and K_{H2} and the values of stability constants log K_{ML} and log K_{M2} found under standard conditions at I = 0.1 (KNO₃) and 20°C are also given in this paper. The results are discussed from the view-point of formation of a coordination bond between the amide group and central ion in the complex ML. That bond does not arise in the complexes ML₂ containing the above cations.

Описывается приготовление N-(карбамоилметил)иминдиуксусной и N-(2-карбамоилэтил)иминдиуксусной кислот, результаты исследования их кислотно-основных свойств при помощи 'H-ЯМР спектроскопии и кислотно-основного потенциометрического титрования, а также данные об образовании комплексов этих соединений с Ca(II), Mg(II), Sr(II), Ba(II), Cu(II), Co(II), Cd(II), Ni(II), Pb(II) и Zn(II), полученные прямым кислотно-основным потенциометрическим титрованием и методом бумажного электрофореза. Приводятся значения констант протонирования $K_{\rm H2L}$ и $K_{\rm HL}$ и также значения констант устойчивости log $K_{\rm ML2}$ при стандартных условиях I = 0,1 (KNO₃) и температуре 20°С. Результаты обсуждаются с точки зрения образования координационной связи амидной группы с центральным ионом в комплексе ML. В комплексах ML₂ с приведенными катионами такая связь не образуется.

This paper deals with N-(2-carbamoylethyl)iminodiacetic acid (KEIDA)



from the view-point of possible coordination of the functional amide group in complexes of this acid with the alkaline earth cations Ca(II), Mg(II), Sr(II), Ba(II) or bivalent cations of the heavy metals Cu(II), Co(II), Cd(II), Ni(II), Pb(II), and Zn(II). Thus, we resume the work of *Schwarzenbach et al.* [1] who studied the possibility of coordination of the amide group with cations of the heavy metals and alkaline earth metals for *N*-(carbamoylmethyl)iminodiacetic acid (KMIDA). Another aim of our work was to find out how the formation of a six-membered chelate ring could affect the stability constants of the investigated complexes when compared with the complexes of KMIDA. In this study, the acid-base properties of both agents have been also studied by ¹H-n.m.r. spectroscopy and the results are confronted with potentiometric data.

Experimental

Preparation of KMIDA and KEIDA

Both substances were prepared by condensing iminodiacetic acid in middly alkaline medium with chloroacetamide (KMIDA) or chloropropionamide (KEIDA) mixed in equimolar amounts in a 50% solution of ethanol. A detailed description of preparation of both substances is the subject of a patent application [2].

The purification of both compounds was carried out by multiple crystallization from warm water at 80°C. After drying in a vacuum furnace, the substances were subjected to elemental analysis and their identity was verified by means of ¹H-n.m.r. and i.r. spectroscopy. The purity of substances was determined by potentiometric neutralization titration with the result KMIDA 99.87% and KEIDA 99.92%.

Potentiometric measurements

We prepared 4×10^{-3} mol dm⁻³ aqueous solutions of the investigated agents. The chemicals used and working procedure were like in preceding work [3, 4], and the instrumental technique was described in [5].

The protonation constants and stability constants of KEIDA with particular bivalent metal cations were calculated from the corresponding experimental pH values of neutralization curves on a calculator HP-97, Hewlett—Packard, according to a programme devised by us.

¹H-N.m.r. spectroscopy

The ¹H-n.m.r. spectra were measured on an NMR spectrometer Tesla BS 487 A (80 MHz) in the frequency sweep mode. The chemical shifts are referred to tetramethylsilane. The samples for measurement were prepared by dissolving KMIDA or KEIDA in D₂O so that their concentration was 0.2 mol dm⁻³. The pD values of solutions were adjusted by means of KOD and DCl and determined according to [6] as pD = pH_m + 0.40 where pH_m is the value read on a pH-meter with a combined microelectrode EA-125, Metrohm, Herisau, Switzerland. Tertiary butyl alcohol was used as an internal reference in the samples. Measurements were also carried out with solutions of KEIDA in trifluoroacetic acid. In this case, tetramethylsilane was applied as an internal reference. The chemical shift of *tert*-butyl alcohol with respect to tetramethylsilane was 1.29 p.p.m.

Electrophoretic measurements

The experimental procedures and evaluating technique of electrophoregrams are described in more detail in [7, 8].

