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Registry No. $K_4[Pt_2(pop)_4Cl_2] \cdot 2H_2O$, 82135-56-6; $K_4[Pt_2(pop)_4Br_2]$, 82135-55-5; $[Ph_4As]_4[Pt_2(pop)_4I_2]$, 82135-54-4; $K_4[Pt_2(pop)_4(CH_3)]I$, 82135-52-2; $K_4[Pt_2(pop)_4]$, 82135-51-1; $[Ph_4As]_4[Pt_2(pop)_4]$, 82149-95-9.

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

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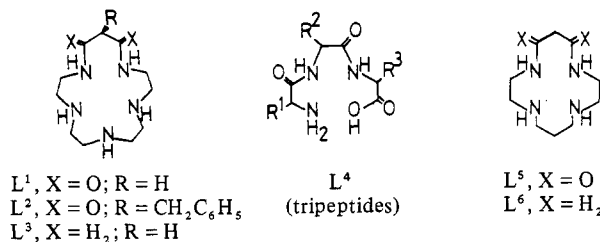
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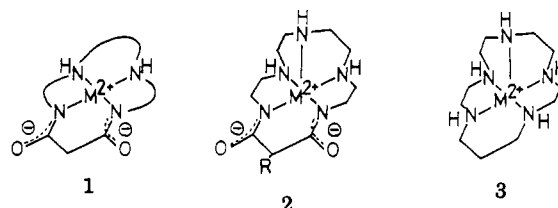
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The chemical interest in interaction and activation (by reduction) of molecular oxygen by copper proteins has grown considerably during recent years.¹ Copper(II)^{2,3} and nickel(II)^{4,5} can promote the reactions between O_2 and peptides, where Cu(III) 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



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 $[MH_2L]^0$, $1^{14,15}$ and tend to lower the redox potentials



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 $[M(H_2L)]^0$ above pH 9: $K_{MH_2L} (= [MH_2L][H^+]^2/[M][L]) = 2.6 \times 10^{-9}$ 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) $\rightarrow d^7$ Ni(III) transition than for the d^9 Cu(II) $\rightarrow d^8$ 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 ($K_{MH_2L} = 7.0 \times 10^{-6} M^{-1}$)¹⁶ at a given pH. In parallel, $Ni^{II}-L^3$ ($K_{ML} = 5.2 \times 10^{17} M^{-1}$) is less stable than $Ni^{II}-L^6$ ($K_{ML} = 5 \times 10^{22} M^{-1}$).

(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 formation was not mentioned: Pillsbury, 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.

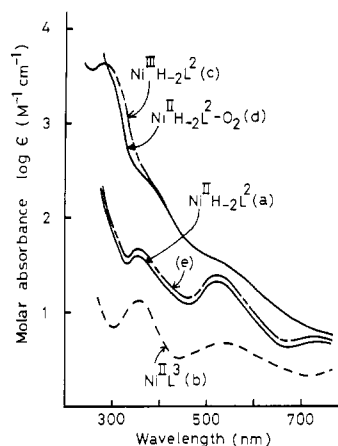


Figure 1. Electronic absorption spectrum of (a) NiH_2L^2 in degassed aqueous solution, (b) NiH_2L^3 , (c) NiH_2L^2 (freshly generated electrochemically), (d) $\text{NiH}_2\text{L}^2\text{-O}_2$ (freshly oxygenated), and (e) solution d after deoxygenation under reduced pressure at room temperature.

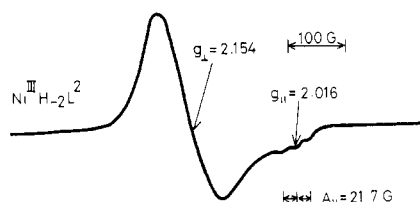


Figure 2. X-band ESR spectrum of electrochemically generated NiH_2L^2 (freshly measured, 5×10^{-3} M in pH 9.4 borate buffers) at liquid nitrogen temperature.

