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Intramolecular Exchange Processes in Cyclohexanediaminetetraacetate Complexes Investigated by Nuclear Magnetic Resonance Technique

PIERO MIRTI, MARIA CARLA GENNARO and CLAUDIO CASALINO

Istituto di Chimica Analitica dell'Università di Torino, via Giuria 5, I 10125, Turin, Italy

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Recent papers deal with the intramolecular rearrangement processes of some diamagnetic complexes formed by polyaminepolycarboxylic ligands, such as ethylenediaminetetraacetic (EDTA) and ethylenebis(oxyethyleneamino)tetraacetic (EGTA) acids [1–3]. A treatment on the nature of these processes, as well as their effects on the related NMR spectra, has been given [1, 4] showing how the occurrence of $\Delta \rightleftharpoons \Lambda$ conversion and nitrogen inversion processes at suitable rates causes the acetate protons to reach progressively their magnetic equivalence in the complex molecule.

Such an investigation has now been extended to the diamagnetic complexes formed by the cyclohexanediaminetetraacetic acid (CyDTA), whose NMR spectra at room temperature consist of two superimposed AB patterns, one of which sometimes collapsed into a single line [5]. The two AB quartets denote the occurrence of slow intramolecular processes on the NMR time scale in the above conditions so as the protons of the two acetate groups bounded to the same nitrogen atom experience different magnetic environments. The kinetics of acetate scrambling reactions may therefore be studied by following the modifications arising in the spectra, if any, when the metal to ligand bonds are labilized by temperature increments.

When dealing with processes which may give acetate exchange in a CyDTA complex, one must still bear in mind that the rigid cyclohexane ring structure prevents any configurational change, so that the only way to reach intramolecular scrambling is *via* the lone pair inversion of the nitrogen atoms [4]. The consequence is the impossibility to reach a whole magnetic equivalence for all the acetate protons and therefore the NMR spectra modifications induced by temperature increments may lead at the most to the formation of a single AB pattern, when the N inversion is a fast process on the NMR time scale and gives rise to two sets of magnetically equivalent acetate protons.

Experimental

Nuclear magnetic resonance spectra were recorded by a Varian T-60 instrument, outfitted with T-6057 (lock-decoupler) and T-6080 (temperature controller) accessories. Probe temperature was controlled by following the chemical shifts of methanol and ethylene glycol according to Van Geet [6]. Maximum homogeneity was verified before each run with the magnetic field locked on the HOD line arising by hydrogen exchange between ligand and solvent (D_2O) molecules. HOD spinning sidebands superimposition on the studied acetate resonances could always be removed by spinning the sample at a proper speed at each working temperature.

Solutions to be investigated were prepared in deuterium oxide by the weighed amounts of dried ligand (BDH) and metal nitrates (C. Erba, Merck and KeK analytical grade chemicals), the metal complex concentration ranging between 5×10^{-2} and 1×10^{-1} *M*. Solutions' pD was adjusted by potassium hydroxide so as to achieve the complete formation of the studied complexes ($\geqslant$99.5%) at each working temperature. No inert electrolyte was added in order to control the total ionic strength because of the intramolecular nature of the investigated processes.

Results and Discussion

The investigated CyDTA complexes were those formed with the calcium(II), strontium(II), barium(II), zinc(II), yttrium(III) and lanthanum(III) ions. For all of them, however, except the barium one, it could not be possible to perform a quantitative treatment of the N inversion process because of the failure to get any appreciable spectral change in the whole investigated range of temperature, up to the upper instrumental limit (373 K). Thus the corresponding metal to ligand bonds have always to be regarded as non labile ones in these conditions, the lone pair inversion requiring higher temperatures to occur at such an extent to allow the acetate protons to average their magnetic environments. This situation does not hold anymore when dealing with the barium chelate, in which case the NMR spectrum changes appreciably when temperature raises, showing the trend to form a unique AB pattern; this, however, is not completely achieved before reaching the highest working temperature. Such a result puts the involved acetate scrambling process inside the kinetic NMR window, so as to allow a quantitative treatment of it. This was carried out

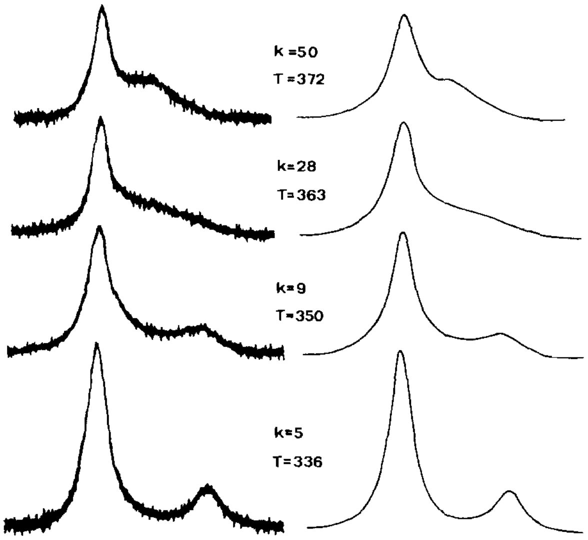

Fig. 1. NMR spectra recorded on BaCyDTA complex containing solutions at the indicated temperature T (K) and best fitting simulated spectra computed by the given rate constant k (s^{-1}). For space reasons, only the most meaningful inner peaks are shown.

