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The Use of Proton Magnetic Resonance in the Study of Complexones

N.A.Kostromina

The available literature data for the protonation of complexones and the formation of their complexes with diamagnetic and paramagnetic ions are reviewed. A systematic and general account is given of studies on the equilibria and kinetics of complex formation and of the structures of the complexes. Typical PMR spectra of complexones and their metal complexes are presented; quantitative characteristics obtained from PMR data (chemical shifts, spin-spin coupling constants, stability constants, and reaction rate constants) are tabulated.
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I. INTRODUCTION

Complexones are now finding extensive application in various branches of the national economy in view of the high stability and solubility of the majority of complexonates and the characteristic features of the structures of complexones responsible for their selective properties in relation to different metals. Therefore the study of metal complexes of complexones is urgently required in connection with the synthesis of new complexones with specified properties [1].

List of Abbreviations

Methylglycine	MGl
Dihydroxyethylglycine	DGl
Iminodiacetate	IMDA
Methyliminodiacetate	MIMDA
Hydroxyethyliminodiacetate	HIMDA
β-Aminoethyliminodiacetate	AEIDA
Nitrilotriacetate	NTA
NN'-ethylenediglycine	EDDA
1,2-dimethyl-*NN'*-ethylenediglycine	DMeEDDA
1,2-diethyl-*NN'*-ethylenediglycine	DEtEDDA
N-(carboxymethyl)-*NN'*-ethylenediglycine	ED3A
N-(carboxymethyl)-*N'*-(2-hydroxyethyl)-*NN'*-ethylenediglycine	HEDTA
(Ethylenedinitrilo)tetra-acetate	EDTA
(Methylethylenedinitrilo)tetra-acetate	PDTA
[(1,2-dimethylethylene)dinitrilo]tetra-acetate	BDTA
[Oxybis(ethylenenitrilo)]tetra-acetate	EEDTA
[Ethylenebis(oxyethylenenitrilo)]tetra-acetate	EGTA
(1,2-cyclohexylenedinitrilo)tetra-acetate	CDTA
[(Carboxymethyl)iminobis(ethylenenitrilo)]-tetra-acetate	DTPA
Tetramethylsilane	tms
Sodium 3-(trimethylsilyl)propanesulphonate	tms*
Nuclear magnetic resonance	NMR
Proton magnetic resonance	PMR

Infrared spectroscopy has yielded much information about the structures of the protonated forms of complexones and also their metal complexes in the crystalline state but has been much less useful in the study of the structures of complexones in solution. However, owing to the complexity of the spectra and in many cases the ambiguity of the band assignments, the data obtained have to be checked by another method.

The method which yields the most complete information about the structures of compounds in solution is that of nuclear magnetic resonance. Many proton magnetic resonance studies have been made on the protonation of complexones and the structures of complexonates in solution. The present review deals with data obtained by this method for the structures of the complexes and the equilibria and kinetics of complex formation and protonation processes.

Since the research technique is based on a comparison of the spectra of the complexones in bound and free states, in the first section of the review we shall consider the PMR spectra of complexones and data on the structures of the protonated forms of the complexones and on the microequilibria in solution as a function of pH.

II. PMR STUDY OF THE STRUCTURES OF COMPLEXONES

Complexones is the name given to compounds containing a nitrogen atom linked to oxygen-containing groups† which can readily split off and combine with protons. In all complexones there are two types of protons: (1) the labile protons of the functional groups which exchange rapidly with the protons of water and other functional groups; (2) non-labile protons forming part of the CH_2, CH, or CH_3 groups of the complexones.

†In this review only complexones containing methylcarboxyls will be considered since NMR data for other types of complexones are not available.

If the study is performed in aqueous solutions, the resonance signals of protons of the first type merge with the signal of the water protons owing to rapid exchange. In this case, the changes in the PMR spectra on protonation are investigated on the basis of the resonance of the non-labile protons [2]. The number of resonance signals in the spectrum depends on the number of non-equivalent protons in the complexone. The positions of the signals depend on the groups with which the CH, CH_2, and CH_3 groups are linked.

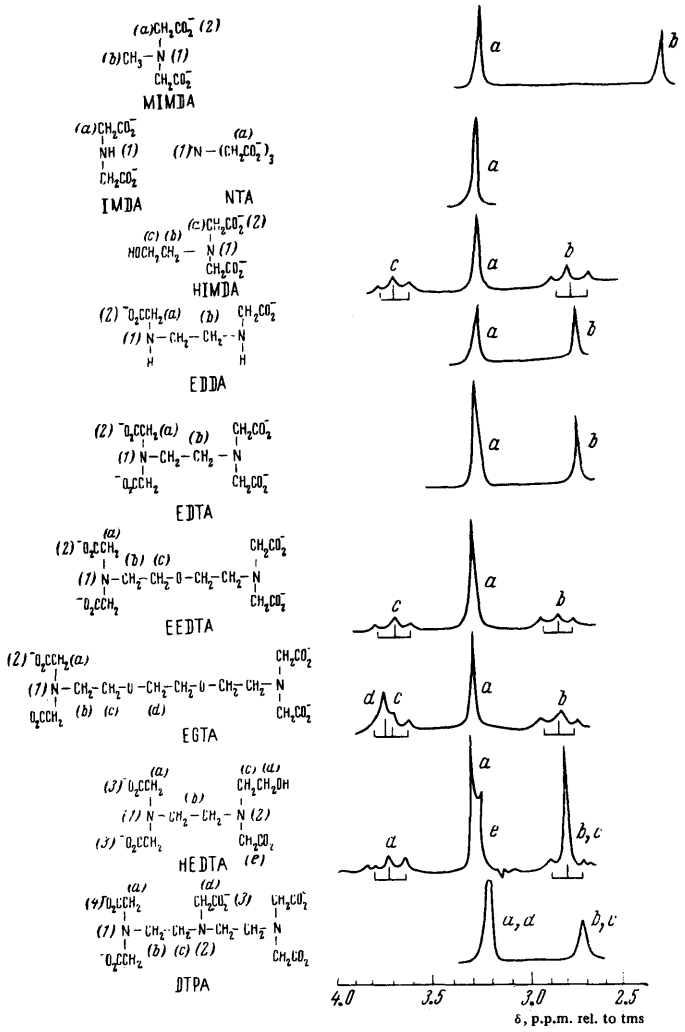


Figure 1. Characteristic proton magnetic resonance spectra of the complexones.

The changes in the position of the CH_2 signal following the addition of electron-donating groups (NR_2, COOH, OH), their protonation, and dissociation have been investigated in detail [2]. The formulae and the designations employed for the complexones investigated, the designations of the non-labile protons (*a*, *b*, *c*, *d*, *e*, ..., *l*) and of the electron-donating groups (1, 2, 3, 4, ..., *L*), and also the PMR spectra of the anions (potassium or tetramethylammonium salts) are presented in Fig. 1. The ratios of the areas and approximate calculations of the signal positions on the basis of the substitution constants carried out by Sudmeier and Reilley [2] were used to assign the signals in the spectra.

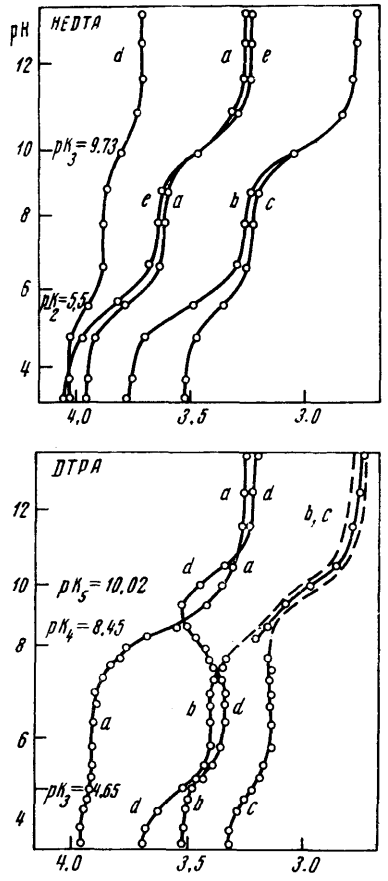


Figure 2. Shifts of the HEDTA and DTPA proton signals as a function of the pH.

If an acid is added to anions with several functional groups capable of combining with protons, microequilibria are established in solution, which include all possible combinations of the protonated and non-protonated forms. Thus, following the addition of one equivalent of acid, each functional group of the complexone may be protonated to a specified degree. This entails the descreening of the methylene protons in the immediate vicinity of the functional group protonated and a shift of their signal to a low field (Fig. 2). The magnitude of the shift depends on the nature of the electron-donating atom, its electronegativity, its position relative to the CH_2 group, and the time during which the proton remains at the electron-donating atom, i.e. on the degree of protonation of each group [2].

In the pH range where signals shifts are observed, there is a mixture of protonated and dissociated forms. The absence of signal splitting shows that rapid proton exchange takes place between these forms.

The position of the signal is defined by the equation

$$\delta_{av.} = N_A\delta_A + N_B\delta_B, \quad (1)$$

where N_A, N_B, δ_A, and δ_B are respectively the mole fractions (N) and the chemical shifts (δ) of the protonated (A) and non-protonated (B) forms. At the point of inflection where $\delta_{av} = (\delta_A + \delta_B)/2$, the concentrations of the protonated and non-protonated forms are equal.

It follows from the dissociation equation

$$\left(K = \frac{N_B[H^+]}{N_A}\right) \quad (2)$$

that, when $N_A = N_B$, the dissociation constant is equal to the hydrogen ion concentration. The dissociation constants determined from the pH–δ relation agree with the literature values [3].

Table 1. Degree of protonation of the electron-donating groups of complexones [2,5].

f_j	MGI^{-}	$IMDA^{2-}$	$MIMDA^{2-}$	NTA^{3-}
	$n=1$	$n=1$	$n=1$	$n=1$
f_1	75±6	93±3	91±5	82±2
f_2	20±5	7±3	6±3	18±2

f_j	$EDTA^{4-}$		$EEDTA^{4-}$	$EGTA^{4-}$		$HEDTA^{3-}$		$DTPA^{5-}$	
	$n=1$	$n=2$	$n=2$	$n=2$	$n=1$	$n=2$	$n=3$	$n=2$	$n=3$
f_1	53±5	96±2	96±11	96±6	42±7	87±6	26±1	85±5	80±11
f_2	−2±3	2±1	2±5	3±3	52±6	97±5	41±1	15±6	64±13
f_3	—	—	—	—	3±18	0±15	7±2	0±16	76±23

Since the addition of a proton causes the greatest shift of the signal of the CH_2 groups linked directly to the electron-donating atoms, the sequence of the protonation of these groups may be established on the basis of the pH–δ relation. The simultaneous shift of the *a* and *b* signals in the spectra of complexones derived from mono- and di-amines following the addition of the first proton to the anion (Fig. 2) shows that the nitrogen atoms are the first to be protonated, in agreement with infrared spectroscopic studies [1]. The study of the spectra of DTPA makes it possible to determine the sequence of the addition of protons to the nitrogen atoms: the middle nitrogen atom is the first to be protonated and is followed by the two extreme atoms, with proton transfer from the middle atom to the extreme atoms and the reprotonation of the middle atom [4].

The PMR method also makes it possible to obtain quantitative data for the degree of protonation of each electron-donating group [2,5]. The calculated degrees of protonation of the electron-donating groups of the complexones are listed in Table 1.

