Alcohol dehydrogenase was prepared by the method of Bonnichsen and Brink and recrystallized 5 times to constant activity/protein ratio, as described earlier. 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 1. 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 $S_{20, w} = 5.1$ 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 activity. More complete data on the molecular weight will be reported shortly.


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The Equilibrium Between Yellow and Blue Nickel(II) Triethylene-tetramine Ions in Strong Salt Solutions

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Lifschitz et al. 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 absorption spectra. Jonassen and Douglas investigated nickel(II) complexes of triethylene-tetramine (= trien) and prepared solid salts of Ni₃trien₂⁺, but not of Ni trien⁺++. 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 μμ, which increases in the yellow solutions, corresponds to the planar, diamagnetic complex. Basolo et al. prepared the yellow Nitemeem₃++ (teneem = C, C, C', C' tetramethyl-ethylenediamine) which has a Gaussian shaped band at 433 μμ with ε = 67. It is interesting that Ni teneem₃++ does not exhibit other spin-allowed, Laporte-forbidden ligand field bands below the ultra-violet absorption limit (ε = 8 at 260 μμ), since the ligand field theory would predict three transitions at not very different wavenumbers (the analogous difficulty occurs in Cu en₃++). The two absorption spectra.

**Fig. 1.** The absorption spectra of 0.1 M Ni trien(NO₃)₂ in water and aqueous solutions of sodium perchlorate. The numbers on the curves indicate the molarity of NaClO₄. The spectra were measured at 19°C on a Cary spectrophotometer.
equally strong bands of PtCl₄⁻ may be caused by effects of intermediate coupling.

However, the height of the new band of yellow Ni₇⁺ 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, s 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(NO₃)₆ alone turns reversibly yellowish. Some salt solutions, such as nine-tenths-saturated CaCl₂ (e = 27 at 443 m) and the same shape of the band as in 4.5 M NaClO₃ and molten Mg(NO₃)₂, 6 H₂O, are equally effective for forming the yellow color, while saturated NaBr and molten Na₂SO₄, 10 H₂O produce only a brownish purple mixture. Since Ni teme₆⁺ neither solvates nor takes up chloride ions, it is not believed that ClO₄⁻ or Cl⁻ directly participate in the first coordination sphere of the yellow Ni trien⁺⁺, even though a general effect of ion-pair formation cannot be excluded. However, a special dehydration effect does not seem to occur in aqueous ethanol, compared to an aqueous solution with identical salt content. Actually, Lifschitz et al. 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-Ni₆X₆⁺⁺, blue trans-Ni₆X₆⁺⁺, and yellow trans-Ni₆A₆, where X is water, alcohol, anions, etc., which are more strongly bound in solutions with low dielectric constant than in water. It is a necessary condition for diamagnetism in d-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 coordinated, 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(ethylenimino)amine)nickel (II) complexes. The spin-allowed transitions from 2F₁ (F) to 2F₆ (F) and 2F₄ (F) are situated at:

Ni trien (H₂O)₆⁺⁺ 564 m 358 m 
Ni trien⁺⁺ 539 346
Ni trien (NH₄)₆⁺⁺ 546 350
Ni trien en⁺⁺ 538 344
Ni trien glyc⁺⁺ 550 332

The last glycine complex resembles more Ni en gly⁺⁺ than Ni tren glyc⁺⁺, which has the bands at 532 and 354 m. It is not easily decided whether trans-Ni trien⁺⁺ also exists as a blue disoquo complex in equilibrium with the anhydrous yellow form. At most 20% 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 (~443 m)). If all the trans-isomer is diamagnetic, this would correspond to a similar deviation from the statistical cis/trans equilibrium constant as in the case of Coen₆(H₂O)₆⁺⁺⁺, J. Bjerrum and Poulsen have reported yellow Ni₇⁺⁺ as an intermediate by low-temperature kinetic studies. Even though Cretun⁺⁺ has mainly the trans-configuration, it has only been possible to prepare cis-Co trienCl₂⁺⁺. Mr. K. Rasmussen and the present author will later discuss a possible blue trans-isomer of the latter ion.

Analogous to the behavior of Ni₇⁺⁺, it is possible to precipitate yellowish pink [Ni trien] [AgBr], Most other salts of Ni trien⁺⁺ seem to be paramagnetic. Thus, thiocyanates produce a copious precipitate of pale blue Ni trien(SCN)₆, which is soluble in excess of trien. If a solution of NiBr₆ and trien is evaporated to dryness, a dark purple salt results, which deliquesces to a brown solution. Ni(CIO₄)₆ and trien produces a sticky reddish brown syrup. On inflaming some mg of this material, it explodes violently. Yellow color of the commercial trien can be removed by treating the 1 M aqueous solution with norit carbon for several weeks.


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