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# 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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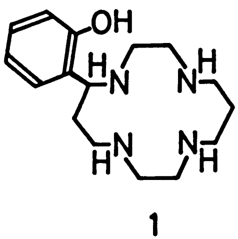
In crystal structure of $Ni^{II}$-phenol-pendent[13]ane$N_4$ complex <u>3</u> the pendent phenolate coordinates to high-spin $Ni^{II}$ in a folded [13]ane$N_4$: in aqueous solution, the equilibrium of phenol ⇄ phenolate directly determines low-spin, square-planar or high-spin, folded macrocyclic structure.

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]ane$N_4$) taking the most stable square-planar configuration (<u>trans</u>-III 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</u>-III 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]ane$N_4$ 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]ane$N_4$ 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-



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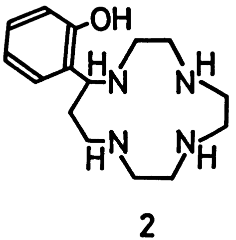

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closes the appropriate positioning of the phenolate at the top of high-spin Ni$^{II}$ residing in the center of the square-planar macrocyclic $N_4$.$^{8)}$ An important consequence of the phenolate axial coordination is the stabilization of higher 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]ane$N_4$(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 cis-configuration of [13]ane$N_4$ with high-spin Ni$^{II}$ in the crystal structure of 3.$^{9)}$ We have also discovered that the cis-trans equilibrium directly depends on the dissociation of the pendant phenol proton.

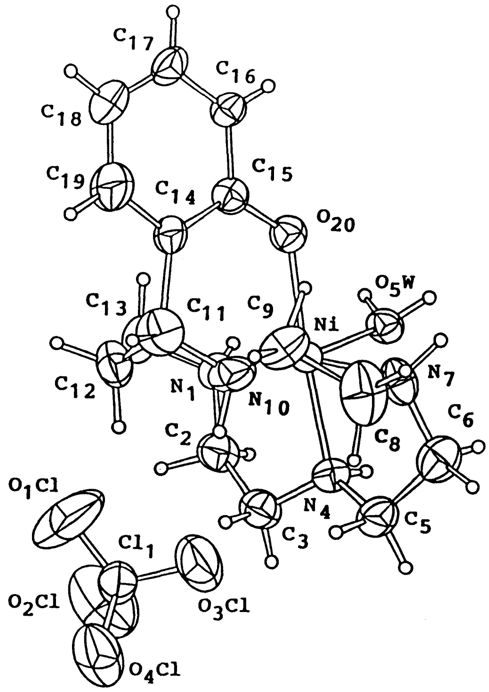


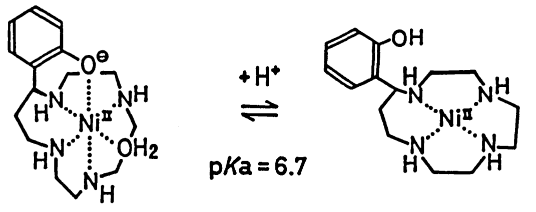
Fig. 1. ORTEP$^{12)}$ drawings of 3·$ClO_4$ Atoms are drawn with 30% probability ellipsoids. Bond angles are as follows: 81.5(2)°, $N_1$-Ni-$N_4$; 96.7(2)°, $N_1$-Ni-$O_{20}$; 81.3(2)°, $N_4$-Ni-$N_7$; 94.1(3)°, $N_{10}$-Ni-$N_1$; 172.8(2)°, $N_4$-Ni-$O_{20}$; 129.0(4)°, Ni-$O_{20}$-$C_{15}$; 173.2(2)°, $N_{10}$-Ni-$O_5W$.

The new ligand 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 p$K_a$ value of 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 3 as a mono $ClO_4^-$ salt ($C_{15}H_{25}N_4ONiClO_4 \cdot H_2O$) were obtained by the reaction of 2 and $NiSO_4$ in the presence of excess $NaClO_4$ in pH 9 aqueous solution. They are monoclinic, space group $P2_1/a$, $a$ = 15.852(8) Å, $b$ = 14.607(8) Å, $c$ = 8.621(5) Å, β = 94.81(5) °, $Z$ = 4, and $D_c$ = 1.514 g cm$^{-3}$, for graphite-monochromated Cu$K_\alpha$ radiation. A total of 2410 reflections above the 2δ(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 $R$ value of 0.076.

Figure 1 shows the [13]ane$N_4$ macrocycle in a folded cis configuration$^{2)}$ with the phenolate oxygen and water oxygen occupying the remaining two cis sites. The Ni-$N_1$, -$N_4$, -$N_7$, and -$N_{10}$ 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 Å[4] but are in the normal range 2.05 - 2.10 Å for high-spin $Ni^{II}$-N bonds.[6,10] The Ni-$O_{20}$(phenolate) bond length is extremely short 2.020(5) Å. The Ni-$O_5$W($H_2O$) 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]ane$N_4$ 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]ane$N_4$ into the cis 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 M ($NaClO_4$)](1 M = 1 mol $dm^{-3}$). The solution intensifies yellow color ( $\lambda_{max}$ 424 nm) at more acidic pH and blue color ( $\lambda_{max}$ 559 nm) at more basic pH and shows an isosbestic point, which indicates an occurrence of an equilibrium for low-spin $\rightleftarrows$ high-spin $Ni^{II}$ [6] depending upon pH. At pH 3.5, the absorption coefficient at 424 nm reaches a limiting $\varepsilon$ value (130 $dm^3mol^{-1}cm^{-1}$), 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 method[11] 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 $\varepsilon$ value of 107 (at $\lambda_{max}$ 425 nm) was reported for yellow, low-spin, square-planar $Ni^{II}$-[13]ane$N_4$.[6] Hence, at pH 7.3, 21% of the low-spin spices is present by estimation of $\varepsilon/\varepsilon_{lim}$. The remaining 79% is the high-spin complex, which is confirmed by a similar calculation using $\varepsilon$ at 559 nm ($\varepsilon_{lim}$ 6 attained at pH >10). The pH 10.5 solution is paramagnetic ($\mu_{eff}$ = 2.90 $\mu_B$) by Evans method[11] at 35 °C. Meanwhile, the same complex solution shows two UV absorption peaks at 291 nm and 272 nm. The measurement of $\varepsilon$ at these peaks indicates 77% of the phenolate anion form and the rest 23% of the phenol form. The calculation is based on the $\varepsilon_{lim}$ value of 3400 $dm^3mol^{-1}cm^{-1}$ at 291 nm for 100% phenolate form of the complex 3 (attained at pH >10; an identical $\varepsilon_{lim}$ value was obtained with free ligand 2 at pH >10) or on the $\varepsilon_{lim}$ value of 2000 $dm^3mol^{-1}cm^{-1}$ at 272 nm for 100% phenol form 4 (attained at



3
folded
blue
high-spin

4
square-planar
yellow
low-spin

Scheme 1.

pH 3.5; an identical $\varepsilon_{\mathrm{lim}}$ value was also obtained with 2 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 $\rightleftarrows$ 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]ane$N_4$ (see Scheme 1). The protonation constant $pK_a$ for the phenolate in 3 is estimated to be 6.7 at 25 °C and $I$ = 0.1 M ($NaClO_4$) on the basis of potentiometric titration as well as spectrophotometric measurements at 291 nm and 272 nm.

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