Following the addition of the number of equivalents of acid equal to the number of nitrogen atoms in the complexone, the nitrogen atoms are protonated preferentially in all the complexones investigated. However, partial protonation of the COO^{-} groups is also observed. In the presence of two nitrogen atoms, there is rapid proton exchange between them (HEDTA, EDTA, EGTA, and EEDTA). If there are three nitrogen atoms (DTPA), there is a slow exchange between the middle and extreme nitrogen atoms and rapid exchange between the extreme atoms.

CDTA, a complexone the structure of which is very close to that of EDTA and is distinguished by the presence of the cyclohexane ring, has somewhat unusual properties.

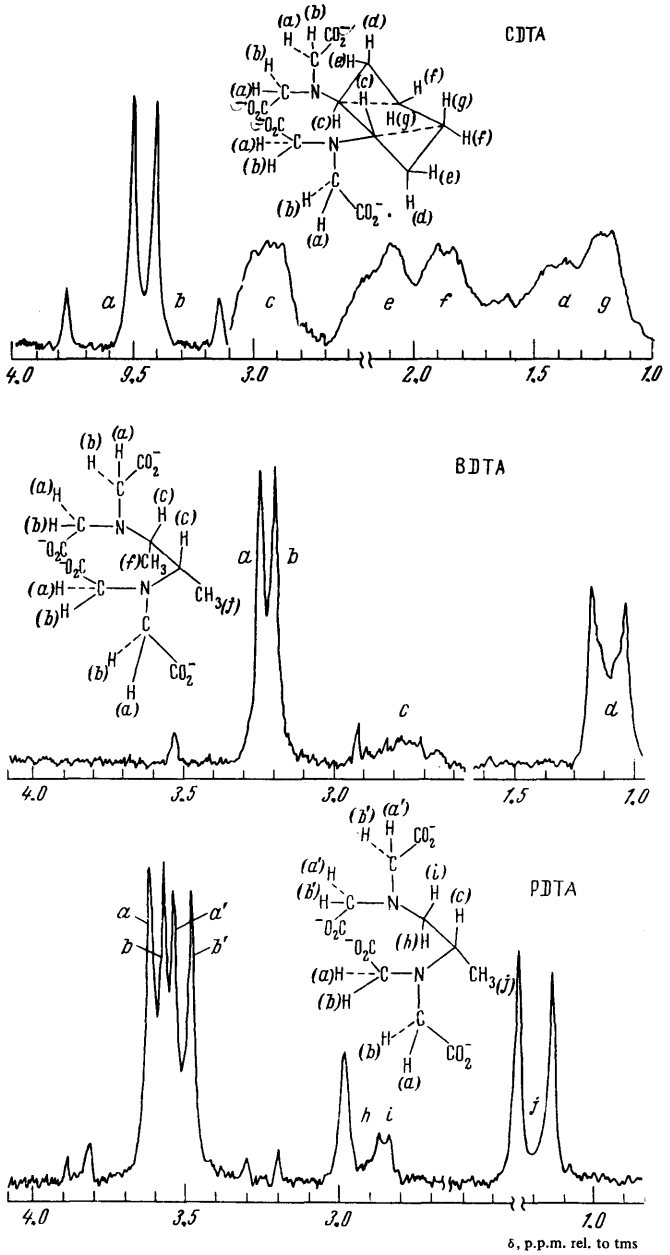


Figure 3. Characteristic spectra of CDTA, BDTA, and PDTA.

The formula of CDTA, the designations of the protons, and the spectrum of the anion are given in Fig. 3. The AB quartet [7], observed in low fields, is due to the protons of

the methylcarboxyls. The two protons in each methylcarboxyl are non-equivalent and give rise to the AB quartet, since the iminodiacetate group is linked to an asymmetric carbon atom [7]‡. The addition of the first two protons causes a shift of the quartet (the *a* and *b* signals) and of the methylidyne proton signals (*c*), the shift of the *c* signals being greater than that of the *a* and *b* signals. Consequently, here too the nitrogen atoms are the first to be protonated. There is further splitting of the *a* and *b* signals after the addition of the first proton, which has been accounted for by the formation of the bridge structure ≥N–H–N<, possibly involving the acetate groups[8].

This difference from EDTA is due to the characteristics of the disposition of the iminodiacetate groups in CDTA. The half-widths of the methylidyne proton signals, which are determined by the spin–spin coupling constant and depend on the positions of the interacting protons, demonstrated that the iminodiacetate groups in CDTA occupy the diequatorial positions. For this disposition, the distance between the nitrogen atoms is 2.2 Å, which favours the formation of a bridge structure. The presence of a linkage with two nitrogen atoms in the monoprotonated form can explain why the reaction becomes much more endothermic following the removal of this proton, in relation to the analogous reaction of EDTA.[6]

III. PMR STUDY OF THE FORMATION OF METAL COMPLEXES OF COMPLEXONES

When complexes are formed, the PMR spectra of the complexones undergo changes which can involve both a shift and a splitting of the bands. To characterise quantitatively the changes occurring in the spectra on formation of complexes with diamagnetic ions, four main parameters are employed: (1) the area of the signal; (2) the chemical shift; (3) the line half-width; (4) the spin–spin coupling constant. For paramagnetic complexes, the main parameters are the relaxation time and the contact and pseudocontact shifts.

Since the methods of investigation and the data obtained for diamagnetic and paramagnetic complexes are significantly different they will be discussed separately.

1. Diamagnetic Complexes

The study of the PMR spectra for the non-labile complexone protons led to the isolation of three groups of complexes: (1) complexes in which the M–N and M–O bonds are labile; (2) complexes in which the M–N bonds are inert and the M–O are labile; (3) complexes in which the M–N and M–O bonds are inert[9]. In the first case, the spectrum of the complex has the same form as that of the free ligand (Fig. 1). Such complexes are formed by the majority of doubly charged metals [except platinum(II) and palladium(II)] with monoamines and EDTA,[10,19] by aluminium and lanthanum with EDTA,[11,17,18] by calcium and lanthanum with HEDTA,[20,21] and by alkali metals with HEDTA.[22]

The signal shifts and the study of the δ –pH relation yielded information in such cases concerning the occurrence of complex formation in the system, and the compositions, stabilities, and structures of the complexes.

‡An analogous splitting into one or two AB quartets is observed in the spectra of other complexones containing an asymmetric carbon atom (Fig. 3).

As an example, Fig. 4 presents δ–pH relations for EDTA complexes with alkali (M : EDTA = 4 : 1) and alkaline earth (M : EDTA = 1 : 1) metals. The δ–pH curve for the potassium salt coincides with the corresponding curve for the tetramethylammonium salt, which implies that potassium does not form a complex with EDTA. The δ–pH relations for sodium, lithium, calcium, strontium, and barium indicate the occurrence of complex formation at pH > 4.

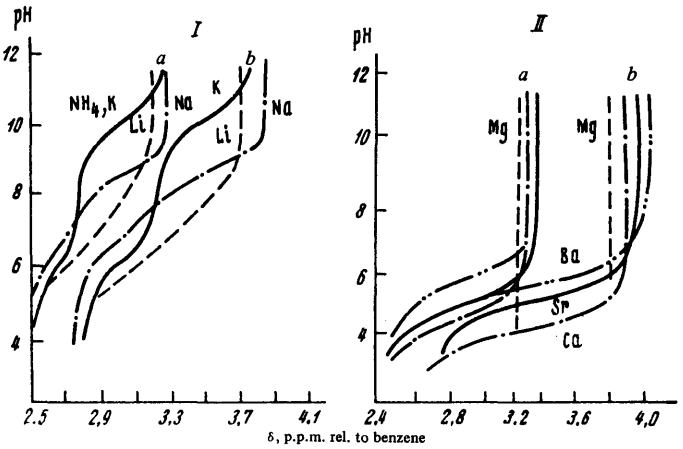


Figure 4. δ–pH relations for the EDTA complexes of alkali (I) and alkaline earth metals (II).

The presence of two rising sections in the curves for the sodium and lithium salts indicates the formation of monoprotonated complexes (in the neutral region). The shift of the signals to low fields in the acid region is due to the decomposition of the complexes. The pH values corresponding to the breakdown of the complexes characterise their stability. The stability constants of the lithium, calcium, strontium, and barium complexes have been calculated[11] from Eqn. (1) in which the subscripts A and B refer to the bound and free ligands. Similar calculations of the constants have been performed for the lanthanum and lutetium complexes of MGl,[14] MIMDA,[12] and DGl[15] and for the cadmium, zinc, and lead complexes of NTA.[16] The calculated stability constants are compared in Table 2 with the values obtained by other methods.

The low stability constants of the lithium, calcium, strontium, and barium complexes of EDTA obtained by the PMR method can be explained by the fact that in the calculation no account was taken of the formation of protonated complexes in the acid region[11].

The formation of a protonated complex in which the proton adds to the carboxy-group (only the *a* signals shift) was observed in a study of the PMR spectra of the lanthanum complex of EDTA at pH < 3.[17] The formation of mixed hydroxo-complexes of zinc and EDTA was established in the alkaline region[25]. The sharp shift of the *d* signal of HEDTA in the lanthanum complex to high fields at the solution pH corresponding to the p*K* for the hydrolysis of the 1 : 1 complex show that in this case a complex is formed in the alkaline region where the hydrogen atom dissociates from the alcoholic group of HEDTA.[21]

The study of the δ–pH relation for stable complexes (the magnesium, calcium, strontium, barium, mercury, aluminium, lead, zinc, and lanthanum complexes of $EDTA^{4-}$, the calcium and lanthanum complexes of HEDTA, and the magnesium, calcium, strontium, and barium complexes with EGTA) yielded information about the regions corresponding to the existence of the complexes: in the pH range where only one complex is present, the positions of the signals remain constant [10,11,17,19,21]. The chemical shifts in the spectra of the 1 : 1 complexes are listed in Table 3, which shows that complex formation entails signal shifts to both low and high fields. The latter are observed for complexes of alkali and alkaline earth metals with large ionic radii [26]. The signal shifts of the CH_2 protons linked to OH groups in DGl and HIMDA indicate the presence of linkages between the metal and the OH group.

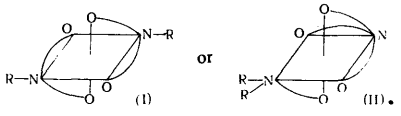
Table 2. Stability constants ($\lg K_1$ and $\lg K_2$) of metal complexes of complexones.

Formula	PMR (Ref.11)	E.m.f.* (Ref.3)	Formula	PMR (Refs. 12, 14 and 15)	pH* (Refs.23 and 24)	Formula	PMR (Ref.16)	pH* (Ref.3)
$Li_2(EDTA)^{2-}$	2.5	2.79	La (HMGl)$^{3+}$	0.6	—	Cd (NTA)$^-$	9.4	9.8
Ca $(EDTA)^{2-}$	9.4	10.6	Lu (HMGl)$^{3+}$	0.9	—	Cd $(NTA)_2^{4-}$	4.9	5.7
Ca_2 (EDTA)	—1	—	—	—	—	—	—	—
Sr $(EDTA)^{2-}$	7.6	8.6	La (MIMDA)$^+$	5.7	5.7	Zn (NTA)$^-$	10.0	10.4
Sr_2 (EDTA)	1		Lu (MIMDA)$^+$	7.07	7.1	Zn $(NTA)_2^{4-}$	3.5	—
Ba $(EDTA)^{2-}$	6.2	7.8	La (DGl)$^{2+}$	4.8	4.39	Pb (NTA)$^-$	11.4	11.39
LaH $(EDTA)_2^{4-}$	1.3	—	Lu (DGl)$^{2+}$	5.2	5.01	Pb $(NTA)_2^{4-}$	2.0	—

*Literature data adjusted to $I = 1$.

