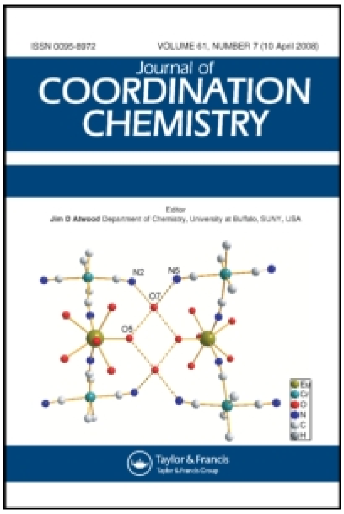

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NUCLEAR MAGNETIC RESONANCE STUDIES OF THE CONFIGURATION AND LIGAND REARRANGEMENT IN COMPLEXES OF NICKEL(II) AND COBALT(II) WITH DIETHYLENETRIAMINEPENTAACETIC ACID AND TRIETHYLENETETRAAMINEHEXAACETIC ACID

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NUCLEAR MAGNETIC RESONANCE STUDIES OF THE CONFIGURATION AND LIGAND REARRANGEMENT IN COMPLEXES OF NICKEL(II) AND COBALT(II) WITH DIETHYLENETRIAMINEPENTAACETIC ACID AND TRIETHYLENETETRAAMINEHEXAACETIC ACID‡

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Coordination of the Ni(II) and Co(II) ions by diethylenetriamine *N,N,N',N'',N''* pentaacetic (DTPA) and triethylenetetraamine *N,N,N',N'',N''',N'''* hexaacetic acid (TTHA) over the entire pH range was studied by means of ^{1}H NMR spectroscopy.

The spectra of the paramagnetic complexes were analyzed based on the relationship between the hyperfine coupling constant and dihedral angle. In the Ni(II) and Co(II) complexes each ionic species exhibits a characteristic NMR spectrum. In the metal ion coordination sphere the unprotonated species contain three amino nitrogens both for DPTA and TTHA. Proton addition decreases the number of coordinating nitrogens. DTPA and TTHA form binuclear and mononuclear complexes. The binuclear complexes consist of two identical subunits linked by an ethylene bridge.

The temperature dependence of the shapes of spectra and of the contact shift exhibits a strong deviation from the Curie law for both mono- and binuclear Ni(II) complexes. This results from rearrangements consisting in a change of the dien ring conformations in the case of mononuclear complexes and from rotation of two subunits around the bridge bonds – for binuclear complexes. Considering the shifts of the Ni(TTHA) and Co(TTHA) complexes as corresponding the "frozen" conformation of the DTPA complexes and assuming a suitable rearrangement mechanism, the isotropic shift averaging diagrams in the spectra of the Ni(DTPA) and Co(DTPA) complexes were deduced. The protons of the acetate methylene groups undergo stereospecific deuteration. For the Ni(TTHA), complex the protons of the central acetate groups are deuterated slower than those of the terminal acetate. For the Ni_2(TTHA) the deuteration rate does not depend on the position of the acetate group in the ligand structure.

INTRODUCTION

Polyaminepolyacetic acids form stable complexes with almost all metal ions. One of the most interesting phenomena typical for these systems are intramolecular rearrangements.[1] Sophisticated studies of these rearrangements have been performed by applying ^{1}H NMR spectroscopy.[2–6] The spectral shape of the acetate methylene protons for diamagnetic complexes is a function of the lifetimes for the metal–ligand bonds.[7]

However, even for relatively long lifetimes an averaged pattern is observed. This renders the interpretation more difficult particularly for more complex ligands.[6,12] The method becomes more applicable in paramagnetic systems where the range of resonances in the spectrum is considerably increased.[3,4,7] The ^{1}H NMR spectrum of the pseudooctahedral Ni(II) complexes contains an abundance of structural information.[7–9]

The situation becomes more complicated for the Co(II) complexes where contribution of the pseudocontact shift is considerable, the differences in the shifts of axial and equatorial protons for the corresponding molecular fragments being maintained.[5,7] The above mentioned effect of the central ion on the ^{1}H NMR spectrum of polyaminepolyacetic acids was extensively applied for investigation of the complexes of diaminepolyacetic acids.[2–5]

Introduction of the $(-CH_2-CH_2-N-CH_2-COOH)_n$ group into the molecular structure of diaminetetraacetic acid leads to the formation of a homologous

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ligand series two members of which: diethylenetriamine *N,N,N′,N″,N″*-pentaacetic acid (DTPA) and triethylenetetraamine-*N,N,N′,N″,N‴,N‴*-hexaacetic acid (TTHA) are dealt in the present paper. Both ligands tend to form either binuclear or mononuclear complexes of different degrees of protonation.[6,10–13] The structure and rearrangements of these complexes in aqueous solutions are poorly known and, therefore, should be studied in detail.

In our previous paper[21] we applied the ^1H NMR spectroscopy to studies of the Ni(II)-DTPA system. From the effect of ligand geometry on the contact shift certain conclusions, concerning the structure of the Ni(H_nDTPA) ionic species in aqueous solutions, were drawn. Similar information may be expected for the corresponding Co(II) complexes.

