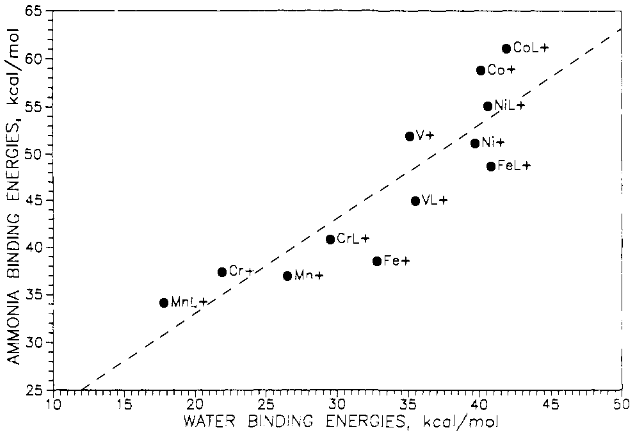
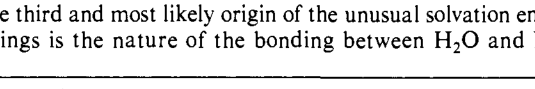


Figure 2. Comparison of water and ammonia binding energies for first-row transition-metal ion clusters. L is either H_2O or NH_3. The dashed line represents a best fit to the data ($R = 0.88$); slope = 1.00, intercept = 13.0 kcal/mol.

kcal/mol), the overall agreement is satisfactory.

Second, the cluster ions may not possess the presumed structures $M^+(H_2O)_n$ and $M^+(NH_3)_n$ but rather exist in metal-inserted forms: $H—M^+—OH$, $H—M^+—OH(H_2O)$ $(H)_2M^+(OH)_2$, $H—M^+—NH_2$, etc. Comparison of the available values for $D[M^+—OH]$, $D[M^+—NH_2]$, and $D[M^+—H]$ in the literature with the bond energies in H_2O and NH_3 suggests that such structures may be thermodynamically accessible.[11] Moreover, V^+ (but *not* the other metals) reacts with H_2O in the central quadrupole by dehydrogenation, and $V^+(H_2O)$ clusters undergo CID to produce $VO^+ + H_2$ in addition to $V^+ + H_2O$. Therefore, O—H insertion by V^+ must occur at some point during an ion-water collision or as a result of collisional activation of the stabilized adduct. We have investigated various ion/molecule reactions of the metal hydrate ions in search of chemical evidence for the presence of insertion structures, operating on the assumption that the $M^+—H$ moiety in such complexes should display characteristic reactivity. Perdeuterated metal hydrates $M^+(D_2O)_n$ formed in the flow reactor fail to undergo H/D exchange with H_2, $CH_2{=}CH_2$, or $CH_3CH{=}CH_2$ in the second quadrupole, whereas diatomic metal hydride ions MH^+ and metal hydride ion complexes readily exchange in the presence of D_2[12] and deuterated olefins.[13,14] Moreover, reactions between each of the $M^+(D_2O)_n$ cluster ions and H_2O in the second quadrupole proceed *exclusively* by water ligand substitution *without* H/D scrambling. Thus, the observed reactivity of the metal hydrates is inconsistent with insertion-type structures.[15]



$$M^+(D_2O)_n + H_2O \longrightarrow \begin{cases} M^+(D_2O)_{n-1}(H_2O) + D_2O \\ \not\longrightarrow M^+(D_2O)_{n-1}(HOD) + HOD \end{cases}$$

The third and most likely origin of the unusual solvation energy orderings is the nature of the bonding between H_2O and NH_3 molecules and the transition-metal ions. Since purely electrostatic models cannot possibly account for the observed trends, then variations in the electronic configuration of the metal ions must play an important role.[16] Moreover, the visible aberrations in the correlation between the water and ammonia binding energies (Figure 2) suggest that the observed effects are a function of not only the metal but the ligand as well. In view of the many low-lying electronic states in atomic transition metal ions[17] and the likelihood of variable mixtures of s, p, and d bonding to H_2O and NH_3 ligands by the different metals,[18] large basis MCSCF calculations will undoubtedly be necessary to account for these unusual solvation energy trends.

Acknowledgment. This work was supported by the National Science Foundation (CHE-8815502). R.R.S. thanks the Alfred P. Sloan Foundation for a fellowship. We are grateful to Prof. J. Michl and Dr. T. Magnera for communication of their results in advance of publication.

Registry No. V^{1+}, 14782-33-3; Cr^{1+}, 14067-03-9; Mn^{1+}, 14127-69-6; Fe^{1+}, 14067-02-8; Co^{1+}, 16610-75-6; Ni^{1+}, 14903-34-5; NH_3, 7664-41-7; H_2O, 7732-18-5.