The study of the PMR spectra of alkaline earth metal, cadmium, zinc, lead, mercury, aluminium, and lanthanum complexes with different component ratios other than 1 : 1 showed that in the presence of an excess of the metal (2 : 1) calcium and strontium form compounds in which there are two metal ions for each EDTA residue, each being linked to one iminodiacetate group [27]. In the presence of an excess of the ligand (1 : 2, 1 : 3, and 1 : 5 component ratios), the formation of cadmium, zinc, lead, and lanthanum complexes containing two NTA residues per metal atom [13,16] and of a lanthanum complex with two EDTA residues [28] was established. The stability constants of the complexes were calculated (Table 2).

Complexes of metals having coordination numbers not exceeding six (lead, zinc, and cadmium), with two NTA residues can have two structures:



To elucidate these structures, use was made of the spin–spin interaction between the ligand protons and the magnetic nuclei of cadmium and lead. In the 1 : 1 complexes, such interaction is observed and is reflected by a broadening of the lines in the spectra. In the complexes with two ligand species, the spin–spin interaction is not observed, i.e. the rate of dissociation increases. This can be accounted for by the decrease of the number of binding sites employed on passing from the 1 : 1 to the 1 : 2 complex, i.e. by the formation of structure(I).

The lanthanum complex with two EDTA residues was shown to have an asymmetric structure in which the second EDTA residue adds to one iminodiacetate group, the form of EDTA involved being that which predominates in solution (the protonated residue at pH 6–9 and the quadruply charged ion at pH > 9). [28] For the remaining metals investigated, only 1 : 1 complexes with EDTA have been detected [11].

Table 3. Chemical shifts of the complexone protons in metal complexes*.

Compound	δ_a	δ_b	Refs.	Compound	δ_a	δ_b	δ_c	Refs.
K_4 (EDTA)	3.14	2.61	26	K_2 (MIMDA)	2.94	2.09	—	19
Na_4 (EDTA)	3.03	2.55	11	Mg (MIMDA)	3.09	2.28	—	19
Li_4 (EDTA)	3.20	2.64	11	Ca (MIMDA)	3.06	2.15	—	19
Cs_4 (EDTA)	3.33	2.82	11	Sr (MIMDA)	2.84	1.99	—	19
Mg $(EDTA)^{2-}$	3.20	2.67	26	Ba (MIMDA)	2.86	1.99	—	19
Ca $(EDTA)^{2-}$	3.13	2.55	26	La $(MIMDA)^+$	3.14	2.18	—	12
Sr $(EDTA)^{2-}$	3.11	2.49	26	Lu $(MIMDA)^+$	3.18	2.25	—	12
Ba $(EDTA)^{2-}$	3.09	2.44	26	K_2 (HIMDA)	3.09	2.60	3.45	19
Hg $(EDTA)^{2-}$	3.34	2.85	26	Mg (HIMDA)	3.25	2.82	3.56	19
Al $(EDTA)^-$	3.56	3.14	11	Ca (HIMDA)	3.05	2.49	3.53	19
Pb $(EDTA)^{2-}$	3.55	3.15	11	Sr (HIMDA)	3.06	2.47	3.53	19
Zn $(EDTA)^{2-}$	3.36	2.85	26	La $(HIMDA)^+$	3.34	2.85	3.67	15
La $(EDTA)^-$	3.40	2.69	17	Lu $(HIMDA)^+$	3.32	2.70	3.70	15
K_4EGTA	3.30	2.65	19	K (DGl)	3.15	2.65	3.65	15
Mg $(EGTA)^{2-}$	3.43	2.75	19	La $(DGl)^{2+}$	3.35	2.70	3.86	15
Ca $(EGTA)^{2-}$	3.35	2.68	19	Lu $(DGl)^{2+}$	3.35	2.75	3.88	15
Sr $(EGTA)^{2-}$	3.24	2.55	19	H (MGl)	3.51	2.67	—	14
Ba $(EGTA)^{2-}$	3.22	2.49	19	La $(HMGl)^{3+}$	3.60	2.65	—	14
				Lu $(HMGl)^{3+}$	3.55	2.55	—	14

In this and all subsequent Tables, the chemical shifts for the diamagnetic complexes are given in p.p.m. relative to tms and the designations of the protons in DGl and MGl are the same as for HIMDA and MIMDA (Fig. 1).

In systems containing two polydentate ligands (EDTA and IMDA or NTA) and lanthanide ions, the formation of mixed complexes incorporating EDTA and IMDA or NTA residues was established [29–31]. In the mixed lanthanum complexes, the chemical shifts of the *a* and *b* signals of EDTA remain the same as in the spectrum of the 1 : 1 complex, i.e. the initial complex does not change and the second ligand species entering the complex displaces a water molecule from the inner sphere. In the spectra of the analogous lutetium complexes, the *b* signals of EDTA are displaced to high fields, which can be accounted for by a weakening of the M–N bonds with increase of the coordination number in these complexes compared with the initial $Lu(EDTA)^-$.

In the lutetium complex $Lu(EDTA)(NTA)^{4-}$, there is a slow exchange between the bound and free NTA, while in the $La(EDTA)(NTA)^{4-}$ and $Ln(EDTA)(IMDA)^{3-}$ complexes the exchange is rapid. The formation constants of the mixed complexes were calculated from the relative signal areas in the first case and from the signal shifts in the second (Table 4). For comparison, Table 4 includes the corresponding constants of the neodymium, europium, and erbium complexes evaluated by a spectrographic method [32–34].

The PMR spectra of complexes of Group I metals in the presence of an excess of ligand can be divided into three groups characterised by the rate of exchange between the bound and free ligand. 1. Rapid exchange: the number of signals does not change, the signals are

broadened, and their positions depend on the pH of the solution and are defined by Eqn. (1)—EDTA complexes of barium, strontium, and aluminium at pH < 6 and calcium and mercury in the highly alkaline region, NTA complexes of cadmium, zinc, lead, and lanthanum and IMDA and MIMDA complexes of lanthanum, yttrium, and lutetium. 2. Slow exchange: two sets of broadened signals, one of which refers to the bound and the other to the free ligand—EDTA complexes of magnesium and lead at pH < 11 and calcium, mercury, aluminium, and lanthanum at pH < 9.5, 9, 6.5, and 7 respectively. 3. Intermediate exchange: two sets of broadened signals close to one another with partial overlapping.

Table 4. Stability constants of mixed lanthanide complexes[31] ($I = 1.0$, $t = 25°C$).

Complex	lg$K$*	lg β	Complex	lg K	lg β
La(EDTA)(IMDA)$^{3-}$**	2.5±0.05	16.6	LaY(NTA)$^{4-}$	2.2±0.1	16.3
NdY(IMDA)$^{3-}$	3.8±0.1	19.2	NdY(NTA)$^{4-}$	4.8±0.1	20.2
EuY(IMDA)$^{3-}$	5.0±0.1	21.3	EuY(NTA)$^{4-}$	5.1±0.1	21.6
ErY(IMDA)$^{3-}$	3.4±0.1	20.7	LuY(NTA)$^{4-}$	2.3±0.1	20.4
LuY(IMDA)$^{3-}$	2.2±0.2	20.3			

*K and β are the successive and overall constants respectively.
**Y = EDTA.

In each of these cases the lifetime of the coordinated ligand (τ) can be represented by the following equations.

For rapid exchange:

$$\tau = \frac{\omega_{Y,MY} - N_Y\omega'_Y - N_{MY}\omega'_{MY}}{4\pi^2 N_Y^2 N_{MY}\Delta\nu_0^2}, \quad (3)$$

where ω and ω' are respectively the observed line width and the line width in the absence of exchange, N is the mole fraction, $\Delta\nu_0$ the difference between the positions of the signals due to the free and bound ligand species in the absence of exchange, and MY and Y represent the complex and the free ligand.

For slow and intermediate exchange:

$$1/\tau_{MY} = \pi(\omega_{MY} - \omega'_{MY}), \quad (4)$$

$$1/\tau_{MY} = \pi\sqrt{1/2(\Delta\nu_0^2 - \Delta\nu^2)}, \quad (5)$$

where $\Delta\nu$ is the difference between the positions of the signals due to the free and bound ligand in the test specimen.

The kinetics of ligand exchange in the systems comprising calcium and strontium with EDTA, calcium with HEDTA, and zinc, lead, and cadmium with NTA have been investigated over a wide pH range[16,20,35]. In systems comprising calcium and strontium with EDTA, the following processes were considered:

$$MY^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} M^{2+} + Y^{4-}, \quad (6)$$

$$MY^{2-} + \overset{*}{Y}{}^{4-} \underset{}{\overset{k_2}{\rightleftarrows}} \overset{*}{MY}{}^{2-} + Y^{4-}, \quad (7)$$

$$MY^{2+} + H\overset{*}{Y}{}^{3-} \underset{}{\overset{k_3}{\rightleftarrows}} \overset{*}{MY}{}^{2-} + HY^{3-}, \quad (8)$$

$$H^+ + MY^{2-} \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} M^{2+} + HY^{3-}, \quad (9)$$

$$HMY^- + H\overset{*}{Y}{}^{3-} \underset{}{\overset{k_5}{\rightleftarrows}} H\overset{*}{MY} + HY^{3-}, \quad (10)$$

$$H^+ + MY^{2-} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} HMY^-, \quad (11)$$

$$HMY^- \underset{k_{-7}}{\overset{k_7}{\rightleftarrows}} HY^{3-} + M^{2+}. \quad (12)$$

The rate of exchange may be represented by the equation

$$-\frac{d[MY^{2-}]/dt}{[MY^{2-}]} = 1/\tau_{MY} = k_1 + k_2[Y^{4-}] + k_3[HY^{3-}] + k_5[HY^{3-}]\frac{[HMY^-]}{[MY^{2-}]} + k_7\frac{[HMY^-]}{[MY^{2-}]}. \quad (13)$$

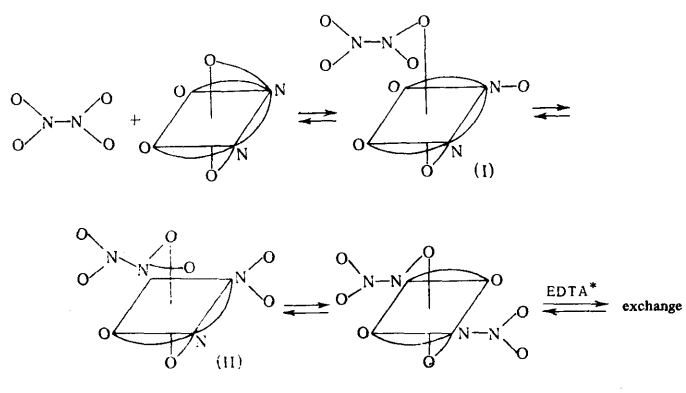
The determination of the quantities $1/\tau_{MY}$ as a function of ligand concentration at different pH permitted the calculations of the rate constants k for the reactions. The results are presented in Table 5, which also includes the rate constants for the analogous exchange reactions of the Ca(HEDTA)$^-$ system. The dissociation rate constant for Sr(EDTA)$^{2-}$ is higher than for Ca(EDTA)$^{2-}$, which agrees with the thermodynamic stabilities of the complexes[3]. The association rate constants are consistent with those for the complexes of the corresponding metals with other ligands[37], which confirms Eigen's mechanism[36].