On the basis of EPR spectra[15–18] the binuclear complexes with TTHA were assigned a different structure in aqueous solutions than in the solid state.[19,20] One may expect that the ^1H NMR spectra, particularly of the binuclear Ni(II) complex, will provide additional information on the structure and rearrangements of binuclear complexes in aqueous solutions.

EXPERIMENTAL

For ^1H NMR measurements the samples were prepared by weighing stoichiometric portions of the metal salt and polyaminepolyacetic acid in order to achieve the metal–ligand molar ratio of 1:1 or 2:1. $NiCl_2 \cdot 6H_2O$ and anhydrous $CoCl_2$ were used as a source of the metal ions. The following acids were used for studies: diethylenetriaminepentaacetic acid (DTPA)–Merck and triethylenetetraaminehexaacetic acid (TTHA)–Fluka.

$NiCl_2 \cdot 6H_2O$ was dissolved in D_2O and evaporated to dryness. The respective complexes were prepared by mixing the solutions of metal salt and polyaminepolyacetic acid in D_2O. The pD required was adjusted by adding KOD or DCl. In order to reduce the residual HOD signal, the solution was evaporated in a vacuum desiccator over P_2O_5. After treating with D_2O the process was repeated several times. Subsequently the solution was treated with D_2O so as to prepare 0.5 M samples.

The deuteration rate of the methylene protons in the acetate groups of the Ni(TTHA) complex was measured in basic solutions at the complex concentration of 0.1 M and KOD concentration of 0.2 M. The solution to be deuterated was heated in a thermostat at the required temperature. Periodically about 0.2 cc samples were taken and cooled down very rapidly to 273 K in order to inhibit the reaction. Then Ni(II) was converted into a diamagnetic $Ni(CN)_4^{-2}$ complex by treating with KCN. By comparing the peak intensities of the acetate and ethylene groups (the latter do not undergo any deuteration) it was possible to follow the hydrogen – deuterium exchange reaction. Deuteration of the methylene hydrogens in the acetate groups facilitated interpretation of ^1H NMR spectra.

Taking into account the results of systematic deuteration studies of the Ni(DTPA),[21] Ni(TTHA) and Ni_2(TTHA) complexes, selective deuteration was performed at 0.5 M concentration. For the Co(II) complexes, heating of the compounds under investigation at elevated temperatures may have resulted in oxidation of Co(II) to Co(III) complexes. However, the deuteration process was carried out under the same conditions as those for the Ni(II) complexes. Another method was also applied, consisting in preparation of selectively deuterated Ni(II) complex. The solution of this complex was then treated with concentrated hydrochloric acid to precipitate white DTPA (TTHA) contaminated with KCl. After drying, the Co(II)-deuterated DTPA (TTHA) samples were prepared. The ^1H NMR spectra in both cases are identical but the latter method allows control of the degree of deuteration.

In order to determine the dependence of the ^1H NMR water half linewidth the 0.1 M solution was used as for IR spectroscopic measurements. In each case the pH-meter reading was recalculated in the following way:[24]

$$pD = pH + 0.40$$

^1H NMR and IR Measurements

The ^1H NMR spectra were measured in a JEOL-PS-100 spectrometer. Sodium 3-(trimethylsilyl)-propanesulphonate (TMS†)–Merck was used as an internal standard. The sweep width was calibrated by means of the side band technique. The spectra were measured in the 270 ppm range. For measurements of the water half linewidth the sweep width of 0.54 or ~~1.08 ppm~~ was applied.

Methyl alcohol and glycol were used for temperature measurements.[23]

IR spectra were measured on a Perkin–Elmer 621 spectrometer in the KRS-5 disks at the film thickness of 0.012 mm, in the 1450–1800 cm^{-1} range.

RESULTS AND DISCUSSION

Ni(H_nTTHA) Complexes

From the stability constants, determined by Bohigian and Martell,[11] a distribution diagram of the ionic species with various degrees of protonation according to pH was developed for the Ni(II)–TTHA system. By comparing this diagram with the characteristic spectral shapes obtained for the Ni(II)–TTHA system for various pD values (Figure 1), particular ionic species were assigned to their corresponding ^{1}H NMR spectra. A description of the dissociation mechanism based on these grounds is presented in Figure 2.

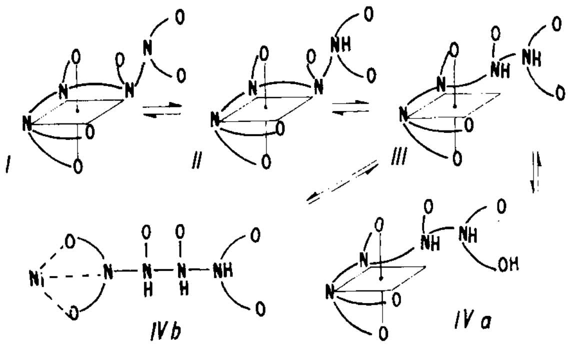

FIGURE 2. Dissociation diagram of the Ni(II)–TTHA system.

The spectra of particular species are observed in the following pD ranges:

I–pD > 10; II–pD = 5–7;
III–pD = 2–3.5; IV–pD = 0.7.

