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Solution Structures of Gd(III) Adducts of Schiff Base Ni(II) Complexes

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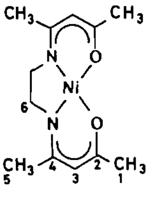
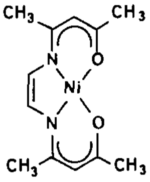
Recently we reported an NMR study of the Gd(fod)$_3$ adduct of N,N'-ethylenebis(acetylacetoneiminato)nickel(II), I, in which the position of Gd(III) relative to the substrate I was determined from analysis of paramagnetic contributions to ^{13}C spin-lattice relaxation rates, T_{1P}^{-1}, in CDCl$_3$ solution [1]. Gd(III) is bound to the oxygens of I in a position ~1.8 Å *out of the plane* of I with estimated errors of only a few tenths of an Angstrom in the Gd coordinates. Steric interactions between the methyl groups of I and the fod ligands were deemed responsible for the out-of-plane coordination.

To explore this further, we have carried out two related spin-lattice relaxation studies. The first involves the Gd(fod)$_3$ adduct of II, which is an oxidation product of I. This serves to provide an independent check on the results obtained for the Gd(fod)$_3$ adduct of I, since the presence of the additional double bond in II is expected to have little effect on binding to Gd(fod)$_3$. In the second study, Gd(NO$_3$)$_3$ is used instead of Gd(fod)$_3$ with substrate I in order to assess the steric and electronic influences of the fod ligands. The results of these two investigations are reported here.



I



II

Experimental

Sample preparations, T$_1$ measurements, and data analyses were carried out as described in detail previously [1]. CDCl$_3$ was used as the solvent for II in the presence of Gd(fod)$_3$, and the Gd/II mole ratio was 7.3×10^{-3}. In experiments involving I and Gd(NO$_3$)$_3$, 0.02 ml of a concentrated stock solution of Gd(NO$_3$)$_3$·5H$_2$O in methanol was added to a CDCl$_3$ solution of I so that the final solution contained ~3% (v/v) methanol and had a Gd/I mole ratio of 1.3×10^{-2}.

Substrate I was prepared by the general procedure of Lindoy *et al.* [2] II was prepared from I using the method of Dilli *et al.* [3].

Results and Discussion

Procedures used in analysis of the NMR data

Crystallographic data are available [4] for I, and it is assumed that bond angles and distances in II are generally close to those of I except for the 5-membered ring. Crystallographic atomic coordinates were transformed to a Cartesian coordinate system, calibrated in Å, with Ni at the origin and with the x-axis bisecting the O–Ni–O angle. Substrates I and II are essentially in the xy plane of this coordinate system. It was assumed, as in our previous study [1], that Gd binds equally to both oxygens of the substrates. Thus Gd is to be found in the xz plane. Initially, a Gd–O distance of 2.45 Å was assumed†. This was subsequently varied in hopes of improving the fit of the model to experimental data. Using a computer program, the Gd position was varied incrementally within the above limits until the ratio of two Gd–C distances, calculated using X-ray coordinates for carbons, showed the best agreement with the corresponding ratio determined from NMR data using eqn. (1):

$$\frac{T_{1P_i}^{-1}}{T_{1P_j}^{-1}} = \frac{r_j^6}{r_i^6} \qquad (1)$$

In the eqn. (1), $T_{1P_i}^{-1}$ is the paramagnetic contribution†† to the observed relaxation rate of carbon i, and r_i is the Gd–C$_i$ distance. The origin of eqn. (1) and the methods used in data analysis are discussed in more detail in reference 1.

Equation (1) is valid only if fast exchange conditions exist, *i.e.* the lifetime, τ_M, of the Gd-substrate adduct is small relative to the relaxation time, T_{1M},

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†This bond distance is reported [5] to be the average of values from several crystallographic studies of lanthanide-substrate complexes.

††Outer-sphere contributions to T_{1P}^{-1} were found previously [1] to be sufficiently small for ^{13}C that they had no effect on the Gd position. Thus they are neglected in the present investigation.

