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M.B. YIM

M.W. MAKINEN

Department of Biochemistry and Molecular Biology
The University of Chicago
Chicago, Illinois 60637
U.S.A.

ENDOR STUDY OF SMALL MOLECULE AND ENZYME COMPLEXES OF Gd^{3+} IN FROZEN SOLUTION

Electron-nuclear double resonance (ENDOR) spectroscopy is applied to the investigation of the coordination structure of Gd^{3+} in small molecule and enzyme complexes in frozen solution. Proton ENDOR spectra of $GdCl_3$ in frozen methanol-water mixtures obtained with H_0 at the turning point of the EPR absorption exhibit single crystal-type line pairs. With use of selectively deuterated solvents, we have assigned the chemical origins of each pair of ENDOR lines. There are two distinguishable sets of protons due to metal-coordinated water and one set belonging to the methyl group of metal-coordinated methanol. Similarly, from the proton ENDOR spectrum of $Gd(CH_3COO)_3$ in frozen solution, we have also identified the set of lines belonging to the methyl group of metal-bound acetate. On the basis of the field dependence of the ENDOR spectra, we have determined the hyperfine coupling (hfc) components of each of the metal-bound ligands.

The hfc components of the protons of Gd^{3+} -bound acetate exhibit axial symmetry, and under the point-dipole approximation, the calculated metal-proton distance is 4.53 ± 0.20 Å. This is in reasonably good agreement with the value of 4.73 Å deduced from crystallographic data. The hfc components of the water and methanol protons do not exhibit axial symmetry, indicating significant spin delocalization. Nonetheless, the metal-proton distances, calculated as lower limit estimates on the basis of the largest anisotropic

hfc component, are in surprisingly reasonable agreement with crystallographic data. Application of this method is made to investigate the environment of lanthanide binding sites in enzymes and proteins.



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C.F.G.C. GERALDES

M.C. ALPOIM

M.P.M. MARQUES

Chemistry Department
University of Coimbra
3000 Coimbra
Portugal

A.D. SHERRY

M. SINGH

Chemistry Department
The University of Texas at Dallas
P.O. Box 830688, Richardson, Texas 75080
U.S.A.

A NMR STUDY OF $Ln(NOTA)$ CHELATES AS AXIALLY SYMMETRIC AQUEOUS SHIFT REAGENTS

The trivalent lanthanide ethylenediaminetetraacetate ($Ln(EDTA)$) chelates are very useful water soluble NMR shift and relaxation probes of the dynamic structure of biological molecules at $pH \sim 7$ [1], including nucleotides [2,3], carboxylates [4,5] and aminoacids [6]. The $Ln(EDTA)$ complexes suffer several disadvantages as aqueous NMR shift reagents including lack of solubility near neutral pH, exchange broadening of the resonances of some ligands to the heavier $Ln(EDTA)$ chelates [6] and structural changes along the series, which complicates the separation of pseudocontact and contact shifts [7,8].

In this work we report ^{13}C and 1H NMR studies of the 1:1 complexes of the axially symmetric macrocyclic ligand 1,4,7-triazacyclononane- N,N',N'' -triacetic acid (NOTA) with the diamagnetic and