The carboxylate stretching frequency (IR spectroscopy data) reflects the manner in which the glycine group is bounded.[14,22] The analysis of the intensity of this band as a function of pD[22] shows that the first two protons are attached at the amino nitrogens only (Figure 3).

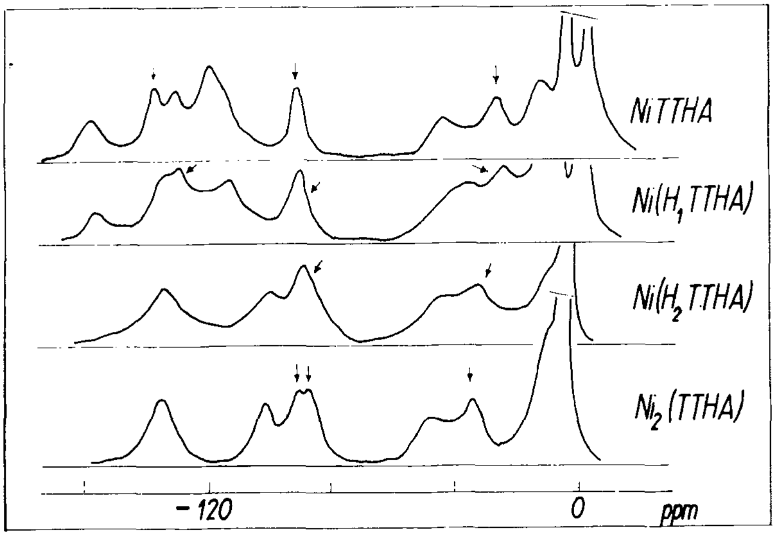

FIGURE 1. Typical shapes of the ^{1}H NMR spectra for the Ni(H_nTTHA) complexes (T= 303 K). Arrows indicate the resonances of the acetate methylene protons.

In the Ni(H_1TTHA) only two carboxyl groups are situated near the protonated nitrogen which corresponds to structure II, while in the Ni(H_2TTHA) species the number of these groups increases to three as for structure III (Figure 2). Further protonation takes place at the carboxyl groups as demonstrated by an increase in line intensity at 1730 cm^{-1} in the IR spectrum. At this degree of protonation changes in the shape of the ^{1}H NMR spectrum occur; this must result from variation in the number of nitrogens in the coordination sphere (ionic species IV).

Since the first proton is attached at relatively high pD values (Figure 3) one should conclude that the nitrogen atom is uncoordinated (Figure 2, ionic form I). Because of the interference of the IR bands corresponding to a fully ionized and fully coordinated carboxyl group[21,22] it is not possible to confirm directly the presence of structure I from these spectroscopic measurements.

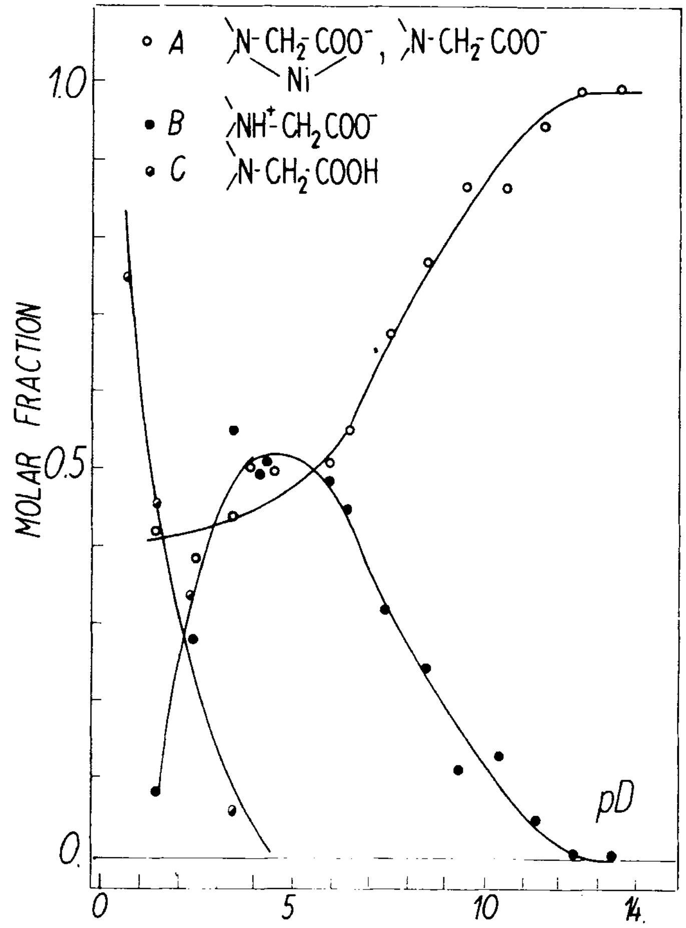

FIGURE 3. Molar fraction of carboxylic group of different coordination and protonation mode as a function of pD for Ni(H_nTTHA) system.

The values were calculated according to the formula: $(I_i/\epsilon_i)/\sum_i (I_i/\epsilon_i)$ where I_i is intensity at maximum, ϵ_i – absorption coefficient (taken from Ref. [22]). Since A and B bands overlap partially, the intensity of each band was estimated by graphical separation assuming symmetric profiles.

