Volume 30
Number 14
July 10, 1991

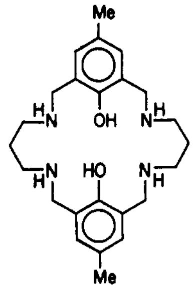
Inorganic Chemistry

Communications

Synthesis, Structure, and Electrochemistry of a Novel Dinickel(II) Complex $[Ni_2L(CH_3OH)_2(ClO_4)_2]\cdot 2(C_2H_5)_3NHClO_4$ Derived from a Tetraamino-Diphenolic Macrocyclic Ligand (H_2L) That Exhibits Stepwise Two-Electron Oxidation and Two-Electron Reduction

Mononuclear Ni(II) complexes of polyazamacrocyclic ligands have been extensively studied[1] over the past two decades. Of more recent origin is the development of binuclear systems obtained either by bridging the metal centers of two mononuclear units[2] or using ditopic bis-macrocyclic ligands.[3] Stabilization of Ni(III) and Ni(I) species and investigation of stereochemistry, size-match selectivity, and thermodynamic and kinetic stability of Ni(II) complexes have been the focus of interest. Recently we have reported[4] structures and magnetic and redox properties of a few dicopper(II) complexes of the tetraamino-diphenolic macrocyclic ligand H_2L. The notable feature of these compounds is that they undergo four one-electron transfers to generate dicopper species with oxidation states varying between +1 and +3. Herein we report that the binuclear Ni(II) complex $[Ni_2L(CH_3OH)_2(ClO_4)_2]\cdot 2(C_2H_5)_3NHClO_4$ (**1**) also undergoes stepwise oxidation to produce $Ni^{II}Ni^{III}$ and $Ni^{III}Ni^{III}$ species and reduction to produce $Ni^{II}Ni^{I}$ and $Ni^{I}Ni^{I}$ species.

Complex **1** was prepared by refluxing a methanol solution of $Ni(ClO_4)_2\cdot 6H_2O$ (2 equiv), H_2L (1 equiv), and triethylamine (2 equiv) for 0.5 h. The wine red solution on concentration over $CaCl_2$ afforded turquoise crystals of **1**, which were recrystallized from methanol by diffusion of diethyl ether.[5]



H_2L

Figure 1 shows the X-ray crystal structure[6,7] of the complex unit $[Ni_2L(CH_3OH)_2(ClO_4)_2]$ of **1**, which consists of two Ni(II) centers bridged by two phenoxide oxygen atoms with two secondary amine nitrogen donors completing the NiN_2O_2 plane. Each of the metal centers obtain pseudooctahedral environments by interacting with trans axially disposed methanol molecules and perchlorate ions. The deviation of the metal centers from the mean plane of the N_2O_2 donor sets does not exceed 0.029 Å. The complex molecule contains a crystallographic center of symmetry, thereby making the two Ni atoms chemically and crystallographically equivalent in the solid state. In the NiN_2O_2 plane the average Ni–O(phenolate) distance is 2.028 Å and the average Ni-N distance is 2.061 Å. The axial Ni–O distance, viz. Ni–O-(CH_3OH) = 2.105 (5) Å, is rather long, and Ni–O(ClO_4) (2.411 (5) Å) is very long, albeit within the range observed for Ni–$OClO_3$ bonds.[8] The two metal centers are separated by 3.135 (2) Å, with a Ni–O(1)–Ni bridge angle of 101.3 (1)°. The packing diagram of **1** (Figure 2) viewed along the *a* axis shows that $[(C_2H_5)_3NH]^+$ cations are interposed between the layers of the complex unit $[Ni_2L(CH_3OH)_2(ClO_4)_2]$, and ClO_4^- ions act as space fillers. Apparently, the triethylammonium perchlorate salt

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(5) Anal. Calcd for $C_{38}H_{74}N_6O_{20}Cl_4Ni_2$: C, 38.21; H, 6.20; N, 7.04; Ni, 9.84. Found: C, 38.05; H, 6.30; N, 7.10; Ni, 10.15. *Caution*! Although the perchlorate salt described here was not found to be shock sensitive, care should be taken in handling this compound.