Infrared spectroscopy

The spectra of KMIDA and KEIDA were measured on a spectrometer Perkin-Elmer 377 in KBr tablets.

Results and discussion

First of all, the structure of the prepared substances was verified by ¹H-n.m.r. spectroscopy. The typical spectra obtained are represented in Fig. 1. The ¹H-n.m.r. spectrum of KMIDA in D₂O solutions was very simple in the whole pD range. It consisted of two singlets with relative integral intensity 1 and 2. We attribute the singlet at higher values of magnetic field intensity to the H^a protons whereas the signal at lower field intensity to the H^b protons (denotation of protons in Fig. 2). The protons of each -CH₂ group are chemically and magnetically equivalent owing to fast inversion of the amine nitrogen similarly as it is in case of other complexanes [9]. The signals of protons belonging to heteroatoms are not observed because of fast exchange for water protons or substitution for D^+ in case of D_2O . The 'H-n.m.r. spectra of KEIDA in the pD range 0-14 were also fairly simple. It was a singlet with relative integral intensity 2 and two triplets, either with relative integral intensity 1. The assignment of signals to individual nonlabile protons based on elementary considerations about electron density on the protons in KEIDA is evident from Fig. 1 and designation of individual protons in Fig. 3. Two triplets in the spectrum are in reality an apparent simple spectrum of the type AA'BB'. This apparent simplification frequently occurs with substituted ethane [10]. The equivalence of both protons in the carboxymethyl --CH₂-- groups was, like in case of



Fig. 1. ¹H-N.m.r. spectra of KEIDA and KMIDA. 1. KEIDA, pD 5.56; 2. KEIDA, pD>14; 3. KEIDA, CF₃COOH; 4. KMIDA, pD 4.40.



Fig. 2. Variation of chemical shifts of signals of the nonlabile protons of KMIDA with pD of the solution.



Fig. 3. Variation of chemical shifts of signals of the nonlabile protons of KEIDA with pD of the solution.

KMIDA, due to fast inversion of the amine nitrogen. The signals of protons on heteroatoms were not observed like in case of KMIDA. By using a sample prepared by dissolving KEIDA in trifluoroacetic acid, a relatively broad signal with relative integral intensity equal to 1 appeared in the spectrum at $\delta = 7.38$ p.p.m. We attribute this signal to the protons which are bonded to the amide nitrogen of KEIDA. With asparagine and glutamine dissolved in CF₃COOH, the signal of the protons bonded to the amide nitrogen was observed as a broad singlet at $\delta = 7.39$ p.p.m. and $\delta = 7.58$ p.p.m., respectively [11]. If KEIDA dissolved in CF₃COOH was used, all signals were broadened and the spin-spin interaction of the H^b and H^c protons manifested itself only by asymmetry of the resonance signals in the spectrum. As for the samples with pD>14, some changes appeared in the spectrum of KEIDA. The signal of the protons H^c (BB' subspectrum of the spin system AA'BB') turns from triplet into multiplet and from the signal of the protons H^b is seen an increase in interaction constants. These changes may be due to a change in conformation of the fragment --CH2--CH2-- and in case of the protons H^c to a change in chemical shifts of their resonance signals (probably nonequivalence of B and B' in the subspectrum BB').

The verification of the structure of KMIDA and KEIDA by means of infrared spectroscopy was based on the identification of absorption bands of the functional groups $-CO(NH_2)$, -COOH or $-COO^-$. The wavenumbers of individual bands identified on the basis of comparison with literature data [12-14] are given in Table 1. The infrared spectra are in harmony with the suggested structures of the investigated substances. The splitting of the band Amide I [v(C=O)] evidences that KMIDA and KEIDA form dimers in the solid state through hydrogen bonds of the amide group.

and N-(2-carbamoylethyl)iminodiacetic acid (cm ⁻¹)									
Vibration	KMIDA	KEIDA	Group						
v(N-H) _{sym}	3280	3310	-NH ₂						
$v(N-H)_{antisym}$	3390	3380	NH ₂						
v(C=O) (Amide I)	1675, 1700	1670, 1685	= N-C ⁺⁰ CH ₂ -						
$\delta(NH_2)$ (Amide II)	1625	1620	-NH ₂						
v(N-H)	3040	3180	-NH ₂ assoc.						
v(C=O)	1720	1710	—СООН						
$v(CH_2)$	2965, 3020, 3090	2950, 2990, 3015	CH ₂						
v(COO ⁻)	1440	1450	COO-						

