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Blue-to-Yellow Equilibrium of a Square Pyramidal Aminocarboxylate Nickel(II) Complex

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A number of linear tetramine ligands yield nickel (II) complexes which exist in solution as an equilibrium mixture of blue paramagnetic octahedral and yellow diamagnetic square planar forms. For example, the nickel(II) complex of 2,3,2-tet (1,4,8,11-tetraazaundecane) exists in dilute aqueous solution as a mixture [1] of approximately 20% planar $Ni(2,3,2\text{-}tet)^{2+}$ and 80% octahedral $Ni(2,3,2\text{-}tet)(H_2O)_2^{2+}$, the latter a mixture of *cis* and *trans* diaquo forms [2, 3]. Addition of certain inert electrolytes, particularly $NaClO_4$, shifts the equilibrium to form more of the planar species, as does an increase in temperature. Nickel(II) complexes of several macrocyclic tetramine ligands have also been shown to involve the same octahedral–planar equilibrium [4, 5].

The present communication reports the observation of an equilibrium between planar and five-coordinate forms of a nickel(II) complex. Moreover, it is the first such equilibrium involving an aminocarboxylate ligand rather than a tetramine ligand.

Ligands which stabilize the square planar form in aqueous solution are those which produce a strong ligand field and those in which steric hindrance limits solvation in the axial positions. The mesocyclic diamine 1,5-diazacyclooctane, for example, forms a square planar complex $Ni(daco)_2^{2+}$ [6] in which the ring methylenes shield the out-of-plane positions. Linear tetradentate ligands incorporating a central mesocyclic diamine ligand form complexes with several transition metal ions which exhibit planar four-coordinate ML or square pyramidal five-coordinate MLX geometries. Legg and his coworkers showed that $[Ni(dacoda)(H_2O)]$ (dacoda = 1,5-diazacyclooctane-N-N′-diacetate) is square-pyramidal in the crystal [7] and this geometry is maintained in solution [8]. The cobalt(II) and zinc(II) complexes are also square pyramidal [8]. Our solution studies on complexes of the related ligand [9] dachden (N,N′-bis(2-aminoethyl)-1,4-diazacycloheptane) demonstrate that although the cobalt(II) and zinc(II) complexes are five-coordinate, the nickel(II) complex is square planar, because of the greater in-plane ligand field of four nitrogen donors compared to two nitrogen and two carboxylate oxygens in the dacoda complex.

In a recent report from this laboratory [10] the planar complex $Ni(dachdpn)^{2+}$ (dachdpn = N,N′-bis(3-aminopropyl)-1,4-diazacycloheptane) was shown to exist in equilibrium with a small amount (9% in dilute solution at 25 °C) of the five-coordinate complex $Ni(dachdpn)(H_2O)^{2+}$, the first reported example of blue-to-yellow equilibrium involving a five-coordinate complex. The dachdpn complex has a small but detectable amount of the paramagnetic form, while the dachden complex is 100% square planar, presumably because of the weaker in-plane field provided by a ligand which forms terminal six-membered chelate rings (energies of the d–d band, a measure of the in-plane ligand field, are 23.0 kK for $Ni(dachden)^{2+}$ and 21.6 kK for $Ni(dachdpn)^{2+}$). In the light of this result we wondered whether the five-coordinate $Ni(dacoda)(H_2O)$ complex could be forced into the yellow square planar form in solutions containing large amounts of $NaClO_4$.

The spectrum of $Ni(dacoda)(H_2O)$, prepared from crystals of $[Ni(dacoda)(H_2O)]\cdot 2H_2O$ [8], in solutions of varying $NaClO_4$ concentration (Fig. 1) demonstrates the occurrence of an equilibrium between blue and yellow forms (equation 1). The

$$\underset{\text{blue, square pyramidal}}{Ni(dacoda)(H_2O)} \rightleftharpoons \underset{\text{yellow, planar}}{Ni(dacoda) + H_2O} \qquad (1)$$

deep blue solution becomes green in 4 *M* $NaClO_4$, as a band appears at 482 nm. The bands at 375 nm and 622 nm decrease, and there are well-defined isosbestic points. The decrease in absorbance at 375 nm permits the calculation of the concentration of the planar species formed and thus the ϵ of the planar species at 482 nm. A correction was made for the presence of the small amount of planar form occurring at $[NaClO_4] = 0$. The bands at 375 nm and 622 nm were approximated by Gaussian band shapes, and the contribution of these bands at 482 nm was found to be negligible. Thus the absorbance at 482 nm of the solution having $[NaClO_4] = 0$ is due to a small amount of the planar form and this was calculated to be 4% of the total. After making this correction the molar absorptivities were found to be $\epsilon_{375} = 85$ (blue form), $\epsilon_{482} = 100 \pm 3$ (yellow form). $Ni(dacoda)(H_2O)$ thus provides the first example of blue-to-yellow equilibrium involving an aminocarboxylate ligand rather than a tetramine ligand. The unusually low energy of the d–d transition of the planar complex (20.7 kK) is consistent with the weak ligand field provided by a two nitrogen–two carboxylate oxygen donor set. The majority of nickel(II) complexes which retain square planar geometry in aqueous solution are complexes of four-nitrogen ligands. Complexes of tripeptides, having three nitrogens and one