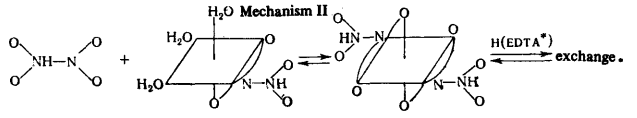
Table 5. Rate constants for exchange in metal complexes of complexones[16,20].

k_n	Ca(EDTA)$^{2-}$	Sr(EDTA)$^{2-}$	Ca(HEDTA)$^-$	k_n	Cd(NTA)$^-$	Zn(NTA)$^-$
k_1, s^{-1}	1	$3\cdot10^1$	$3\cdot10^1$	k_1, s^{-1}	<1	<1
k_{-1}, mole^{-1} s^{-1}	$2.5\cdot10^9$	$8.1\cdot10^8$	$1.3\cdot10^8$	k_2, mole^{-1} s^{-1}	$2.9\cdot10^5$	$1.8\cdot10^5$
k_2, mole^{-1} s^{-1}	$1.2\cdot10^2$	$1.1\cdot10^3$	$1.1\cdot10^3$	k_{-2}, mole^{-1} s^{-1}	$2.1\cdot10^5$	$5.1\cdot10^5$
k_3, mole^{-1} s^{-1}	5	$1.6\cdot10^2$	$2.3\cdot10^2$	k_3, mole^{-1} s^{-1}	$2.9\cdot10^2$	$5.3\cdot10^2$
k_4, mole^{-1} s^{-1}	$2\cdot10^7$	$1\cdot10^8$	—	k_4, mole^{-1} s^{-1}	$1.8\cdot10^7$	$2.0\cdot10^6$
k_5, mole^{-1} s^{-1}	$2\cdot10^5$	$1\cdot10^5$	—	k_5, mole^{-1} s^{-1}	$1.3\cdot10^7$	$6.0\cdot10^8$
k_7, mole^{-1} s^{-1}	$1\cdot10^7$	$5\cdot10^5$	—	k_6, s^{-1}	$2.2\cdot10^2$	$6.3\cdot10^2$
k_{-1}, s^{-1}	$5\cdot10^4$	$2\cdot10^4$	—	k_7, mole^{-1} s^{-1}	$1.4\cdot10^2$	—
				k_8, mole^{-1} s^{-1}	$1.2\cdot10^3$	—

The exchange reaction between the bound and free ligand species in the calcium and strontium complexes can take place either in one stage without the formation of an intermediate or in many stages with formation of an intermediate where both ligand species are linked simultaneously to the metal ion[38]. Mechanisms have been proposed for the exchange reactions (10) and (11), with formation of intermediates as the rate-limiting stage, on the basis of the available data[20,35].

Mechanism I





In mechanism(II), it is postulated that the EDTA residue in the protonated calcium and strontium complexes is linked via one iminodiacetate group. In this case, the exchange rate constants for the protonated EDTA complexes should be the same as for the complexes of the corresponding metals and IMDA. Such agreement has been observed for the strontium complexes[20].

A study has been made[16] of the kinetics and mechanism of the formation of NTA complexes of cadmium and zinc. The exchange rate constants have been determined for the following reactions:

$$M(NTA)^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} M^{2+} + NTA^{3-}, \quad (14)$$

$$H^+ + M(NTA)^- \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} M^{2+} + HNTA^{2-}, \quad (15)$$

$$H^+ + Cd(NTA)_2^{4-} \underset{k_6}{\overset{k_5}{\rightleftarrows}} Cd(NTA)^- + HNTA^{2-}, \quad (16)$$

$$Cd(NTA)_2^{4-} \underset{k_4}{\overset{k_3}{\rightleftarrows}} Cd(NTA)^- + NTA^{3-}, \quad (17)$$

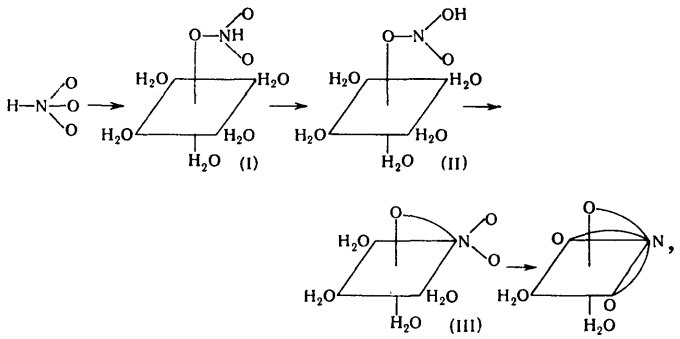
$$N\overset{*}{T}A^{3-} + Cd(NTA)_2^{4-} \underset{}{\overset{k_3}{\rightleftarrows}} Cd(NTA)\,N\overset{*}{T}A^{4-} + NTA^{3-}, \quad (18)$$

$$HN\overset{*}{T}A^{2-} + Cd(NTA)_2^{4-} \underset{}{\overset{k_7}{\rightleftarrows}} Cd(NTA)\,N\overset{*}{T}A + HNTA^{2-}, \quad (19)$$

$$N\overset{*}{T}A^{3-} + Zn(NTA)^- \underset{}{\overset{k_8}{\rightleftarrows}} Zn(N\overset{*}{T}A)^- + NTA^{3-}. \quad (20)$$

The results are compiled in Table 5.

The data obtained demonstrated that in the exchange reaction of Cd^{2+} and Zn^{2+} with H(NTA) the rate-limiting stage is not dissociation of the water in the aquo-ion and that the rate of reaction determines proton transfer from the nitrogen atom to the carboxy-group, which can proceed either via exchange with water molecules or directly from N to O.[39] A mechanism was proposed for the formation of the complexes:



in which the rate-limiting stage is the formation of the intermediate (II).

Lutetium complexes of NTA,[13] molybdenum(V) and molybdenum(VI) complexes of IMDA, MIMDA, and NTA[40-42], cadmium[19], molybdenum[40,43,44], zirconium, hafnium[45], yttrium, and lutetium[17] complexes of EDTA, yttrium and lutetium complexes of HEDTA[21], lanthanum complexes of DTPA[46], and the majority of BDTA and CDTA[26] complexes may be included among compounds with labile M–O and non-labile M–N bonds.

If the nitrogen atom of the complexone is linked to different substituents (IMDA, MIMDA, EDTA, HEDTA, and DTPA), the formation of a non-labile M–N bond makes the two protons of the acetate group non-equivalent (H_A and H_B). The situation remains unchanged on rotation: there are three rotational configurations (Fig. 5) in each of which the H_A and H_B protons have different environments, which lead to the splitting of the signals of the protons of this group into an AB quartet[47]. Owing to the rotation of the $>N-CH_2-CH_2-N<$ group in diamine derivatives, the signals of the ethylene protons are averaged out and a singlet is produced.

A typical spectrum of the protons of the CH_2COO^- group in the EDTA, HEDTA, IMDTA, and DTPA complexes in the presence of inert M–N and labile M–O bonds is presented in Fig. 5. The PMR spectra of such complexes show new features: the spin–spin coupling constant J and the difference between the chemical shifts ($\delta_A - \delta_B$) of the non-equivalent H_A and H_B protons.

A second distinctive feature of the complexes with non-labile M–N and labile M–O bonds is slow interchelate exchange: exchange between the bound and free ligand species or ligand species in complexes with different compositions or structures. This characteristic permits the determination of the number and composition of the complexes formed in metal–ligand systems as a function of the conditions governing complex formation and can yield information about the structures of these complexes.

In the study of the spectra of the molybdenum(VI) complexes of IMDA and MIMDA[41-43], the simultaneous formation of different 1 : 1 complexes (monomers, dimers) in solution was established, the compositions of the complexes corresponding to non-stoichiometric component ratios was determined (from the signal areas), and in some cases the constants were determined and complex formation equilibrium diagrams were plotted (Fig. 6).

Data were obtained for the structures of the complexes. In the MoO_4^{2-}–$IMDA^{2-}$ system, the spin–spin interaction between the CH_2 protons and the NH proton was employed for this purpose. The spin–spin coupling constants (J_{AX} = 7.3 Hz and J_{BX} = 1.0 Hz) show that the H_A protons interact with the NH protons to a greater extent than the H_B protons. A theoretical calculation showed that the

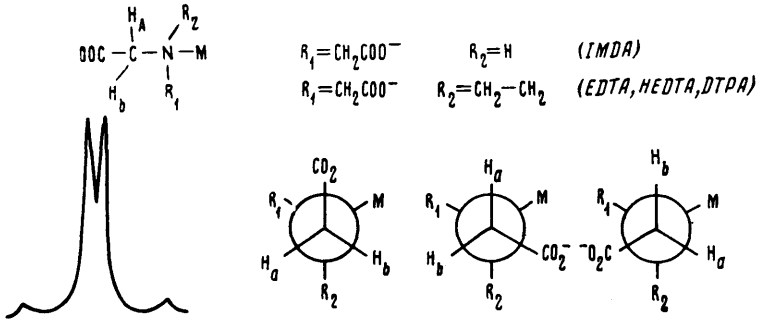


Figure 5. Characteristic spectrum of the CH_2 protons in the presence of non-labile M–N bonds.

7.3 Hz constant corresponds to an angle $\theta AX = 12°$ and the 1.0 Hz constant corresponds to an angle $\theta BX = 110°$.[41,48]

The molybdenum(VI) complexes of MIMDA give rise to a complicated spectrum with spin–spin interaction between the protons of one acetate branch and those of the other. Calculation of the spectra on the hypothesis of such interaction by a standard method[49] agreed with the experimental data[42].

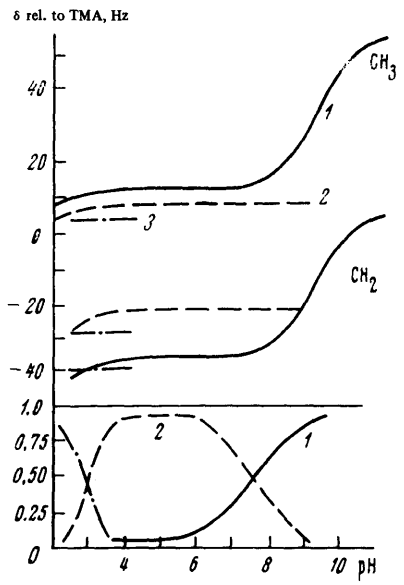


Figure 6. Complex formation equilibrium diagram for the molybdenum–MIMDA system according to PMR data: 1) free complexone; 2) monomeric complex; 3) dimer.

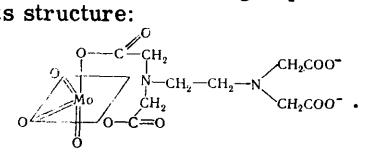
Differences were discovered between the molybdenum complexes of MIMDA and IMDA: (1) the chemical shift difference between the H_A and H_B protons in the IMDA complex is 0.65 p.p.m. in contrast to 0.27 p.p.m. for the MIMDA complex and 0.17–0.30 p.p.m. which is characteristic of all the complexes investigated with NR_3 groups. This can be explained by the fact that the substitution of a proton at the nitrogen atom by an alkyl group reduces the differences between the magnetic environments of H_A and H_B. (2) In molybdenum complexes of IMDA, the rate of exchange is higher [at a high pH the resonance signals of different specimens are averaged out ($k = 1.6 \times 10^2$ mole^{-1} s^{-1})] than for the MIMDA complexes. The reasons for this may be a decrease of steric hindrance, which facilitates attack by the free ligand.

In EDTA complexes with non-labile M–N and labile M–O bonds, the ratio of the signal areas of the bound and free ligands established that in the presence of an excess of the ligand all the metals investigated, except yttrium, form only 1 : 1 complexes. In the yttrium–EDTA system with 1 : 2 and 1 : 5 reactant ratios, a 1 : 2 complex is formed in which the second EDTA residue adds via one iminodiacetate group. This entails an increase of the mobility of the M–N bonds: the AB quartet disappears and the ethylene proton signal (*b*) shifts to a higher field[28].