The ^{1}H NMR spectra of the Ni(DTPA)[21] and Ni(TTHA) complexes are identical (Figure 1, Table I). Thus, it was assumed that in form I of Ni(TTHA) (Figure 2), as in Ni(DTPA), three succesive nitrogens coordinate with identical configurations for both complexes (Figure 4).

The resonances of these molecular fragments, which were not coordinated, could not be found in the ^{1}H NMR spectrum of the Ni(TTHA), probably because of the dynamic processes taking place in solution. One should note the appearance of the central acetate group resonance at extremely low field (−140 ppm, T = 303 K) which must result from a considerable distortion of the chelate ring formed by it.

The transition of Ni(TTHA) into Ni(H_1TTHA) results in spectral peak broadening. No change of the contact shifts take place. Two new resonances appear in the equatorial range. It may be assumed that the presence of a proton on the amino nitrogen slows down the rotation around N—C bond of the uncoordinated molecular fragment. This results in an increase of population of one of the rotamers with respect to that bond and in the appearance of two spectral lines, each one being assigned to one of the methylene protons in the α position with respect to the bonding nitrogen atom. This degree of protonation does not affect the water half linewidth which confirms the suggested course of the process.[25,26] Further protonation results in an

TABLE I
Contact shifts and spectral assignments of Ni(II) complexes at 303 K

Complex	am, eq	ac, eq	am, eq	am, eq	ac, eq	am, ax	ac, ax	am, ax
Ni(TTHA)	−159.6	−138.8[a]	−132.3	−120.6	−92.5[b]	−39.4	−26.3[b]	−11
Ni(DTPA)	−160.0	[c]	−129.0	−114.0	−90.0[b]	−35.0	−25.0[b]	−15
Ni_2(TTHA)	–	–	−138.9	−104.5[d]	−95.6	−46.6[d]	−36.0	−10
Ni(H_2TTHA)	–	–	−140.6	−102.9[e]	−93.0	−46.9[e]	−36.0	−10
Ni(H_1DTPA)	–	–	−140.0	−101.0[e]	−95.0	−50.0[e]	−35.1	−10
Ni(MED3A)[f]	–	–	−133	–	−93	–	−33	−5

Shifts in ppm; referenced to uncomplexed, diamagnetic ligand in basic solution (pD > 11)

[a] – central acetate group
[b] – side acetate group
[c] – broad
[d] – bridging ethylene protons
[e] – lines of unchelated $N-CH_2-C$
[f] – from Ref. 4,,MED3A – $^{-}O_2C-CH_2-N-(CH_3)-CH_2-CH_2-N-(CH_2-COO^{-})_2$
ax – axial; eq – equatorial; ac – acetate; am – $(CH_2-CH_2N)_n$ group

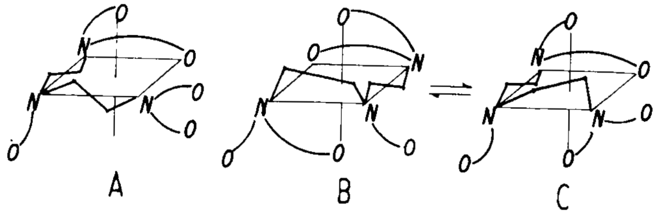

FIGURE 4. Suggested structures and rearrangement of the M(DTPA) and M(TTHA) complexes where M = Ni(II); Co(II).

increases of the water half linewidth from 5 Hz to 25 Hz, due to the structure opening (Figure 2).

The attachment of the succesive protons varies the spectrum so that its shape is identical by pairs: Ni(H_2TTHA) and Ni(H_1 DTPA) (Table I,[2 1]) as well as Ni(H_3 TTHA) and Ni(H_2DTPA), respectively. On the grounds of this comparison these ionic species may be assigned to the structures III and IV (Figure 2). The Ni_2(TTHA) complex (well soluble in the pD range 3 ÷ 12) exhibits a relatively simple spectrum (Figure 1). It was assumed that the complex consists of two identical subunits of the Ni(MED3A) structure linked by an ethylene bridge (Figure 5).

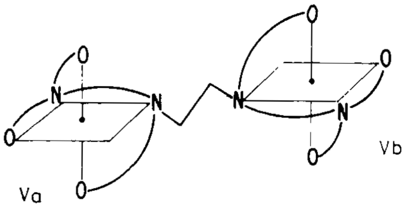

FIGURE 5. "Extended" structure of the Ni_2(TTHA) ion.

Various authors offer controversial views as to the structure of the binuclear complexes with TTHA.[15-20]

The results for the Ni_2(TTHA), presented in this paper, indicate that in solution, at least for Ni(II) systems, TTHA forms complexes with an "extended" structure (Figure 5). The "closed" forms differ substantially in their structures from the EDTA complexes and their analogues[1 5-1 7] and, as a rule, the environment of each Ni(II) ion should differ from that for the Ni(MED3A) complex. The ^{1}H NMR spectrum of the Ni_2(TTHA) which indicates presence of the Ni(MED3A) type subunits (Table I), enables to eliminate "closed" structures in solution. The "extended" structure may also be suggested for the Ni(II)–DTPA system (pD = 2 ÷ 4). At the molar ratio Ni(II)–DTPA = 2 : 1 the ^{1}H NMR spectrum, as compared with the Ni(H_1DTPA) complex exhibits two new resonances of methylene protons of the acetate groups in position which are characteristic of the Ni(II) complexes with iminodiacetic acid and its derivatives.[7] One of the Ni(II) ions is coordinated by two amino nitrogens and three carboxyl groups (Ni(MED3A) type structure) and another one by one nitrogen and two carboxyl groups (Ni(IDA) type structure).