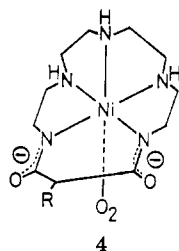
Table I. Standard Electrode Potentials (E°) for $\text{M}^{\text{II}}\text{H}_2\text{L} \rightleftharpoons \text{M}^{\text{III}}\text{H}_2\text{L}$ (or $\text{M}^{\text{II}}\text{L} \rightleftharpoons \text{M}^{\text{III}}\text{L}$)

ligand	E° , V vs. SCE ^a	
	NiH_2L (or NiL)	CuH_2L (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_2SO_4 , and the specified pH in bracket. ^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 $d_{x^2-y^2}$ 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) dioxopentamine 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_2L)- O_2 adducts 4*. The supporting evidence for



the novel 1:1 Ni-O_2 complexes is given as follows: (1) The NiH_2L^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 NiH_2L^2 with air in unbuffered pH 9.8 aqueous solutions at 25 °C yields 0.5 mM $\text{NiH}_2\text{L}^2\text{-O}_2$ 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 $\text{NiH}_2\text{L}^2\text{-O}_2$ at potentials below its $E_{1/2}$ proceeds to a quantitative recovery of the starting pink NiH_2L^2 , as determined spectrophotometrically. (5) When the 0.5 mM $\text{NiH}_2\text{L}^2\text{-O}_2$ 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 $[(2.35 - 0.88)/2.35 = 63\% \text{ decomposition}]$. (6) The electrochemically generated $\text{Ni}^{\text{III}}\text{H}_2\text{L}$ complexes do not release free O_2 at all when acidified with acetic acid. (7) The pH titration curve of NiH_2L^1 in aerobic conditions fits only to the equation derived for the formation of 1:1 O_2 adducts; the determined K_{O_2} ($= [\text{NiH}_2\text{L}^1\text{-O}_2]/[\text{NiH}_2\text{L}^1][\text{O}_2]$) = $1.8 \times 10^4 \text{ M}^{-1}$ 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_2L^2 (but not from NiH_2L^1) in aqueous solution under reduced pressure ($\sim 20 \text{ mmHg}$) 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 $\text{Ni}^{\text{III}}\text{H}_2\text{L}^2$ (electrochemically generated) does not absorb O_2 at all. In light of the fact that the coordinated O_2 cannot be released from NiH_2L^1 under comparable conditions, we postulate that the benzene ring of L^2 ligand may displace 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 $\text{NiH}_2\text{L}^2\text{-O}_2$ aqueous solutions with benzene or, more simply, air-bubbling through a mixture of NiH_2L^2 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 biomimetic model of aromatic oxygenations. So far we have obtained ca. 40% yield (based on the used NiH_2L^2 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_2L^2 complex (solution d) exhibited an ESR spectrum very similar to the one obtained for $\text{Ni}^{\text{III}}\text{H}_2\text{L}^2$ (see Figure 2). Referees suggested that this spectrum is most likely of an oxidized Ni^{III} contaminant and that the $\text{Ni}^{\text{II}}\text{-O}_2$ 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^{II} character in the $\text{Ni}^{\text{II}}\text{-O}_2$ bonding. Certainly, more evidence is needed to enforce this notion.

cidation of the $\text{NiH}_2\text{L}-\text{O}_2$ and the reaction mechanism and synthetic applications of aromatic hydroxylations.²⁴

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Registry No. $\text{Ni}^{\text{III}}\text{H}_2\text{L}^1$, 80400-19-7; $\text{Ni}^{\text{III}}\text{H}_2\text{L}^2$, 80389-72-6; $\text{Ni}^{\text{III}}\text{L}^3$, 77321-28-9; $\text{Ni}^{\text{III}}\text{H}_2\text{L}^2$, 82135-48-6; $\text{Ni}^{\text{II}}\text{H}_2\text{L}^2\text{-O}_2$, 82149-93-7; $\text{Cu}^{\text{II}}\text{H}_2\text{L}^1$, 80386-21-6; $\text{Cu}^{\text{II}}\text{H}_2\text{L}^2$, 80386-22-7; $\text{Cu}^{\text{II}}\text{L}^3$, 80389-68-0; $\text{Cu}^{\text{II}}\text{L}^6$, 52304-87-7.

