

Alcohol dehydrogenase was prepared by the method of Bonnichsen and Brink⁶ and recrystallized 5 times to constant activity/protein ratio, as described earlier⁷. The sedimentation constant was measured in the Spinco ultracentrifuge at 59 780 r.p.m. and 20°C with various protein, chloride and hydrogen ion concentrations. The results are shown in Table. I. There is no evidence of any significant effect of chloride or hydrogen ion concentration on the sedimentation constant. Extrapolation to infinite dilution of the protein gives $S_{20}^0 = 5.1 S$.

These data give a value of 4.8 *S* at a protein concentration of 10 mg/ml, slightly greater than Pedersen's value. The difference is probably to be ascribed to the greater purity of our material indicated by higher specific activity⁷. More complete data on the molecular weight will be reported shortly.

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The Equilibrium Between Yellow and Blue Nickel(II) Triethylenetetramine Ions in Strong Salt Solutions

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Lifschitz *et al.*^{1,2} prepared solid nickel(II)bis(stilbenediamine) complexes in two isomers, one yellow, diamagnetic, and one blue, paramagnetic. The equilibrium between two such forms in solution has not yet been studied by means of the ab-

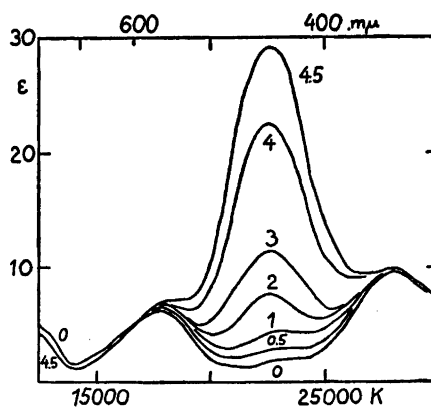


Fig. 1. The absorption spectra of 0.1 M Ni trien(NO_3)₂ in water and aqueous solutions of sodium perchlorate. The numbers on the curves indicate the molarity of NaClO_4 . The spectra were measured at 19°C on a Cary spectrophotometer.

sorption spectra. Jonassen and Douglas³ investigated nickel(II) complexes of triethylenetetramine (= trien) and prepared solid salts of $\text{Ni}_2\text{trien}_3^{+2}$, but not of Ni trien^{+2} . The latter violet-blue ion turns brownish yellow in strong salt solutions. Fig. 1 gives the absorption spectra at 19°C in different concentrations of sodium perchlorate. The absorption band at 443 μ , which increases in the yellow solutions, corresponds to the planar, diamagnetic complex. Basolo *et al.*⁴ prepared the yellow Nitemeen₂⁺⁺ (temeen = C, C, C', C' tetramethyl-ethylenediamine) which has a Gaussian shaped band at 433 μ with $\epsilon = 67$. It is interesting that Ni temeen_2^{++} does not exhibit other spin-allowed, Laporte-forbidden ligand field bands below the ultra-violet absorption limit ($\epsilon = 8$ at 260 μ), since the ligand field theory⁵ would predict three transitions at not very different wavenumbers (the analogous difficulty* occurs in Cu en_2^{++}). The two

* However, the band at 422 μ of Ni(II) in ethanolic sodio-succinimide has a shoulder at 470 μ , and the band at 440 μ of Ni(II) in 1 M NaOH with caseine has a shoulder at 510 μ . These orange solutions do not seem to contain paramagnetic nickel, according to the spectra. Sodium caseinate is very effective for formation of tetragonal complexes; its biuret reaction with Cu(II) has the band maximum at 547 μ .

equally strong bands of PtCl_4^{2-} may be caused by effects of intermediate coupling ⁶.

