Solvent and Temperature Effects on the Electronic Spectra of Mixed Nickel(II) Chelates with *N*,*N*,*N'*,*N'*-Tetramethylethylenediamine and Acetylacetone

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When equimolar quantities of $Ni(ClO_4)_2 \cdot 6H_2O$, *N*, *N*, *N'*, *N'*-tetramethylethylenediamine(TMEN), acetylacetone(acaH) and sodium carbonate are mixed in ethanol, and the resulting mixture is concentrated under reduced pressure, blue crystals of the composition Ni TMEN aca $(ClO_4) \cdot 2H_2O$ separate out. This compound is stable in open air but is easily dehydrated in a P_2O_5 dessicator, and a red anhydrous compound is obtained which slowly reverts to the blue dihydrate in moist air.[1] The blue compound has a magnetic moment (μ_B) of 3.04 B.M. at 14°C, while the red one is only slightly paramagnetic ($\mu_B \sim 0.6$ B.M.).[2]

These values, and the spectral data shown below, indicate that they should be formulated as the mixed chelates, [Ni TMEN aca $(H_2O)_2$] (ClO_4) (octahedral) and [Ni TMEN aca] (ClO_4) (square-planar).

Both of these chelates are decomposed by water, but they are soluble in many organic solvents. Fig. 1 shows their spectra in some alcohols and acetone. It can be seen that in methanol both of the chelates exist as the blue octahedral species, [Ni TMEN aca $(X)_2]^+$ ($X = H_2O$ or solvent); the spectra of these solutions (Curves A) are also very similar to the solid reflection spectrum of the blue chelate. On the other hand, the spectra in the other solvents show that they exist in part as blue species and in part as a red square-planar species, very probably [Ni TMEN aca]$^+$. The amount of this red species increases in the order MeOH$\ll$EtOH$<$*n*-PrOH$<$Acetone$\ll$$CHCl_3$ or $C_2H_4Cl_2$, *i.e.* the order of decreasing coordination ability of the solvents. Corresponding to this spectral change, the color of the solution becomes gradually reddish from methanol to acetone, and the solutions in chloroform or 1,2-dichloroethane are quite red. In these two solvents, the red species clearly predominate ($\nu_{max} = 20.5$ kK; log $\varepsilon = 2.1$—2.2).

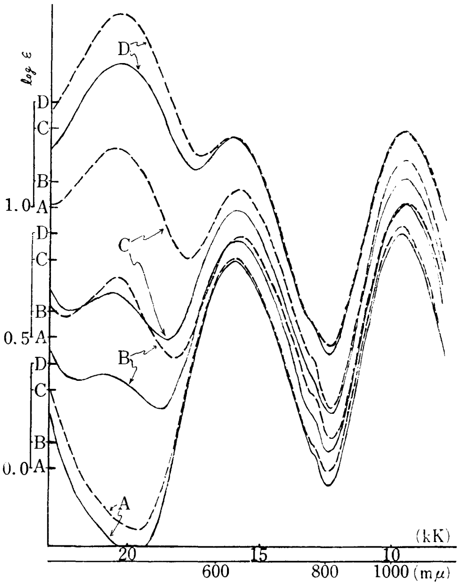

Fig. 1. Absorption spectra of the blue and red chelates at room temperature (18°C). Curves A,B,C and D refer respectively to the solutions in MeOH, EtOH, *n*-PrOH and acetone (0.8×10^{-1}—1.2×10^{-1}M); each curve is drawn in the same scale but displaced vertically (*cf.* the scale for log ε). The solid-line curves are those for the blue chelate, and the dotted-line curves for the red.

All the alcoholic and acetone solutions are thermochromic and become more reddish on heating. Spectral studies on the thermochromism show that the intensity of the band at 20.5 kK increases remarkably with the rise of temperature, showing that the equilibria [Ni TMEN aca $(X)_2]^+$ (octahedral)$\rightleftarrows$[Ni TMEN aca]$^+$ (square-planar)$+2X$ are shifted to the right hand side even by slight heating. It is interesting, however, to note that this type of reversible thermochromism is observed only in solvents of medium coordination ability (alcohols and acetone); the red solutions in poorly coordinating solvents($CHCl_3$ and $C_2H_4Cl_2$) as well as the blue ones in strongly coordinating solvents (DMSO and DMF) are not thermochromic, *i.e.* their colors do not changes by heating.

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[1] Elementary analyses of these compounds are as follows. Found for the blue compound: C, 32.40; H, 6.89; N, 6.88%. Calcd for [Ni TMEN aca $(H_2O)_2$](ClO_4): C, 32.26; H, 6.66; N, 6.84%. Found for the red compound: C, 34.65; H, 6.42; N, 7.42%. Calcd for [Ni TMEN aca](ClO_4): C, 35.37; H, 6.22; N, 7.50%.

[2] The moments obtained with different samples of the red compound do not agree well with each other, and they all tend to increase slowly with time. It is therefore possible that this compound is in fact diamagnetic, and the observed moment is due to a small amount of the blue dihydrate which is readily formed in the sample. Work is now going on to confirm this view.