system (**2**) is highly sensitive to the tetraamine ligand structure. Consistent with the above results, X-ray structures of $[(\mathrm{trpn})\mathrm{Co}(\mathrm{CO_3})]^+$ and $[(\mathrm{tren})\mathrm{Co}(\mathrm{CO_3})]^+$ reveal that the trpn ligand is better able to stabilize four-membered rings. Both O–Co–O bond angles in $[(\mathrm{trpn})\mathrm{Co}(\mathrm{CO_3})]^+$ (68°)[12] and $[(\mathrm{tren})\mathrm{Co}(\mathrm{CO_3})]^+$ (68°)[13] are highly distorted from that found in regular octahedral complexes (90°). All the N–Co–N bond angles are rigidly held (87°) with the tren ligand, whereas the N–Co–N bond angle opposite the O–Co–O bond angle in $[(\mathrm{trpn})\mathrm{Co}(\mathrm{CO_3})]^+$ is free to expand to 100°.[12] We[10d] recently showed that the much higher reactivity of $[(\mathrm{trpn})\mathrm{Co}(\mathrm{OH_2})(\mathrm{OH})]^{2+}$ over $[(\mathrm{tren})\mathrm{Co}(\mathrm{OH_2})(\mathrm{OH})]^{2+}$ in hydrolyzing phosphate diesters is due to the relative ease of formation of a four-membered ring transition state with $[(\mathrm{trpn})\mathrm{Co}(\mathrm{OH_2})(\mathrm{OH})]^{2+}$.

In conclusion, we have shown that $[(\mathrm{trpn})\mathrm{Co}(\mathrm{OH_2})(\mathrm{OH})]^{2+}$ hydrolyzes unactivated phosphate monoesters with unprecedented efficiency. The mechanism of the hydrolysis reaction involves a 2:1 metal to substrate complex leading to the formation of a binuclear cobalt(III) complex with a novel doubly bidentate phosphato bridge. The stability of the binuclear complex and the reactivity of $[(\mathrm{trpn})\mathrm{Co}(\mathrm{OH_2})(\mathrm{OH})]^{2+}$ are highly sensitive to the tetraamine ligand structure.

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Mixed-Valence, Conjugated Semiquinones

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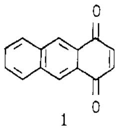
On inspection, the semiquinone **4**$^{\bullet-}$ is expected to have a delocalized π-electronic structure. Indeed, it has been shown that the three-ringed analogue **3**$^{\bullet-}$ is delocalized.[1] We now report evidence that **4**$^{\bullet-}$ and **5**$^{\bullet-}$ are not delocalized and propose that they have mixed-valence structures. In accord with this hypothesis are IR and electrochemical data as well as unusually broad and featureless optical absorption bands for **4**$^{\bullet-}$ and **5**$^{\bullet-}$ which extend from the visible region to the infrared. Upon the basis of molecular orbital calculations, we ascribe the surprising structure and properties of **4**$^{\bullet-}$ and **5**$^{\bullet-}$, at least in part, to the extraordinary polarizability of these species which allows small geometry or solvent perturbations to trap the charge at one end of the molecule.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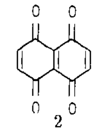
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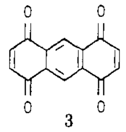
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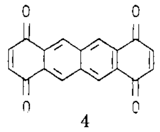
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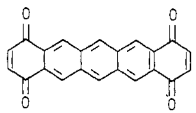
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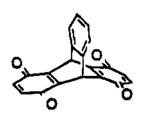
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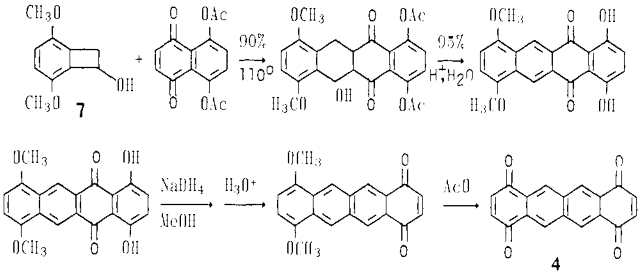
The neutral quinones **1** and **2** were prepared using literature methods.[2,3] Quinones **3**–**5** were prepared as follows: **3** (**7**[5] plus benzoquinone and then $\mathrm{Ce(NH_4)_2(NO_3)_6}$), **4** (see below), **5** (pyromellitic dianhydride plus hydroquinone[6] and then $\mathrm{NaBH_4}$).