TABLE I. Paramagnetic Contributions to Carbon-13 Spin-Lattice Relaxation Rates for Substrates I and II.

Position	#[a]	Substrate I[b]		Substrate II[c]	
		δ^{d}	T_{1P}^{-1} [e]	δ^{d}	T_{1P}^{-1} [e]
$CH_3(O)$	1	24.3	0.596(89)	25.4	10.19(40)
C=O	2	176.8	1.167(120)	179.5	16.77(165)
CH	3	99.7	0.243(89)	101.5	3.26(26)
C=N	4	164.8	0.187(39)	157.9	1.92(10)
$CH_3(N)$	5	21.0	0.087(19)	20.4	0.505(50)
CH_2, CH	6	53.1	0.171(51)	125.0	1.10(5)

[a] Numbering scheme shown in I. [b] Experiments carried out in $CDCl_3$ containing ~3% (v/v) MeOH at 308 K in the presence of $Gd(NO_3)_3$ at a Gd/I mole ratio of 1.3×10^{-2}. [c] In $CDCl_3$ solution at 308 K in the presence of $Gd(fod)_3$ at a Gd/II mole ratio of 7.3×10^{-3}. [d] Chemical shifts in ppm from TMS. [e] Observed relaxation rate less relaxation rate in the absence of Gd(III); in sec^{-1}; numbers in parentheses are errors in the least significant digits determined using Student's t-distribution with a 95% confidence interval.

of a nucleus on the (short-lived) adduct. The temperature dependences of paramagnetic contributions to proton nmr linewidths were used, as previously [1], to test for fast exchange of Gd(III) with both substrates. The results indicated fast exchange in each case in the 290–325 K range. This is corroborated by the facts that T_{1P}^{-1} values differ considerably among the carbons and the data fit reasonable models for the adducts in each case.

$Gd(fod)_3$ and Substrate II

The T_{1P}^{-1} data for the carbons of II parallel those found earlier for I, indicating the structures of the adducts are similar. Previously [1] we used T_{1P}^{-1} data for carbons 1 and 2 to locate Gd, since errors are relatively small for these carbons. The model for the adduct was then tested by comparing distances from Gd to the remaining carbons calculated using crystallographic coordinates ('X-ray' distances), with corresponding distances determined using eqn. (1) and the 'X-ray' Gd–C_2 distance. The same procedure is followed here.

Using T_{1P}^{-1} data for carbons 1 and 2 of substrate II and a Gd–O distance of 2.45 Å, we find Gd at x = 2.82(23), z = 1.56(23)*. The best data obtained previously for the $Gd(fod)_3$–I adduct located Gd at x = 2.58(24), z = 1.75(17) [1]. Since these positions are within error of one another, it may be concluded that I and II bind Gd in a very similar manner. A comparison of ‚NMR' and 'X-ray' distances to the remaining carbons of II is presented in Table II. The values agree within the limits of error, thus substantiating the Gd position. The overall fit is improved somewhat by assuming a Gd–O distance of 2.6–2.7 Å, in which case Gd is located at x = 2.77, z = 1.83, but this is of questionable significance in view of the errors in Gd–C distances. Using either value for Gd–O, however, it is clear that in the adduct *Gd is significantly out of the molecular plane of II* and is near the position found earlier in the adduct of I.

TABLE II. Comparison of Structural Data for Gd(III) Adducts of Substrates I and II.

		Substrate I	Substrate II
Gd(III) Coordinates, Å[a,b]		x = 2.71(45)	x = 2.82(23)
		y = 0	y = 0
		z = 1.66(40)	z = 1.56(23)
Comparison of Gd–C Distances, Å[a,c]			
Gd–C(3)	NMR	4.38(85)	4.43(40)
	X-ray	4.47(41)	4.49(21)
Gd–C(4)	NMR	4.59(77)	4.84(41)
	X-ray	4.95(48)	5.00(25)
Gd–C(5)	NMR	5.21(87)	6.04(58)
	X-ray	6.41(46)	6.45(24)
Gd–C(6)	NMR	4.66(85)	5.31(44)
	X-ray	5.68(54)	5.75(28)

[a] Errors in the least significant digits are given in parentheses. [b] Gd constrained to the xz plane with a Gd–O distance of 2.45 Å. [c] NMR distances were determined using the Gd–C(2) distance and ratios $T_{1P_i}^{-1}/T_{1P_2}^{-1}$. X-ray distances were determined using experimental Gd coordinates and crystallographic coordinates for the carbon atoms.