In the lutetium–EDTA, zirconium–EDTA, and hafnium–EDTA systems, only 1 : 1 complexes were detected. The position of the signal of the LuY complex remains unchanged over a wide pH range (from 3 to 12), but above pH 11 a mixed hydroxo-complex is formed. This results in an increase of the mobility of the Lu–N bonds (the AB quartet disappears and the *a* and *b* signals shift to higher fields)[28]. The zirconium and hafnium complexes of EDTA give rise to spectra with signals in different positions depending on the pH of the solution, which corresponds to the two types of complexes formed: one at pH $\leq$ 3.5 (I) and the other at pH $>$ 6 (II). In the intermediate region between pH 3.5 and 6, there is a gradual transition from form (I) to form (II). Comparison with potentiometric titration data[50] established that in the region of pH $\sim$ 3, a simple chelate is formed and at pH 3.5 an OH group adds to the complex with possible polymerisation.

The complex formation equilibria in the molybdenum(VI)–EDTA system have been investigated as a function of the pH of the solution for Mo : EDTA $\geq$ 1.[40,44] Several complexes are formed in the system, the relative proportions of which and of the free EDTA are variable. The number of complexes in the solution was determined from the number of signals and their variation with the pH of the solution: a 1 : 1 complex, a complex with the ratio Mo : EDTA = 2 : 1, and a polymeric complex in the acid region was detected. A diagram illustrating the distribution of molybdenum among the complexes was plotted on the basis of the relative signal areas as a function of the solution pH and the stability constants of the complexes were determined ($\lg K_{MoO_3Y} = 10.7 \pm 0.3$, $\lg K_{(MoO_3)_2Y} = 19.5 \pm 0.3$).

The presence in the spectrum of the 1 : 1 complex of the signals due to two free acetate groups made it possible to establish its structure:



The complexes are protonated at pH $<$ 8 with formation of MoO_3HY^{3-}. In the complex with two MoO_3 groups, each is linked to an iminodiacetate group.

The molybdenum(V) complexes of MIMDA, NTA, and EDTA were also investigated. The paramagnetic molybdenum(V) ion forms diamagnetic complexes, which can be explained either by the formation of dimers with a linear coordination Mo–O–Mo or by the formation of dioxo-bridge complexes[43].

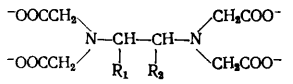
The study of the yttrium and lutetium complexes of HEDTA revealed two types of complexes with non-labile M–N and labile M–O bonds: complexes with a triply charged HEDTA residue in the pH range between 2 and 6–7 and with a quadruply charged HEDTA residue at pH $>$ 7. As for lanthanum, the formation of a complex in which the hydrogen atom in the alcoholic group has dissociated was indicated by the shift of the signal of the CH_2 group linked to the hydroxyl towards higher fields[21] and in all cases the pH at the point of inflection on the curve corresponded to the p*K* for the formation of the hydroxo-complex[51].

In the lanthanum complex of DTPA, the presence of non-labile equivalent linkages with three nitrogen atoms (C_3 symmetry) and labile linkages with the methylcarboxyls (one signal due to the ethylene proton) was established[46].

The spectroscopic parameters of certain complexes with non-labile M–N and labile M–O bonds are presented

in Table 6, which shows that in all cases where the M–O bonds in the complexes are labile the constant J is close to 17 Hz, which corresponds to unstrained bonds.

Hexadentate ligands with the general formula



(CDTA, PDTA, BDTA; Fig. 3) are very similar to EDTA.

Table 6. Spectroscopic parameters of metal complexes with non-labile M–N and labile M–O bonds.

Compound	δ_a^*	δ_b^*	J	$\sigma_A - \delta_B$	References
$(Mo^V\text{—NTA})_n^{**}$	4.35	—	—	—	43
$Lu(NTA)_2^{3-}$	3.38	—	—	—	13
$MoO_3(IMDA)^{2-}$	3.73	—	17.3	0.65	44
$MoO_3(MIMDA)^{2-}$	3.55	3.05	16.5	0.27	42
$Cd(EDTA)^{2-}$	3.11	2.64	17.1	0.17	45
$Y(EDTA)^-$	3.38	2.76	16.8	0.19	17
$Lu(EDTA)^-$	3.41	2.81	17.0	0.30	17
Zr (EDTA)	3.84	3.22	17.1	0.26	45
Hf (EDTA)	3.83	3.18	17.1	0.20	45
$MoO_2(EDTA)^{2-}$	3.57	3.73	16.7	0.31	45
$(MoO_2)_2(EDTA)^{4-}$	3.43	2.64	17.6	0.30	45
$La(DTPA)^{2-}$	3.47	2.92	17	0.20	46

*If the signals are split, the centre of the multiplet is given (δ in p.p.m. and J in Hz).
**The composition of the complex has not been established.

All these ligands differ from EDTA by the fact that the introduction of substituents into the ethylene chains hinders interconversion which in turn should be reflected in an inhibition of the M–O exchange. This is shown particularly markedly in the presence of the rigid cyclohexane ring (CDTA). Moreover, the presence of the CH_3 groups in PDTA and BDTA can lead to the appearance of isomeric forms of the complexes differing in the positions of these groups. The spectra of the complexes of BDTA with various metals are presented in Fig. 7.[26]

In the spectra of the majority of the bivalent metal complexes§, signals of two types of acetate groups are observed—two AB quartets and a doublet due to the methyl group, which is consistent with the presence of non-labile M–N and labile M–O bonds. Isomeric forms of the complexes were not observed.

Owing to the stereochemical requirements of the ring in CDTA, the methylidyne protons can have only one configuration. The inversion of nitrogen atoms is impossible and therefore the acetate groups are not involved in exchange. If two of these groups are located in one plane and the other two are in a plane at right angles to it, there should be two types of acetate groups regardless of the lifetime of the M–O bond. To obtain information about bond mobility, one can employ the constant J_{AB}: labile bonds are unstrained and J_{AB} is close to 17 Hz. However, unstrained bonds can arise also for long lifetimes. Therefore one employs also an additional method based on the broadening of the lines due to the labile bonds following the addition of a paramagnetic ion[26]. It has been established that Ag^+, all bivalent metals, and lanthanum[26,52] form complexes in which the M–N bonds are inert and the M–O bonds are labile (Fig. 8): $J_{AB} \simeq 17$ Hz.

§Exceptions are the barium and strontium complexes in which the M–N bonds are labile and the cobalt complexes in which the M–N and M–O bonds are non-labile.

The degeneration of the AB quartet to a singlet is observed for strontium, barium, zinc, hafnium(II), and lanthanum, which implies that the difference between the chemical shifts is < 0.1 p.p.m. The spectroscopic parameters of a number of metal complexes of BDTA and CDTA are presented in Table 7.

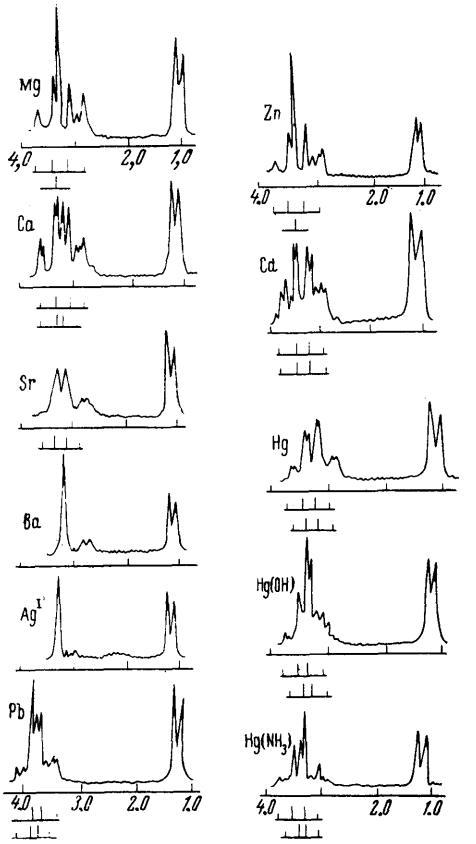


Figure 7. Characteristic spectra of metal complexes of BDTA.

In the third group of complexes (M–N and M–O bonds are inert), there is an additional splitting of the proton signals due to the non-equivalence of the groups and the inhibition of exchange and inversion. The number of AB quartets due to acetate protons varies from one (if all the acetate groups are equivalent) to two, three, or four (if all the acetate groups are non-equivalent). AB or A_2B_2 splitting is also observed.

This group includes the majority of cobalt(III), rhodium(III), platinum(II), and palladium(II) complexes. In all the complexes of the third group, there is a slow exchange between the bound and free ligand species and also between the ligand species bound in different complexes. Therefore when the solution contains two complexes or a complex and a free ligand, the spectrum becomes much more complex. Such spectra yield valuable information about the structure of the complexes, the number of binding sites in the ligand employed, the disposition of the electron-donating

group, the occurrence of *cis–trans* isomerism, and also about the equilibria and kinetics of the exchange between isomeric forms.

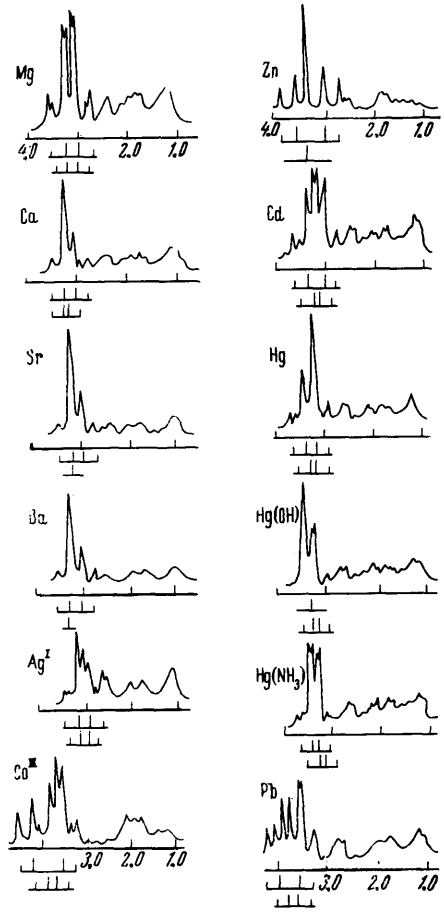


Figure 8. Characteristic spectra of metal complexes of CDTA.

The cobalt(III) and rhodium(III) complexes of monoamine derivatives (MIMDA, IMDA, and NTA) [53–57], diamine derivatives (EDDA, ED3A, HEDTA, EDTA, PDTA, BDTA, and CDTA) [58–67], and DTPA [96] have been investigated. The metals form with each ligand complexes of similar structure. Accordingly, their PMR spectra are also similar.

The spectra of the complexes with monoamine derivatives [53–56] show the AB quartets due to the protons of the acetate groups. In the spectra of the IMDA complexes, the AB quartets are broadened or split owing to the spin–spin interaction with NH protons. The signals of the NH groups are observed immediately after the solutions have been prepared. After the exchange with deuterium (D_2O), the signals disappear and the spectrum becomes simpler.