Table 1

Wavenumbers of the vibrational bands of N-(carbamoylmethyl)iminodiacetic acid and N-(2-carbamoylethyl)iminodiacetic acid (cm⁻¹)

The data from ¹H-n.m.r. spectroscopy may be profitably used for studying the acid-base properties of aminopolycarboxylic acids [9]. The protonation or dissociation of proton from heteroatom of a particular functional group brings about a change in electron density on nonlabile protons in the vicinity of this functional group and thus a change in chemical shifts of their ¹H-n.m.r. signals. The magnitude of the change in chemical shift is usually determined by induction effect so that the magnitude of this change for different nonlabile protons enables us in most cases to estimate unambiguously at which pH values of solution the particular functional groups protonize (or their protons dissociate). The experimental results of this study are summarized in Fig. 2 for KMIDA and in Fig. 3 for KEIDA. As for KEIDA, the chemical shifts for the protons H^a and H^b have been determined from resonance frequency of the most intensive signal in the subspectrum AA' and BB'. The error thus committed is smaller than $\Delta \delta = \pm 0.01$ p.p.m. in every case and can be neglected in the study of acid-base properties. It results from the experimental data in Fig. 2 that the protonation of KMIDA takes place in the pD region 9.2-5.5 and the change in chemical shift accompanying the protonation is $\Delta \delta = 0.58$ p.p.m. for the protons H^a and $\Delta \delta = 0.83$ p.p.m. for the protons H^b. The bonding of another proton is to be observed in the region pD < 3.4 and the change in chemical shift of the signal of the protons H^a and H^b is $\Delta \delta = 0.66$ p.p.m. and $\Delta \delta = 0.30$ p.p.m., respectively. It is obvious from the magnitude of the changes in chemical shifts that a protonation of the amine nitrogen of KMIDA must take place first and afterwards a protonation of the carboxyl groups succeeds. An equal conclusion is also valid for KEIDA. In this case, the change in chemical shift accompanying protonation in the pD region 11–7 is $\Delta \delta = 0.59$ p.p.m. for the protons H^a, $\Delta \delta = 0.67$ p.p.m. for the protons H^b, and $\Delta \delta = 0.36$ p.p.m. for the protons H^e. If the protonation takes place in the pD region 4-0, the change in chemical shift is $\Delta \delta = 0.54$ p.p.m. for the protons H^a, $\Delta \delta = 0.18$ p.p.m. for the protons H^b, and $\Delta \delta = 0.08$ p.p.m. for the protons H^c. Especially in the last case, the minimum change in chemical shift of the signal H^{c} is a direct evidence that the oxygen atoms of the carboxyl groups of these two complexanes are protonated only in the acid pD region. Thus the results of ¹H-n.m.r. spectroscopy unambiguously confirm that both KMIDA and KEIDA in aqueous solutions have betaine structure.

The signals of all nonlabile protons of KEIDA are shifted in the region pD > 14 to higher values of the intensity of magnetic field. The cause of this shift is not clear. A possibility of splitting off a proton from the amide nitrogen is little probable because the change in chemical shift of the H^a signal ought to be very small in this case. However, the experimental values are comparable for all three kinds of protons (H^a, H^b, H^c) in a molecule. It is not out of the question that the change in structure of the intramolecular hydrogen bonds (which is testified by the change in the spectrum in Fig. 1) or changes in character of the solvation of molecule are

responsible for the observed change in chemical shift.

The resulting values of protonation constants of the investigated substances obtained from potentiometric neutralization titration and ¹H-n.m.r. spectroscopic data are given in Table 2. It appears from potentiometric measurements as well as ¹H-n.m.r. spectroscopic measurements that the dissociation of protons takes place in separated buffered regions. The first proton dissociates much easier than the second one, which is in harmony with the assumption of betaine structure of the investigated substances in solution. The resulting values of protonation constants obtained from potentiometric measurements differ from the protonation constants obtained from ¹H-n.m.r. measurements. This is logical because of different solvents (H₂O and D₂O), ionic strengths, and concentrations of the solutions used for these measurements. It ensues from the resulting values of protonation constants thus obtained that a considerable increase in basicity of the amine nitrogen of KEIDA took place, which manifested itself by an increase in the value of $\log K_{\rm HI}$ by 1.77 units in comparison with KMIDA. The increase in this value may be explained by different structure of both substances. The negative induction effect of the amide group on nitrogen basicity in KEIDA is impaired by displacing the amide group from the amine nitrogen and shielding its effect by elongation of the side chain with

