Novel Nickel(II) Complexes with Doubly Deprotonated Dioxopentaamine Macrocyclic Ligands for Uptake and Activation of Molecular Oxygen

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The chemical interest in interaction and activation (by reduction) of molecular oxygen by copper proteins has grown considerably during recent years.[1] Copper(II)[2,3] and nickel(II)[4,5] can promote the reactions between O$_2$ and peptides, where Cu(III) and Ni(III) peptide complexes were considered as intermediates. Cu(III) and Ni(III) ions have been obtained with complexes of peptides (such as L^4)[6–8] and macrocyclic polyamines such as L^3
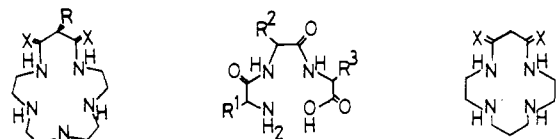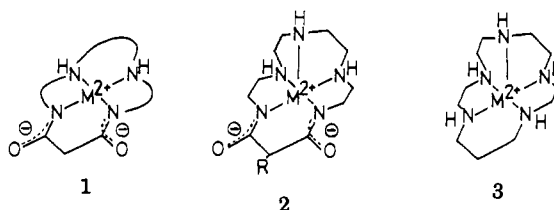

L^1, X = O; R = H
L^2, X = O; R = CH$_2$C$_6$H$_5$
L^3, X = H$_2$; R = H

L^4
(tripeptides)

L^5, X = O
L^6, X = H$_2$

or L^6.[9–13] Very recently, we have shown that dioxotetraamine macrocycles (e.g., L^5) possess dual characters of macrocyclic tetraamines (e.g., L^6) and of tripeptide L^4 to form square-planar

complexes [MH$_{-2}$L]^0, **1**,[14,15] and tend to lower the redox potentials

1   **2**   **3**

E^0 for M(II) $\rightleftharpoons$ M(III) couples.[16] However, the E^0 values so far reported in our models were not low enough to make M(III) states readily accessible in biological conditions (e.g., air-oxidation).

In developing a closer mimic to redox enzymes, we have synthesized new ligands, the dioxopentaamine macrocycles L^1 and L^2.[17] Herein we communicate that *the special steric and electronic effects imposed by the basal two imide anions and an axial N donor of the pentaamine macrocyclic ligands in the rigid square-pyramidal structure* **2** *facilitate the generation of nickel(III) ion and further permit the formation of hitherto unknown 1:1 Ni–O$_2$ adducts at room temperature in air oxidation. Moreover, the benzyl substituent in L^2 effects a reversible Ni–O$_2$ interaction.* We have also discovered that *dioxygen is activated by coordinating with the nickel(II) complexes so as to convert benzene into phenol.*

The 1:1 M(II)–L^1 pH metric titrations in N$_2$ atmosphere and their analysis (as for L^5)[14] established formation of the doubly deprotonated complexes [M(H$_{-2}$L)]^0 above pH 9: $K_{MH_{-2}L}$ (= [MH$_{-2}$L][H$^+$]^2/[M][L]) = 2.6 × 10^{-9} M for Ni(II) and 9.3 × 10^{-3} M for Cu(II) at 25 °C and I 0.2 M. In contrast to the yellow Ni(II)–L^5 and –L^6 complexes,[16] the pink Ni(II)–L^1, –L^2, and –L^3 show d–d absorption spectral patterns (see Figure 1) indicative of octahedral high-spin species, to lend a support to the square-pyramidal structures **2** and **3**.[18] The conjugated two imide anions of L^1 and L^2 should lie at the basal part of the square-pyramidal ring, which may add rigidity and constriction to the in-plane N$_4$ ligand field of L^3, as illustrated by the higher intensities of d–d transitions for L^1 and L^2 complexes than for the L^3 complex with Ni(II).