by determining the intramolecular rate constant (k) at each temperature via complete line shape analysis of the corresponding experimental spectrum by aid of a DNMR computer program [7], searching for the best fitting between recorded and computed ones. The generation of the theoretical spectra was achieved by the input data of chemical shifts, coupling constants and transverse relaxation time drawn out from the 'frozen' spectrum and taking into account the exchange limitations due to the chelate structure (*i.e.*, each acetate proton is exchanged between two sites only). The most significant among the so obtained spectra, computed by the given k value, are collected in Fig. 1, together with the corresponding experimental ones recorded at the indicated temperature. Figure 2 shows, on the other hand, the resulting activation plot, by whose data a least square treatment allowed the evaluation of the activation enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$), which, according to the absolute rate theory, are related to rate constant and temperature by the equation

$$k = \chi \frac{KT}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT}$$

and therefore

$$\ln (k/T) = \ln \frac{\chi K}{h} + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{R} \frac{1}{T} \qquad (1)$$

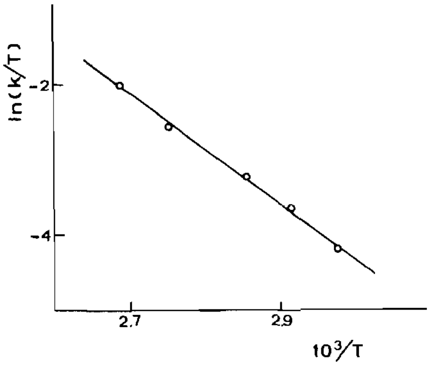

Fig. 2. Activation plot of the BaCyDTA nitrogen inversion process.

K and h in eqn. (1) are the Boltzman and Planck constants, and χ, the transmission coefficient, was taken as one half for the studied exchange process.

The so calculated activation parameters for the BaCyDTA complex are $\Delta H^{\ddagger} = (14.7 \pm 0.5)$ Kcal/mol and $\Delta S^{\ddagger} = (-10 \pm 1)$ e.u.

Exchange mechanisms suitable to describe acetate scramblings in metal polyaminepolycarboxylates have been discussed already [1–3]: they include water assisted displacements and twist paths via trigonal prisms and consist of the nitrogen to metal bond breaking as the rate determining step when the process is the lone pair inversion. The rigid cyclohexane backbone of the CyDTA molecule, however, does not allow the trigonal prism to form as the activated state, limiting the choice between the two mechanisms; this, in turn, prevents any configurational change, being also hindered an acetate shift by water displacement in the octahedral state and simple metal to oxygen bonds breaking. So, any acetate scrambling requires the metal to nitrogen bond rupture so as to occur only as nitrogen inversion *via* a displacement mechanism.

The above may give reason of some deactivation of the process as compared with the EDTA and EGTA chelates; as a matter of fact, even if the obtaining of activation parameters rewards the only barium complex, the informations drawn out by the NMR spectra of the studied CyDTA chelates give evidence of not labile intramolecular bonds, which cause the two AB quartets to persist uncoalesced up to the highest working temperatures. On the contrary, the lability of such metal to ligand bonds comes out to be higher when the same ions are bound to the EDTA and EGTA molecules, placing itself below or just inside the NMR kinetic window by giving single acetate resonances or unique AB patterns able to collapse in the working temperature range. An exception is given by the lutetium

EGTA complex, which, however, as further support to the above considerations, was interpreted in terms of the more rigid ether oxygen coordinating structure, thus excluding, as the CyDTA one, the trigonal prism formation as activated state [3].

The fairly little negative $\Delta S^{\ddagger}$ value shown by the BaCyDTA complex is in agreement again with the occurring of the nitrogen inversion by a displacement mechanism, as far as it is consistent with a diminished order in the arrangement of the solvent molecules in the activated state as compared with the situation arising with the trigonal intermediate, which leads to $\Delta S^{\ddagger}$ values of about –40 (EDTA complexes) or –30 e.u. (LaEGTA; but the value comes down to –21 e.u. for the LuEGTA complex, in agreement with its structural differences).

No wonder then in the finding out the barium complex as the more labile among the studied CyDTA systems; the ion, in fact, is by far the biggest one and likely the most suitable to increase the possibility for the solvent molecules to push the nitrogen atom away and lower the energy barrier required to achieve nitrogen inversion; by the other hand the strength of the prevalently electrostatic metal to ligand bonds is also depending upon the charge density of the ion, whose lower value among the studied ones is given by the barium ion again.

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