The semiquinones were prepared electrochemically in DMF, 0.1 M $\mathrm{Bu_4N(BF_4)}$ at a carbon cathode, and cyclic voltammetry utilized a glassy carbon working electrode. In Table I are the $E^{\circ\prime}$ values for the first two reduction processes (there are others at more negative potentials). These two processes were reversible (60 ± 4 mV peak separation and nearly equal anodic and cathodic peak currents) for all the compounds investigated. Preparative reduction carried out to 1.05 electron/molecule gave stable solutions of the anion radicals. Electrochemical reoxidation regenerated the neutral in high yield and did not leave residual vis-NIR absorptions.

Table I. Electrochemical $E^{\circ\prime}$ and Computed Dipole Moments

compd	$-E^{\circ\prime a}$ (V, SCE)	$\mu(\mathrm{D})^b$	$\mu(\mathrm{D})^c$
1$^-$	0.69, 1.41		
2$^-$	−0.14, 0.59	1.27	6.6
3$^-$	0.26, 0.74	2.49	13.2
4$^-$	0.50, 0.75	13.2	19.8
5$^-$	0.72, 0.84	18.0	26.4
6$^-$	0.30, 0.53		

[a] From CV on ~1 mM neutral in DMF, 0.1 M $\mathrm{Bu_4N(BF_4)}$ at 100 mV $\mathrm{s^{-1}}$. [b] Dipole moments relative to the nuclear center of mass, calculated for an ion distorted along the B_{1u} mode (see text). [c] Dipole moments for the completely localized model (see text).

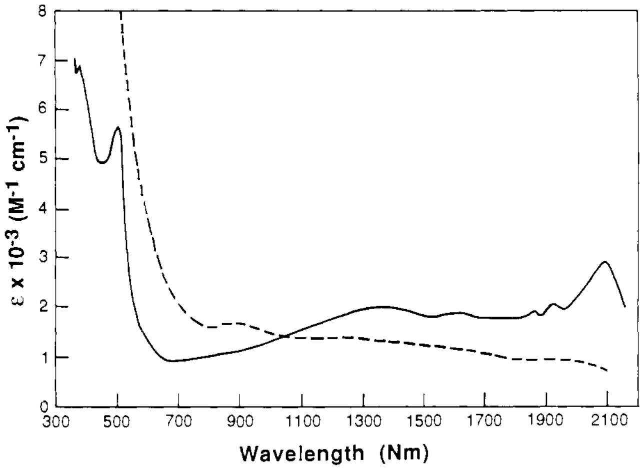


Figure 1. Vis NIR spectra of **4**$^{\bullet-}$ (—) and **5**$^{\bullet-}$ (– –) in DMF, $\mathrm{Bu_4N(BF_4)}$.

The optical spectra of **4**$^{\bullet-}$ and **5**$^{\bullet-}$ are shown in Figure 1. Instead of a sharp band in the NIR as found for **2**$^{\bullet-}$ and **3**$^{\bullet-}$, **4**$^{\bullet-}$ and **5**$^{\bullet-}$ have nearly flat absorption spectra from 600 to 2100 nm with $\epsilon \sim 2000$. The complete change in shape of the spectrum which results from addition of one benzene ring is unexpected, and the very broad absorption of **4**$^{\bullet-}$ and **5**$^{\bullet-}$ is quite unusual. Broad bands in the NIR are, however, characteristic of mixed-valence compounds,[7] and we hypothesize that the ions adopt a

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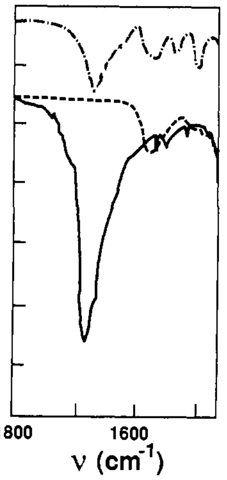

Figure 2. IR of $\mathbf{4}^{\bullet-}$ (—■—), $\mathbf{4}^{2-}$ (--), and **4** (—) formed sequentially from reduction of **4** and reoxidation to **4** in DMF,$Bu_4N(BF_4)$. The spectrum of $\mathbf{4}^{\bullet-}$ is offset for clarity.

mixed-valence structure which tends to temporarily localize the anion radical charge on one quinone moiety.