Cyclic voltammetry was used to determine the redox potentials E^0 for M(II) $\rightleftharpoons$ M(III) in L^1, L^2, L^3 complexes.[19] An interesting result with L^1 and L^2 (Table I) is that the Ni^{III,II} potentials are much smaller than the corresponding Cu^{III,II} potentials, reflecting coordinate environments much more favorable for the d^8 Ni(II) → d^7 Ni(III) transition than for the d^9 Cu(II) → d^8 Cu(III). A more remarkable fact is that the E^0 values of Ni (+0.24 V *vs.* SCE) are the lowest of all the reported M^{III,II} values for the relevant polyamines (inclusive of the dioxo-free counterpart L^3 complex)[11,12,16] and oligopeptides.[5–8,20] The dark brown developed as the pink solution (unbuffered, initial pH 10.1) of Ni(II)–L^1 and –L^2 complexes were oxidized electrochemically (final pH 7.1). The UV–visible spectra of the oxidation products (λ_{max} 300 nm, ϵ 6900 M^{-1} cm^{-1} for L^1 and λ_{max} 270 nm, ϵ 7400 M^{-1} cm^{-1} for L^2 (see Figure 1c)) are indicative

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(17) Synthesized from tetraethylenepentaamine and diethyl malonate in refluxing ethanol for a week. Both L^1 (mp 174 °C) and L^2 (mp 194 °C) gave satisfactory elemental analysis and NMR data.

(18) The high-spin Ni(II) complex of the N$_5$-donor L^1 is less stable than the low-spin complex of the N$_4$-donor L^5 ($K_{MH_{-2}L}$ = 7.0 × 10^{-6} M^{-1})[16] at a given pH. In parallel, Ni^{II}–L^3 (K_{ML} = 5.2 × 10^{17} M^{-1}) is less stable than Ni^{II}–L^6 (K_{ML} = 5 × 10^{22} M^{-1}).

(19) The voltammograms show quasi-reversible behavior by similar criteria (the separation of the anodic and cathodic peaks by E = ca. 80 mV and peak current ratios nearly unity, etc.) applied to those for Ni^{II}–L^4 and –L^5 complexes.[16]

(20) Much more negative potentials for the Ni^{2+}/Ni^{3+} couple in organic solvents were previously reported with planar macrocyclic tetraamine ligands having dianionic, charge-delocalized chelate rings. However, their O$_2$ adducts formtion was not mentioned: Pillsburg, D. G.; Busch, D. H. *J. Am. Chem. Soc.* **1976**, *98*, 7836. Streeky, J. A.; Pillsbury, D. G.; Bush, D. H. *Inorg. Chem.* **1980**, *19*, 3148.
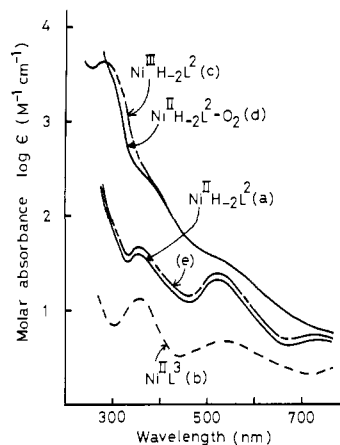
Figure 1. Electronic absorption spectrum of (a) $Ni^{II}H_{-2}L^2$ in degassed aqueous solution), (b) $Ni^{II}L^3$, (c) $Ni^{III}H_{-2}L_2$ (freshly generated electrochemically), (d) $Ni^{II}H_{-2}L^2O_2$ (freshly oxygenated), and (e) solution d after deoxygenation under reduced pressure at room temperature.
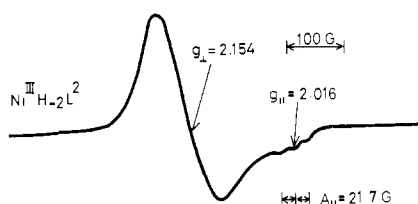

Figure 2. X-band ESR spectrum of electrochemically generated Ni^{III}-$H_{-2}L^2$ (freshly measured, 5×10^{-3} M in pH 9.4 borate buffers) at liquid nitrogen temperature.

