The Electric Field Gradient of $^{111}$Ag in Macroyclic Crown Thioethers

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Abstract. Time differential perturbed angular correlation experiments and ab-initio density functional theory calculation were used to determine the electric field gradients of the metal centres of the macrocyclic crown thioethers Ag(15S5)[BF$_4$], Ag(18S6-CH$_2$OH)[CF$_3$SO$_3$], Ag(18S6)$^+$, Ag(19S6-OH)[Tosylat] and Ag(20S6-OH)[CF$_3$SO$_3$]. The density functional theory calculations have been performed with the Amsterdam Density Functional code ADF. A “fingerprint system” is introduced, which allows to assign electric field gradients to certain Ag coordinations in these crown thioether complexes.

Key Words: Amsterdam density functional (ADF), Ag crown thioether, density functional theory (DFT), electric field gradient (EFG), PAC, time differential perturbed angular correlation (TDPAC).

Abbreviations: TDPAC – time differential perturbed angular correlation; EFG – electric field gradient; NQI – nuclear quadrupole interaction; ACCN – acetonitrile; THF – tetrahydrofuran; DMSO – dimethyl sulfoxide.

1. Introduction

The electric field gradient tensor (EFG) at a metal centre in a biological molecule can be determined by various hyperfine interaction spectroscopy methods, e.g., time differential perturbed angular correlation (TDPAC) [1]. The EFG, which arises from all extra-nuclear charges, reveals information about the coordination sphere of the metal probe, e.g., binding angles, bond distances, valence state and dynamics [1]. With the Amsterdam Density Functional code (ADF) [2–4] a density functional program package is available which allows to calculate reliable electric field gradients in molecules with a reasonable computational effort [5]. Therefore, ab-initio EFG calculations serve to validate proposed structures of metal centres or to establish “fingerprint systems” which allow to assign an experimentally determined EFG to a certain metal coordination.
Here, we present TDPAC measurements and ADF calculations on macrocyclic crown thioethers. Crown thioethers consist of a cyclic ligand of carbon and sulphur atoms saturated by hydrogen which coordinates an Ag$^+$ ion in its centre. A negatively charged counter ion assures the neutral charge of the whole complex. Figure 1 shows the Ag(18S6-CH$_2$OH)[CF$_3$SO$_3$] crown thioether which consists of a ring with 12 carbon and six sulphur atoms. A CH$_2$OH group is connected to the ring and as the negatively charged counter ion serves CF$_3$SO$_3$. These crown thioethers are used for the formation of complexes with radioactive $^{111}$Ag, a $\beta^-$-emitter with some potential for the application in nuclear medicine [6]. For this purpose the in-vivo stability of the $^{111}$Ag complex is essential. In order to achieve this in vivo stability several macrocyclic crown thioethers with different ring sizes have been prepared and investigated. Since $^{111}$Ag can also be used for TDPAC studies, this family of molecules is ideally suited to test the capabilities and limits of the ADF calculations of the electric field gradient by TDPAC experiments.

2. Experimental

The theory of TDPAC is well described in standard textbooks [7], the data analysis in [8]. All TDPAC measurements were performed with a 6-detector TDPAC-spectrometer equipped with BaF$_2$ detectors [9]. In the present study, we make use of the radioactive isotope $^{111}$Ag($\beta^-$)$^{111}$Cd (half-life $t_{1/2} = 7$ d) which decays by the successive emission of two $\gamma$-quanta via an intermediate state of the nuclear spin $I = 5/2$ (half-life $\tau_{1/2} = 84$ ns, quadrupole moment $Q = 0,83(13)$ barn). Prior to the $\gamma-\gamma$-cascade used for the TDPAC measurement a $\beta^-$-decay occurs. The $^{111}$Ag($\beta^-$)$^{111}$Cd was extracted from neutron irradiated Pd [10]. The nuclear quadrupole frequency $\omega_Q$ and the asymmetry parameter $\eta$, which are obtained by the TDPAC experiment are related to the main tensor components of the EFG $V_{xx}$, $V_{yy}$ and $V_{zz}$ as follows: $\omega_Q = 2\pi eQV_{zz}/(4I(2I-1)\hbar)$, $\eta = (V_{xx} - V_{yy})/V_{zz}$. The Lorentz-type line broadening $\delta$ of the TDPAC signal takes into account

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure1.png}
\caption{The structure of Ag(18S6-CH$_2$OH)[CF$_3$SO$_3$].}
\end{figure}