Both units are linked by the ethylene bridge. Such a spectral shape may be observed up to 373 K without any visible changes, which might have resulted from a change in environment of the Ni(II) ions within the same molecule.

Rearrangements of the Ni(II) Complexes

Figure 4 shows possible structures of the Ni(DTPA) and Ni(TTHA) ions, considering the conformation of the ligand amino part. In structures B and C (Figure 4) the envelope conformation of the five-membered ring, found in certain chelated compounds[2,7–31] was taken into account. In addition, structures B and C are optical isomers.

For each of the structures shown in Figure 4 one should expect four peaks in the equatorial region of the NMR spectrum, of which two may interfere yielding one peak as found in the experimental spectrum. An increase in temperature causes averaging of the proton shifts in the amino region of the Ni(DTPA) spectrum, leaving axial-equatorial differentiation of the acetate methylene protons.[21] Each of the rearrangement mechanisms known hitherto for the polyaminepolyacetic acid complexes acts in a non-selective way. These mechanisms lead to complete averaging of all isotropic shifts or, as in the case of inversion on nitrogen atom, axial-equatorial differentiation remains.[2] For the sake of clarity, it should be added that conversion of optical isomers may leave residual differentiation of shifts but it should be much lower than the difference in shifts of the Ni(DTPA) acetate methylene protons, which amounts to 60 ppm ($T = 353$ K).

The structures suggest in Figure 4 require to take additionally into consideration the conformational equilibrium of the envelope—δ (λ) type. The process was presented schematically in Figure 6.

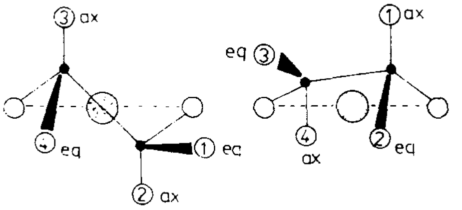

FIGURE 6. Conformations of the five-membered chelate ring with proton position taken into consideration. ax – axial; eq – equatorial

The conformational equilibrium shown in Figure 6 makes it possible to average ^{1}H NMR resonance positions. For Ni(DTPA), it would be equivalent to an equilibrium between isomers B and C (see Figure 4). A rapid scrambling of the acetate groups is the reason for conformation changes of two ethylenediamine type chelate rings in the ligand. The interpretation of the acetate group spectrum is not so straightforward. The process does not pass through the symmetric transition form and does not average, as for Ni(IDA)$_2$ complex,[4] the equatorial and axial acetate proton contact shifts. The contact shift of the equatorial protons in terminal (side) acetate groups ($T = 353$ K) is an arithmetic mean of the acetate equatorial proton shifts of the Ni(TTHA) complex. This is a confirmation of the fact that the rearrangement process, in the case of acetates, proceeds with preservation of the chelate ring conformations.

It was assumed that the contact shifts of the Ni(TTHA) complex ($T = 353$ K) equal to the shifts for the Ni (DTPA) complex with 'frozen" conformations of the chelate rings at corresponding temperature. According to that rearrangement mechanism suggested above, it is possible to conclude that the observed shifts is the arithmetic mean of contact shifts of the two different configurations of the Ni(DTPA) complex (B and C, Figure 4).

A diagram of shift averaging, resulting from structural rearrangements of the Ni(DTPA) ion, was proposed (Figure 7).

As can be seen from Figure 7 the agreement between calculated and experimental spectra is satisfactory.

The central acetate group resonance is found in low fields which may be related to the predominance of a specific rotamer with respect to the N—C bond ($\theta = 60°$).

For the Ni(TTHA) complex the contact shifts of the equatorial and axial protons are not averaged. As shown by the relationship between the product of contact shift and temperature /($\delta \cdot T$)/ versus T each proton exhibits a deviation from the Curie law which indicates that a dynamic process takes place.[8] The mechanism of that process is probably similar to the rearrangement mechanism of the Ni(DTPA) complex, the two equilibrium forms for the latter one being equivalent and equally probable. The Ni(TTHA) ion is asymmetric as compared with Ni(DTPA) (absence of one acetate at nitrogen 3) and one of the two forms B or C (Figure 4) may predominate. A certain role also may be played by exchange between the coordinated and free end of the TTHA molecule.