Table I. Standard Electrode Potentials ($E°$) for $M^{II}H_{-2}L \rightleftharpoons M^{III}H_{-2}L$ (or $M^{II}L \rightleftharpoons M^{III}L$)

	$E°$, V vs. SCE^a	
ligand	$NiH_{-2}L$ (or NiL)	$CuH_{-2}L$ (or CuL)
L^1	+0.24 (pH 9.5)^b	+0.68 (pH 9.0)^b
L^2	+0.24 (pH 10.4)^b	+0.74 (pH 10.5)^b
L^3	(+0.66)^b	irreversible^b
L^4 (triglycine)	+0.60^c	+0.67^c
L^5	+0.81^c	+0.64^c
L^6	(+0.51)^c	irreversible^b

^{a} Taken from the midpoint between the oxidation peak and the reduction peak in the cyclic voltammograms at 100–200 mV s^{-1} with a glassy carbon electrode, 25 °C, I 0.5 M Na$_2$SO$_4$, and the specified pH in blacket. ^{b} This study. ^{c} Reference 16.

of Ni(III) complexes.[12,13] The ESR spectra at liquid nitrogen temperatures showed $g_\perp$ = 2.17 (L^1) and 2.15 (L^2), which are greater than $g_\parallel$ = 2.02 (L^1 and L^2) and which are consistent with the unpaired electron in the d_{z^2} orbital for d^7 Ni(III) (see Figure 2). The Ni(III) species are kinetically fairly stable at pH 7 but decompose immediately at pH 10, as judged from the visible and ESR spectra.

In view of the unusually low oxidation potential of Ni(II) dioxopentaamine complexes, their air oxidation was attempted. An intense brown color developed as in the electrochemical oxidation (see the spectral change from a to d in Figure 1). A further elaborate study established that the *air-oxidation products are the 1:1 (NiH$_{-2}$L)-O$_2$ adducts 4*. The supporting evidence for

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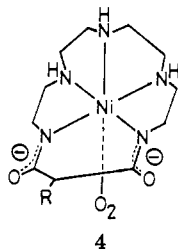
the novel 1:1 Ni–O$_2$ complexes is given as follows: (1) The Ni^{II}H$_{-2}$L^1 complex uptakes equimolar O$_2$ in pH 9.5 borate buffers at 25 °C and I 0.2 M. (2) The freshly oxygenated products show the intense bands (possibly assignable to CT from Ni to O$_2$) at λ_{max} 310 nm (ϵ 2200) for L^1 and 290 nm (4700) for L^2 (see Figure 1d) and possess similar oxidizing abilities (such as oxidation of I$^-$ and ascorbic acid) as the electrochemically prepared Ni^{III} species. (3) After several hours equilibration of 0.7 mM Ni^{II}-H$_{-2}$L^2 with air in unbuffered pH 9.8 aqueous solutions at 25 °C yields 0.5 mM NiH$_{-2}$L^2–O$_2$ species (determined by the absorbance at 290 nm).[21] The solution after deaeration (with N$_2$) exhibits a new polarographic wave at $E_{1/2}$ +0.17 V vs. SCE, which is ascribable to the reduction of the Ni-bound O$_2$. (4) The electrochemical reduction of NiH$_{-2}$L^2–O$_2$ at potentials below its $E_{1/2}$ proceeds to a quantitative recovery of the starting pink Ni^{II}H$_{-2}$L^2, as determined spectrophotometrically. (5) When the 0.5 mM NiH$_{-2}$L^2–O$_2$ solution is acidified (to pH 3.0) by a few drops of acetic acid in N$_2$ atmosphere, its wave height at $E_{1/2}$ +0.17 V diminishes from 12 to 4.5 cm to indicate 63% [=(12 – 4.5)/12] decomposition of the oxygenated species. This wave decrease matches the emergence of a new wave (7.5 cm high) at −0.1 V vs. SCE, which is assigned to the reduction of free O$_2$, as separately confirmed. These polarographic observations are consistent with the spectroscopic evidence of the diminished absorbance at 290 nm from 2.35 to 0.88 [(2.35 – 0.88)/2.35 = 63% decomposition]. (6) The electrochemically generated Ni^{III}H$_{-2}$L complexes do not release free O$_2$ at all when acidified with acetic acid. (7) The pH titration curve of Ni^{II}–L^1 in aerobic conditions fits only to the equation derived for the formation of 1:1 O$_2$ adducts; the determined K_{O_2} (= [NiH$_{-2}$L^1–O$_2$]/[NiH$_{-2}$L^1][O$_2$]) = 1.8 × 10^4 M^{-1} at 35 °C and I 0.2 M.