(6) X-ray data were collected on a prismatic crystal of dimensions 0.36 × 0.34 × 0.42 mm at 295 K on a Nicolet R3m/V diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). With use of 1.80° ω scans at 3.00–30.00 min^{-1}, 6445 reflections were collected in the range $2 < 2\theta < 55°$ and 4246 with $F > 6\sigma(F)$ were used in structure analysis. The structure was solved by direct methods and refined by the full-matrix least-squares programs of SHELXTAL-PLUS. Crystallographic data: triclinic, space group $P\bar{1}$, $a = 11.270$ (6) Å, $b = 11.554$ (6) Å, $c = 12.670$ (6) Å, $\alpha = 99.69$ (4)°, $\beta = 104.34$ (6)°, $\gamma = 118.58$ (3)°, $V = 1321.5$ (11) Å^3, $Z = 1$, $d_{calcd} = 1.50$ g cm^{-3}, $R = 6.35\%$, and $R_w = 8.54\%$.

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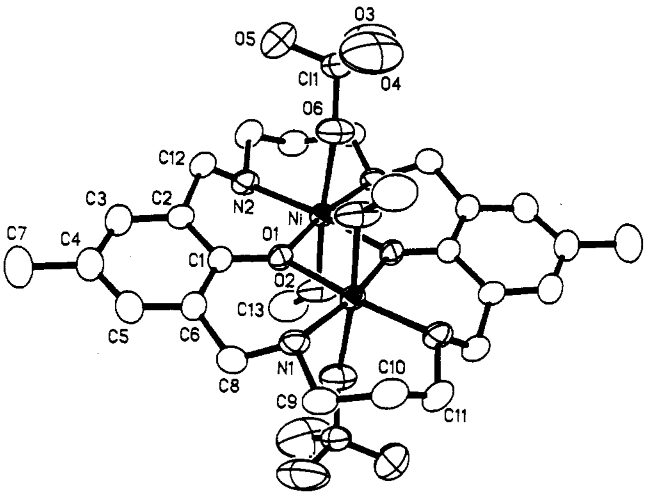

Figure 1. Perspective view of the complex unit $[Ni_2L(CH_3OH)_2(ClO_4)_2]$. Selected bond distances (Å) and angles (deg) are as follows: Ni–O(1) = 2.027 (3), Ni–O(1A) = 2.028 (4), Ni–O(2) = 2.105 (5), Ni–O(6) = 2.411 (5), Ni–N(1A) = 2.064 (3), Ni–N(2) = 2.057 (5), Ni–Ni(A) = 3.135 (2); Ni–O(1)–Ni(A) = 101.3 (1), O(1)–Ni–N(2) = 91.1 (1), O(1)–Ni–O(1A) = 78.7 (1), N(2)–Ni–N(1A) = 98.6 (2), O(1)–Ni–O(2) = 90.0 (1), N(2)–Ni–O(2) – 95.7 (2), N(2)–Ni–O(1A) = 169.7 (1), O(1)–Ni–N(1A) = 170.1 (2).

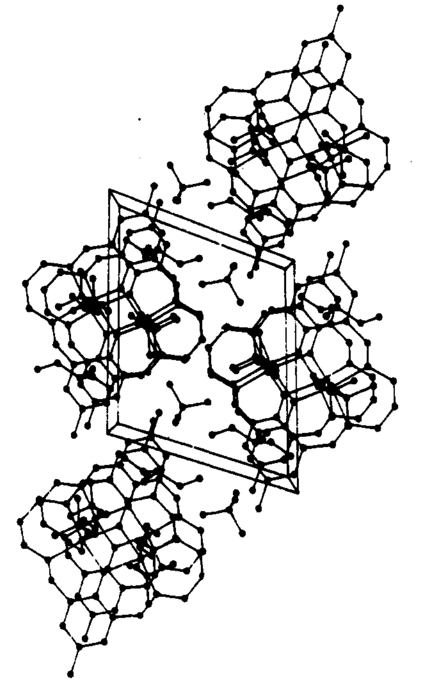

Figure 2. Packing diagram of $[Ni_2L(CH_3OH)_2(ClO_4)_2]\cdot 2(C_2H_5)_3NH\text{-}ClO_4$ viewed along the *a* axis.

is held in space by electrostatic and van der Waals forces.