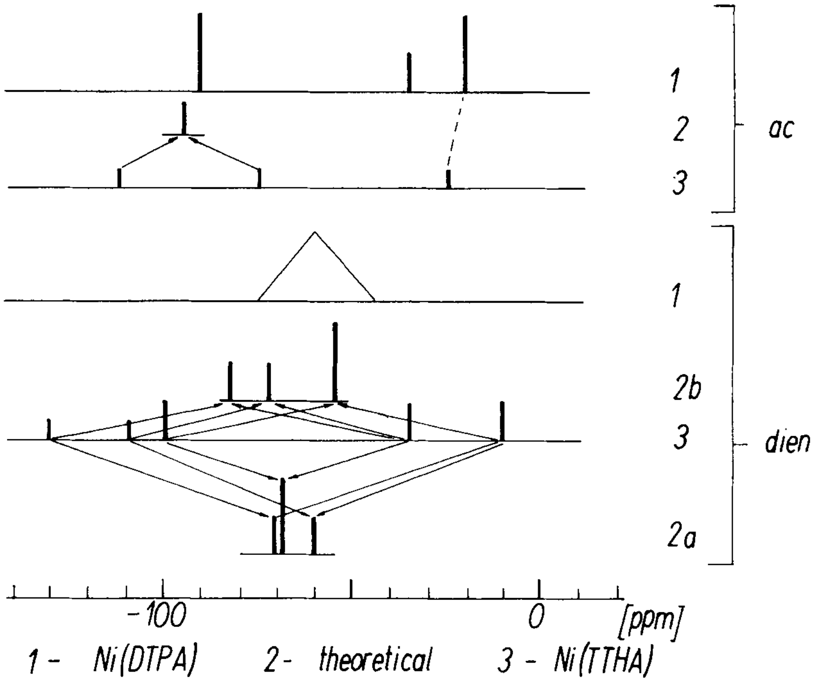

FIGURE 7. Diagram of the contact shift averaging, resulting from structural rearrangements in the Ni(DTPA) complex (T = 353 K).
ac – acetate methylene protons
dien – amino part methylene protons

In the case of the Ni(H_2TTHA) and Ni(H_1DTPA) a plot of ($\delta \cdot T$) versus T indicates that the resonances assigned to the protons of the coordinated part of the ligand molecule obey the Curie law. This assignment differs from the previous one for Ni(H_1DTPA).[21] On the other hand, the deviation from the Curie behaviour found for the N–CH_2–C (uncoordinated ligand part) resonances is related to the exchange process of the methylene group positions with respect to the Ni–N bond. The metal ion–protonated molecule end interaction stabilizes one of the three main conformations with respect to the N–C bond in which a maximum differentiation of contact shifts occurs (rotamer with the radical in gauche position to the Ni–N bond). An increase in temperature augments the populations of less stable rotamers which, in effect, is manifested by the deviation from Curie law.

A similar process takes place for the Ni_2(TTHA) complex. A plot of ($\delta \cdot T$) versus T shows that the subunit protons satisfy the Curie law whereas the bridging ethylene protons are exchanged between various positions owing to the rotation of two subunits each around another.

Deuteration of the Ni(TTHA) and Ni_2(TTHA) Complexes

Assuming the averaging processes of proton positions proceed very rapidly in comparison with deuteration processes, the deuteration rate constants and the corresponding thermodynamical functions were found (Table II). These values do not differ considerably from those found for Ni(EDTA),[2] and Ni(DTPA).[21]

It was found that for the Ni(TTHA) complex the deuteration process of the methylene protons in acetate groups, linked to the central nitrogens, is much slower than for the terminal (side acetate) groups. Under conditions in which the deuteration kinetics was investigated, no proton-deuterium exchange took place in these groups.

On the other hand, in the Ni_2(TTHA) complex the deuteration proceeds always in the same way, irrespective of the position of acetate groups.

On the basis of the selective deuteration, it was possible for the Ni(H_nTTHA) complexes ($n = 0 \div 3$) to distinguish peaks corresponding to the protons of

TABLE II
Pseudo first-rate constants (k·10^4 [s^{-1}]) and activation parameters for exchange of acetate protons

		Acetate group		
		Side		Central
		Ni(TTHA)	Ni$_2$(TTHA)	Ni$_2$(TTHA)
T(K)	359.2	7.56	10.70	12.90
	338.0	1.52	3.15	2.38
	318.2	0.32	0.56	0.43
	307.6	0.12	0.20	0.16
	277.1	0.008	0.014	0.005
E$_a$, kcal		15.7	17.2	18.5
ΔH$^{\neq}$, kcal		16.6	16.1	17.8
ΔS$^{\neq}$, cal/K		−26±3	−29±3	−21±3

the amino ligand part and acetate groups, and even peaks of the central acetate protons from those of the terminal acetate protons (Figure 1, Table I).

The spectrum of the Ni(TTHA) complex shows that at least one of the central acetate group is involved in the coordination. It is known[2] that the deuteration rate of the diaminepolyacetic acid complexes depends considerably on the position of the acetate group in the complex. The results obtained suggest that for Ni(TTHA) and Ni(DTPA)^{2}[1] complexes, one of such positions protects the acetate methylene protons against deuteration.

According to the analysis of the effect of structural rearrangements on the deuteration processes[2] equal deuteration rates of all acetate groups found for binuclear complex are an evidence of the inversion process on the nitrogen atom. Since this exchange takes place between the equally filled molecular states without any change in the relative proton positions in the chelate ring, it is not reflected in temperature dependences of contact shifts.