It is of much interest to note that *the coordinated O$_2$ can be removed from NiH$_{-2}$L^2* (*but not from NiH$_{-2}$L^1*) *in aqueous solution under reduced pressure* (~20 mmHg) *at room temperature*: see the generation of spectrum e from d (Figure 1). Exposure of the solution e to O$_2$ again produces spectrum d. Thus the reversible oxygenation of the solution state was followed through several cycles by monitoring changes in the UV spectrum. The degree of reversibility was ca. 80% per oxy–deoxy cycle, by judging from the spectral data and the reabsorption of ca. 0.8 mol of O$_2$/1 mol of Ni. Possible irreversible oxidation to the Ni(III) complex accounts for the gradual drop in the volume of O$_2$ absorption. Separately, we have confirmed that Ni^{III}H$_{-2}$L^2 (electrochemically generated) does not absorb O$_2$ at all. In ligth of the fact that the coordinated O$_2$ cannot be released from NiH$_{-2}$L^1 under comparable conditions, we postulate that the benzene ring of L^2 ligand may dispel the coordinated O$_2$ for steric and/or electronic reasons.[22]

The chemical reactivity of the Ni-bound O$_2$ is as remarkable as its occurrence. *Mere stirring of the NiH$_{-2}$L–O$_2$ aqueous solutions with benzene or, more simply, air-bubbling through a mixture of NiH$_{-2}$L in borate buffers and benzene yields phenol*. Of further interest mechanistically is the reaction with toluene to yield only o- and p-cresol. Thus our system may offer a biomimetric model of aromatic oxygenations. So far we have obtained ca. 40% yield (based on the used NiH$_{-2}$L complex) of phenol from benzene with the presence of reducing agents such as NaBH$_4$.[23] We are currently investigating the structural elu-

(21) Under this condition with L^2 complex, the oxygenation equilibrium lies partially in the reverse direction (see the following paragraph). For the complete oxygenation, higher pH (~11) was required.

(22) The freshly oxygenated brown NiH$_{-2}$L^2 complex (solution d) exhibited an ESR spectrum very similar to the one obtained for Ni^{III}H$_{-2}$L^2 (see Figure 2). Referees suggested that this spectrum is most likely of an oxidized Ni^{III} contaminant and that the Ni^{II}–O$_2$ species should be ESR silent, as is the case for heme–O$_2$. However, we observed this spectrum decrease in signal intensity upon deoxygenation in vacuo. The final spectrum, if quantified by integration, accounts for only 20–30% of the initial oxygenated Ni species. Upon reoxygenation we obtained almost the same spectrum as the first one. These ESR data, supported by the UV data, seem to imply an ESR-active Ni^{III} character in the N^{II}–O$_2$ bonding. Certainly, more evidence is needed to enforce this notion.

cidation of the NiH₋₂L–O₂ and the reaction mechanism and synthetic applications of aromatic hydroxylations.[24]

(23) The electrochemically generated Ni^III^H₋₂L species are not active at all in the oxygenation of benzene. In the NiH₋₂L–O₂ reactions, the ligand L¹ and L² are gradually oxidized to dehydrogenated species (determined by the mass spectroscopy), which results in loss of activity in the oxygenation of benzene. It is common that Ni(III) complexes tend to undergo self oxidation–reduction in which the ligands are frequently dehydrogenated (Kirksey, S. T.; Neubecker, T. A.; Margerum, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 1631).

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Figure 1. Core structure of HRh₂(CH₃C₆H₄C=C(H)C₆H₄CH₃)[P(O-*i*-C₃H₇)₃]₄ with isopropoxy groups omitted for clarity. The *p*-tolyl groups are oriented trans to one another in the bridging vinyl linkage. The X-ray crystal structure of HRh₂(CH₃C=C(H)CH₃)[P(O-*i*-C₃H₇)₃]₄ revealed an essentially identical structure for the core atoms. Isostructural also is the vinyl complex derived from C₆H₅C≡CC₆H₅ as determined by NMR spectroscopy (see supplementary material). The full details of these crystal structures will be described elsewhere.

