Crystal and Solution Structures of Nickel(II)-13-Membered Macrocyclic Tetramine [1,4,7,10-Tetraazacyclotridecanenickel(II)] Effected by a Pendent Phenol

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In crystal structure of Ni^{II}-phenol-pendent[13]aneN₄ complex <u>3</u> the pendent phenolate coordinates to high-spin Ni^{II} in a folded [13]aneN₄: in aqueous solution, the equilibrium of phenol $\stackrel{+}{\leftarrow}$ phenolate directly determines low-spin, square-planar or high-spin, folded macrocyclic structure.

Structures of complexes of saturated tetra-amine macrocycles are closely controlled by the relative size of metal ions and the macrocyclic cavity.¹⁾ For 13-membered saturated tetraaza macrocycle 1,4,7,10-tetraazacyclotridecane ([13]aneN₄) taking the most stable square-planar configuration (<u>trans-III</u> form),²⁾ the best-fit metal-nitrogen bond length is calculated to be 1.92 Å.³⁾ Ni^{II} ion squeezed in a center of the <u>trans-III</u> configuration indeed takes low-spin state with its Ni-N bond length (1.86 Å)⁴⁾ being close to the ideal one (1.89 Å).⁵⁾ In an aqueous solution at 25 °C, Ni^{II}-[13]aneN₄ takes overwhelmingly a low-spin, square-planar <u>trans</u> form (87%) over a high-spin, folded <u>cis</u> form (13%).⁶⁾

Recently, we have designed $[14]aneN_4$ attached with a phenol pendent <u>1</u>.⁷⁾ In Fe^{II 7)} and Ni^{II 8)} (both high-spin) complexes this intramolecular phenolate becomes the fifth, axial ligand. The crystal structure of the Ni^{II} complex dis-



closes the appropriate positioning of the phenolate at the top of high-spin Ni^{II} residing in the center of the square-planar macrocyclic N₄.⁸) An important consequence of the phenolate axial coordination is the stabilization of higher oxidation states of the central metals.^{7,8)} Then it was wondered how such a LF strength of the intramolecular phenolate might affect the spin state and structure of Ni^{II}-phenol-pendent[13]aneN₄($\underline{2}$) complex that otherwise would adopt a rigid square-planar macrocyclic configuration around the low-spin Ni^{II}. We have now found hitherto unknown, folded <u>cis</u>-configuration of [13]aneN₄ with high-spin Ni^{II} in the crystal structure of 3.9 We have also discovered that the <u>cis-trans</u> equilibrium directly depends on the dissociation of the pendant phenol proton.



Fig. 1. ORTEP¹²⁾ drawings of <u>3</u>°ClO₄ Atoms are drawn with 30% probability ellipsoids. Bond angles are as follows: $81.5(2)^{\circ}$, N₁-Ni-N₄; 96.7(2)°, N₁-Ni-O₂₀; $81.3(2)^{\circ}$, N₄-Ni-N₇; 94.1(3)°, N₁₀-Ni-N₁; 172.8(2)°, N₄-Ni-O₂₀; 129.0(4)°, Ni-O₂₀-C₁₅; 173.2(2)°, N₁₀-Ni-O₅W.

The new ligand $\underline{2}$ (mp 72-74 °C) was synthesized in the same manner as before,⁷⁾ except using 1,8-diamino-3,6-diazaoctane instead of 1,9-diamino-3,7-diazanonane. The pK_a value of $\underline{2}$ are 11.54, 10.31, < 2, < 2 (for nitrogens), and 8.71 (phenol), as determined by pH-metric and spectrophotometric titrations. Light blue crystals of $\underline{3}$ as a mono ClO_4^- salt ($C_{15}H_{25}N_4ONiClO_4 \cdot H_2O$) were obtained by the reaction of $\underline{2}$ and NiSO₄ in the presence of excess NaClO₄ in pH 9 aqueous solution. They are monoclinic, space group $\underline{P2}_1/\underline{a}$, $\underline{a} = 15.852(8)$ Å, $\underline{b} = 14.607(8)$ Å, $\underline{c} = 8.621(5)$ Å, $\beta = 94.81(5)$ °, $\underline{Z} = 4$, and $\underline{D}_c = 1.514$ g cm⁻³, for graphite-monochromated CuK_{α} radiation. A total of 2410 reflections above the 2 δ (I) level out of 4237 theoretically possible ones were collected on a Philips PW1100 diffractometer. The structure was solved by the heavy-atom method and refined by the block-diagonal-matrix least-squares method to final <u>R</u> value of 0.076.

