**77Se NMR SPIN-LATTICE RELAXATION INVESTIGATIONS OF HEXARHENIUM CHALCOGENIDE CLUSTER ANALOGUES**

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**Introduction**

The aim of our investigations is to understand the $^{77}$Se T$_1$ relaxation mechanisms in the hexarhenium chalcogenide clusters in solutions. The principal relaxation mechanisms in liquids are dominated by chemical shift anisotropy (CSA) relaxation and spin-rotation (SR) interactions. For both mechanisms, the relaxation rate is proportional to the square of the magnetic field. The relaxation rate due to the CSA mechanism is also proportional to the square of the total chemical shift anisotropy. Therefore, to separate the contribution of each from other mechanisms, e.g., dipolar relaxation, it is favorable to determine the relaxation rates at more than one Larmor frequency. Furthermore, to separate the contribution of SR from CSA, the relaxation rates must be measured at different temperatures. Keeping the above points in consideration, we have carried out $^{77}$Se T$_1$ experiments at multiple Larmor frequencies and as a function of temperature in these clusters.

**Experimental**

$^{77}$Se T$_1$ measurements were carried out at Larmor frequencies of 95 MHz and 137 MHz. The experiments at 137 MHz were carried out in the NMR facility (720 MHz solution state spectrometer) at the NHMFL. A Varian-Inova spectrometer console was used with a broadband Nicolet probe for all the experiments. The temperature of the sample was varied between $90^\circ$C and $-55^\circ$C using dry air and nitrogen gas as exchange gases. To reach temperatures below $0^\circ$C nitrogen gas was passed through a freezing mixture consisting of dry ice and petroleum ether, and the temperature near the sample space was controlled using a heater located near the NMR coil. Inversion recovery as well as saturation recovery pulse sequences were employed to measure T$_1$. Typical $\pi/2$ pulses for the 137 MHz experiments were 25 $\mu$s. Before measuring the $T_1$ values, a Bloch decay spectrum of $^{77}$Se in both the clusters were recorded at room temperature and referenced to the $^{77}$Se NMR resonance in diphenyl selenide, a secondary standard, which is at 402 ppm relative to dimethylselenide (0 ppm).

**Results and Discussion**

The $^{77}$Se NMR spectra of both clusters consisted of two peaks, the high frequency (HF) peak and the low frequency (LF) peak. For the cluster with Cl$^-$ ligand, the LF peak is very broad; therefore, T$_1$ measurements on this peak have high error bars due to poor signal to noise ratio. The T$_1$ of HF and LF peaks in both the clusters increases with increasing temperature and goes through a minimum as the temperature is decreased. The T$_1$ values of the HF peak were found to be smaller than that of the LF peak for both the clusters, due their different CSA’s. T$_1$ also showed a dependence on Larmor frequency. T$_1$ values at 137 MHz were found to be less than those at 95 MHz in the temperature range studied for both clusters. Such dependence of T$_1$ on Larmor frequency indicates that the relaxation mechanism in these clusters is via CSA. As T$_1$ did not show any sign of decrease with increasing temperature in the range studied, we cannot conclusively state the contribution of SR interaction towards relaxation. However, a slope change in T$_1$ in the high temperature range of the LF peak in the CN$^-$ cluster may be an indication of the onset of SR interaction towards relaxing the $^{77}$Se nuclear spins. We could not go beyond $90^\circ$C as the sample starts disintegrating above this temperature.

**Conclusions**

Our $^{77}$Se NMR T$_1$ investigations indicate that chemical shift anisotropy is the dominant mechanism in the spin-lattice relaxation of $^{77}$Se nuclear spins in both clusters. The different T$_1$ values of the peaks indicate their different CSA.

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