This structural hypothesis is supported by comparison of the IR spectrum of $\mathbf{4}^{\bullet-}$ (Figure 2) with the spectra of the delocalized $\mathbf{3}^{\bullet-}$ and the localized[8] $\mathbf{6}^{\bullet-}$. In DMSO $\mathbf{3}^{\bullet-}$ has a C=O band[9] at 1581 cm^{-1} as expected[10] if both quinones share the extra electron, while $\mathbf{6}^{\bullet-}$ has both a quinone C=O at 1650 and semiquinone C=O at 1505 cm^{-1}. In contrast to both, $\mathbf{4}^{\bullet-}$ has no clearly recognizable band in the C=O region (1700–1450 cm^{-1}). This is similar to the spectrum of the anion radical of an unconjugated bis-indanone anion radical studied by Mazur and Schroeder and precociously explained in terms of a mixed-valence structure.[11]

Also in agreement with this hypothesis are the $E^{\circ\prime}$ values (Table I). Since the anion of $\mathbf{4}^{\bullet-}$ is largely localized, it is relatively easy to add a second electron, and the separation (ΔE) between the first and second peaks is small. For comparison, consider the localized **6** (ΔE = 230 mV) and the delocalized **3** (ΔE = 480 mV) along with **4** (ΔE = 250 mV). It is also notable that the first $E^{\circ\prime}$ for **5** is essentially the same as that for the model monoquinone **1**.

The hypothesis of charge localization in the larger ions was tested with ab initio, restricted Hartree–Fock level calculations using both single- and double-ζ basis sets.[12] Such calculations showed that because the longer ions are extraordinarily polarizable, extremely small perturbations lead to substantial localization of the odd electron on one quinone moiety. A localized ion necessarily has a nonsymmetric charge distribution relative to the center of mass, giving rise to a dipole moment. Therefore, as a measure of localization we have subjected the ions to small perturbations and calculated the dipole moments of these perturbed ions. For comparison, we also calculated the dipole moments of hypothetical, completely localized ions, which have one-half of a negative charge on each oxygen of one quinone moiety. For example, a calculation using a geometry with the two C–O distances on one end lengthened by 0.01 Å and the two on the other end shortened by 0.01 Å (corresponding to a B_{1u} vibrational distortion) gave large dipole moments for $\mathbf{4}^{\bullet-}$ and $\mathbf{5}^{\bullet-}$ (Table I). These dipole moments were about 70% as large as the moments calculated using the completely localized models. Calculations including a small electrostatic field (like a solvent field) along the long molecular axis gave similar results. Thus, the calculations show $\mathbf{2}^{\bullet-}$ and $\mathbf{3}^{\bullet-}$ are different from $\mathbf{4}^{\bullet-}$ and $\mathbf{5}^{\bullet-}$ and that small perturbations lead to localization of the odd electron for $\mathbf{4}^{\bullet-}$ and $\mathbf{5}^{\bullet-}$.

The surprising conclusion of this study is that at least on the IR time scale the extra electron of $\mathbf{4}^{\bullet-}$ and $\mathbf{5}^{\bullet-}$ is largely localized on one quinone unit. This is in spite of the fact that the two quinones are connected by what is considered an excellent π delocalizing, conjugated framework.

Acknowledgment. This work was supported by NSF, SDIO/NRL, and the Minnesota Supercomputer Institute. We thank Professor Adrian Docken for the sample of **6**.

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Surface Methylene, Hydrogen, and C_xH Species from the Dissociative Adsorption of Diazirine on W(100) at 100 K

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Diazirine is found to be a suitable precursor for the isolation of C_1 fragments on W(100). The catalytic transformation or synthesis of hydrocarbon molecules on surfaces may often involve the formation of adsorbed C_1 intermediates. A knowledge of the identity and the chemistry of such species is crucial to the determination of surface reaction mechanisms as well as the factors which govern selectivity in heterogeneous catalysis. Vibrational spectroscopy in the form of electron energy loss spectroscopy (EELS), and more recently FT-IRAS, has led to the detection of adsorbed CH, CH_2, CCH, CCH_2, CCH_3, and $CHCH_2$ on single crystal metal surfaces following the decomposition of adsorbed parent molecules such as ethylene or acetylene.[1a–d] However, as yet, there is no clear evidence that the decomposition of these molecules on metal surfaces leads to adsorbed methylene.[2] Interest in adsorbed CH_2 stems from the role it is proposed to play in a variety of surface reactions such as methanation, metathesis, homologation, and Fischer–Tropsch reactions.[3] The chemistry and structure of the CH_2 ligand has been explored in detail by inorganic chemists. Among the many fascinating results of the latter studies is the observation that ethylene reacts with methylene bridged dinuclear complexes to yield propene.[4] The conversion of the μ-CH_2 ligand to μ-CH_2CO and μ-C_3H_6 ligands has also been reported.[5,6] Clearly there is a need for a parallel exploration of CH_2 chemistry on metal surfaces. A delineation of the similarities and the differences in the chemistry of such a reactive

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