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OBSERVATION OF LANTHANOID-INDUCED Pt-195 SHIFTS FOR THE ADDUCT OF BIS(ACETYLACETONATO)Pt(II) WITH TRIS(8,8,8,7,7,6,6-HEPTAFLUORO-2,2-DIMETHYLOCTANE-3,5-DIONATO)Pr(III) IN $CDCl_3$ SOLUTION

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The lanthanoid-induced ^{195}Pt shifts were observed on the successive addition of $Pr(fod)_3$ (L) to a 0.46 mol·dm^{-3} $CDCl_3$ solution of $Pt(acac)_2$ (S) at an ambient probe temperature (25°C). The equilibrium constant and ^{195}Pt intrinsic shift were estimated with the least squares fits of data to a plausible equilibrium between S and its 1:1 adduct with L formed via bidentate interaction.

It has recently been demonstrated in our laboratory that lanthanoid-induced shifts (LIS's) of ^{59}Co,1) ^{27}Al,2) and ^{9}Be3) are successfully observed for β-diketonato-complexes of these metals in non-polar solvents at an ambient probe temperature. It has also been found for the adduct formation of the metal complex incorporating several oxygen donor atoms with $Ln(fod)_3$4) that, in the case of the bonding via three bridging oxygens, the chemical exchange between free complex and its 1:1 adduct in solution is very slow on the NMR time scale at room temperature,1,2,5) while via two bridging oxygens it is rapid.3,6) As an extension of these studies, we now report the paramagnetic ^{195}Pt shifts induced by lanthanoid shift reagent (LSR) for $Pt(acac)_2$.4)

Figure 1 shows the plots of ^{195}Pt-LIS (δ_{obs}) vs. concentration ratios of $Pr(fod)_3$ (L) to $Pt(acac)_2$ (S) obtained on the successive addition of L to a 0.46 mol·dm^{-3} $CDCl_3$ solution of S at 25°C. ^{195}Pt NMR spectra were recorded on a Varian CFT-20 spectrometer equipped with a broad band accessory at 17.089 MHz using the ^{13}C signal of TMS observed simultaneously as an internal standard and the deuterium external-lock system. The aquisition time was taken as 0.5 s for the spectral width of 8065 Hz, the number of transients being ~1000.

It can be seen from Fig. 1 that the exchange of S between its free form and its adduct with L in solution is very rapid on the NMR time scale under the present conditions. The ability of lanthanoid ion to expand its coordination number from six to eight has been well documented and the lone pair electrons of cis oxygen donors in this complex can be expected to be capable of coordinating simultaneously to a second metal ion, from analogy with a few examples for related complexes.7) From this view, it seems likely that LS including the bidentate interaction as shown in Fig. 2 represents a most probable structure. An equilibrium is then given by

$$L + S \rightleftharpoons LS \qquad (1)$$

In the fast exchange limit, the calculated LIS of ^{195}Pt should be given by

$$\delta_{cal} = f_{LS} \cdot \Delta_{LS} \tag{2}$$

where f_{LS} and Δ_{LS} are the fraction of LS and the intrinsic shift of LS, respectively. The f_{LS} is determined by the equilibrium constant K for Eq. 1 and total concentrations of L, $[L_0]$, and of S, $[S_0]$:

$$f_{LS} = \frac{1}{2}\left[\left(1 + \frac{[L_0]}{[S_0]} + \frac{1}{K \cdot [S_0]}\right) \pm \left\{\left(1 + \frac{[L_0]}{[S_0]} + \frac{1}{K \cdot [S_0]}\right)^2 - 4\frac{[L_0]}{[S_0]}\right\}^{1/2}\right] \tag{3}$$

The optimum values of K and Δ_{LS} were calculated from the least squares fits of δ_{obs} to Eq. 2 by the computer iteration method using the program in the literature.[8] The estimated results are 10.3 and -89.7 ppm for K and Δ_{LS}, respectively.

This K-value seems consistent with those estimated from the analyses of ^1H and ^{13}C LIS's observed for the same system[9] within experimental errors and furthermore is fairly smaller in magnitude than those for the N_2O_2-quadridentate ligand Pt(II)-$Eu(fod)_3$ system in $CDCl_3$ at 32°C.[6b] Since the approximation of axial symmetry cannot strictly be applied to such the case with bidentate interaction, the graphical analysis using LIS's with a series of LSR cannot simply be carried out.

In the near future, the simultaneous analyses of LIS's from ^1H, ^{13}C and ^{195}Pt nuclei in this adduct will be performed by employing the complete equation describing the total shift via the iterative fitting procedure.[10] The contact shift contribution to ^{195}Pt-LIS separated consequently should be expected to be very effective for the detailed discussion on the nature of Pt—O bonds in this complex.

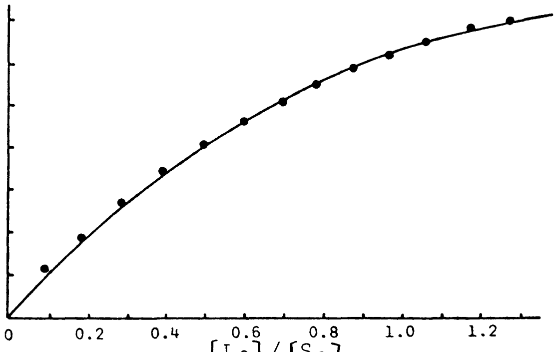
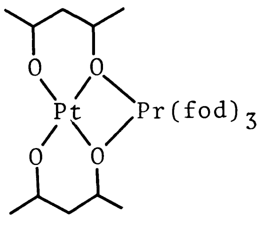


Fig. 1. ^{195}Pt-LIS vs. $[L_0]/[S_0]$ plots



LS

Fig. 2. The structure of adduct

References

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