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*Gd is found at approximately these same coordinates using T_{1P}^{-1} data for other pairs of carbons. For examples, using data for C_1 and C_3–C_5, Gd is found in the range x = 2.49–2.67, z = 1.69–1.81. Using C_3 and C_4 only, x = 2.43, z = 1.85.

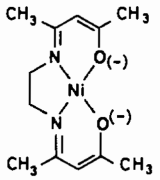
$Gd(NO_3)_3$ and Substrate I

In these experiments, $Gd(NO_3)_3$ is introduced into the $CDCl_3$ solution of I *via* a methanol stock solution. The paramagnetic species is perhaps best represented as $Gd(NO_3)_x(MeOH)_y^{+3-x}$, since nitrate ligands may remain coordinated. T_{1P}^{-1} values for the carbons of I in this solution show the same *relative* order as they do for I and II in the presence of $Gd(fod)_3$ (see Table I). However they are smaller by more than an order of magnitude even though the Gd/substrate mole fraction is larger here. Apparently the equilibrium constant for adduct formation is considerably smaller for solvated $Gd(NO_3)_3$ than for $Gd(fod)_3$*.

The T_{1P}^{-1} data were treated as described above. Using data for carbons 1 and 2 and a Gd–O distance of 2.45 Å, Gd is found at x = 2.71(45), z = 1.66(40)**. The relatively large error limits here result from large errors in T_{1P}^{-1}'s which, in turn, are due to the small extent of adduct formation. These coordinates are close to those found for Gd in the $Gd(fod)_3$ adducts of I and II, and in spite of the large errors resulting when solvated Gd(III) is used, it is clear that Gd is significantly out of the substrate plane in this case also.

The structural model for the solvated Gd(III)–I adduct may be tested by comparing 'NMR' and 'X-ray' distances to carbon atoms not used in locating Gd. As a result of the large errors in T_{1P}^{-1}'s, the agreement (Table II) is not as satisfactory as when $Gd(fod)_3$ is used. However, for each carbon the two distances are within the error limits of each other. A slight overall improvement in the model is found using a Gd–O distance of 2.65 Å, but as in the case of substrate II, this is of questionable significance.

The two substrates used in this investigation are normally represented as I or II, showing π delocalization in the six-membered rings. The oxygen non-bonding electron pairs are assumed to be in sp^2 orbitals in the molecular plane, thus it was initially expected that Gd in the adduct would be found in or very near this plane. The occurrence of out-of-plane bonding to Gd suggests that resonance hybrid III, where the oxygen non-bonding electron pairs are out-of-plane, makes a significant contribution to the electronic structures of the Gd-bound substrates. The electron pairs in III are in sp^3 orbitals which would point approximately in the direction of Gd(III) in the adducts.



III

If Gd were in the substrate plane with Gd–O distances of 2.45 Å, the closest approach of a methyl proton to the Gd(III) ion would be 2.6 Å. This is only ~0.4 Å greater than the sum of ionic and Van der Waals's radii of Gd(III) and H, respectively. Thus it becomes clear why other ligands as small as MeOH or NO_3^- in the first coordination sphere of Gd(III) are able to generate steric interactions which result in out-of-plane bonding.

References

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*An alternative explanation is that most of the added Gd(III) is unavailable for adduct formation due to precipitation in the 97% $CDCl_3$ solution. We were unable to detect any precipitate visually, but the small amounts of $Gd(NO_3)_3$ used may preclude this.

**The coordinates found using carbons 1 and 3 and carbons 2 and 3 are x = 2.39, z = 1.87 and x = 2.16, z = 1.97, respectively.