The room-temperature magnetic moment of **1** (4.35 μ_B) probably indicates a spin-exchange interaction between the two Ni(II) centers. Electronic spectra[9] of **1** both in the solid state and in methanol solution are typical of six-coordinate tetragonal Ni(II) complexes. The IR spectrum of **1** exhibits[10] vibrations associated with the NH stretch of the ligand (3260 cm^{-1}) and the $[(C_2H_5)_3NH]^+$ ion (2670, 2490 cm^{-1}).

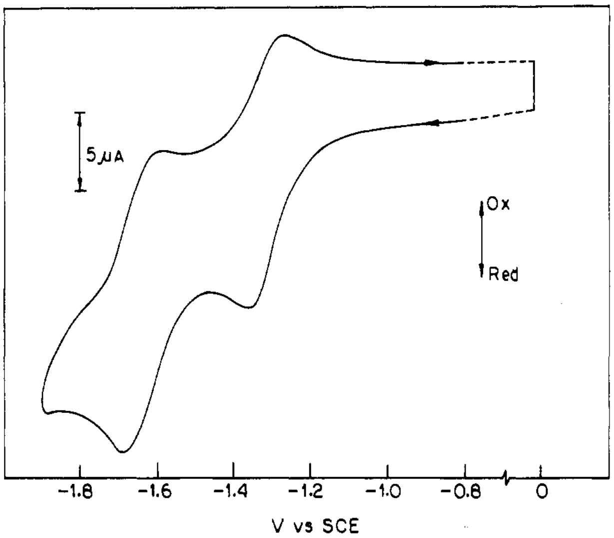

Figure 3. Cyclic voltammogram of **1** in Me_2SO containing 0.1 M TBAP with a 100 mV s^{-1} scan rate at a glassy-carbon electrode.

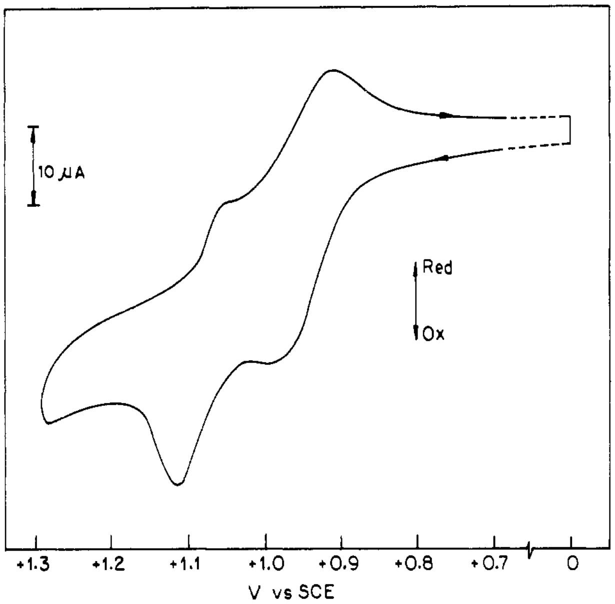

Figure 4. Cyclic voltammogram of **1** in MeCN containing 0.1 M TBAP with a 50 mV s^{-1} scan rate at a Pt electrode.

Figure 3 shows the cyclic voltammogram[11] for the stepwise reduction of **1** in Me_2SO with a glassy-carbon electrode. The two one-electron reduction steps ($E_{1/2}$ = −1.32, −1.65 V vs SCE) occur quasireversibly.[12] The formation of $Ni^{II}Ni^{I}$ species was confirmed coulometrically, but $Ni^{I}Ni^{I}$ species were not stable in the coulometric time scale. The cyclic voltammogram of **1** in MeCN with a Pt electrode at positive potential range (Figure 4) exhibits two reversible[13] one-electron oxidation steps ($E_{1/2}$ = 0.94, 1.08 V vs SCE). The occurrence of these two waves at the indicated potentials was also observed in differential-pulse voltammetric

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(9) UV-vis (Nujol mull; λ_m, nm): 1170, 760, 620, 490, 350. UV-vis (MeOH; λ_m, nm (ϵ, L mol^{-1} cm^{-1})): 1160 (7), 810 (8), 750 (9), 495 (100), 375 (400).

