

### The Solvation of (*R,S,R,S*)(1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)nickel(II) in Aqueous Solution

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The complexes of nickel(II) with the ligand 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (known commonly as tetramethylcyclam or TMC) have been very widely studied since they can exist as four-, five- or six-coordinate species depending on ligand conformation and the presence or otherwise of other coordinating ligands [1-4]. TMC can also allow stabilisation of some unusual oxidation states [5]. Depending on the method of synthesis, two different TMC complex conformations, *R,S,R,S* and *R,S,S,R* (sometimes known as *trans* I and *trans* III, respectively), can be obtained in the solid state [2, 6]. In solution, interconversion of the two species is generally negligible in most solvents and at reasonable temperatures [7]. The *R,S,R,S* conformer is generally believed to exist as four-coordinate planar diamagnetic, five-coordinate paramagnetic or an equilibrium between the two. There is NMR evidence that the five-coordinate structure is trigonal bipyramidal with the solvent ligand in an axial position [3]. The *R,S,S,R* conformer is generally believed to be four-coordinate, six-coordinate or an equilibrium between the two [3]. There are two exceptions to the above, however. In the presence of excess hydroxide, the *R,S,S,R* conformer is reported to give a five-coordinate hydroxy species [3] and in excess thiocyanate, the *R,S,R,S* conformer gives a water insoluble, organic soluble complex containing two thiocyanates [1]. Single crystal X-ray diffraction studies on this compound suggest that the complex is *trans* octahedral, but there is serious TMC disorder which prevents a definitive structure from being obtained [8].

The assignment of five- or six-coordinate is generally made on the basis of the larger extinction coefficients for the lower coordination, but such an approach can be criticised since even the six-coordinate species can be far from local octahedral symmetry and hence exhibit enhanced extinction coefficients. Studies on the equilibria between the various solvated species can be made using both NMR and UV-visible absorption spectroscopy but it is necessary to be able to shift the equilibria close to completion so as to obtain limiting spectra. For example, in aqueous solution, for equilibria of the form

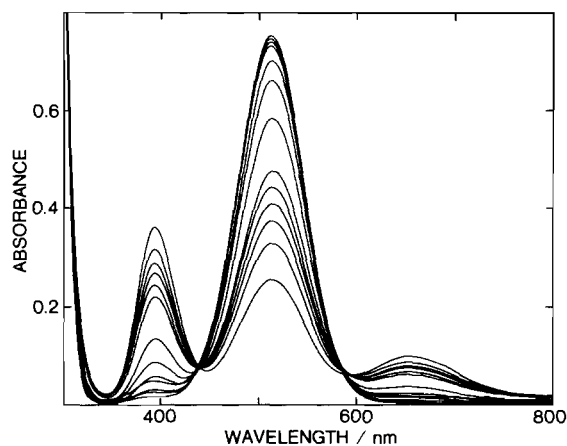


Fig. 1. UV-visible spectrum of  $3.99 \times 10^{-3} M$  solution of the title compound as a function of  $\text{NaClO}_4$  concentration at  $295 \pm 0.5 K$ .



the equilibrium can be pushed almost totally to the left by addition of  $\text{NaClO}_4$  which are thought to compete for the water molecules [3]. Under such an approach, the apparent equilibrium constant at any given  $\text{NaClO}_4$  concentration should be proportional to the water activity raised to the power  $n$ . It is the purpose of this paper to explore this approach as a means of obtaining the value of  $n$ . Recently, Merbach, Tregloan and coworkers [9] used a related approach of reducing the activity of acetonitrile by diluting with an inert solvent so as to obtain significant proportions of both planar and five-coordinate species in solution in equilibrium.

### Experimental

The title complex was prepared according to published procedures [1] and was characterised by elemental analysis, UV-visible spectroscopy and  $^1\text{H}$  NMR. Solutions were made up by volume, but since water activities are tabulated by molality [10], solutions were made up to given  $\text{NaClO}_4$  molalities by using available density data. UV-visible absorption spectra were obtained on a Varian Cary 210 spectrometer using the automatic solvent baseline recording/subtraction facilities. Sample and reference were contained in 1 cm glass cells. In order to limit effects due to changes in solution refractive index, the reference solution was the corresponding  $\text{NaClO}_4$  solution. Such an approach improved the quality of the isobestic points obtained. Figure 1 shows the spectra as a function of  $\text{NaClO}_4$  concentration; it is clear from the very good isobestic points

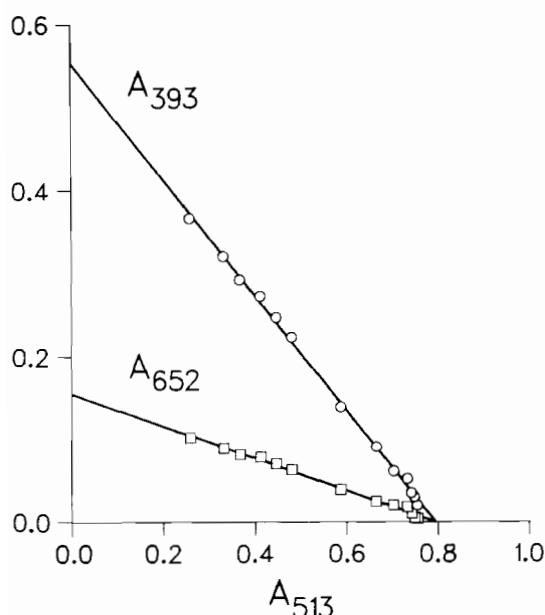


Fig. 2. Plot of the variation of the absorbance of the 513 nm peak with that of the 393 and 652 nm peaks (see text for details).

obtained that there are but two absorbing species in equilibrium.