	KMI	IDA	KEIDA			
	a	b	С	b		
log К _{н2L} log К _{HL}	2.30 6.60	1.8 7.3	2.23 8.37	2.3 9.1		

 Table 2

 Protonation constants of KMIDA and KEIDA (I = 0.1 (KNO₃); $t = 20^{\circ}$ C)

a) Data taken from [1]; b) data obtained by 'H-n.m.r. spectroscopy; c) data from potentiometric measurements.

In relation to increasing basicity of nitrogen in KEIDA, an increase in stability constants of its complexes with bivalent metal cations when compared with those of KMIDA could be expected. If the amide functional group takes part in coordination in these complexes, a six-membered chelate ring is formed from KEIDA. This ring is energetically less preferable than the five-membered ring of the complexes arising from KMIDA. Therefore this factor affects the stability constants in the opposite way to the basicity of the amine nitrogen. As the influence of these factors cannot be appreciated, we studied the formation of the complexes containing KMIDA and KEIDA in more detail.

The curves of electrophoretic mobility of the complexes containing the investigated cations and KMIDA or KEIDA at varying pH value of the fundamental electrolyte solution are represented in Fig. 4. A formation of complexes with



Fig. 4. Electrophoretic mobility of the complexes of KEIDA and KMIDA. $U = \text{Actual electrophoretic mobility relative with respect to } (C_2H_5)_4\text{N}^+$; I = 0.1 (KNO₃); $t = 20^{\circ}\text{C}$, u = +1.00; pA = concentration of free ligand.

Analytical concentration of agents in the fundamental electrolyte $c_{\rm L} = 2 \times 10^{-2} \text{ mol dm}^{-3}$; analytical concentration of metals at application $c_{\rm M} = 5 \times 10^{-2} \text{ mol dm}^{-3}$.

KMIDA and KEIDA was not evidenced by means of these curves for Ba(II), Sr(II), and Mg(II) because the curves of mobility could not be recorded in anodic region owing to low stability of the arising complexes. The stability constants of the normal ML complexes of KMIDA and KEIDA with the ions of alkaline earths calculated by extrapolating the electrophoretic data on the assumption of zero mobility of ML are given in Table 3. A plateau corresponding to zero mobility which indicates formation of a neutral ML complex in the pH region 2.5-4.5 is outlined on the curves of mobility of Cd(II), Ni(II), Co(II), Cu(II) with KMIDA and Ni(II), Co(II), Cu(II) with KEIDA. It is obvious that a neutral complex of Pb(II) or Zn(II) with KMIDA is formed in the pH region 3.5-6.5 whereas an analogous complex with KEIDA arises in the pH region 2.5-6.0. An increased anodic mobility of all above-mentioned ions appears in alkaline region. In case of KEIDA, this mobility successively attains a steady value with increasing pH. This fact indicates formation of ML₂²⁻ complexes containing KEIDA. The stability constants of the ML and ML_2^{2-} complexes calculated from electrophoretic data are given in Table 3. The stability constants determined electrophoretically are in good agreement with the values obtained by potentiometric method. In most cases, the differences do not exceed the scope of deviations due to a smaller accuracy of the electrophoretic method.

Table 3

S	tability constants of	the complexes of h	MIDA [1] and I	KEIDA containing bi	valent metal cations	

Method		Constant	Mg	Ca	Sr	Ba	Со	Ni	Cu	Zn	Cd	Pb
KMIDA	1	$\log K_{\rm ML}$ $\log K_{\rm ML_2}$	2.47	3.96	3.03	2.88	6.91 3.30	8.02 3.88	9.68 3.26	7.30 2.24	7.08 3.60	8.40 2.24
	2	$\log K_{\rm ML}$	2.1	3.2	2.0	2.1	6.8	>7	>7	7.3	6.9	>7
KEIDA	1	log K _{ML} log K _{ML2}	3.78	3.93	2.94	2.90	8.13 4.05	9.34 4.71	10.47 4.24	8.12 3.82	6.52 4.60	8.09 1.94
	2	log K _{ML} log K _{ML2}	4.2	4.1	3.3	3.2	8.3 3.2	>9 3.6	>9 3.5	8.2 3.1	7.3 3.9	8.4 1.3

Data obtained by: 1. potentiometric method (I = 0.1 (KNO₃), $t = 20^{\circ}$ C); 2. paper electrophoresis.