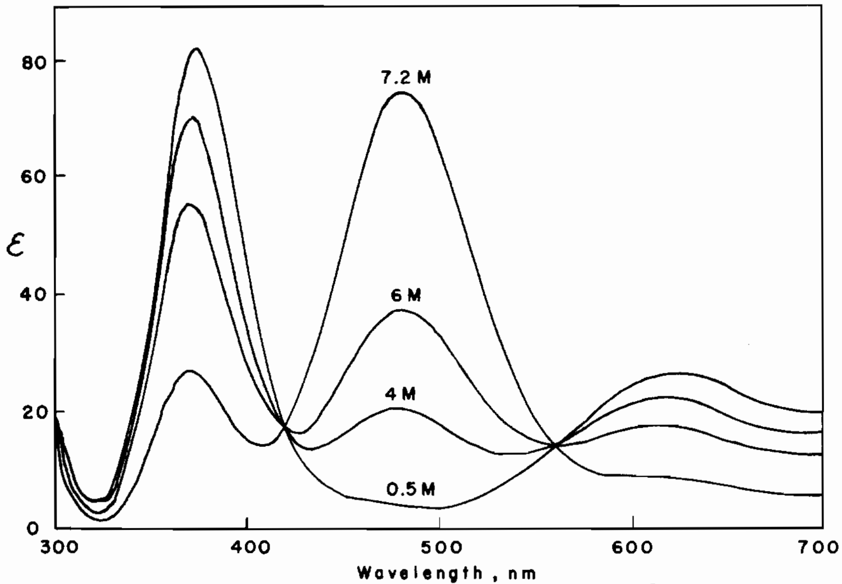

Fig. 1. Visible absorption spectrum of Ni(dacoda)(H_2O) (2.12×10^{-3} *M*) in $NaClO_4$ solutions at 25 °C.

TABLE I. Thermodynamic Parameters for the Blue-to Yellow Equilibrium of Ni(dacoda)(H_2O).

[$NaClO_4$] *M*	ΔG° kcal/mol	ΔH° kcal/mol	ΔS° cal/deg mol
1.0	1.8 ± 0.1	5.6 ± 0.6	13 ± 2
4.0[a]	0.8 ± 0.1	5.1 ± 0.1	14.4 ± 0.5
4.0[b]	0.8 ± 0.1	4.8 ± 0.1	13.6 ± 0.5

[a] Calculated using absorbance data at 482 nm. [b] Calculated using absorbance data at 375 nm.

carboxylate, are also planar. However, two nitrogens and two oxygen donors are not sufficient to cause spin-pairing, and it is only with the steric effect of the 1,5-diazacyclooctane ring that the conversion from blue to yellow occurs at high concentrations of sodium perchlorate.

The spectrum of [Ni(dacoda)(H_2O)] in 4 *M* $NaClO_4$ was recorded at various temperatures (from 26° to 77 °C). The temperature was measured using a thermistor probe inserted through a hole drilled in the Teflon cover of a 1 cm cell. The equilibrium constant for equation (1) was calculated from the relationship $K = E/(\epsilon - E)$, where $E = A_{meas}/(bc)$ and $\epsilon = 100\ M^{-1}\ cm^{-1}$, using absorbance measurements at 482 nm. A plot of lnK *vs.* 1/T was linear (correlation coefficient 0.998) and the thermodynamic values listed in Table I were obtained. Within the expected experimental error, identical results were obtained using data at 375 nm. Spectra were also recorded for a solution 1 *M* in $NaClO_4$ over the temperature range 27° to 81 °C. Here the spectral changes were much smaller and ΔH° and ΔS° values are less precise. ΔH° values are similar to those found for the blue ⇌ yellow conversion of nickel(II) complexes of cyclam [11] and isocyclam [5]. The ΔS° value is greater* than that expected for the release of a single water molecule, which according to Fabbrizzi is about 8–10 cal/deg mol. Values of 19–20 cal/deg mol were found for the release of two water molecules from cyclam and isocyclam. The ΔS° value of approximately 13–14 cal/deg mol thus corresponds to release of more than one water molecule from [Ni(dacoda)(H_2O)]. The additional positive entropy change may be the result of a decrease in solvation of the planar complex. Conversion from either six- or five-coordinate to planar four-coordinate nickel(II) results in an increase in nickel(II)–N bond strength, with a concomitant, well-documented decrease in bond length. A similar increase in nickel(II)–O (carboxylate) bond strength undoubtedly occurs, and this would tend to decrease electron density on the carbonyl oxygen of the carboxylate. The carbonyl oxygens would thus be less solvated in the planar complex than in the five-coordinate form, and the mobilized water molecules would contribute to the positive entropy change. Solvation of the carbonyl oxygens in the five-coordinate complex but to a lesser degree in the planar form is indicated by the fol-

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*A referee has stated that ΔS values are expected to increase markedly with increasing concentration of inert electrolyte and therefore the ΔS values for Ni(dacoda)(H_2O) cannot be compared with ΔS values determined for other systems in dilute solution. However, work in this laboratory has indicated that for other octahedral–planar interconversions, increasing the sodium perchlorate concentration to *e.g.* 2 *M* results in a decrease in ΔH and, within experimental error, does not affect ΔS. The same effect is seen here for the dacoda complex (Table I).

lowing. The crystal structure of [Ni(dacoda)(H_2O)] · $2H_2O$ shows the two water molecules of solvation hydrogen bonded to the carbonyl oxygens of the carboxylate groups [7]. When the blue [Ni(dacoda)(H_2O)] ·$2H_2O$ is heated *in vacuo* it is converted to yellow, diamagnetic Ni(dacoda) [8]. These observations support the expectation that the planar form, Ni(dacoda), is less solvated and may well account for the anomalous entropy change observed.

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