

Synthesis of a Novel Octaamino Tetraphenol Macrocyclic Ligand and Structure of a Tetranuclear Nickel(II) Complex

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In the past two decades there have been extensive studies on metal complexes of the Schiff base binucleating macrocyclic ligands² derived from condensation reactions of 2,6-diformyl-4-methylphenol or its analogues with amines. The focus of attention has been on probing of electron-transfer potentials,³ intramolecular electron-transfer rates,⁴ magneto-structural relations,⁵ and selective activation of substrates.⁶ In the recent past these studies have been extended to polynuclear systems. Organization of more than two metal centers in predetermined arrays has led to the isolation of several novel structural motifs in which certain anions are trapped in unusual environments.⁷ For example, tetranickel(II),^{7a,b} tetrazinc(II),^{7a} and hexacopper(II)⁸ complexes have been obtained by [2 + 2] or [3 + 3] condensation reactions between 2,6-diformyl-4-methylphenol and 2,6-bis(aminomethyl)-4-methylphenol in the presence of the metal salts. On the other hand, the reactions involving 2,6-diformyl-4-methylphenol and 1,5-diamino-3-hydroxypentane, under different conditions, have produced tetracopper(II),⁹ octacopper(II),^{7c,9} and dodecacopper(II)¹⁰ complexes.

In contrast to the above metal-induced macrocyclization reactions, the use of preformed ligands in generating polynuclear complexes is restricted by the ready hydrolytic cleavage of the metal-free Schiff base macrocycles. During the course of our studies on phenoxy-bridged binuclear complexes obtained by using preformed tetraamino diphenol macrocyclic ligands we have noted¹¹ that, owing to the greater flexibility and stronger σ -donor capacity of secondary amines, the stereochemistry and redox and magnetic properties of these complexes differ significantly from their Schiff base analogues. We report here the facile synthesis

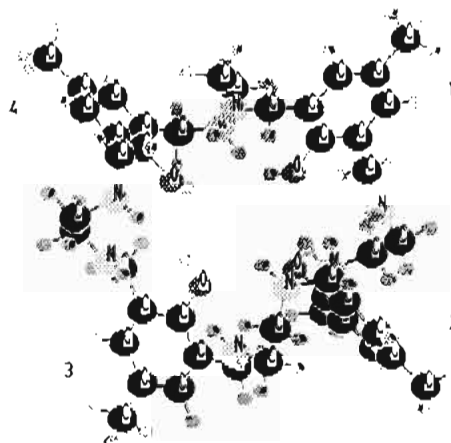


Figure 1. Minimum-energy configuration of H₄L.

of a novel 36-membered potentially tetranucleating macrocyclic ligand H₄L and the structure of the nickel(II) complex [Ni₄L-(μ_3 -OH)(μ -H₂O)₂(ClO₄)](ClO₄)₂·2CH₃COCH₃·H₂O (1).

Ligand H₄L was synthesized by reacting 2,6-diformyl-4-methylphenol (4 equiv), 1,2-diaminoethane (4 equiv), Mg(OAc)₂·4H₂O (2 equiv), and Mg(NO₃)₂·6H₂O (2 equiv) in methanol at 50 °C over a period of 6 h. An orange yellow magnesium complex that deposited was collected and reduced with NaBH₄ in methanol. Acidification of the solution with HCl (8 M) followed by cooling afforded the colorless crystals of H₄L·8HCl, an aqueous solution of which on treatment with NH₃ followed by extraction with CH₂Cl₂ and recrystallization from CHCl₃-CH₃OH gave H₄L¹² (50%).

