Proton Chemical Shifts in NMR Spectra of Diamagnetic Metal–Aminopolycarboxylate Complexes

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The proton chemical shifts of 2-hydroxy-1,3-propanediamine-N,N,N',N'-tetraacetic acid and 1,3-propanediamine-N,N,N',N'-tetraacetic acid in 1:1 complexes with diamagnetic metal ions have been investigated as a function of the metal ion charge Z and crystal ionic radius r. The chemical shifts correlate with Z/r linearly but separately in (II)A, (II)B, and lanthanide group. The inductive effects, long-range shielding and solvent ordering effects of metal ions are discussed as the possible contributions to the proton chemical shifts.

Introduction

In a recent paper [1] it was shown that proton chemical shifts in NMR spectra of aqueous solutions of diamagnetic alkaline, alkaline earth and rare earth metal ion–EDTA complexes correlate with Z^2/r, where Z is the charge and r is the ionic radius of metal ion. It was suggested that this correlation is reflective of ordering in the solvation shell rather than a result of direct metal–ligand electrostatic or inductive effects, and might be used as a probe of the order–disorder effects in the solvent, selective solvation in mixed solvents, and of the effect of ion pairing on the solvation layer.

On the other hand, it has been shown by another group of authors [2], that proton chemical shifts of nitrilotriacetic acid (NTA) complexes with the same metal ions correlate with the valence force constant of the C–H bond, calculated from the antisymmetrical valence vibrations of the C–H bond, and these results have been interpreted in terms of the inductive effects.

The aim of the present study is to measure the proton chemical shifts of I,3-propanediamine-N,N,N',N'-tetraacetic acid (PDTA) and 2-hydroxy-1,3-propanediamine-N,N,N',N'-tetraacetic acid (HPDTA) in complexes with diamagnetic closed-shell and/or rare earth metal ions. These ligands have been chosen as subject for the examination because it is possible to study the inductive effects in their complexes more specifically than in the EDTA or NTA complexes.

Experimental

PDTA and HPDTA were prepared according to [3] and [4], respectively, and their purity was checked by elemental analysis and potentiometric titration. All samples were prepared from PDTA, HPDTA, reagent grade metal salts, reagent grade EDTA, DCl, KOD and D_2O. D_2O solutions were 0.1–0.2 M in ligand. The PMR spectra were taken on CW TESLA 80 MHz or FT JEOL 100 MHz spectrometers. Tert-butylalcohol-OD was used as an internal standard. All spectra were obtained at 25 °C.

Results and Discussion

The PMR spectra of HPDTA and PDTA complexes are dependent on the coordination bond lifetimes and symmetry of complexes. AB quartet for each of the four acetate proton pairs could be observed in complexes with long metal ion–nitrogen lifetimes, which precludes inversion of the nitrogen. We have observed one singlet for all the acetate protons in the SrPDTA, BaPDTA, CaPDTA, MgPDTA, LaPDTA, YPDTA, and SrHPDTA complexes, one AB quartet in the ZnPDTA, CdPDTA, MgHPDTA, CaHPDTA, BaHPDTA, CdHPDTA and YHPDTA complexes, two quartets in ZnHPDTA and LaHPDTA complexes, and three AB quartets in LuHPDTA complexes. For the sake of simplicity, in this paper only the arithmetical mean values of the chemical shifts for the non-equivalent acetate protons (H^d) are presented.

ABCDX and A_4B_2 patterns were observed for the protons of $\backslash$N–$CH^aH^bCH^x(OH)CH^aH^b$–N$\langle$ and $\rangle$N–$CH_2^aCH_2^xCH_2^a$–N$\langle$ fragments of HPDTA and PDTA, respectively. Whenever possible, spectra were simulated and iterated with the LAOCOON III
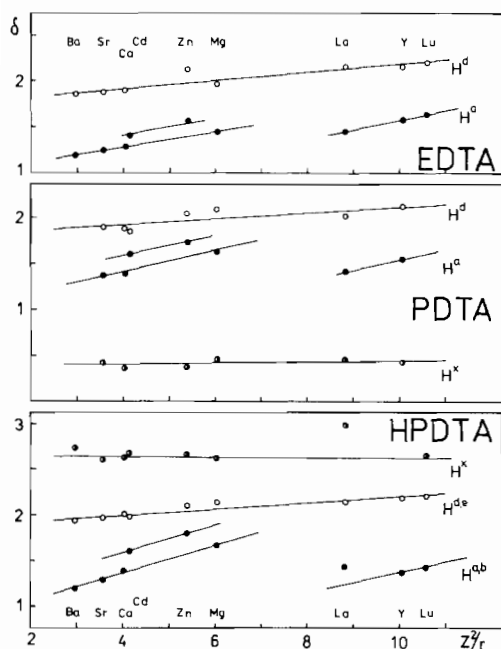
Fig. 1. Chemical shift variation with Z^2/r for aminopoly-carboxylate complexes with diamagnetic metal ions.

program [5]. The chemical shifts of H^a and H^b protons presented in this paper are the mean values of shifts obtained from the simulated spectra. The more detailed description of the spectra, as well as the effects of pD and temperature on the spectra, will be published elsewhere [6]. The chemical shifts of nonlabile protons of HPDTA, EDTA and PDTA complexes obtained as described are plotted *vs.* Z^2/r in Fig. 1.