Co(II) Complexes with TTHA and DTPA

For the Co(II)–TTHA system a similar pattern of coordination and structural rearrangements as that for Ni(II)–TTHA is observed. On the basis of the ^{1}H NMR (Tables III–V) and IR spectra, selective deuteration of the acetate groups and also on the basis of water half linewidth consideration it was possible to establish the mechanism of the dissociation process by similar reasoning as that for the Ni(II) complexes (Figure 2). It was possible to assign the resonances to the corresponding protons (Tables III–V).

TABLE III
Isotropic shifts for Co(TTHA) complex at 303 K

Shift	Assignment	Shift	Assignment
−166.0	am, eq	−56.0	ac, uncoord.
−146.0	ac, eq	−53.0	ac, ax
−140.3	am, eq	−36.6	am, ax
−113.1	ac, eq	6.9	am uncoord.
−105.5	ac, eq	12.1	am
−103.7	am, eq	33.2	am, ax
−91.5	am, ax + eq	51.0	am, ax
−66.0	ac, ax	69.0	ac, ax

[a] Shifts in ppm; referenced to uncomplexed, diamagnetic ligand in basic solution. Denotation as in Table I.

For Co(TTHA) an increase in temperature alters only the isotropic shifts of resonances, as for Co(H$_1$TTHA) the ^{1}H NMR spectrum demonstrates the presence of rearrangement processes (broadening and even disappearance of certain peaks).

The spectra of the Co(DTPA) complex (Table IV) differ substantially in their shapes from those of the Ni(II) complex. This is more interesting in that for TTHA the spectral shapes for both metal ions are similar and substantially different from that for Co(DTPA). Thus, the observed spectrum should neither be related to the specific structure of the complex ion nor to the different spectroscopic properties but rather to its structural rearrangements.

An identical rearrangement mechanism as for Ni(DTPA) was proposed. However, the activation energy of the Co(DTPA) rearrangement is lower than that for Ni(DTPA), which is usually observed when comparing Ni(II) and Co(II) complexes with

TABLE IV
Isotropic shifts for Co(DTPA) complex at 303 K

Shift	Assignment
−121.1	ac side, eq
−89.6	am
−60.9	ac side
−56.3	ac central
−56	am, visible from T = 333 K
−35	am, visible from T = 333 K
33.5	ac side, ax

[a]Shifts in ppm; referenced to uncomplexed, diamagnetic ligand in basic solution; denotation as in Table I

diaminepolyacetic acids.[4,5] Therefore, even at 303 K the shifts for particular protons become averaged. The two resonances of the dien ligand part are broadened for the Co(DTPA) up to 333 K. The Co(DTPA) complex is in the course of permanent structural rearrangements and for these two resonances the exchange rate corresponds to the intermediate exchange rate where the half linewidth is at maximum[32] (i.e. the distance of shifts in Hz for "frozen" conformation is the largest). The dependence of the isotropic shifts on temperature exhibits considerable deviation from the Curie law which results mainly from the shift-averaging structural rearrangements.

The analysis of the half linewidth for the acetate methylene proton resonances indicates that from T = 343 K the half linewidth increases considerably (from 7 ppm at 343 K to 22 ppm at 373 K).

The subsequent process, responsible for the acetate resonance broadening, alters the conformations of glycine chelate rings. On the basis of the values of isotropic shifts for Co(TTHA) an attempt was made to reconstruct the isotropic shift averaging scheme resulting from the rearrangement mechanism shown in Figure 4. The assumptions accepted for the Ni(DTPA) complex were considered to be also valid here. The result of such an averaging is shown in Figure 8.