The formulae of the rhodium and cobalt complexes are isolated and their spectroscopic parameters are given in Table 8. The configurations are designated as follows:

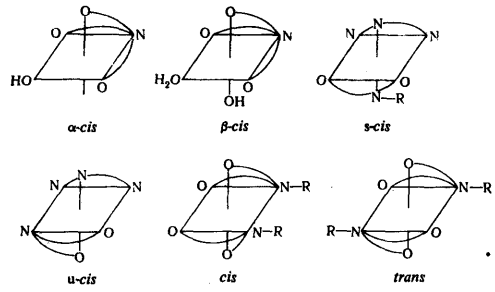


Table 7. Spectroscopic parameters of metal complexes of BDTA and CDTA. [26]

M^{n+}	BDTA						CDTA			
	methylene			methylidine	methyl		methylene			methylidyne
	δ	δ_{AB}	J^*_{AB}	δ	δ	J	δ	δ_{AB}	J_{AB}	
K_4	3.19	0.14	15.9	2.82	1.12	6.3	3.19	0.24	16.4	2.60
Mg	3.22 3.27	0.52 0.1	0.1 —	2.86 —	1.05 —	6.8 —	3.10 3.11	0.30 0.39	16.2 17.2	2.36 —
Ca	3.21 3.24	0.44 0.25	17.4 16.5	2.81 —	1.09 —	6.6 —	3.11 3.19	0.37 0.14	16.3 16.8	2.41 —
Sr	3.18	0.38	17.5	2.75	1.08	6.6	3.12 3.22	0.37 0.1	16.2 —	2.45 —
Ba	3.16	0.1	—	2.72	1.08	6.8	3.12 3.25	0.39 0.1	16.1 —	2.54 —
Zn	3.32 3.39	0.51 0.1	17.7 —	2.97 —	1.09 —	6.9 —	3.25 3.35	0.82 0.1	17.9 —	2.55 —
Cd	3.19 3.22	0.44 0.43	17.3 16.6	2.9 —	1.13 —	6.8 —	3.12 3.14	0.18 0.51	16.4 16.9	2.44 —
Pb	3.73 3.77	0.32 0.20	17.1 16.5	3.51 —	1.22 —	7.0 —	3.68 3.72	0.40 0.60	16.3 16.4	2.77 —
Hg	3.26 3.30	0.35 0.36	17.5 16.4	3.04 —	1.15 —	6.8 —	3.17 3.32	0.1 0.4	16.0 —	2.57 —
Ag	3.24	0.1	—	2.98	1.10	6.9	3.03 3.07	0.48 0.27	17.4 25.5	2.56 —

*Here and henceforth J is quoted in Hz.

The spectra of the *trans*-configurations of the 1 : 2 complexes and the s-*cis*-configurations of the 1 : 1 complexes show only one AB quartet and those of the *cis*- and u-*cis*-configurations show two AB quartets. In the spectra of the 1 : 2 complexes, the singlet corresponds to the free-carboxy-group. This is also indicated by the shift of the singlet towards higher fields as the pH of the solution is increased. Complexones with a tertiary nitrogen atom (NTA and MIMDA) give rise only to the *trans*-configurations owing to steric requirements.

The trend in the H_A and H_B proton shifts in the spectra of substituted IMDA can be accounted for on the basis of the magnetic anisotropy of the C–N bonds [57]. In the *trans*-complexes, substitution of the amino-proton by a CH_3 group leads to a greater screening of the H_A proton and to a smaller screening of the H_B proton. The *cis*-complex gives rise to a signal in higher fields than the corresponding *trans*-complexes.

In the cobalt complexes of diamine derivatives, the glycinate rings can be of two types: polar (out-of-plane) and equatorial (in-plane). Depending on this, one or two acetate groups at the nitrogen atom are bound in the complex, being designated by R_1 and R_2 for the polar groups and by G_1 and G_2 for the equatorial groups. The ring in which two nitrogen atoms are linked is designated by the letter E.

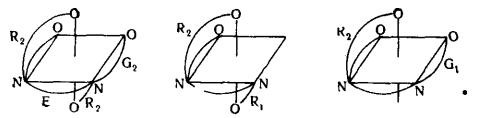


Table 8. Chemical shifts in the spectra of the cobalt(III) and rhodium(III) complexes of NTA, MIMDA, and IMDA. [55,56]

Complex	δ_A	δ_B	δ_R	J_{AB}	J_{NH-H_A}	J_{NH-H_B}
αK [Co (NTA) (OH) (OH_2)]·$2H_2O$	4.60	3.89	3.97	16.1	—	—
β-K [Co (NTA) (OH) (OH_2)]·$3H_2O$	4.34	3.75	3.91	16.1	—	—
Co (NTA) $(OH_2)_2$	4.41	3.79	4.11	16.5	—	—
Rh (NTA) $(OH_2)_2$	4.46	4.11	4.23	16.3	—	—
trans-H [Co (HNTA)$_2$]·$2H_2O$	4.34	4.11	4.51	17.6	—	—
trans-H [Rh (HNTA)$_2$]·$2H_2O$	4.30	4.16	4.55	17.5	—	—
trans-Co $(IMDA)_2^-$	4.42	3.61	9.0	17	—	—
trans-H [Rh $(IMDA)_2$]·$3H_2O$	4.25	3.55	8.25	17.4	7.6	1.5
after exchange	4.23	3.34	—	17.5	—	—
trans-(Co $(MIMDA)_2]^-$	4.25	3.86	3.17	17	—	—
trans-H [Rh $(MIMDA)_2$]·$2H_2O$	4.09	3.82	3.25	17.1	—	—
cis-[Co $(IMDA)_2]^{2-}$	4.24	3.26	7.6	17	—	—
	4.00	3.27	—	17	—	—
cis-H [Rh $(IMDA)_2$]·$2H_2O$	3.98	3.47	—	16.8	—	—
	4.28	3.44	—	17.9	—	—
s-cis-[Co (dien) (IMDA)]$^+$	4.29	3.45	—	17	—	—
s-cis-[Co (dien) (MIMDA)]$^+$	4.19	3.69	2.99	17	—	—
u-cis-[Co (dien) (IMDA)]$^+$	4.45	3.47	7.0	17	—	—
	4.35	3.41	—	17	7.8	1

Cobalt complexes of ED3A containing a monodentate ligand residue (Cl^- and NO_2) [58], the isomeric forms of complexes containing the EDDA and $AEIDA^X$ residues and bidentate ligand residues [CO_3^{2-}, ethylenediamine (en), oxalate (ox), and malonate (mal) [59-63]], and complexes of the type Co(HY)X and Co(Y)X, where Y =EDTA, PDTA, and HEDTA [26,64], have been synthesised.

The study of the PMR spectra established the number of polar and equatorial glycinate rings on the basis of the number of bands in the spectrum [60,62,65] and proton–deuterium exchange involving the CH_2 group [61] and permitted the assignment of the bands in the spectra.

Table 9 lists the possible forms of the complexes with diamine derivatives, the shifts of the H_A and H_B protons in rings of different types, and the positions of these signals in the spectra of the hexa- and penta-dentate EDTA and HEDTA complexes. Their comparison shows that in the cobalt(III) spectra the H_A and H_B protons in each type of glycinate ring give rise to characteristic band positions, varying in the range 4–4.2 and 3.1–3.4 for R_1, 4.2–4 and 4–3.9 for R_2, and 3.9–4.2 and 3.7–4 for G_2. The differences between the H_A and H_B chemical shifts remain approximately constant: 0.7–0.9 for R_1, 0–0.2 for R_2, and 0–0.2 for G_2. The spectra corresponding to the R_2 and G_2 rings are similar.

These values may be useful for the elucidation of the structure in those cases where isomers can be formed.

Thus two glycinate rings of type G_2 and one ring of type R_2 ($\delta AB = 0$) are observed in the complexes with the pentadentate EDTA and HEDTA residues, which confirms the *trans*-position of the NO_2 groups relative to the acetate group in these compounds. The degeneration of the CH_2 quartet of the R_2 ring to a single is due to the small chemical shift difference between the H_A and H_B protons [66].

Table 9. Positions of the signals due to the CH_2 protons in various rings of the cobalt(III) and rhodium(III) complexes of diamine derivatives*.

Complex	H_A	R_1	H_B	H_A	G_1	H_B	E**	Refs.
trans-[Co (en) EDDA]$^+$	4.19		3.37	—		—	3.10	62
trans-[Co (ox) EDDA]$^-$	4.28		3.33	—		—	—	59
trans-[Co (mal) EDDA]$^-$	4.20		3.25	—		—	—	59
cis-[Co (en) EDDA]$^+$	4.02		3.15	—	3.71	—	—	59
cis-[Co (ox) EDDA]$^-$	3.92		3.09	—	3.56	—	—	59
cis-[Co (mal) EDDA]$^-$	3.99		3.09	—	3.48	—	—	59
[Co (ED3A) $NO_2]^-$	4.16		3.42	3.96	G_2	3.88	—	59
[Co (EDTA) $Cl]^{2-}$	4.27		3.28	4.02		3.82	—	26
[Rh (EDTA) $Cl]^{2-}$	4.50		3.85	4.14		3.89	—	67
[Rh (EDTA) $Cl]^{2-}$	4.23		3.75	4.20		4.09	—	67
trans-[Co (en) (DMeEDDA)]$^+$	4.11		3.69	—		—	2.83	62
trans-[Co (en) (DEtEDDA)]$^+$	4.10		3.62	—		—	2.78	62
[CoEDTA]$^-$	3.96	R_2	3.88	3.91		3.58	3.85	67
[RhEDTA]$^-$	4.07		3.97	4.00		3.83	3.71	67
[Co (EDTA) $NO_2]^{2-}$		4.12		4.11		3.86	—	59
		4.2		4.26		3.78	—	59
[Co (HEDTA) $NO_2]^-$		4.13		4.09		3.87	—	59
				4.36		3.46	—	
cis-[Co (AEIDA) en]$^+$	4.21		4.05	4.18		4.02	—	59
Co (PDTA)$^-$	4.11		3.41		3.70		—	26
	3.91		3.53	4.03		3.82	—	
[CoBDTA]$^-$	4.02		3.36	3.87		3.59	—	26
	4.14		3.43	3.96		3.86	—	
[CoCDTA]$^-$	4.25		3.37	3.83		3.52	—	26

*δ in p.p.m.; J = 11–19 Hz.

**The chemical shifts of the ethylene protons for the remaining complexes are not quoted in the original papers.

In the analogous EDTA complex with a chloride ion, the latter is located in the plane [of the ring ?] (only the R_1 ring is observed).

Complexes of EDDA and its *C*-substituted derivatives with cobalt and neutral ligands have been investigated. For the *trans*-coordination of EDDA, the acetate groups are identical and there is only one AB quartet (due to the R_1 ring), while in the *cis*-isomer there are two types of acetate rings (R_1 and G_1) and the spectrum contains an AB quartet and a singlet.

The E ring of the *trans*-complex has two equivalent proton sets, each of which contains equatorial (eq) and axial (ax) protons giving rise to A_2B_2 splitting. The chemical shifts in the spectra of these compounds have been accounted for on the basis of the magnetic anisotropy of the C–N bond [57]. The application of molecular models to cobalt complexes showed that the angles between the $C-H_{eq}$ and $C-H_{ax}$ bonds on the one hand and the molecular axis on the other are different, varying on alkyl substitution from 80° for H_{eq} and 40° for H_{ax} in the EDDA complex to 65° and 85° for the corresponding protons in the DMeEDDA and DEtEDDA complexes, which leads to a change of the chemical shift of the ethylene protons from 3.10–3.12 p.p.m. to 2.83–2.78 p.p.m.