### Discussion

Visual inspection of Fig. 1 suggests that at 8 molal  $\text{NaClO}_4$  the desolvation is almost complete whereas, in pure water, about 70% of the complex is solvated. The ratio of the peak heights at 394 nm and 650 nm remains constant for all solutions, which is strong evidence that the desolvated species absorbs negligibly at these wavelengths. Let  $\alpha$  be the fraction of complex which is solvated. Then

$$\alpha = \frac{A_{394}}{A_{394}^{\circ}} \quad (2)$$

where  $A_{394}$  is the absorbance at 394 nm and  $A_{394}^{\circ}$  is the absorbance when  $\alpha = 1$ . A similar expression applies at 652 nm. Assuming only the desolvated form absorbs at 394 nm, then we may similarly write

$$1 - \alpha = \frac{A_{513}}{A_{513}^{\circ}} \quad (3)$$

Eliminating  $\alpha$  from eqns. 2 and 3, we obtain

$$A_{394} = A_{394}^{\circ} - \frac{A_{394}^{\circ}}{A_{513}^{\circ}} A_{513} \quad (4)$$

A similar equation applies for the 652 nm rather than the 394 nm data. Figure 2 shows the results of plot-

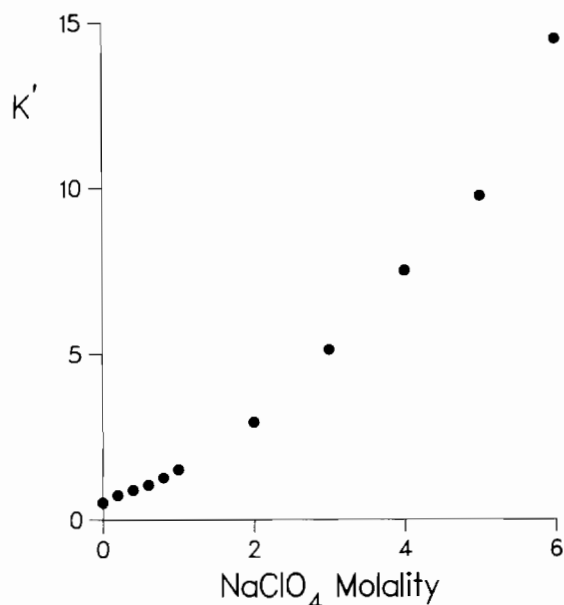


Fig. 3. Variation of the apparent value of the equilibrium constant  $K'$  with  $\text{NaClO}_4$  concentration.

ting both the 394 and 652 nm data *versus* the 513 nm results. The straight lines correspond to a simultaneous fit of the two data sets to the three unknowns. The values of the intercepts with the x and y axes correspond to these parameters. The quality of the fit gives confidence to the assumptions embodied in eqns. 2 and 3.

We may define an apparent equilibrium constant  $K'$  for the reaction 1, neglecting the water activity in terms of the activities of the solvated and unsolvated forms:

$$K' = \frac{a_{\text{Ni}(\text{TMC})(\text{H}_2\text{O})_n}}{a_{\text{Ni}(\text{TMC})}} \quad (5)$$

It is clear that, although the activity coefficients for both the solvated and unsolvated complex ions will differ markedly from unity in concentrated  $\text{NaClO}_4$ , their ratio being very close to unity and thus equation 5 may be approximated to

$$K' = \frac{\alpha}{1 - \alpha} \quad (6)$$

Figure 3 shows the value of  $K'$  as a function of  $\text{NaClO}_4$  concentration. It is immediately apparent that the variation of  $K'$  does not relate to the water activity; going from pure water to 2 molal  $\text{NaClO}_4$ , the water activity only changes from 1.0 to 0.934 [10] whereas  $K'$  changes from 0.505 to 2.94. The initial linearity of  $K'$  with  $\text{NaClO}_4$  concentration would imply some form of anion assisted desolvation. However, it is clear that the desolvated species

is diamagnetic and hence planar [2]. The interaction must thus be fairly long range. The two possible sites could be *trans* to the solvating solvent molecule (assuming  $n = 1$ ), the TMC ligand preventing close approach of the  $\text{ClO}_4^-$  or alternately the  $\text{ClO}_4^-$  could compete for the solvent site but with the ligand preventing the anion from approaching closely enough to give a paramagnetic complex. Another explanation could be that the anion induced conformational changes perhaps between square pyramidal and trigonal bipyramidal. Further work would be needed to evaluate these possibilities. In order to check that the value of  $K'$  in the absence of added  $\text{NaClO}_4$  was truly an infinite dilution value, *i.e.*, showed no concentration dependence, the spectra were also run on solutions of approximate composition  $2.0$  and  $1.0 \times 10^{-3} M$  in water; no variation in  $K'$  could be discerned.

The effect of different electrolytes in promoting desolvation was estimated approximately by comparing spectra run in pure water with those run in  $1 M$  electrolyte solution. It is immediately apparent that the order efficiency of desolvation is  $\text{ClO}_4^- \gg \text{NO}_3^- > \text{SO}_4^{2-}$  and in addition a less sensitive trend  $\text{Na}^+ > \text{K}^+$ . The anionic trend is strongly reminiscent of the Hofmeister or lyotropic ion series which would imply that water structure changes are responsible for the observed changes [11]. However, such an approach would predict the reverse order for the cations.

It is clear that the solvation–desolvation equilibria is considerably more complicated than as described by eqn. 1. In addition, the very large sensitivity of the equilibrium to the presence of added salts would suggest that care should be taken when comparing the results from different groups. Where possible, comparisons of the solvating efficiencies at different solvents should only be made from measurements in the absence of added salts.

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