Selective Formation of Trans Olefins by a Catalytic Hydrogenation of Alkynes Mediated at Two Adjacent Metal Centers

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Cis olefins are the ubiquitous first products in catalytic alkyne hydrogenations with metals and also mononuclear metal complexes; appearance of trans olefins in such reactions usually can be traced to a subsequent step of olefin isomerization. Earlier, we[1] noted the possibility that trans olefins could be initial products in homogeneous systems if there were two metal centers involved in the catalytic sequence. We describe here a system in which trans olefins are so formed with a dinuclear metal catalyst. A late step in the catalytic cycle was rate determining, enabling a definition of intermediates in the catalytic cycle,[2] including the key bridging vinyl intermediate with trans substituents, through low-temperature studies and by spectroscopic and crystallographic investigations. This novel catalytic system has no synthetic utility because of a short catalyst lifetime. However, utility is not the immediate issue; the key scientific point is that a unique catalytic outcome at adjacent metal centers in a polynuclear complex has been unequivocally demonstrated.

Alkynes are converted[3] to olefins at low rates (~1 turnover/min) at 20 °C and <1 atm by the catalyst precursor (μ-H)₂Rh₂[P(O-*i*-C₃H₇)₃]₄ (**1**), a bridged square-planar[4] dinuclear complex. This dimer[3] has been shown to undergo fast, reversible reaction with hydrogen to form (μ-H)₃(H)Rh₂[P(O-*i*-C₃H₇)₃]₄ (**2**). We have found that the dimer also reacts with alkynes (but not with olefins) in the absence of hydrogen to form first (μ-H)₂(η²-μ-RC₂R)Rh₂[P(O-*i*-C₃H₇)₃]₄, which then transforms to a bridged vinyl complex. Relative rates of reaction of **1** with
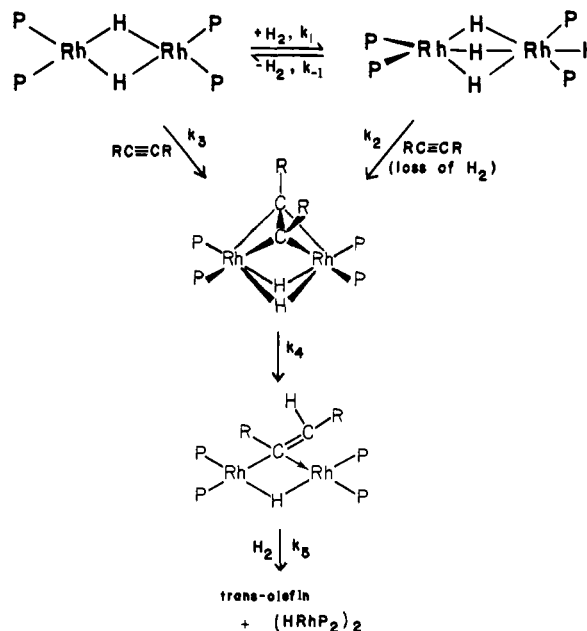
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(2) No homogeneous catalytic hydrogenation of alkynes had been mechanistically established in reasonable detail prior to this study.
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Figure 2. Scheme depicting the catalytic hydrogenation of acetylene to olefins by (μ-H)₂Rh₂[P(O-*i*-C₃H₇)₃]₄. In the bridging vinyl structure, the arrow represents a π bonding of the vinyl carbon atoms to the rhodium atom on the right (see Figure 1). All compounds shown in this scheme have been spectroscopically or crystallographically defined. For R = C₆H₅ or CH₃C₆H₄, $k_1 > k_2 > k_4 > k_3 > k_5$; for R = CH₃, $k_1 > k_2 > k_4 \cong k_3 > k_5$. Undetected in these reactions have been H₄Rh₂(RC≡CR)[P(O-*i*-C₃H₇)₃]₄ (from reaction of H₄Rh₂[P(O-*i*-C₃H₇)₃]₄ with RC≡CR) and H₃Rh₂(RC=C(H)R)[P(O-*i*-C₃H₇)₃]₄ (from reaction of the vinyl complexes with H₂). The last step of the cycle undoubtedly comprises several elementary steps including hydrogen addition, carbon–hydrogen bond formation, and olefin elimination. The first of these elementary steps is probably the rate-determining step.

H₂ and with alkynes is H₂ > dialkylacetylenes > diarylacetylenes. The tetrahydride **2** also reacted with alkynes to form hydrogen and the bridged vinyl complex, but more rapidly than did dimer **1** form the vinyl complex directly from alkyne.

The bridged vinyl complexes derived from various dialkyl- and diarylacetylenes appeared to be structurally identical by NMR data, but the stereochemistry in the vinyl group could not be