(23) The electrochemically generated $\text{Ni}^{\text{III}}\text{H}_2\text{L}$ species are not active at all in the oxygenation of benzene. In the $\text{NiH}_2\text{L}-\text{O}_2$ reactions, the ligand L^1 and L^2 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 $\text{Ni}(\text{III})$ 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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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, we¹ 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 converted³ to olefins at low rates (~ 1 turn-over/min) at 20 °C and <1 atm by the catalyst precursor $(\mu\text{-H})_2\text{Rh}_2[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_4$ (1), a bridged square-planar⁴ dinuclear complex. This dimer³ has been shown to undergo fast, reversible reaction with hydrogen to form $(\mu\text{-H})_3(\text{H})\text{Rh}_2[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_4$ (2). We have found that the dimer also reacts with alkynes (but not with olefins) in the absence of hydrogen to form first $(\mu\text{-H})_2(\eta^2\text{-}\mu\text{-RC}_2\text{R})\text{Rh}_2[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_4$, which then transforms to a bridged vinyl complex. Relative rates of reaction of 1 with

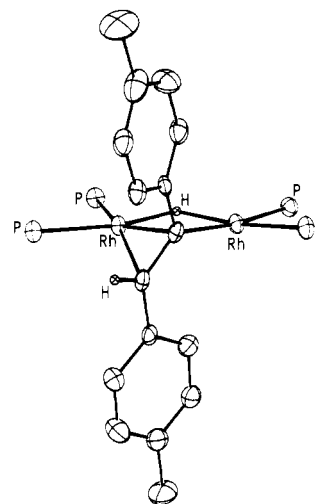


Figure 1. Core structure of $\text{HRh}_2(\text{CH}_3\text{C}_6\text{H}_4\text{C}\equiv\text{C}(\text{H})\text{C}_6\text{H}_4\text{CH}_3)[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_4$ with isopropoxy groups omitted for clarity. The *p*-tolyl groups are oriented trans to one another in the bridging vinyl linkage. The X-ray crystal structure of $\text{HRh}_2(\text{CH}_3\text{C}\equiv\text{C}(\text{H})\text{CH}_3)[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_4$ revealed an essentially identical structure for the core atoms. Isostructural also is the vinyl complex derived from $\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$ as determined by NMR spectroscopy (see supplementary material). The full details of these crystal structures will be described elsewhere.

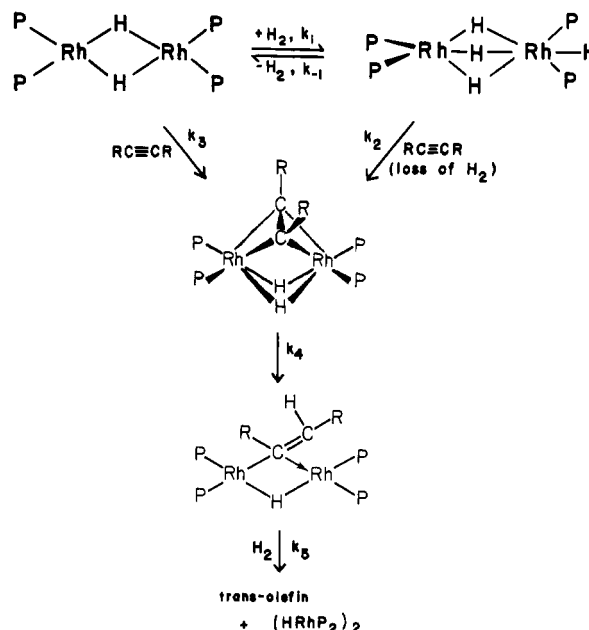


Figure 2. Scheme depicting the catalytic hydrogenation of acetylene to olefins by $(\mu\text{-H})_2\text{Rh}_2[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_4$. In the bridging vinyl structure, the arrow represents a π bonding of the vinyl carbon atoms to the rhodium atom on the right (see Figure 1). All compounds shown in this scheme have been spectroscopically or crystallographically defined. For $\text{R} = \text{C}_6\text{H}_5$ or $\text{CH}_3\text{C}_6\text{H}_4$, $k_1 > k_2 > k_4 > k_3 > k_5$; for $\text{R} = \text{CH}_3$, $k_1 > k_2 > k_4 \approx k_3 > k_5$. Undetected in these reactions have been $\text{H}_4\text{Rh}_2(\text{RC}\equiv\text{CR})[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_4$ (from reaction of $\text{H}_4\text{Rh}_2[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_4$ with $\text{RC}\equiv\text{CR}$) and $\text{H}_3\text{Rh}_2(\text{RC}\equiv\text{C}(\text{H})\text{R})[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_4$ (from reaction of the vinyl complexes with H_2). 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.

H_2 and with alkynes is $\text{H}_2 > \text{dialkylacetylenes} > \text{diarylacetylenes}$. 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

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