However, the height of the new band of yellow Nitrien⁺⁺ cannot be implied with certainty from the Figure, since the decrease of the concentration of the blue form cannot be determined, due to salt effects. However, ϵ seems to be between 50 and 80, as expected. The formation of the yellow isomer is endothermic; a boiling solution of 0.1 M Ni trien(NO_3)₂ alone turns reversibly yellowish. Some salt solutions, such as nine-tenths-saturated CaCl_2 ($\epsilon=27$ at 443 μm) and the same shape of the band as in 4.5 M NaClO_4) and molten $\text{Mg}(\text{NO}_3)_2$, 6 H_2O , are equally effective for forming the yellow colour, while saturated NaBr and molten Na_2SO_4 , 10 H_2O produce only a brownish purple mixture. Since Ni temeen⁺⁺ neither solvates nor takes up chloride ions ⁷, it is not believed that ClO_4^- or Cl^- directly participate in the first co-ordination sphere of the yellow Ni trien⁺⁺, even though a general effect of ion-pair formation cannot be excluded. However, a special de-hydration effect does not seem to occur in aqueous ethanol, compared to an aqueous solution with identical salt content. Actually, Lifschitz *et al.*¹ observed blue solutions in chloroform and other non-polar solvents of salts, which are yellow in aqueous solution. Thus an equilibrium may be postulated between blue *cis*- NiA_4X_2 , blue *trans*- NiA_4X_2 and yellow *trans*- NiA_4 , where X are water, alcohol, anions, etc., which are more strongly bound in solutions with low dielectric constant than in water. It is a necessary condition ⁸ for diamagnetism in d^8 -systems to have a much weaker ligand field along the tetragonal axis than in the plane of the four strongly bound ligands.

The blue isomer is not tetrahedrally co-ordinated, but is rather *cis*-octahedral. Thus, the water can be exchanged by other ligands, and the absorption spectra greatly resemble those of the corresponding tren- (= β , β' , β'' tris(ethylamino)amine)nickel (II) complexes ⁷. The spin-allowed transitions from 3T_2 (F) to 3T_4 (F) and 3T_4 (P) are situated at:

Ni trien (H_2O) ₂ ⁺⁺	564 μm	358 μm
Ni_2 trien ₃ ⁺⁴	539	346
Ni trien (NH_3) ₂ ⁺⁺	546	350
Ni trien en ⁺⁺	538	344
Ni trien gly ⁺	550	352

The last glycinate complex resembles more Ni en₂gly⁺ than Ni tren gly⁺, which ⁷ has the bands at 532 and 354 μm . It is not

easily decided whether *trans*-Ni trien⁺⁺ also exists as a blue diaquo complex in equilibrium with the anhydrous yellow form. At most 2 % of the yellow form occurs in the most dilute solution of the Figure (a spin-forbidden band may be the cause of the weak shoulder $\sim 443 \mu\text{m}$). If all the *trans*-isomer is diamagnetic, this would correspond to a similar deviation from the statistical *cis/trans* equilibrium constant ⁹ as in the case of Coen₂(H_2O)₂⁺⁺⁺. J. Bjerrum and Poulsen ⁹ have reported yellow Nien₂⁺⁺ as an intermediate by low-temperature kinetic studies. Even though Cutrien⁺⁺ has mainly the *trans*-configuration, it has only been possible ¹⁰ to prepare *cis*-Co trienCl₂⁺. Mr. Kjeld Rasmussen and the present author will later discuss a possible blue *trans*-isomer of the latter ion.

Analogous ⁵ to the behaviour of Nien₂⁺⁺, it is possible to precipitate yellowish pink [Ni trien] [AgBrI]₂. Most other salts of Ni trien⁺⁺ seem to be paramagnetic. Thus, thiocyanates produce a copious precipitate of pale blue Ni trien(SCN)₂, which is soluble in excess of trien. If a solution of NiBr₂ and trien is evaporated to dryness, a dark purple salt results, which deliquesces to a brown solution. Ni(ClO_4)₂ and trien produces a sticky reddish brown syrup. On inflaming some mg of this material, it explodes violently. Yellow colour of the commercial trien can be removed by treating the 1 M aqueous solution with norite carbon for several weeks.

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