Figure 1 shows the [13]aneN₄ macrocycle in a folded <u>cis</u> configuration²) with the phenolate oxygen and water oxygen occupying the remaining two <u>cis</u> sites. The Ni-N₁, -N₄, -N₇, and -N₁₀ bond lengths are 2.125(6), 2.082(5), 2.154(7), and 2.064(7) Å, respectively, which are undoubtedly longer than the average low-spin Ni^{II}-N bond length of 1.86 Å⁴) but are in the normal range 2.05 - 2.10 Å for high-spin Ni^{II}-N bonds.^{6,10}) The Ni-O₂₀(phenolate) bond length is extremely short 2.020(5) Å. The Ni-O₅W(H₂O) bond length is 2.150(5) Å, completing the octahedral structure. Thus, ClO_4^- ion is not in the 6th coordination site, like the Ni^{II}-[14]aneN₄ homologue complex.⁸) The present crystal structure study vividly demonstrates the strong LF strength by the intramolecular phenolate, under which Ni^{II} is rendered high-spin with the enlarged metal ion forcing [13]aneN₄ into the <u>cis</u> configuration.

The crystals of 3 form a blue-yellow aqueous solution [1 mM, resulting pH 7.3 at 25 °C and $\underline{I} = 0.1 \text{ M} (\text{NaClO}_4)](1 \text{ M} = 1 \text{ mol } \text{dm}^{-3})$. The solution intensifies yellow color (λ_{max} 424 nm) at more acidic pH and blue color (λ_{max} 559 nm) at more basic pH and shows an isosbestic point, which indicates an occurrence of an equilibrium for low-spin ⁺/₂ high-spin Ni^{II 6}) depending upon pH. At pH 3.5, the absorption coefficient at 424 nm reaches a limiting ε value (130 dm³mol⁻¹cm⁻¹), which is taken as the molar absorption coefficient of the low-spin, square-planar chromophore. This acidic solution was confirmed to be diamagnetic by the Evans method¹¹⁾ at 35 °C. Moreover heating (to 50 °C) and raising the ionic strength (to 6 M $NaClO_4$) do not increase the absorbance any further. The limiting ϵ value of 107 (at λ_{max} 425 nm) was reported for yellow, low-spin, square-planar Ni^{II}-[13]aneN₄.⁶⁾ Hence, at pH 7.3, 21% of the low-spin spices is present by estimation of ϵ/ϵ_{lim} . The remaining 79% is the high-spin complex, which is confirmed by a similar calculation using ϵ at 559 nm (ϵ_{lim} 6 attained at pH >10). The pH 10.5 solution is paramagnetic (μ_{eff} = 2.90 μ_{B}) by Evans method¹¹) at 35 °C. Meanwhile, the same complex solution shows two UV absorption peaks at 291 nm and 272 nm. The measure-

ment of ε at these peaks indicates 77% of the phenolate anion form and the rest 23% of the phenol form. The calculation is based on the ε_{lim} value of 3400 dm³mol⁻¹cm⁻¹ at 291 nm for 100% phenolate form of the complex <u>3</u> (attained at pH >10; an identical ε_{lim} value was obtained with free ligand <u>2</u> at pH >10) or on the ε_{lim} value of 2000 dm³mol⁻¹cm⁻¹ at 272 nm for 100% phenol form <u>4</u> (attained at



Scheme 1.

pH 3.5; an identical $\varepsilon_{1\text{im}}$ value was also obtained with <u>2</u> at pH 3.5). The good agreement in the high-spin/low-spin Ni^{II} ratio and the pendent phenolate/phenol ratio proves that the equilibrium of pendent phenolate $\stackrel{+}{\leftarrow}$ phenol directly determines the high-spin (folded) or low-spin (square-planar) structure; in other words, only with deprotonation, the pendant phenol can perturb the strong low-spin LF of the square-planar [13]aneN₄ (see Scheme 1). The protonation constant pK_a for the phenolate in <u>3</u> is estimated to be 6.7 at 25 °C and <u>I</u> = 0.1 M (NaClO₄) on the basis of potentiometric titration as well as spectrophotometric measurements at 291 nm and 272 nm.

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