The Formation of Tetrahedral Tetrachloronickelate(II) in Aqueous Solution

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DURING a systematic study of the effects of cations upon the absorption spectra of tetrahedral tetrahalogenonickelate(II) complexes in nonaqueous media it was observed that, as halide ions were added, complete conversion into the tetrahedral complex occurred more readily as the size of the cation associated with the halide decreased. In co-ordinating solvents, lithium ions were solvated and hence appeared large in size, but quaternary ammonium cations were not so solvated. It is also known that the octahedral ⇌ tetrahedral equilibrium for chloro-nickel complexes is driven to the right on heating.[1,2] We therefore predicted that tetrahedral $NiCl_4^{2-}$ might be obtained in aqueous solution in the presence of chloride ions supplied by the small cation Me_4N^+ and if the solution were warmed. The blue colour typical of tetrahedral $NiCl_4^{2-}$ was obtained on warming to about 50° a solution containing 0·015M-$Ni(ClO_4)_2,6H_2O$ and 2·5M-Me_4NCl. The spectrum shown resembles closely that established for tetrahedral or very slightly distorted tetrahedral $NiCl_4^{2-}$.[3] Experiments with Et_4NCl and larger quaternary chlorides did not produce blue solutions. No evidence for tetrahedral $NiBr_4^{2-}$ or NiI_4^{2-} could be obtained on adding Me_4NBr or Me_4NI respectively, even in saturated solutions at their boiling point.

Angell and Gruen[4] have obtained tetrahedral $NiCl_4^{2-}$ in molten salt hydrates, such as $MgCl_2,6H_2O$, at high temperatures, but we believe that this is the first evidence for tetrahedral $NiCl_4^{2-}$ in aqueous solution. Russian workers[5] have recently suggested that tetrahedral NiI_4^{2-} can be obtained in 9M-HI solution at −10° but, on examination, their reported spectra can only be explained in terms of an octahedral ⇌ tetrahedral equilibrium with the equilibrium well to the left. Further, the concentrations they used parallel the salt hydrates of Gruen.[4]

Gill and Nyholm[6] originally suggested an explanation for the inability of nickel to form $NiCl_4^{2-}$ in aqueous solution and this has recently been extended.[7] The conclusion was drawn that CFSE values appear capable, *in themselves*, of providing a semiqualitative guide to the relative stabilities of tetrachlorometallate ions of the first transition series. We now suggest that some other energetic feature is of major importance or that the formation of some kind of "ion-pair"[8] should be considered in accounting for this phenomenon; a detailed explanation is being prepared.

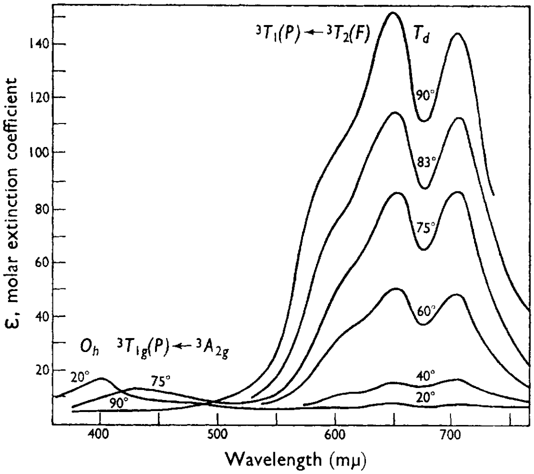

FIGURE. *The effect of temperature upon the electronic absorption spectrum of nickel*(II) *in aqueous* Me_4NCl *solution.*

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