(10) IR (KBr): 3400 (br), 3260, 2670, 2490, 1605, 1100 (br), 630 cm^{-1}.

(11) Electrochemical measurements were carried out by using a BAS 100 A electrochemistry system. The complex was 1 + 0.2 mM in Me_2SO or MeCN, and the supporting electrolyte $[Bu_4N](ClO_4)$ had a fixed concentration, 0.1 M. The potentials measured against a saturated calomel electrode (SCE) were compared to those for the ferrocene–ferrocenium couple, which under the same experimental condition gave $E_{1/2} = 0.5(E_{pc} + E_{pa}) = 0.465$ V and $\Delta E_p = E_{pc} - E_{pa} = 70$ mV.

(12) The $E_{1/2}$ values did not change with the variation of scan rates (v = 100–600 mV s^{-1}), and ΔE_p, which was 90 mV for the $Ni^{II}Ni^{I}$ couple and 100 mV for the $Ni^{I}Ni^{I}$ couple at v = 100 mV s^{-1}, increased by a small difference with the increased of scan rate. The ratio i_{pc}/i_{pa} was close to unity at different scan rates, and $i_{pc}v^{-1/2}$ remained constant.

(13) For both the $Ni^{II}Ni^{III}$ and $Ni^{III}Ni^{III}$ couples $E_{1/2}$ (0.94, 1.08 V) and ΔE_p (70 mV) values remained cosntant when scan rates were varied between 50 and 500 mV s^{-1}.

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measurements. Controlled-potential electrolysis at 1.3 V consumed 2 equiv of charge implicating the two-electron oxidation of **1** to a dinickel(III) species. The ligand itself and $[Zn_2L(H_2O)_2](ClO_4)_2$ do not show any electrochemical response in the entire potential range −2.0 to +1.7 V. The stability of the mixed-valence $Ni^{II}Ni^{I}$ and $Ni^{II}Ni^{III}$ species can be related to their conproportionation constants, K_{con}.[14,15] A greater value of K_{con} indicates greater stability of the mixed-valence species with respect to the isovalent species. Although $K_{con} = 3.8 \times 10^5$ for the reduction process implies considerable stability of the $Ni^{II}Ni^{I}$ species, a much lower value of K_{con} (2.3×10^2) for the oxidation process suggests easier access to the dinickel(III) species.

We note that there are many examples[1,16] of mononuclear macrocyclic Ni(II) complexes undergoing both oxidation and reduction. Also, there are limited number of examples[2,3] in which binuclear Ni(II) complexes undergo stepwise oxidation. However, to our knowledge, **1** provides the first example of a binuclear Ni(II) system exhibiting two successive one-electron oxidation steps as well as one-electron reduction steps.

Acknowledgment. We are very thankful to Dr. Debashis Ray for the X-ray structural work and to the Department of Science and Technology, New Delhi, for establishing a National Single Crystal Diffractometer Facility at the Department of Inorganic Chemistry, Indian Association for the Cultivation of Science. Thanks are also due to Dr. S. K. Mandal for his assistance in the electrochemical measurements.

Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, H atom coordinates, NiN_2O_2 least-squares planes, and crystallographic details for **1** (8 pages); a listing of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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[15] K_{con} is defined in the following equation:

$$[Ni^{m+} - Ni^{m+}] + [Ni^{n+} - Ni^{n+}] \underset{}{\overset{K_{con}}{\rightleftharpoons}} 2[Ni^{m+} - Ni^{n+}]$$

$K_{con} = \exp(nF(\Delta E)/RT)$, where $\Delta E = |E_{1/2}(1) - E_{1/2}(2)|$.