Inasmuch as the four phenyl rings of H₄L are connected by 28 single bonds, the molecular can be subjected to considerable deformation and twist. A stereoview of the minimum-energy configuration, as obtained by molecular mechanics calculations,¹³⁻¹⁵ is shown in Figure 1. It may be noted that the -C-N-C-N-C- linkages are twisted to different extents and the benzylic carbons of ring 2 are linked in a crosswise manner to the amino nitrogens. The planes of the phenyl rings are inclined to each other in the following way: 1-2, 76.8°; 1-3, 52.6°; 1-4, 50.8°; 2-3, 86.6°; 2-4, 26.2°; 3-4, 78.3°. The hole size of the macrocycle, taken as the average distance between the diagonally opposite

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- (12) Analytical data are as follows: Mp 157-158 °C; IR (KBr) 3310 (ν_{NH}), 3190 (ν_{OH}), 1610 (δ_{NH}) cm⁻¹; ¹H NMR (CDCl₃) 2.21 (s, 12H, CH₃), 2.74 (s, 16H, CH₂-CH₂), 3.80 (s, 24H, ArCH₂NH), 6.78 (s, 8H, C₆H₂); ¹³C NMR (CDCl₃) 20.44 (CH₃), 47.91 (CH₂), 50.83 (CH₂), 124.26 (4-C₆H₂), 127.46 (2,6-CH₂), 128.80 (3,5-C₆H₂), 151.14 (1-C₆H₂); FAB-MS, *m/e* 769 (MH⁺, 40%). Anal. Calcd for C₄₄H₆₄N₈O₄: C, 68.75; H, 8.33; N, 14.58. Found: C, 68.88; H, 8.28; N, 14.48.
 (13) The total energy of the molecular system was approximated as the sum of nonbonded, electrostatic, bond-stretching, angle-bending, torsion, stretch-bend, and compression energy terms and calculated by an MMPI and MMP2 force field.¹⁴
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 (15) For the minimum-energy configuration: total energy = 72.3 kcal/mol; heat of formation (300 K) = -71 kcal/mol; dipole moment = 1.96 D.