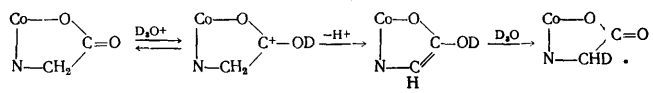
One can also investigate the effect of C–N bonds on the protons of the glycinate ring. The protons located on the

same side of the ring as the amino-proton or the substituent are designated by H_A and those on the other side by H_B. These protons are symmetrical in relation to the C–N bond in the R ring and are screened by this bond to an equal extent, but H_B is located above the C–N bond in the ring, while H_A is at an angle of 40° relative to the C–N axis. Therefore H_B should be screened more than H_A. Such a situation arises in the EDDA complex. If the proton linked to the nitrogen atom is substituted by an alkyl group, the protons of the R ring are distributed in a different way: H_A at right angles and H_B at an angle of about 35° relative to the bond axis. Under these conditions H_A is screened and H_B descreened. Indeed in the DMeEDDA and DEtEDDA complexes, the signal due to H_A shifts towards higher fields and that due to H_B towards lower fields.

Probably the change in the disposition of the H_A and H_B protons is responsible also for the increase of the difference $\delta A - \delta B$ in the spectra of the cobalt complexes of PDTA, BDTA, and CDTA.

To elucidate the structures of the complexes, one also employs the ability of the acetate group protons located in the vertical planes to undergo exchange with deuterium of heavy water in an acid medium at high temperatures, which leads to a gradual decrease of the intensity and the final disappearance of the signal due to these protons [67].

The study of the kinetics of the exchange of the protons of the acetate groups led to a tentative mechanism of the exchange reaction involving the formation of an intermediate enolic form of the complex:



These investigations also made it possible to determine the relative positions of the CH_2 protons in the complexes [58].

The study of the PMR spectra of rhodium complexes of EDTA established the mechanism of the complex formation process as a function of the solution pH and the number of EDTA binding groups employed in the complexes $Rh(EDTA)(H_2O)$, $RhH(EDTA)X$, and $RhH_2(EDTA)X_2^-$¶, where X = Cl or Br. [68] In the first complex, the composition and the number of EDTA binding sites employed change with increase of the pH:

$$\underset{(I)}{Rh(HY)(H_2O)} \leftrightarrow \underset{(II)}{RhY} \leftrightarrow \underset{(III)}{RhY(OH)^{2-}}.$$

The number of binding sites employed is five in complexes (I) and (III) and six in complex (II); this is confirmed by the presence in the spectra of the first two complexes of signals due to the free acetate group, which are displaced as the pH is varied. The number of free and bound groups was determined from the ratio of the signal areas (1 : 3). Under conditions close to neutrality, the signals of the free acetate groups were not observed.

The signals of the free acetate groups were also noted in the spectra of the complexes $Rh(HY)X^-$ and $Rh(H_2Y)X_2^-$, the ratio of the bound and free groups being 3 : 1 and 2 : 2 in the first and second cases respectively, corresponding to penta- and tetra-dentate EDTA residues. In the last case, the presence of only two AB quartets shows that the EDTA oxygen atoms are in the *trans*-positions, which is consistent with the presence of the R_1 rings in the complexes $[Rh(EDTA)Cl]^{2-}$ and $[Rh(EDTA)Cl_2]^{3-}$.

¶ $RhY(H_2O)$, $Rh(HY)X$, and $Rh(H_2Y)X_2^-$.

Platinum(II) and palladium(II) complexes differ from those of cobalt(III) and rhodium(III) by the fact that the metal coordination number in them is four. In the PMR spectra of the majority of platinum and palladium compounds, AB quartets are also observed [69–71]. The number of binding sites in the complexones (IMDA, MIMDA, and NTA) employed in the 1 : 1 platinum and palladium complexes does not exceed three; the oxygen atoms of the acetate groups are located in the *trans*-positions and are equivalent (one AB quartet). The angles between the C–H_{AB} and C–N bonds were determined from the chemical shifts and the spin–spin coupling constants of the H_A and H_B protons: $\theta_{HA} = 80°$ and $\theta_{HB} = 155°$.

After the addition of ammonia to the palladium complexes of IMDA and MIMDA, initially one water molecule is substituted and then one and two oxygen atoms of the complexone are displaced.

The 1 : 2 complexes were found to have *cis*- and *trans*-isomers for IMDA and only the *trans*-isomers for MIMDA and NTA. The chemical shifts of the platinum and palladium complexes investigated are presented in Table 10, which also includes the constants for spin–spin coupling to the magnetic nuclei of platinum.

Table 10. Spectroscopic parameters of the platinum and palladium complexes of IMDA, MIMDA, and NTA. [69–71]

Complex	δ_A	δ_B	δ_R	J_{AB}	J_{PtH_A}	J_{PtH_B}	J_{Pt-R}
[HPt(MIMDA)Cl]·2HCl	4.53	4.08	3.17	17.1	5.5	33.5	27.1
[KPt(IMDA)Cl]·2HCl	4.5	3.76	—	17.5	5.5	35.5	—
Pd(MIMDA)OH·H_2O	4.31	3.35	2.86	16.1	—	—	—
Pd(MIMDA)NH_3	4.25	3.42	2.83	16.1	—	—	—
Pd(IMDA)(OH_2)·H_2O	3.93	3.42	—	16.0	—	—	—
Pd(IMDA)(NH_3)	3.71	3.18	—	16.1	—	—	—
Pt(NTA)	4.58	4.44	4.09	16.5	18.0	37.0	10.5
Pt$(H_2NTA)_2$	3.87	3.78	4.02	15.9	28.0	18.5	26.5
Pd$(H_2NTA)_2$	—	—	3.78	—	—	—	—
$PtH_2(IMDA)_2$	3.78	3.42	—	16.8	43.0	22.0	—
	3.56	3.39	—	16.7	22.0	18.0	—
$PdH_2(IMDA)_2$	3.64	3.46	3.27	16.5	—	—	—

The PMR spectra of the platinum complexes hardly change with temperature and those of the palladium complexes of NTA show only one signal due to acetate protons, which can be accounted for by the averaging of the signals owing to rapid exchange (lability of M–O bonds). The increase of the lability of the bonds from platinum(II) to palladium(II) is consistent with the known rates of substitution reactions involving the complexes of these metals [72] and may be due to a weakening of the bonds in the palladium(II) complex. The latter is consistent with the shift of the acetate proton signal towards high fields relative to the signals in the spectra of the corresponding platinum complexes.

Mixed cobalt [73–78] and platinum(II) [79] complexes containing an aminoacid as one of the ligands have been studied. The aim of these investigations was to establish the absolute configuration of the complexes and to study the rate of proton exchange and of the mutarotation of the chelated aminoacids.

Some data on the structure of the complexes and the delocalisation of electrons on complex formation may be obtained by analysing the chemical shifts. The chemical

shift is determined by the screening constant, which may be represented by the formula

$$\sigma = \sigma_{dia} + \sigma_{para} + \Delta\sigma + \sigma_{ring} \quad (21)$$

where σdia is the local diamagnetic term, σpara the local paramagnetic term, $\Delta\delta$ represents the effect of the anisotropy of the neighbours, and σring represents the interatomic ring currents [80]. In a study of the proton resonance of acyclic compounds, only the first and third terms should be taken into account.

By considering a series of complexes of various metals with the same ligand, it is possible to distinguish three cases. (1) σdia $> \Delta\delta$; the chemical shift is determined by σdia, which is a function of electron density. Since complex formation involves the delocalisation of electrons with decrease of electron density at the ligand, a correlation should be observed between z/r or the ionisation potential and the shift towards lower fields. (2) σdia $\simeq \Delta\delta$; the correlation between the chemical shift and the electronegativity breaks down and the signal shift on complex formation may be close to zero if σdia and $\Delta\delta$ have opposite signs. (3) σdia $< \Delta\delta$; the chemical shift is determined by the symmetry of the complex and is independent of z/r or I for the same symmetry.

Comparison of the chemical shifts of the complexone anions and various complexes shows that in the spectra of certain metal (Li, Na, Mg, Ca, Sr, and Ba) complexonates no signal shift is observed or only a slight shift towards higher fields. This can be accounted for by the fact that the degree of descreening on formation of the metal complexes is caused by the disposition [81] assumed by the complexone atoms on complex formation.

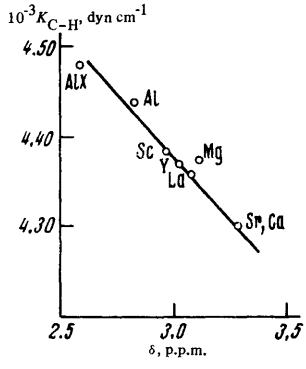


Figure 9. Relation between the chemical shift and the valence-force constant of the C–H bonds for AlX and MX_2 complexes (M = Al, Mg, Ca, Sr, Sc, Y, or La).

In the spectra of the majority of the complexes of the remaining metals, there are signal shifts towards lower fields. If complexes of identical symmetry are formed, the $\Delta\delta$ term will remain approximately constant and the increase of the shift towards lower fields is due to the increase of the delocalisation of electrons on bond formation.

For the NTA complexes, a correlation between the chemical shift and the bond force constant was observed (Fig. 9) [82]. For rhodium and cobalt complexes of the same structure, the chemical shift of the acetate protons in monoamine derivatives and of the ethylene protons in diamine derivatives was found to increase from rhodium to cobalt, which is consistent with the increase of the ionic and ionisation potentials.

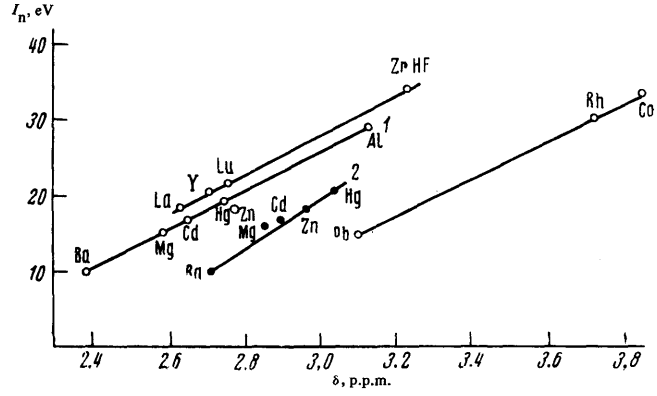


Figure 10. Relation between the ionisation potential of the metal and the chemical shift for EDTA (lines *1*) and BDTA (line *2*) complexes.

Three correlations were found between the ionisation potential I_n, where n is the charge of the metal, and the chemical shift of the EDTA ethylene protons for three groups of metals: (1) lead, rhodium, and cobalt; (2) lanthanum, yttrium, lutetium, zirconium, and hafnium; (3) barium, magnesium, mercury, zinc, and cadmium (Fig. 10). The correlation indicates an identical symmetry of the complexes within the limits of each group and a change in symmetry (with a change in $\Delta\delta$ by a constant amount) on passing from one group of metals to another.

In the first group there is an octahedral symmetry with two nitrogen atoms and two oxygen atoms of the carboxy-groups located in the same plane with the metal atom and two oxygen atoms of the acetate group located in the plane at right angles (a coordination number of six). The formation of polyhedra of lower symmetry (C_1, C_2) with a coordination number greater than six [83,84], in which only the nitrogen atoms are in the same plane as the metal, is characteristic of the second group of metals. The third group includes metals with a noble gas outer shell, in the complexes of which the coordination number may be less than six. These complexes have presumably a *trans*-structure with rapid exchange of the nitrogen atoms along the vertical axis and with the oxygen atoms of the carboxy-groups located in the same plane as the metal ion.

A correlation between the stability constants and the chemical shifts is not always observed. Nor is a linear correlation observed between the stability of the EDTA complexes and the rate of intrachelate and interchelate exchange: with increase of the stability constants, there is both an increase and a decrease of the rate of exchange.