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Received September 28, 1990

A High-Valent Oxomanganese Dimer Containing Bridging and Terminal Inorganic Phosphate Ligands

The aqueous chemistry of high-valent manganese complexes has been the focus of our recent efforts both in terms of understanding the interactions of the water oxidation catalyst in photosystem II (PS II) with its substrate[1] and elucidating the primary process in the photoactivated assembly of this catalyst.[2] An important aspect of this work has been identifying ligands that are hydrophilic, oxidation resistant, and capable of stabilizing high-valence manganese centers. We report here the first bis(μ-oxo)manganese cluster with a bridging inorganic phosphate ion, a ligand that is attractive from all of the above standpoints. Additionally, the polyprotic character of ligated phosphate provides both a potential source and a sink for hydrogen ions in proton-coupled redox chemistry. Recently, we have demonstrated the presence of such proton-coupled electron transfer (PCET) for a bis(μ-oxo)dimanganese(III,IV) cluster.[3] In the water oxidation cycle of PS II, several of the individual light-induced oxidation events in the Mn cluster have been shown to be accompanied by hydrogen ion release,[4] which helps ameliorate the buildup of charge in the cluster; at present, there is no experimental evidence intimately coupling the electron transfer and proton release in these events in the PS II oxidation cycle. Since the coordination environment of the water oxidation catalyst in PS II is thought to involve primarily oxygen donor ligands,[5] incorporation of phosphate ligands into model clusters provides a route to a largely oxygen coordination environment about high-valent manganese. Our results indicate that inorganic phosphate promotes the stabilization of Mn(IV) in aqueous solution.

Wieghardt and co-workers[6] have reported the crystal structure of a μ_3-PO_4 trimeric manganese(IV) cluster, $[Mn_3(\mu\text{-}O)_3(tacn)_3(\mu_3\text{-}PO_4)]^{3+}$, which is the only other Mn cluster containing a bridging inorganic phosphate of which we are aware. The bridging phosphate bis(μ-oxo) dimer that we report here may provide a useful structural model for the dinuclear metal center in the purple acid phosphatase (PAP) enzyme. Current evidence suggests that phosphate can bind to the Fe(II,III/III,III) site in PAP as both a terminal and a bridging ligand.[7] Synthetic efforts have provided oxoiron complexes bridged by phenylphosphates,[8,9] and although a complex thought to contain bridging inorganic phosphates has been isolated, it has yet to be characterized crystallographically.[8] Such crystalline bridging phosphates may be elusive because of the hydrophilic nature of inorganic phosphate. PAPs have also been reported to contain Fe,Zn[10a] and Mn_2[10b] cofactors in place of the dinuclear iron center.

We have been investigating the aqueous chemistry of oxomanganese clusters such as $[(bpy)_2Mn(O)_2Mn(bpy)_2]^{3+}$ (**1**, bpy = 2,2′-bipyridine) in an effort to develop an understanding of the factors governing the coordination chemistry of high-valent Mn in H_2O in relation to photosynthetic water oxidation.[1,3] A number of simple Mn(III)–phosphate coordination compounds showing stability in aqueous solution are known.[12] We have previously reported that in acidic solution (pH 2, HNO_3), **1** undergoes disproportionation and cluster rearrangement to form the trinuclear complex $[Mn^{IV}_3(O)_4(bpy)_4(OH_2)_2]^{4+}$ (**2**), which consists of an $(Mn^{IV}(\mu\text{-}O)_2Mn^{IV})$ unit bridged by an O–Mn^{IV}–O linkage.[1] We now find that an unexpected version of this reaction occurs in H_3PO_4 solutions to give a species in which a $(Mn^{IV}(\mu\text{-}O)_2Mn^{IV})$ group is bridged by inorganic phosphate.

Treatment of an aqueous solution of **1** with H_3PO_4 (pH 2.3) generates a stable green solution, exhibiting a weak ($\epsilon \sim 100$ M^{-1} cm^{-1}) absorption at 600 nm but now lacking the characteristic intervalence charge-transfer bands of **1** in the 700–900-nm region.[13] Slow crystallization from a 0.5 M H_3PO_4 aqueous solution yields[14] thin red-brown plate crystals of $[(bpy)(H_2PO_4)Mn(\mu$-

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