The titration curves of KEIDA alone and in mixture with individual alkaline earth metal cations are represented in Fig. 5. Curves 1-5 in the diagram exhibit identical course in the region a < 1 and a > 2, which indicates the absence of processes involving a formation of complexes in the corresponding pH regions. This enables us to assume that neither hydrogen complexes nor hydroxo complexes are formed in the investigated solutions. In contrast, a different course of curves in the region 1 < a < 2, *i.e.* in that region where the ligand exists, in principle, in the form of the L^{2-} ions points to a formation of the ML complexes. Besides, we titrated the solutions of KEIDA which contained a tenfold excess of M^{2+} . The titration curves obtained are in full harmony with curves 2-5 which were got by titrations at equimolar ratio M^{2+} : KEIDA = 1 : 1 and are represented in that diagram. This fact indicates that no dinuclear complexes arise in the investigated systems or the stability of these complexes is very low.



According to the course of the titration curves of KEIDA with heavy metal ions, a gradual formation of the ML and ML_2 complexes may be observed. The titration curves in Fig. 6 corresponding to the mole ratio metal : ligand = 1 : 2 may serve for illustration. The course of these curves demonstrates formation of the ML and ML_2 complexes in separate buffered regions. We did not pursue investigations of the formation of hydrogen and hydroxo complexes in these systems though the character of these curves suggests a formation of hydroxo complexes for Cu(II),



KEIDA in the presence of half concentration of Pb(II) (2); Zn(II) (3); Co(II) (4); Cu(II) (5); Ni(II) (6).

I = 0.1 (KNO₃); $t = 20^{\circ}$ C; a = mol NaOH/mol KEIDA.

Pb(II), Zn(II), and Cd(II) at a > 2. The resultant values of stability constants of the ML and ML₂ complexes are given in Table 3.

The solution of the problem of participation of the amide group of KMIDA and KEIDA in coordination of bivalent ions may be based on two criteria. The first one is a comparison of log K_{ML} and K_{HL} for a particular complexane and a series of other typical tridentate or tetradentate complexanes which form two or three chelate cycles in the HL complexes. The comparison usually shows whether the increase in log $K_{\rm ML}$ is due to a formation of another chelate ring or to an increase in basicity of the amine nitrogen [1, 15]. We carried out such comparison for all ions investigated by using all available data concerning stability constants of the derivatives of iminodiacetic and nitrilotriacetic acid [16]. For illustration, we give the results obtained for stability constants of the Mg(II) complexes in Fig. 7. The correlation in this figure demonstrates that the stability constants of the ML complexes of KMIDA and KEIDA with Mg(II) correspond to stability constants of the complexes of the derivatives of Complexone I which are tetradentate substances and form complexes of the ML type by means of three chelate rings. Equal result was obtained for KMIDA and KEIDA and all other ions investigated except Cu(II). In this case, the value of $\log K_{ML}$ of the complex containing KEIDA corresponded to $\log K_{\rm ML}$ of tridentate agents.



Fig. 7. Correlation between $\log K_{ML}$ and $\log K_{HL}$ for tridentate derivatives of iminodiacetic acid.(1) and tetradentate derivatives of nitrilotriacetic acid (2).

Linear relationships were obtained by the method of least squares for (1) from 11 data and for (2) from 27 data found in literature [16].

