94. Spectrophotometric and Nuclear Magnetic Resonance Study of Temperature- and Pressure-induced Changes in the Intimate Solvation of Neodymium (III) in N, N-Dimethylformamide and Trimethylphosphate

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Summary

The temperature- and pressure-dependent equilibria for the addition of an extra N, N-dimethylformamide (DMF) or trimethylphosphate (TMP) ligand onto $[Nd(DMF)_8]^{3+}$- and $[Nd(TMP)_6]^{3+}$-species respectively have been measured by visible spectrophotometry. Complementary NMR. studies on other lanthanide ions show a gradual shift in preference for the lower coordination number across the lanthanide series.

The tripositive lanthanide ions are very labile towards ligand substitution in solution and consequently it has proved difficult to establish precise coordination numbers. For aqueous solutions, a large body of indirect evidence [1] suggests a change in coordination number (nine to eight) across the series but universal agreement has not been reached. The absorption band, $^4I_{9/2} \rightarrow {}^2P_{1/2}$, in the electronic spectrum of Nd^{3+} is sensitive to the environmental changes [2] mentioned above and, accordingly, a preliminary spectrophotometric study of neodymium (III) solvent complexes at variable temperature and pressure is now reported.

Anhydrous solutions of $[Nd(DMF)_8](ClO_4)_3$ [3] in DMF[1]) exhibit temperature and pressure dependent visible absorption bands[2]) in the region 425–435 nm as indicated in *Figure 1*. The spectra recorded for Nd^{3+} in DMF at high temperature approach those of $[Nd(DMF)_8](ClO_4)_3$ dissolved in either of the inert diluents, nitromethane or dichloromethane. Plots of the paramagnetic-induced NMR. shifts of the solvent formyl proton in Ln^{3+}/DMF solutions *versus* inverse temperature *(Fig. 2)* show points of inflection[3]) for Ln = Ce-Nd but not for Tb-Yb [4]. The behavior of the visible absorption bands and NMR. shifts for Nd^{3+} with temperature are consistent with an equilibrium between two solvated Nd^{3+}-species. Whilst

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[1])   There is no evidence for perchlorate in the first coordination sphere of Ln^{3+}/DMF solutions by ^{35}Cl-NMR. [4].

[2])   No such spectral modifications are observed for aqueous solutions of $Nd(ClO_4)_3$.

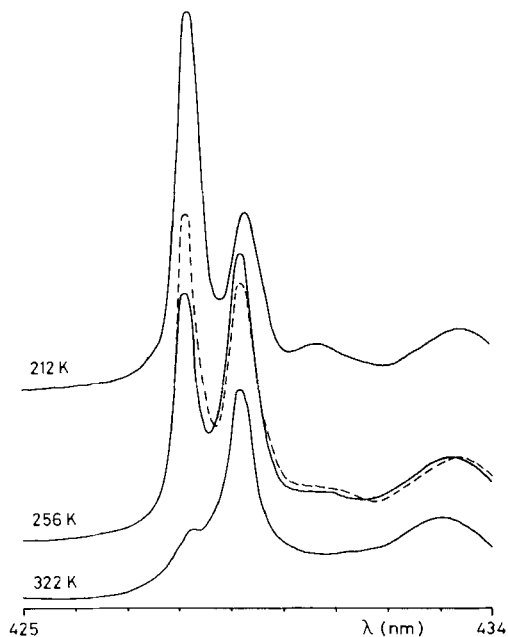[3])   At this point, equal amounts of two paramagnetic species are implied.

Fig. 1. *Visible absorption spectra for a [Nd(DMF)₈](ClO₄)₃/DMF solution at the temperatures indicated.* Solid lines represent spectra at ambient pressure. Dashed line shows the spectrum at 120 MPa.
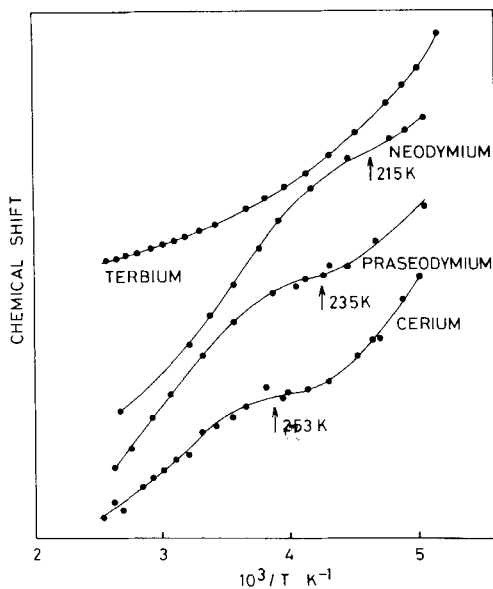

Fig. 2. *Plots of the paramagnetic-induced NMR. shift* (arbitrary scales) of the DMF formyl proton *versus* inverse temperature for [Ln(DMF)₈](ClO₄)₃/DMF solutions when Ln = Ce, Pr, Nd and Tb. The approximate temperatures corresponding to the inflection points are indicated.

