

10 kHz the device turns on to nearly the same extent as at 1 Hz. The polyaniline device shows an easily detected variation in drain current, I_D , for flow of only 10^{-12} C in the gate circuit accompanying ΔV_G in the V_G region of maximum transconductance. Thus, the device can respond to a small fraction of a femtomole (10^{-10} C) of charge.

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The *o*-Methoxyphenol-Pendant Cyclam Complexes. A Novel Molecule Designed for Intramolecular Redox Coupling between Monodentate Catecholate and Metal Ions in an N_4 Macrocyclic

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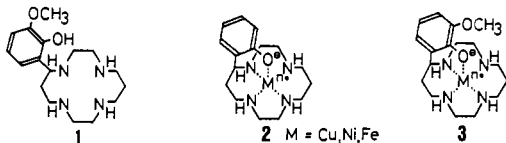
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This paper describes the synthesis and characterization of the *o*-methoxy-phenol- pendant cyclam complexes. Synergistic, simultaneous oxidation has been revealed by unusually low potentials at -0.30 V vs. SCE for Fe^{2+}/Fe^{3+} and for *o*-methoxyphenolate.

The coordination chemistry of bidentate catechol ligands (cat^{2-}) has long been a subject of chemical²⁻⁷ as well as biochemical interest.⁸ Recently, however, monodentate catecholate ($catH^-$) coordination to Fe^{3+} was proposed as an active intermediate in catechol-cleaving dioxygenases, whereupon the catechol becomes susceptible to O_2 attack.^{9,10}

With the intention of exploring the redox coupling between the monodentate catecholate and metal ions, we have designed a new cyclam ligand **1**¹¹ that strategically places the N_4 macrocycle to



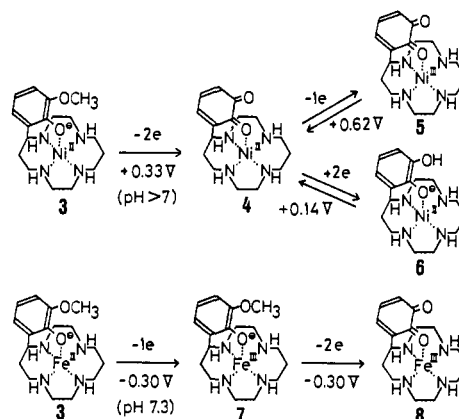
hold metal ions during the course of the redox process close to the *o*-methoxyphenol, an equivalent of catechol.¹² Earlier,^{13,14}

we reported the X-ray structure¹⁵ of the axial phenolate coordinating complexes (structure **2**), along with the mutually affected redox behavior of the phenolate ion and metal ions.

The new *o*-methoxyphenol- pendant cyclam **1** has pK_a values [determined pH metrically at 25 °C, $I = 0.1$ M (NaClO₄)] of 12.0, 11.16, 8.99 (for phenol, confirmed spectrophotometrically), <2, and <1 and the following UV spectra: λ_{max} 276 nm (ϵ 2500, pH 6.2) for the phenol form; λ_{max} 292 nm (ϵ 4500) and 243 nm (ϵ 8000) for the phenolate form (pH 12.0). In the cyclic voltammogram (CV)¹⁶ of **1**, the anodic oxidation, like *o*-methoxyphenol itself,¹⁷ starts with irreversible 2e oxidative dimethylation to *o*-quinone at +0.58 V (pH 4.0 acetate buffer), +0.45 V (pH 7.3 Tris buffer), and +0.30 V (pH 10.0 carbonate buffer), followed by a reversible¹⁸ *o*-quinone/catechol 2e redox process at +0.33, +0.13, and 0 V, respectively.

Under argon atmosphere¹⁹ **1** forms 1:1 complexes in situ having structure **3** with Ni^{2+} (pH > 7), Cu^{2+} (pH > 9), and Fe^{2+} (pH > 6),²⁰ as established by pH metric titration. The UV absorptions [λ_{max} 293 nm (ϵ 3600) and 247 nm (ϵ 8600) for Ni^{2+} (pH 8.2), 288 nm (ϵ 5700, *sh*) and 246 nm (ϵ 12000) for Cu^{2+} (pH 10.0), and 287 nm (ϵ 3700) and 243 nm (ϵ 7600) for Fe^{2+} (pH 8.3)], being similar to corresponding features in **2**, support the phenolate coordination in **3**. In electrochemical behavior, the Cu^{2+} complex **3** displays an identical CV (Figure 1-I) with that of the uncoordinated ligand, indicating little influence of Cu^{2+} on oxidation of the axial *o*-methoxyphenolate. Cu^{2+} is not oxidized in the measured potential range.

The CV and RDE of the Ni^{2+} complex **3** Figure 1-II) indicate the 2e oxidation (to **4**) at +0.33 V (pH > 7), followed by 1e



(12) We have previously synthesized the catechol- pendant cyclam (ref 14); the metal interactions were more complex due to the ligand's rapid decomposition in air.