A linear correlation between the stability of bivalent metal complexes and the rate of exchange is observed for the base-catalysed substitution of CH_2 protons in the

acetate residues by deuterium: the rate of proton exchange increases with the stability of the complexes and of the ionisation potential (Fig. 11) [85].

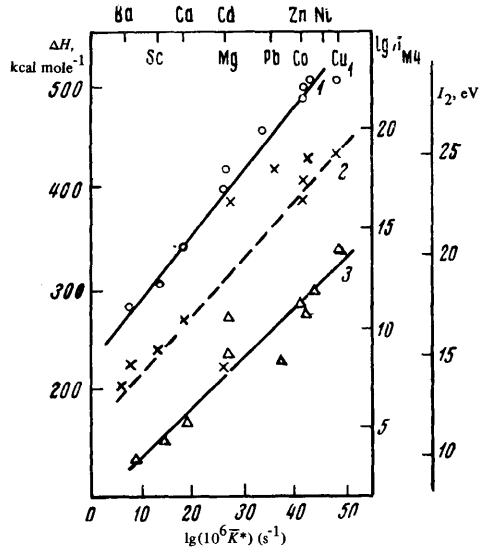


Figure 11. Correlation between the thermodynamic characteristics [1) heat of formation of gaseous MY ions; 2) lgK_{MY}; 3) ionisation potentials] and the rate of proton exchange.

On formation of mixed hydroxo-complexes with substitution of one acetate group by a hydroxide ion, the rate of proton exchange decreases [$Zn(EDTA)(OH)^{2-}$]. If a mixed hydroxo-complex is formed without the dissociation of the linkage with the acetate groups [$Cd(EDTA)(OH)^{2-}$], the rate of proton exchange remains unchanged. Thus the rate of proton exchange serves as an indicator whereby it is possible to establish the structure of the mixed hydroxo-complexes.

The chemical shifts of the acetate protons and their variation in a series of BDTA complexes with various metals are approximately the same as for the EDTA complexes (Fig. 10).

In the CDTA complexes, the chemical shift is almost independent of the metal (apart from the lead complexes). The absence of a dependence on z/r or the metal ionisation potentials can be explained by approximately equal contributions of inductive (σ_{dia}) and long-range ($\Delta\delta$) effects. This is confirmed by similar differences between the chemical shifts of the H_A and H_B protons, the latter being determined by long-range screening [26].

2. Paramagnetic Complexes

The paramagnetic complexes differ from the diamagnetic complexes by higher contact and pseudocontact shifts and considerable changes in the relaxation times on complex formation [47]. Nickel(II), cobalt(II), and copper(II) complexes of aminoacids and complexones and EDTA complexes of uranium(IV) and paramagnetic lanthanide ions have been investigated.

The spectra of complexes with ligands containing NH_2 and NH groups, show lines in the region of high fields (between +50 and +200 p.p.m.), which are attributed to the protons of these groups. It has been shown that these protons exchange with the water protons at the rate of 1×10^3 s^{-1}. The water molecules bound to the ion do not give rise to a separate line (rapid exchange). The majority of lines in weak fields are attributed to the protons of the CH_3, CH_2, and CH groups bound to the nitrogen atom.

The signals of the protons in the CH_2 groups bound to COO^- groups are displaced towards higher fields. The observed directions of the shifts can be accounted for by a contact interaction on formation of the covalent bond [47,86].

However, pseudocontact interaction (the effect of anisotropy) also plays a considerable role. The presence of the CH_3 group in the sarcosine complexes of nickel leads to a disposition of the chelate ring such that the two C–N bonds involving methylene groups form different angles with the Ni–N–C plane, which results in a splitting of the methylene proton signal into two lines (–100 and –40 p.p.m.). In the corresponding glycinate complex there is only one resonance of CH_2 groups, which can be explained by the planarity of the glycinate ring [86].

In complexes with polydentate ligands, a rigid structure may be formed, incorporating several rings which are not planar, which should lead to a splitting of the CH_2 proton signals.

Proton resonance of the nickel(II) complexes of tridentate complexones and nickel(II) and cobalt(II) complexes of tetra- and hexa-dentate complexones has been investigated [86,87]. 1 : 1 complexes with iminodiacetic acids and NTA were shown to have the *cis*-configuration. The following ratios of the *cis*- and *trans*-configurations were found in the complexes with two ligand species: 80 : 20 for IMDA, 40 : 60 for MIMDA, and < 10 : 90 for NTA. [88]† In complexes with two tetradentate ligand species (HIMDA and NTA), the number of binding sites of the ligand employed decreases to 3. The lifetimes of the Ni–N and Ni–O bonds have been determined. In complexes with one NTA residue, the exchange is faster than in the complexes with two NTA residues, which can be explained by the fact that the substitution of water molecules is faster than the substitution of the acetate group. The rate constant is of the order of 10^5 s^{-1}. In $Ni(IMDA)_2^{2-}$ and $Ni(MIMDA)_2^{2-}$, the rate of exchange is lower than in the NTA complex, owing to the absence of a free acetate group [56] ($\bar{k} < 10^3$ s^{-1}) [88].

The spectra of the nickel(II) and cobalt(II) complexes of hexadentate ligands depend on the pH of the solution: the bands are displaced and their width changes. The spectra of the cobalt complexes contain sharper lines and their structure is more complicated, which can be explained by a lower rate of exchange in these complexes [86].

In the spectra of all the metal compounds with complexones investigated, the signals of the CH_2 group linked to a nitrogen atom are split into two components, which can be accounted for by the anisotropy of the linkage (different angles between the Ni–N–C plane and the CH_2 protons). The difference between the chemical shifts of the CH_2 protons increases in the spectra of complexes with six-membered rings compared with complexes having five-membered rings. The explanation may be that the angles between the Ni–N–C plane and the C–H vector

† *cis*- and *trans*- in relation to the oxygen atoms.

differ more on formation of six-membered rings. All these conclusions are consistent with X-ray diffraction studies [89,90,91] and with studies on the PMR spectra of the diamagnetic complexes (see p. 271). The shift of the N–CH_2 protons and the angle between the Ni–N–C plane and the C–H vector have been found to be correlated (Fig. 12).

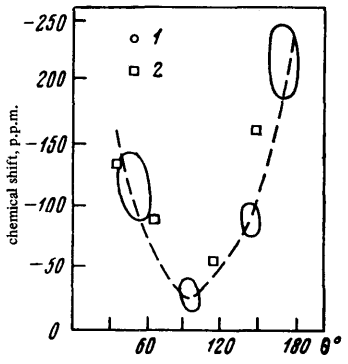


Figure 12. Correlation between the shift of the CH_2 proton signals and the NiNC–H angle: 1) angles determined from the model; 2) X-ray diffraction data.

The study of mixed complexes containing an EDDA residue and an aminoacid established the conformation of the glycine ring in the unsubstituted and methyl-substituted glycinate complexes: the number of binding sites of the tridentate aminoacids employed in the mixed complexes was found to be reduced, the stereochemistry of the mixed complexes was established, and stereoselective coordination of the aminoacids in the mixed complexes was found [92].

Mixed complexes of asymmetric aminoacids give rise to diastereoisomers, which can be detected in the PMR spectra.

Interesting studies have been made on complex-formation equilibria with simultaneous investigation of the structure of the complexes in the cobalt(II)–histidine system [93]. Fig. 13 illustrates the variation of the contact shift of the protons in water and histidine,

$$(\overset{+}{N}H_3\text{—}\underset{\displaystyle COOH}{\underset{|}{CH}}(\alpha)\text{—}CH_2(\beta)\text{—}),$$

as the pH of the solution is varied. At a low pH, there is a greater contact shift of the water protons, while the histidine protons do not exhibit a shift relative to the free ligand, i.e. there is no complex formation. With increase of the pH, the signals of the Hα and Hβ histidine protons are displaced, which indicates coordination via the nitrogen atom and the COO^- group. At pH > 4, the contact shift of the water proton signals decreases with a simultaneous increase of the contact shift of the signals due to the protons in the imidazole ring and at pH > 6 the position of the water proton signal becomes the same as in pure water. This shows that under these conditions water does not enter the inner sphere of the complex.

Four complexes were discovered in the system, in which the linkages are formed either with the COO^- group alone or with the COO^- group and one or two nitrogen atoms. In the latter case, there is a transition from octahedral to tetrahedral configuration [93].

The hydration and structures of certain copper(II) aminoacid complexes have been investigated [94]. The hydration numbers of copper and the distances between the copper atom and the oxygen atoms of water in complexes with aminoacids and in the normal and protonated EDTA complexes were determined from the relaxation time of the water protons (Table 11).

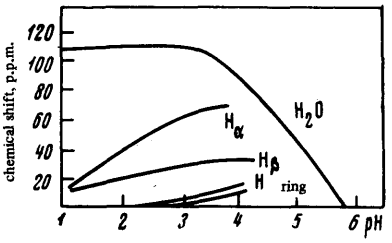


Figure 13. Variation of the contact shifts of the proton signals of water and histidine (Hα, Hβ, H_{ring}) with the pH of the solution.

The spectra of EDTA complexes with paramagnetic lanthanide ions (cerium, neodymium, praseodymium, and samarium) show one AB quartet due to the methylene protons and a singlet due to the ethylene protons. The presence of one AB quartet can be accounted for either by the equivalence of the methylcarboxyls or by a rapid exchange between them. The latter is more likely. In a mixture of complexes of two lanthanides, two sets of signals due to these complexes are observed. The relative concentrations of the complexes were determined from the relative intensities and the stability constants were calculated from the exchange equilibrium constants [97]. The constants obtained agree with the values quoted in the literature [3].

Table 11. Cu–OH_2 distances in complexes with aminoacids and EDTA.

Ligand	$[CuA(H_2O)_4]^+$ Cu–OH_2, Å		$CuA_2(H_2O)_2$ Cu–OH_2, Å	
	soln.	crystal	soln.	crystal
Glycine	2.12		2.29	
α-Alanine	2.18		2.34	
β-Alanine	2.16	2.20*	2.26	2.43*
Sarcosine	2.16		2.28	
Dimethylglycine	2.21		2.39	
	$[CuA(H_2O)]^{2-}$		$[CuHA(H_2O)_2]^-$	
EDTA	2.03	2.08**	2.08	

*Refs. 95 and 96.

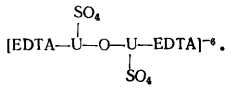
**In $Ni(H_2EDTA)H_2O$ which is isomorphous with the copper(II) complex [89].

In the uranium(IV) complex of EDTA in the presence of sodium sulphate above 27 °C, the U–O bonds are labile and the U–N bonds are non-labile, while below 27 °C the U–O

bonds also become non-labile [98]. This is reflected in an additional splitting of the signals due to the methylene and ethylene protons. Measurements of the rate of exchange and inversion at different temperatures and of the activation parameters for these processes showed that the ethylene ring undergoes inversion without dissociation of the metal–ligand bonds ($\Delta G = 10.22$, $\Delta H = 10.8$, and $\Delta S \simeq 0$).

The study of the spectra at different pH revealed two types of complexes (at pH 0–3 and at pH > 6). At lower pH values, the signals due to free EDTA are also observed.

The complex formed in the acid region is a monomer with a distorted cubic structure. At pH > 6, dimeric species with an oxygen bridge and incorporating sulphate groups are formed:



The structure of the monomeric complex was deduced by analysing the chemical shifts on its formation [92].

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Institute of General and
Inorganic Chemistry,
Academy of Sciences of
Ukrainian SSR, Kiev