The first conclusion from Fig. 1 is that the chemical shifts of H^x protons in HPDTA and PDTA complexes are independent of metal ion. The shift for the LaHPDTA complex shows a significant deviation to the lower field. The independence of shifts of H^x protons on the Z^2/r ratio, and the deviation of LaHPDTA suggest that the shift of H^x protons is dominated mainly by the inductive effects. These effects are very small in all complexes because of long distance between the metal ion bonding sites and H^x except for LaHPDTA, where coordination of the La(III) ion to the hydroxyl oxygen occurs [7, 8]. The formation of this coordination bond leads to the decrease of electron density on the H^x proton and thus to the downfield shift of the H^x signal.

The chemical shifts for both the acetate H^d protons and $H^a(H^b)$ protons of PDTA and HPDTA complexes move toward lower field with increasing Z^2/r, in comparison to the K^+ salts of free ligands. For the acetate protons the dependence of chemical shift on Z^2/r is approximately linear. However, the linear correlation for $H^a(H^b)$ protons occurs only

within each of the three distinct groups of metal ions. The La(III) HPDTA complex shows again a significant deviation — the signals of $H^a(H^b)$ protons are shifted downfield in comparison to the Y(III) and Lu(III) complexes because of electron density decrease due to the hydroxyl oxygen coordination to the La(III) ion. The chemical shifts of acetate protons are not affected by this bond because of a rather large distance from the hydroxyl oxygen.

It has been found in paper [1] that linear correlations of chemical shifts of acetate (H^d) and ethylenic (H^a) protons of EDTA complexes display the same slopes, and this finding has been taken as the main argument against the inductive and electrostatic effects of the metal ion on the proton chemical shifts. Because of different slopes of acetate and H^a-(H^b) proton chemical shifts in HPDTA and PDTA complexes, we have reinvestigated also the EDTA complexes. The results are shown in Fig. 1. We have found that chemical shift of acetate (H^d) protons of EDTA complexes changes approximately linearly with Z^2/r, but we have not observed linear correlation of ethylenic proton shift with Z^2/r. Again, as in the case of HPDTA and PDTA complexes, the shift of H^a protons is linear only within each of the three groups of metal ions. Furthermore, acetate and ethylenic protons display different slopes.

We have also reevaluated data from [1] for N-hydroxyethylenediamine-N,N',N'-triacetic acid and N-methylethylenediamine-N,N',N'-triacetic acid complexes. We have found again that the shift of acetate protons is a linear function of Z^2/r for both the alkaline earth and rare earth metal ion complexes, while the shift of ethylenic protons is linear with Z^2/r only within each of the two groups of metal ions. The slopes for the acetate and ethylenic protons are different.

The different slopes for $H^a(H^b)$ and H^d protons indicate the importance of the inductive effects due to the nitrogen and carboxylate oxygen interactions with the metal ion. The downfield shift for $H^a(H^b)$ protons increases with the increase of Z^2/r faster than that for the H^d (acetate) protons, in accordance with the different inductive pathways from the metal ion.

Because the ratio of Z^2/r is proportional to the ion solvation energy [9], we have tried to correlate the chemical shifts also with Z/r and Z/r^2. The best results in terms of correlation coefficients have been obtained with Z/r — an 'electrostatic potential' of the ion. This result might indicate the importance of electrostatic effects. However, it is necessary to test this hypothesis in the series of complexes with the known structural data.

The long range shielding is an important contribution to the chemical shift and its importance may be visualized in structurally different complexes. It is seen in Fig. 1 that the shift of $H^a(H^b)$ protons

changes monotonically only within each group of metal ions. We suggest that the differences between three various groups are caused mainly by the different geometries of the ligands in complexes. We suggest further that the abrupt changes of chemical shift within a given group of metal ions might indicate the changes in the geometry of complexes. However, it is interesting to note the chemical shift is insensitive to the geometry changes in the case of acetate (H^d) protons. Furthermore, the slopes of chemical shift against Z/r are approximately the same for all ligands investigated. We suppose this phenomenon is caused by the very short carboxylate oxygen—metal ion bond lifetime. Weakness of this bond permits the similar geometry of acetate arms in all complexes in water solution, which results in similar long range shielding.

Conclusions

The proton chemical shifts in diamagnetic metal ion—aminopolycarboxylate complexes consist of several contributions. Changes of chemical shift between complexes of various metal groups are caused mainly by the long range shielding, which is sensitive to changes in the geometry of complexes.

Within each group of metal ions the chemical shift increases linearly with Z/r, rather than with Z^2/r. The slope of the linear correlation is affected by inductive effects, and possibly also by the electrostatic and solvent effects of metal ions. The contribution of the proton-ordered solvation shell interaction is rather small in comparison to the long range shielding and the inductive effects of the metal ions.

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