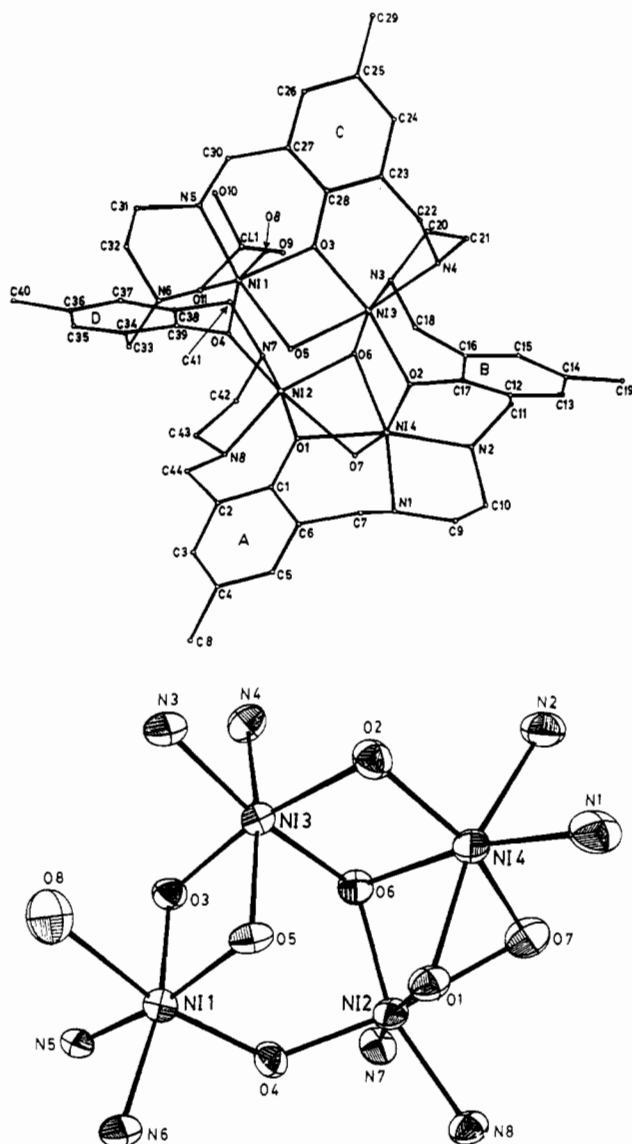


Figure 2. Structure of the cation $[\text{Ni}_4\text{L}(\mu_3\text{-OH})(\mu\text{-H}_2\text{O})_2(\text{ClO}_4)]^{2+}$. (a) Top: Perspective view showing the numbering scheme employed. (b) Bottom: Coordination environment for the four nickel centers. Selected bond lengths (Å) and angles (deg): Ni(1)–Ni(2) = 4.583(7), Ni(1)–Ni(3) = 3.128(6), Ni(1)–Ni(4) = 5.128(8), Ni(2)–Ni(3) = 3.724(7), Ni(3)–Ni(4) = 3.136(6), Ni(2)–Ni(4) = 2.933(5), Ni(1)–O(3) = 1.986(6), Ni(1)–O(4) = 2.033(5), Ni(1)–O(5) = 2.121(5), Ni(1)–O(8) = 2.426(8), Ni(2)–O(1) = 2.047(5), Ni(2)–O(4) = 2.031(6), Ni(2)–O(6) = 2.042(5), Ni(2)–O(7) = 2.421(6), Ni(3)–O(2) = 2.009(5), Ni(3)–O(3) = 2.022(6), Ni(3)–O(5) = 2.180(7), Ni(3)–O(6) = 2.109(5), Ni(4)–O(1) = 2.163(6), Ni(4)–O(2) = 2.004(5), Ni(4)–O(6) = 2.098(5), Ni(4)–O(7) = 2.192(7), Ni(1)–N(5) = 2.086(7), Ni(1)–N(6) = 2.093(9), N(2)–N(7) = 2.133(8), Ni(2)–N(8) = 2.087(6), Ni(3)–N(3) = 2.094(8), Ni(3)–N(4) = 2.082(9), Ni(4)–N(1) = 2.070(6), Ni(4)–N(2) = 2.120(9); O(3)–Ni(1)–N(6) = 168.4(2), O(4)–Ni(1)–O(8) = 157.6(2), O(5)–Ni(1)–N(5) = 171.2(2), O(1)–Ni(2)–N(7) = 170.5(3), O(4)–Ni(2)–O(7) = 170.2(3), O(6)–Ni(2)–N(8) = 160.0(2), O(2)–Ni(3)–O(3) = 168.1(2), O(5)–Ni(3)–N(4) = 172.1(2), O(6)–Ni(3)–N(3) = 170.3(2), O(1)–Ni(4)–N(2) = 166.8(2), O(2)–Ni(4)–O(7) = 159.8(2), O(6)–Ni(4)–N(1) = 161.7(3).

oxygens, is 4.75(8) Å. The uncomplicated NMR spectra of H_4L indicate that, in fluid, conformational changes are very rapid.

From a consideration of molecular models it has become apparent that self-assembly of metal ions with L^{4-} is governed primarily by the steric requirements of the metals. When a metal ion prefers six-coordination the presence of other auxiliary bridging and/or coordinating molecules or anions are essential. On the other hand, a square planar orienting metal ion will force the ligand to adopt a helically twisted configuration.