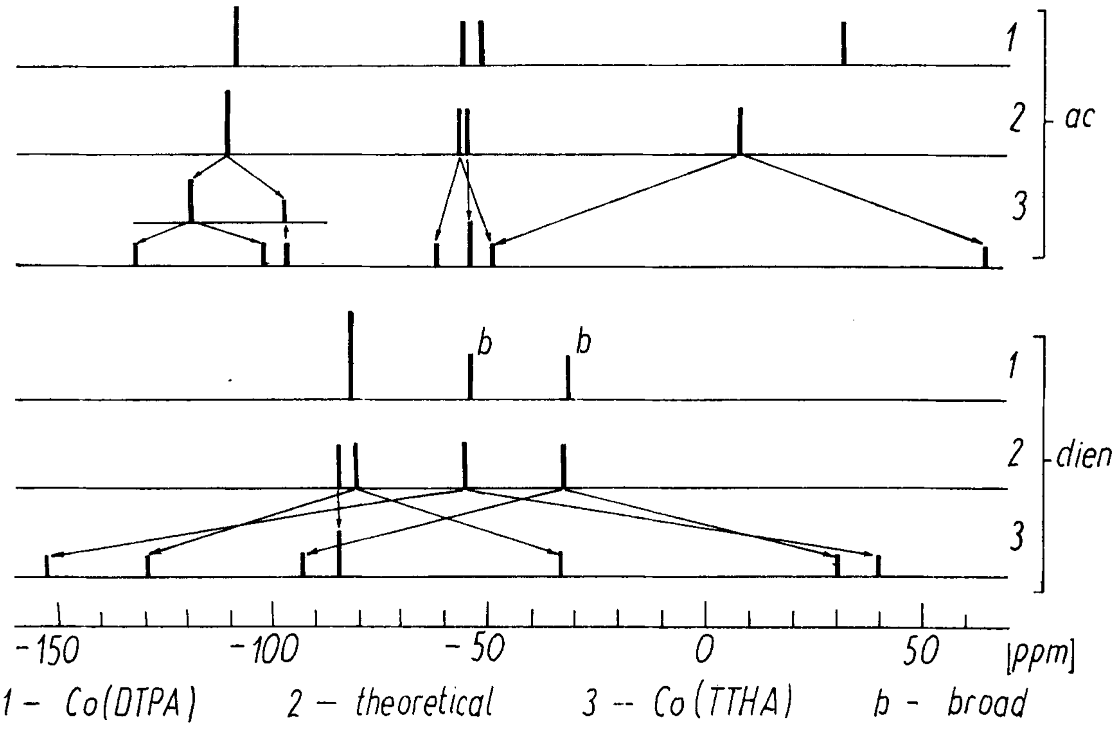

FIGURE 8. Diagram of the isotropic shift averaging, resulting from structural rearrangements in the Co(DTPA) complex (T = 323 K).
Denotation as in Figure 7.

Co_2(TTHA) Complex

The shape of the ^1H NMR spectrum (Table V) for such a specific complex as Co_2(TTHA) is determined by three effects which are possible only for binuclear form of the complex:

a) rotation of the two Co(MED3A) type subunits around the bridging ethylene (see Figure 5);

b) inversion, independently on each central ion (for each subunit there are four possible geometric and optical isomers and thus one expects ten isomers of the binuclear complex, assuming that the rearrangement processes of both parts of the molecule are independent);

c) the pseudocontact shift is a sum of two contributions resulting from the two central ions. Although the enantiomeric forms are usually indistinguishable by NMR spectroscopy in achiral media, it is quite possible to distinguish the diastereoisomeric forms appearing for a binuclear complex.

The spectral assignments are tabulated in Table V. The systems of four peaks (doublet of two doublets) situated at −65.5 and 25.8 ppm (T = 303 K) were assigned to the four protons of the ethylene bridge. These protons, owing to the rotation of two subunits around bridge bonds, change their position with respect to both paramagnetic centres and thus the magnitude of the isotropic shift. The peaks from the band broadened at 303 K, become sharp doublets at 373 K. The equal resonance intensities and participation in the same dynamic process (changes on both doublets proceed in parallel) confirm both such an assignment. All other resonances alter the half linewidth insignificantly. Taking into account the results obtained by Everhart and Evillia[5] one should assume that a rapid inversion takes place on the cobalt ion. The contribution of the pseudocontact shift differentiates the magnitudes of isotropic shifts in such a way that, even after racemization, the differentiation of shifts is maintained. It is worth mentioning that most resonances in the spectrum, particularly at elevated temperatures occur in the form of doublets (Table V).

Each component of the doublet was assigned to a different Co(MED3A) type subunit of the Co_2(TTHA) complex (Figure 5).

The magnitude of differentiation decreases with the increasing second metal ion–reasonating proton distance. The differentiation of shifts (T = 373 K) is about 8–10 ppm for bridge ethylene protons and 3–4 ppm for the acetate and ethylenediamine protons (en in the chelate ring). The contribution of rotamers (with respect to the bridge ethylene bonds) with lowered symmetries results probably in different effects of the pseudocontact shifts for each part of molecule. It should be emphasized that the rotation must lower the complex symmetry even for initial dimeric structure shown in Figure 5. This effect did not cause any spectroscopic problems in the Ni_2(TTHA) spectrum because of the absence of any pseudocontact shift in that complex.

TABLE V
Isotropic shifts for Co_2(TTHA) complex

T = 303 K		T = 373 K	
Shift	Assignment	Shift	Assignment
−129.8	ac	−98.9	ac
−84.6	am	−97.0	ac
−80.8	am + ac	−70.9	am
−71.9	ac	−68.2	am
−70.4	ac	−63.9	ac
−65.5	am, very broad (bridging en)	−56.4 −49.5	am(bridging en) + ac
−47.5	ac	−31.5	ac
−25.9 ÷ −13.6	am	−29.2	ac
25.8	am, very broad (bridging en)	−22.9 + ÷ −12.6	am
115.1	ac	14.8 22.7	am (bridging en)
		76.1	ac

[a] Shifts in ppm; referenced to uncomplexed, diamagnetic ligand in basic solution; denotation as in Table I.

CONCLUSION

^1H NMR spectroscopy was applied to studies of the Ni(II) and Co(II) complexes with DTPA and TTHA, i.e. with ligands whose number of donors are higher than coordination number of the metal ions. A large number of their functional groups is an origin of interesting dynamic and structural properties of these complexes. The ^1H NMR spectroscopy of the paramagnetic complexes made it possible to trace these processes and to make an attempt to describe them. These processes differ substantially from those found in diaminepolyacetic acid complexes.

The properties of the Ni(II) and Co(II) complexes with DTPA and TTHA are similar. However, the activation energy of the rearrangement processes in the DTPA complexes is lower than that for TTHA complexes and this energy is lower for the Co(II) complexes than for corresponding Ni(II) complexes.

Rearrangements found for the paramagnetic complexes proceed probably in a similar way for the diamagnetic metal ion–DTPA or TTHA systems.

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