tions of $UCl_4$ in tetrahydrofuran with the corresponding potassium salts were followed simultaneously by $^{11}B$ NMR spectroscopy, electronic absorption spectroscopy and by conductivity measurements. In one of the experiments an intermediate species was found as shown by the $^{11}B$ NMR spectrum.

The first $^{11}B$ NMR variable temperature measurements of poly(pyrazol-1-yl)borates were made with the second compound dissolved in toluene and showed a Curie Weiss behaviour for one paramagnetic species.

In contrast with the above two compounds which show two $^{11}B$ NMR distinct lines, all the other analogous compounds studied, display only a single line.

Results from $T_1$ measurements obtained by the inversion recovery method will also be presented for the ligands and for some uranium species.

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## B24

### $^1H$ and $^{13}C$ Nuclear Magnetic Resonance Study of the Complexation of Uranyl Ion with (D)-Tartaric Acid

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The interaction of uranyl ion with tartaric and malic acids has been studied by means of the potentiometric method in the pH range 2–8 [1]. However a full pH range study of uranyl–malic acid complexation by NMR reveals the existence of more species [2]. This is also the case reported here. At least four uranyl–tartrate complexes are identified in $^1H$ (at 80 and 300 MHz) and $^{13}C$ (at 20 MHz) spectra. At low pH the ligand is mono or bidentate while at higher pH values tridentate chelates are dominating. Work is in progress to establish the stoichiometry of these complexes and to elucidate the exchange phenomena involving the various species present.

1 K. S. Rajan and A. E. Martell, *J. Inorg. Nucl. Chem., 26,* 1927 (1964).
2 M. T. Nunes, V. M. S. Gil and A. V. Xavier, *Can. Jour. Chem., 60,* 1007 (1982).

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## B25

### Variable Pressure NMR and Spectrophotometric Study of Lanthanide Solvation in DMF

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The equilibrium $[Ln(DMF)_8]^{3+}$ + DMF $\rightleftarrows$ $[Ln(DMF)_9]^{3+}$ has been studied in solutions of lanthanide perchlorates. For Nd the following thermodynamic parameters were obtained from spectrophotometric studies: $\Delta H = -14.9 \pm 13.$ kJ $mol^{-1}$, $\Delta S = -69.1 \pm 4.2$ J $K^{-1}$ $mol^{-1}$ and $\Delta V = -9.8 \pm 1.1$ $cm^3$ $mol^{-1}$. The NMR study of Ln = Ce–Nd and Tb–Yb shows that the proportion of the nine coordinate solvates rapidly becomes insignificant across the lanthanide series. Characteristic $^{17}O$, $^{13}C$ and $^1H$ NMR shifts for $[Ln(DMF)_8]^{3+}$ are also reported.

Kinetic parameters for the exchange of DMF on $[Ln(DMF)_8]^{3+}$ (Ln = Tb–Yb) have been determined in neat DMF, by variable temperature and pressure $^1H$- and $^{13}C$-NMR at 1.4, 4.7 and 8.5 Tesla. For the high field high pressure experiments, a high resolution multinuclear probe fitting into the tubular wide-bore 4.7 Tesla superconducting magnet was built. The probe works between –60 to +130 °C and has been used to 250 MPa. The spectral resolution measured by $^1H$-NMR is about 1 Hz, that is $5 \times 10^{-9}$. For the DMF exchange on Tb, the activation parameters, $\Delta H^*$ (kJ $mol^{-1}$), $\Delta S^*$ (J $mol^{-1}$ $K^{-1}$) and $\Delta V^*$ ($cm^3$ $mol^{-1}$), are respectively, 14.1 ± 0.4, –58 ± 2 and +5.2 ± 0.2 whilst for Yb the corresponding values are 39.3 ± 0.6, +40 ± 3 and +11.8 ± 0.4. The observed systematic variations in activation parameters from Tb to Yb are interpreted in terms of a mechanistic crossover at Er. Kinetic rate law determinations in $CD_3NO_2$ diluent indicate that an interchange mechanism operates for Tb ($k_{os}$ = 0.5 at 231 K) whereas a D mechanism is operative for Yb.