Table. *Thermodynamic parameters for solvent addition* ($NdS_n^{3+} + S \rightleftharpoons NdS_{n+1}^{3+}$) *and average coordination numbers*[a]

	La C.N.	Nd C.N.	ΔH, kJ mol^{-1}	ΔS, JK^{-1} mol^{-1}	ΔV, cm^3 mol^{-1}	Eu C.N.	Tb C.N.	Tm C.N.	Yb C.N.	Lu C.N.
DMF	–	6.8±0.3	– 14.9±1.3	– 69.1±4.2	– 9.8±1.1[b]	–	–	7.7±0.2	7.8±0.2	–
TMP	6.8±0.2	–	– 32.7±3.3	– 114±11	– 23.8±1.5[c]	6.9±0.3	5.9±0.2	–	–	5.9±0.2

[a]) Coordination numbers determined in CD$_2$Cl$_2$-diluent in which the concentrations of free and coordinated ligand were arranged to be approximately equal.
[b]) At 256 K and 231 K.
[c]) At 298 K.

attempts to measure the coordination number of Nd^{3+} in DMF/CD_2Cl_2 solutions by NMR. integration were unsuccessful due to rapid DMF-exchange even at 170 K, eight-coordination was established for the more slowly exchanging Tm^{3+}- [4] and Yb^{3+}-systems *(Table)*. The latter (and smaller) lanthanide ions are expected to favour the lower coordination number and, hence, the equilibrium being examined here is between $[Nd(DMF)_8]^{3+}$ and $[Nd(DMF)_9]^{3+}$ with the former species being favoured at higher temperature.

The visible spectrophotometric behaviour of $Nd(SO_3CF_3)_3/TMP$ solutions with temperature and pressure is similar to that for $Nd(ClO_4)_3/DMF$ solutions and is again consistent with an equilibrium between two solvated Nd^{3+}-species but, now, exchange is sufficiently slow in TMP/CD_2Cl_2 to permit direct NMR. integration of the ^{31}P-signals arising from free and coordinated TMP at 175 K. The average coordination numbers measured in this way for several $Ln(SO_3CF_3)_3/TMP/CD_2Cl_2$ solutions are shown in the *Table*. It is evident that equilibrium is between $[Nd(TMP)_6]^{3+}$ and $[Nd(TMP)_7]^{3+}$. The observation of the coexistence of two solvated lanthanide species in DMF and TMP should not be considered unique to these solvents but, rather it suggests that such equilibria do occur for many solvents (*e.g.* water) somewhere along the series.

The thermodynamic parameters, ΔH, ΔS and ΔV for the addition of one solvent molecule were determined by analysis of the visible spectra in neat solvent and are listed in the *Table*. They provide for obvious comparison with activation parameters from solvent exchange kinetic studies and, especially, provide the previously missing limits needed for proper mechanistic evaluation of the enthalpy, entropy and volume profiles of closely related exchange systems. As an example, comparison of the activation parameters for TMP-exchange on $[In(TMP)_6]^{3+}$ ($\Delta H^{\pm} = 32.8$ kJ mol^{-1}, $\Delta S^{\pm} = -118$ J K^{-1} mol^{-1}, $\Delta V^{\pm} = -21.4$ cm^3 mol^{-1}) [5] with ΔH, ΔS and ΔV for $[Nd(TMP)_6]^{3+}$ suggests an almost completely associative (A) exchange mechanism for $[In(TMP)_6]^{3+}$.

REFERENCES

[1] *Y. Marcus*, Gmelin Handbuch *D3*, 1 (1981).
[2] *K. B. Yatsimirskii & N. K. Davidenko*, Coord. Chem. Rev. *27*, 223 (1979).
[3] *S. S. Krishnamurthy & S. Soundararajan*, Can. J. Chem. *47*, 995 (1969).
[4] *D. L. Pisaniello & A. E. Merbach*, Helv. Chim. Acta *65*, 503 (1982).
[5] *C. Ammann*, Ph. D. Thesis, EPF-Lausanne 1981.