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(16) Electrodes used in CV and RDE (rotating disk electrode voltammetry) are all glassy carbons which should be well-polished before every measurement, which were checked by using a reversible redox system of $Ni^{2+/3+}$ -cyclam complex in 0.2 M Na_2SO_4 at 25 °C.

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(18) Reversibility in this and the following redox systems in 0.2 M Na_2SO_4 was checked by log plots of $\log[i/(i_d - i)]$ against the dc potential being invariably linear with reciprocal slope of 30 mV, which corresponds to a reversible two-electron oxidation.

(19) In this and the following electrochemical studies, O_2 is rigorously excluded by using a stream of argon prepurified with an alkaline pyrogallol solution.

(20) Due to rapid decomposition, isolation of these complexes was unsuccessful, except for the pink (high-spin) Ni^{2+} complex (with very low yield) out of a pH 8 aqueous solution of $NiCl_2$ and **1** under argon atmosphere. Anal. Calcd for $C_{17}H_{29}N_4O_2NiCl \cdot H_2O$: C, 47.09; H, 7.21; N, 12.92. Found: C, 47.05; H, 7.40; N, 12.50. The Ni^{2+} complex isolated has shown identical solution behaviors as the one prepared in situ.

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 (11) The new ligand **1** was synthesized as follows: Refluxing methyl 2'-(benzyloxy)-3'-methoxycinnamate and 1,9-diamino-3,7-diazanonane in dry CH_3OH for 3 weeks afforded the 14-membered oxotetraamine (mp 170-171 °C, from CH_3CN in 20% yield), and reduction of the oxotetraamine with B_2H_6 in tetrahydrofuran yielded the cyclam derivative **1** (mp 106-107 °C, from CH_3CN in 60% yield).

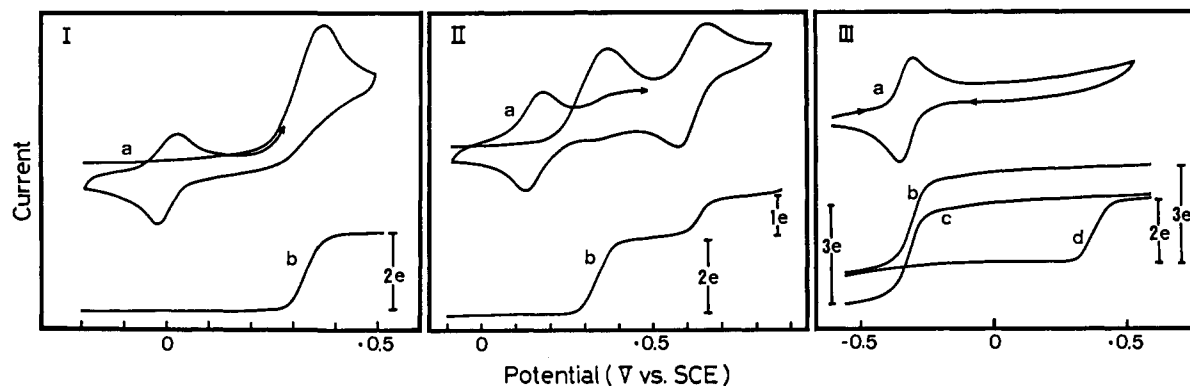


Figure 1. Cyclic voltammograms (I-a, II-a, III-a) at a scan rate of 100 mV s^{-1} , rotating disk electrode voltammograms (I-b, II-b, III-b-d) at an electrode rotation rate of 1000 rpm, and a scan rate of 10 mV s^{-1} on a glassy carbon disk electrode with $0.2 \text{ M Na}_2\text{SO}_4$ at 25°C . I for 1 mM Cu^{2+} complex **3** at pH 10.0. II for 1 mM Ni^{2+} complex **3** at pH > 7.0 . III for 1 mM free ligand and Fe complex at pH 7.3 (Tris buffer); curve a and b for Fe^{2+} complex **3**, curve c for Fe^{3+} complex **7** (aeration product of Fe^{2+} complex **3**), curve d for free ligand **1**. No further oxidation wave was seen up to $+0.5 \text{ V vs. SCE}$.

oxidation (to **5**) at $+0.62 \text{ V}$; in the subsequent CV sweep the reversible *o*-quinone/catechol (**4** \rightleftharpoons **6**) wave appears at $+0.14 \text{ V}$, as was seen with the free ligand. In view of the fact that the oxidation potential ($+0.35 \text{ V}$) for $\text{Ni}^{2+}/\text{Ni}^{3+}$ in the phenolate-pendant cyclam complex **2**¹⁵ is in a similar range with the present oxidation potential ($+0.30 \text{ V}$) of the *o*-methoxyphenolate, we have attempted to determine formal charges for the initial $2e$ oxidized product that was obtained by applying constant potential of $+0.45 \text{ V}$ at pH 8.3.²¹ Its ESR silent behavior supports nonradical structure **4**, excluding the electron-transferred semiquinone- Ni^{3+} structure. The magnetic susceptibility of **4** measured by the Evans method²² was $2.8 \mu_B$, indicating a high-spin Ni^{2+} complex for **4**. The further $1e$ oxidized (at $+0.70 \text{ V}$) product has structure **5** with its ESR spectrum²³ characteristic to Ni^{3+} and magnetic moment of $1.7 \mu_B$. This electrochemically oxidized solution showed an identical CV as those before the $1e$ oxidation.

