

Influence of Zn-Cd Substitution: An NMR and Theoretical Study of the Complexes of 8-Hydroxyquinoline

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Abstract: The ^{13}C and ^{113}Cd NMR experimental and theoretical data of 8-Hydroxyquinoline complexes of Zn and Cd are reported. The geometry and chemical shifts (GIAO method) were calculated using the Gaussian 98 program with LanL2DZ and B3LYP/6-31G** basis sets, and the experimental ^{13}C and ^{113}Cd - CP/MAS NMR chemical shifts were obtained in a 300 MHz spectrometer. According to the results, there are modifications of the metal coordination environment when substitution occurs. Compensation between the electronic and the structural effects of complexes are proposed.

It is now well known that zinc is crucial for the synthesis of nucleic acids and, consequently, for cellular division.¹ However, ^{67}Zn , an NMR-detectable isotope, is one of the isotopes most poorly studied by NMR. This difficulty lies in the low natural abundance (4.11%), low magnetogyric ratio ($1.68 \times 10^7 \text{ rad} \cdot \text{T}^{-1} \cdot \text{s}^{-1}$) and high quadrupolar moment ($0.15 \times 10^{-28} \text{ m}^2$) of ^{67}Zn . The strategy used for NMR studies is the substitution of Zn by ^{113}Cd . Since 1976 more than 20 metalloproteins have been studied using this method.¹ The objective of this work was to use molecular modelling methods, ^{13}C and ^{113}Cd NMR, to study the electronic and structural effects of Zn^{2+} substitution by Cd^{2+} on the ^{13}C NMR chemical shifts in complexes of quinoline (Figure 1).

The geometry and chemical shifts (GIAO method) were calculated using the Gaussian 98 program² with LanL2DZ and B3LYP/6-31G** basis sets (in ppm relative to the

chemical shift of TMS calculated at the same level).

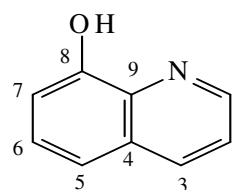


Figure 1. Quinoline

They were considered to be in tetrahedral (TD) and octahedral (OT, adding two water molecules) coordination environments. ^{13}C and ^{113}Cd - CP/MAS NMR spectra were obtained in a 300 MHz spectrometer. According to the results shown in Table 1 there is an average error in the calculated chemical shift of ± 3.0 ppm and ± 4.2 ppm for Zn and Cd complexes, respectively.

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Table 1. Calculated and Experimental ^{13}C Chemical Shifts for Zn and Cd Quinoline Complexes

<i>Carbon</i>	<i>Experimental</i>		<i>Theoretical</i>	
	<i>Zn</i>	<i>Cd</i>	<i>Zn-TD</i>	<i>Cd-OT</i>
C-1	127.55	122.72	125.03	120.65
C-2	118.97	114.21	122.04	115.30
C-3	---	140.18	---	138.50
C-4	135.64	131.44	137.05	128.47
C-5	110.07	109.59	112.14	113.42
C-6	138.07	137.97	135.05	133.98
C-7	112.50	111.85	109.15	114.50
C-8	159.11	161.68	162.40	156.49
C-9	145.19	148.59	140.70	151.04

The chemical shift differences between the two complexes are very small, varying between 0.65 and 4.83 ppm. This chemical shift non-variation is possibly due to compensation between the electronic and structural effects due to metal exchange. Cadmium tends to form octahedral complexes as it coordinates with solvent molecules, while Zn tends to remain in a tetrahedral geometry. Thus, this study indicates that there are severe modifications of the metal coordination environment when Zn-Cd substitution occurs.

Acknowledgements

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References

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