The second criterion is based on comparison of $\log K_{ML}$ with $\log K_{ML}$, for the ions with coordination number 6 [1, 17]. If the ligand in the ML complex is tridentate, then the bonding of another molecule of the ligand involves possible formation of other three coordination bonds. In this case, the stability constant $K_{\rm ML_2}$ is relatively high and the difference $\Delta \log K_{\rm D} = \log K_{\rm ML} - \log K_{\rm ML}$, is small. However, if the ligand in the ML complex is tetradentate, the formation of the ML_2 complex must be connected with breaking of one coordination bond, which results in a relative decrease in $K_{\rm ML}$, and the difference $\Delta \log K_{\rm D}$ is thus relatively great. Such a comparison for typical tridentate (A) and tetradentate (B) agents and the structural analogues of KMIDA (C) is given in Table 4. It is obvious directly from the table without any more detailed analysis of the data that both KMIDA and KEIDA coordinate the ions Co(II), Ni(II), Zn(II), and Pb(II) as tetradentate agents in the ML complexes and as tridentate agents in the ML₂ complexes. As for Cu(II) and Cd(II), the situation is not clear. For Cu(II), the ratio $K_{\rm ML}/K_{\rm ML}$, is exceedingly high and has been preferably so explained that the coordination number of Cu(II) in complex compounds is equal to four [1]. Recently, it has been, however, revealed that the coordination number of Cu(II) in iminodiacetates and nitrilotriacetates is six while nitrilotriacetic acid in the ML complexes is tetradentate [18] and nitrilotriacetic and iminodiacetic acids in the ML_2 complexes are tridentate [19, 20]. The increase in $\Delta \log K_{\rm D}$ for the complexes KMIDA by more than one unit, therefore, gives evidence that KMIDA is tetradentate in the ML complexes at i tridentate in the ML₂ complexes. As for KEIDA, the situation is not clear and it seems that KEIDA in the presence of Cu(II) functions as a tridentate agent in both ML and ML₂ complexes. This conclusion is in agreement with the data concerning the correlation between log $K_{\rm ML}$ and log $K_{\rm HL}$ already discussed. As for the Cd(II) complexes, the value of $\Delta \log K_D$ indicates that KMIDA is tetradentate in the ML complex and tridentate in the ML_2 complex while KEIDA

Table 4

(4004409 _ 0.2)											
Cation		A			В			С			
	Ι	II	Ш	IV	V	VI	VII	VIII	IX	KMIDA	KEIDA
Co(II)	1.6	1.3	1.5	6.4	4.0	2.4	1.9	2.1	7.7	3.6	4.1
Ni(II)	2.1	1.5	1.3	6.6	4.4	3.4	2.2	2.4	7.8	4.1	4.6
Cu(II)	4.6	4.3	5.0	8.5	7.8	_	4.2	4.2	_	6.4	5.9
Zn(II)	1.9	1.2	1.7	7.1	4.9	2.4	3.1	3.2	_	5.1	4.3
Cd(II)	1.3	1.0	1.1	5.1	2.1	1.5	2.6	2.4	4.5	3.5	1.9
Pb(II)	_	3.9	3.8		5.3		_		9.3	6.2	6.2
CH₂—COOH				R					F	ł	
CH₂-COOH			I II III IV V	H CH ₃ CH ₃ (CH ₂ ((CH ₂)	С(СН ₃) СООН),ОН	2(CH2)	2	v	VI (VII C III C IX H	CH₂)₃OH CH₃(CO)CH C₅H₅(CO)CI I₂N(CH₂)₂	I2 H2

Difference $\log K_{\rm D} = \log K_{\rm ML} - \log K_{\rm ML_2}$ for the derivatives of iminodiacetic and nitrilotriacetic acid (accuracy ± 0.2)

From the values of stability constants for substances I-IX are taken from paper [16].

is tridentate in either case. However, this conclusion is in disagreement with the correlation between $\log K_{\rm ML}$ and $\log K_{\rm HL}$ which has shown unambiguously that KEIDA is tetradentate in the ML complex.

Finally, we confronted the influence of basicity of the amine nitrogen and the influence of steric factors on stability of the ML complexes. As the authors of paper [21] have shown, the dependence of $\log K_{\rm ML}$ on $\log K_{\rm ML'}$ for two structurally similar complexanes is linear with unit slope. Provided the formation of complexes is not affected by steric factors but only by basicity of the amine nitrogen, it must pass through the point log K_{LH} , log $K_{L'H}$. Two such graphs for KMIDA and KEIDA and KMIDA and its structural analogue, i.e. N-(2-oxopropyl)iminodiacetic acid (OPIDA) are represented in Fig. 8. A comparison of KMIDA with OPIDA shows clearly that the functional group --- NH₂ of KMIDA has a positive effect on stability of the ML complexes when compared with the -CH₃ group. As for KEIDA, the extension of chain between the amine and amide nitrogen by one ---CH₂--- group has a negative effect on stability of all investigated ML complexes except the complex with Mg(II). This negative effect manifests itself especially with the Cd(II), Pb(II), and Cu(II) ions. Except for Mg(II), the positive effect of increased basicity of nitrogen is overcome by the negative effect of steric factors.