The most unusual synergistic oxidation behavior was revealed by the definite $3e$ oxidation²⁴ of Fe^{2+} complex **3** simultaneously at -0.30 V (pH 7.3 Tris buffer) on RDE (see Figure 1-IIIb). The CV of **3** in Figure 1-IIIa shows no other redox wave up to $+0.5 \text{ V}$! The potential of -0.30 V is too low for the $2e$ oxidation of 2H^+ , Cu^{2+} , or Ni^{2+} -binding *o*-methoxyphenolate. The $1e$ oxidation potential for $\text{Fe}^{2+}/\text{Fe}^{3+}$ in **2** was -0.16 V .¹³ We are thus tempted to conclude that Fe^{2+} is initially oxidized to Fe^{3+} **7** at the lower potential of -0.30 V under the influence of stronger σ -donor, *o*-methoxyphenolate and thereupon that Fe^{3+} catalytically drains $2e$ out of this ligand to a possible quinone pendant **8**.²⁵ All the attempts to prepare **8** in large quantity for further identification by electrochemical oxidation at -0.10 V resulted in failure, mostly due to the immediate halt of the electric current. We suspect that this is because kinetically reactive **8** undergoes immediate intramolecular (e.g., Michael addition) as well as intermolecular reactions whose unidentified products stick to the electrode surface. Mild aeration (20 min) of **3** initially oxidizes Fe^{2+} to Fe^{3+} [**7**, deep violet, λ_{max} 278 nm (ϵ 5500), 518 nm (ϵ 2150) at pH 7.0, in analogy to Fe^{3+} complex of **2**¹³], which undergoes further $2e$ oxidation to **8** at -0.30 V (curve c).

Although the final product structure **8** remains open to question, the present Fe macrocyclic complexes **3** and **7** have offered the first prototype for synergistic intramolecular redox coupling between monodentate catecholate and metal ions to render the catechol unusually vulnerable to oxidation. We are currently studying the catechol-cleaving reaction with **3**. Further modification of metal ions or macrocyclic structure with catechol pendant would find the novel redox system. Moreover, the reactivity of the remaining 6th axial position would be extremely interesting as a catalytic site.

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Determination of the Charge on Carbon in a Bridging Methylene Iron Dimer with Solid-State Deuterium NMR Spectroscopy

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The chemistry of bridging methylene metal dimers and the value of the ^{13}C NMR chemical shifts have been interpreted as due to a partial negative charge on the carbon atom.² PES yields a C_{1s} binding energy indicative of $-0.5 e$ charge.³ However, for $(\mu\text{-CH}_2)[\text{MnCp}(\text{CO})_2]_2$, a high-resolution X-ray diffraction electron density map shows no excess charge buildup.⁴ We are attempting to resolve the dilemma by using solid-state deuterium NMR techniques. In the results for *cis*-($\mu\text{-C}^2\text{H}_2$)($\mu\text{-CO}$)[$\text{FeCp}^d(\text{CO})$]₂ ($\text{Cp}^d = 5\%$ deuteriated cyclopentadienyl) presented here, we find no evidence for an excess negative charge on the bridging methylene carbon atom.

(21) The products **4** [λ_{max} 458 nm (ϵ 11200) and 508 nm (*sh*, ϵ 10700) at pH 5.3] and **5** [λ_{max} 279 nm (ϵ 6400), 441 nm (*sh*, ϵ 10800), 489 nm (ϵ 11600) at pH 5.0] reveal characteristic UV-vis absorption spectra, which differ from those of noncoordinating *o*-benzoquinone (λ_{max} 390 nm, ϵ 1800 at pH 5.0) or of the *o*-quinone-pendant cyclam (λ_{max} 406 nm, ϵ 1900 at pH 3.5).

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(24) The number of electrons involved were calibrated by using well-established $2e$ and $1e$ oxidation RDE wave heights of the Ni^{II} complex **3**, as illustrated in Figure 1-II.

(25) The $2e$ oxidation of another part of the ligand (e.g., the cyclam part) at this potential is very unlikely, in view of the fact that phenolate-cyclam in **2** ($M = \text{Fe}^{3+}$) is not oxidized up to $+0.9 \text{ V}$ (Kimura, E., unpublished data.).

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