The tetranuclear nickel(II) complex $[\text{Ni}_4\text{L}(\mu_3\text{-OH})(\mu\text{-H}_2\text{O})_2(\text{ClO}_4)](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{COCH}_3 \cdot \text{H}_2\text{O}$ (**1**) has been synthesized¹⁶ and characterized,¹⁷ and the structure has been determined.¹⁸ The complex cation $[\text{Ni}_4\text{L}(\mu_3\text{-OH})(\mu\text{-H}_2\text{O})_2(\text{ClO}_4)]^{2+}$ (Figure 2a) completely lacks symmetry. Within the macrocycle, the four noncoplanar nickel atoms are in a distorted octahedral environment (Figure 2b), and each metal ion is coordinated to two amine nitrogens and two bridging phenoxide oxygens. Three of these metal centers, Ni(2), Ni(3), and Ni(4), are anchored by the tricoordinated hydroxyl oxygen, O(6), while each pair of metals is bridged by the water molecules. The sixth coordination site of Ni(1) is occupied by the perchlorate oxygen, O(8). The intramolecular distances between the nickel atoms lie in the range 2.93–5.13 Å. The interplanar angles between the phenyl rings in the complex are as follows: A–B, 81.2°; A–C, 54.7°; A–D, 45.8°; B–C, 105.1°; B–D, 37.1°; C–D, 74.5°. A large number of intra- and intermolecular hydrogen bonds, in which donor-acceptor distances lie between 2.6 and 3.1 Å, reinforce the asymmetric structure of **1**. Thus, there are ten intramolecular hydrogen bonds involving NH, phenoxide, and aqua bridges and six intermolecular hydrogen bonds involving ClO_4^- , NH, acetone, and water.

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Supplementary Material Available: Tables of atomic coordinates and thermal parameters, anisotropic thermal parameters, complete bond lengths and bond angles, and hydrogen bond distances and angles for **1** (13 pages). Ordering information is given on any current masthead page.

- (16) Complex **1** was prepared by refluxing a methanol solution of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (4 equiv), H_4L (1 equiv), and $(\text{C}_2\text{H}_5)_3\text{N}$ (4 equiv) for 1 h, during which time the deep green solution turned red. The product was isolated by concentration of the solution and recrystallized from acetone. *Caution!* Perchlorate salts are potentially explosive and therefore should be prepared and handled in small quantities.
- (17) Data for **1** are as follows: IR (KBr) 3420 (br, ν_{OH}), 3280 (ν_{NH}), 3190 ($\nu_{\mu_3\text{-OH}}$), 1700 (ν_{CO}), 1145, 1110, 1090, 640, 630 ($\nu_{\text{ClO}_4^-}$) cm^{-1} ; UV-vis (acetone) λ_{max} (ϵ , $\text{L mol}^{-1} \text{cm}^{-1}$) 980 (45), 650 (55), 365 (sh) nm; $\mu_{\text{eff}}/\text{Ni}^{2+}$ (300 K) 2.84 μ_{B} . Anal. Calcd for $\text{C}_{50}\text{H}_{79}\text{N}_9\text{O}_{22}\text{Cl}_3\text{Ni}_4$: C, 40.43; H, 5.32; N, 7.55; Ni, 15.82. Found: C, 40.32; H, 5.36; N, 7.63; Ni, 15.94.
- (18) Crystallographic data for **1**: triclinic, space group $P\bar{1}$; $a = 12.167(1)$ Å, $b = 12.673(1)$ Å, $c = 22.652(2)$ Å, $\alpha = 101.05(1)^\circ$, $\beta = 91.61(1)^\circ$, $\gamma = 111.66(1)^\circ$, $V = 3167.2(1)$ Å³, $Z = 2$, $d_{\text{calcd}} = 1.557$ g cm^{-3} , $\mu(\text{Cu K}\alpha) = 31.80$ cm^{-1} ; $R = 0.052$, $R_w = 0.058$.
- (19) X-ray data were collected at 293 K on an Enraf-Nonius CAD-4 diffractometer using monochromated $\text{Cu K}\alpha$ radiation ($\lambda = 1.54184$ Å) in the 2θ range 4–130°. Out of 9352 reflections measured 5526 with $I > 3\sigma(I)$ were used in the structure analysis. Lorentz, polarization, and absorption corrections were made. The structure was solved by direct methods using the program MULTAN-82²⁰ and refined by block-diagonal least-squares calculations. At the final stage of refinement the difference map showed peaks between -0.7 and 0.8 e Å⁻³.
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