N



Fig. 8. Stability constants log K_{ML} of the complexes of KMIDA, KEIDA, and OPIDA with bivalent cations.
 Full line: linear relationship passing through the point log K_{HL}, log K_{HL}, with unit slope.

Conclusion

Two new complexanes derived from iminodiacetic acid, *i.e.* N-(carbamoylmethyl)iminodiacetic acid and N-(2-carbamoylethyl)iminodiacetic acid, were prepared by a simpler method than the method described in literature [1]. These complexanes have betaine structure in aqueous solution. They form the ML complexes with the ions Mg(II), Ca(II), Sr(II), and Ba(II) and both ML and ML₂ complexes with the ions Co(II), Ni(II), Cu(II), Cd(II), and Pb(II). In the ML₂ complexes, the investigated complexanes are tridentate substances and the amide group does not take part in coordination. In the ML complexes KMIDA is a tetradentate complexane with respect to all ions and KEIDA is also a tetradentate complexane with respect to all ions except Cu(II) and likely Cd(II). The stability constants of the complexes of KEIDA except for Cd(II) and Pb(II) are higher than those of the complexes of KMIDA. However, the increase in stability constants does not correspond (except for Mg(II)) to increased basicity of the amine nitrogen in KEIDA with reference to KMIDA because of the steric hindrance due to the replacement of one five-membered ring by a six-membered ring accompanying formation of the complexes of KEIDA.

References

- 1. Schwarzenbach, G., Anderegg, G., Schneider, W., and Senn, H., Helv. Chim. Acta 38, 1147 (1955).
- 2. Majer, J. and Benedikovič, I., Czech. Appl. PV 1841-78.
- 3. Majer, J., Dvořáková, E., and Nagyová, M., Chem. Zvesti 20, 313 (1966).
- 4. Dvořáková, E. and Majer, J., Chem. Zvesti 20, 233 (1966).
- 5. Riečanská, E., Majer, J., Bumbálová, A., and Kalina, M., Chem. Zvesti 28, 332 (1974).
- 6. Mikkelson, K. and Nielson, S. O., J. Phys. Chem. 64, 632 (1960).
- 7. Jokl, V., Majer, J., and Mazáčová, M., Chem. Zvesti 18, 584 (1964).
- 8. Jokl, V. and Majer, J., Chem. Zvesti 19, 249 (1965).
- 9. Leyden, D. E. and Cox, R. H., Analytical Applications of NMR. J. Wiley, New York, 1977.
- 10. Bovey, F. A., Nuclear Magnetic Resonance Spectroscopy. Academic Press, New York, 1969.
- 11. Bak, B., Dambmann, C., Nicolaisen, F., and Pedersen, E. J., J. Mol. Spectrosc. 26, 78 (1968).
- 12. Horák, M. and Papoušek, D., Infračervená spektra a struktura molekul. (Infrared Spectra and Structure of Molecules.) Academia, Prague, 1976.
- 13. Silverstein, R. M., Bassler, G. C., and Morril, T. C., Spectrometric Identification of Organic Compounds. J. Wiley, New York, 1974.
- 14. Rajaballe, F. J. M., Spectrochim. Acta 30A, 891 (1974).
- 15. Irving, H. M. N. H. and Miles, M. G., J. Chem. Soc. A1966, 1268.
- 16. Martell, A. E. and Smith, R. M., Critical Stability Constants, Vol. 1, Amino Acids. Plenum Press, New York, 1974.
- 17. Ando, T., Bull. Chem. Soc. Jap. 36, 1593 (1963).
- 18. Fomenko, V. V., Polynova, T. N., and Porai-Koshits, M. A., Zh. Strukt. Khim. 16, 645 (1975).
- 19. Kramarenko, F. G., Polynova, T. N., Porai-Koshits, M. A., Chalyj, V. P., and Mitrofanova, N. D., Zh. Strukt. Khim. 14, 1113 (1973).
- 20. Fomenko, V. V., Thesis. Chemical Faculty, State University of Moscow, Moscow, 1972.
- 21. Irving, H. M. N. H. and Rosotti, H., Acta Chem. Scand. 10, 72 (1956).

Translated by R. Domanský