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NMR STUDY OF STRUCTURE OF LANTHANIDE COMPLEXES IN SOLUTION

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Thermodynamic and optical spectroscopic studies of lanthanide complexes in aqueous solution have provided much interesting speculation on the structures of these complexes. Unfortunately, however, these studies cannot provide the basis for definitive models of these structures. We have investigated the use of nuclear magnetic resonance as a tool for obtaining more direct insight into the structure of lanthanide complexes in solution.

In recent years the use of paramagnetic lanthanide ions as 'shift reagents' has been studied intensively. Although the paramagnetic induced shifts are useful, the spectra of complexes of the diamagnetic lanthanides are also a fertile source of structural information. In this paper the diagnostic value of PMR studies of diamagnetic lanthanide complexes to define the nature of the species in the lanthanide-pyruvate system is discussed. Then the use of NMR spectra of both diamagnetic and paramagnetic lanthanide complexes to obtain detailed structural information is reviewed.

Pyruvate Complexes

MASTER

Pyruvate has been shown to form several types of complexes in solution in which the ligand is in the keto form, the diol(hydraté) form and in a dimeric form. We measured the overall values of  $\Delta G_1$ ,  $\Delta H_1$ , and  $\Delta S_1$  of complexation with the lanthanides, then used PMR to obtain information on the types and concentration of the different complexes in a series of

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solutions. The proton shifts are different for the various ligand forms in both free and complexed states. With this data, from a set of mass balance equations it was possible to resolve the overall stability constant into individual constants for the keto, diol and dimer complexes. The keto form had a stability constant similar to acetate complexes, indicating no interaction of the ketonic oxygen with the metal ion. The values of the diol and dimer stability constants were both similar to that of the glycolate complexes, supporting a model of chelation involving the  $\alpha$ -hydroxy group (Fig. 1).

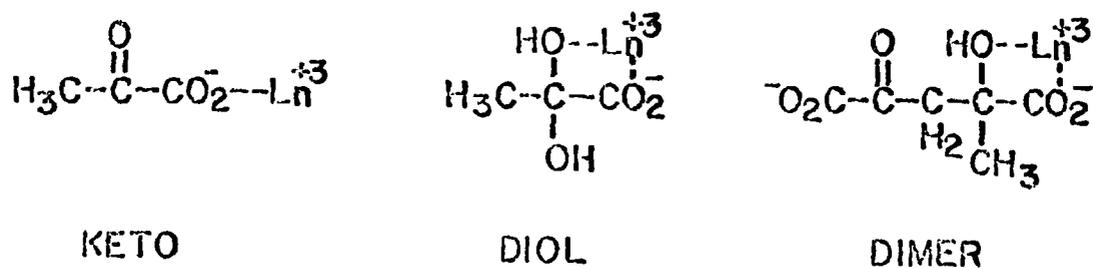


FIGURE I  
Complexes Formed by Pyruvate

Measurement of the relative shifts in the paramagnetic complexes of Pr(III) agreed with a model of weaker complexing with the keto ligand (only the bulk susceptibility shift was observed) and stronger complexing with the diol and dimer ligands (the induced paramagnetic shift was observed).

#### Diamagnetic Aminocarboxylate Complexes

PMR spectra of 1:1 alkaline earth and diamagnetic lanthanide (La, Lu, Y) complexes of MEDTA, HEDTA, EDTA and DPTA (Fig. 2) showed a linear correlation between the relative proton shift and the metal charge density,  $Z^2/r$ . This correlation aided in the assignments of the shifts and confirmed the ionic character of these complexes.



coordinated in the Lu(III) complexes but not (or much more weakly so) in the La(III), Y(III) and alkaline earth complexes. The spectra of the DTPA complexes are consistent with hexacoordination with the alkaline earth cations and heptacoordination with the lanthanides. In the latter case, the unbound ligand donor group is the lone acetate on the middle nitrogen.

#### Paramagnetic Complexes

Pr, Eu and Yb complexes show significant paramagnetic shifts with adequate resolution to be easily observed. The complexes studied should be of known stoichiometry either with slow exchange with free ligand or with an insignificant amount of the latter present. Ligand rigidity is also necessary if estimates of precise geometries are to be attempted.

The thermodynamics of complexation of lanthanides with *o,o'*-phenylenedioxydiacetate indicated that this was a promising system for NMR investigation. The  $^1\text{H}$  and  $^{13}\text{C}$  spectra were obtained for solutions of metal:ligand ratios from 0.05 to 3.0. Values of  $\beta_1$  were used with these spectral data to determine values of  $\beta_2$  which agreed with the earlier thermochemical values. Shifts of the  $\text{ML}$  and  $\text{ML}_2$  complexes could be assigned from the net shifts and the  $\beta_i$  values.

In order to use the theory for dipolar shifts to calculate the geometry of complexes, it is necessary to determine the relative magnitude of the dipolar (pseudocontact) and the contact terms. Proton shifts in lanthanide complexes generally have negligible contact terms whereas for the  $^{13}\text{C}$  shifts the two terms may be of comparable magnitude. In these complexes, using  $^1\text{H}$  and  $^{13}\text{C}$  shifts, we found that the contact term is always smaller.

The very similar pattern of the shifts of the complexes for each of the three lanthanide ions suggests that the structure of the complex

is essentially identical for all three systems. An analysis of the signs and the magnitudes of the shifts indicates that the lanthanide ion is located between the ether oxygens and the single bonded oxygen of the two carboxylate groups. Consequently, the ligand is coordinated to the lanthanide ion through four of its oxygen atoms which are located in the same plane as the metal (Fig. 3). Computer analysis of the data has provided values for M-C and M-H distances and angles, allowing a precise geometric description of the complex.

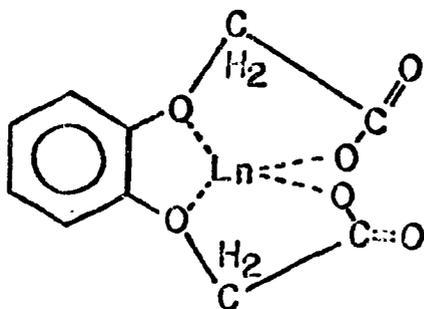


FIGURE 3  
Lanthanide-*o,o'*-phenylenedioxydiacetate

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