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(15) Inserted structures are not necessarily ruled out, however, since a mobile equilibrium between $M^+(H_2O)$ and $H—M^+—OH$ isomers could exist and still give the same results with the chemical probes.

(16) Dative bonding interactions are proposed to account for the large decrease between the second and third water and ammonia binding energies of Ag^+ and Cu^+, cf. ref 8.

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Highly Efficient Hydrolytic Cleavage of Adenosine Monophosphate Resulting in a Binuclear Co(III) Complex with a Novel Doubly Bidentate μ^4-Phosphato Bridge

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Received January 13, 1989

Cobalt complexes of the type *cis*-$[(N_4)Co(OH_2)_2]^{3+}$ where N_4 is any tetraamine ligand have been used extensively by various research teams as ATPase models and phosphatase models. Most of the model studies have been focused on phosphate anhydrides[1] (e.g., adenosine triphosphate (ATP)) or phosphate monoesters with good leaving groups[2] (e.g., *p*-nitrophenyl phosphate). Unactivated phosphate monoesters (e.g., adenosine monophosphate (AMP), methyl phosphate) are much more resistant to hydrolysis.[3] Here we report on a novel mechanism for efficient hydrolytic cleavage of unactivated phosphate monoesters leading to the formation of a binuclear cobalt(III) complex with a doubly bidentate phosphato bridge.

Stirring 2 equiv of $[(trpn)Co(OH_2)_2]^{3+}$ with disodium salts of adenosine monophosphate (AMP) or hydroxyethyl phosphate in water at 25 °C for about 6 h gave the corresponding alcohol and $[((trpn)Co)_2PO_4]^{3+}$ (**2**, Scheme I) in quantitative yield.[4] The

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(4) Trpn: tris(aminopropyl)amine. Alcohol confirmed by ^1H NMR. Compound **2**: ^{31}P NMR, D_2O, (trimethylphosphate) δ 40.5 ppm. Anal. Calcd for $C_{18}H_{46}N_8Co_2O_4P{\cdot}3ClO_4$: C, 24.35; H, 5.45; N, 12.62; Cl, 11.98; P, 3.49. Found: C, 24.52; H, 5.38; N, 12.63; Cl, 12.12; P, 3.48. We are trying to obtain a crystal structure of **2**.

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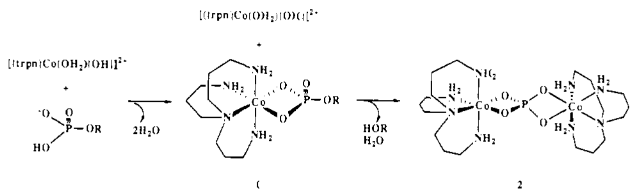
Scheme I



binuclear cobalt complex (**2**) could also be made from inorganic phosphate and $[(\mathrm{trpn})\mathrm{Co}(\mathrm{OH_2})_2]^{3+}$. In order to carry out a more detailed kinetics study, 1 equiv of $[(\mathrm{trpn})\mathrm{CO}(\mathrm{OH_2})_2]^{3+}$ was first added to the phosphate monoester (AMP or hydroxyethyl phosphate) solution. This resulted in immediate formation of a stable cobalt complex adduct of the phosphate monoester (**1**, Scheme I) in quantitative yield (Figure 1a).[5] Although **1** is stable in neutral water, it was rapidly hydrolyzed to **2** upon addition of $[(\mathrm{trpn})\mathrm{Co}(\mathrm{OH_2})(\mathrm{OH})]^{2+}$. The rate of formation of **2** increased linearly with amount of $[(\mathrm{trpn})\mathrm{Co}(\mathrm{OH_2})(\mathrm{OH})]^{2+}$ added. In a typical kinetics experiment, the hydrolysis reaction was initiated by addition of $[(\mathrm{trpn})\mathrm{Co}(\mathrm{OH_2})(\mathrm{OH})]^{2+}$ (1–4 equiv) to a solution of **1** (0.025 M) in D_2O (pD 5.0, 25 °C).[6] The progress of the reaction was monitored by following the increase in the ^{31}P NMR signal due to **2** and decrease in the ^{31}P NMR signal due to **1** (Figure 1) as well as increase in ^{1}H NMR signal due to the alcohol formation. The second-order rate constant for formation of **2** from **1** and $[(\mathrm{trpn})\mathrm{Co}(\mathrm{OH_2})(\mathrm{OH})]^{2+}$ is $3.6 \pm 0.5 \times 10^{-3}\ \mathrm{M^{-1}\ s^{-1}}$ when AMP is involved and $1.2 \pm 0.2 \times 10^{-2}\ \mathrm{M^{-1}\ s^{-1}}$ when hydroxyethyl phosphate is involved.

^{31}P NMR have been widely used to monitor various Co(III) complex promoted hydrolysis of ATP, diphosphate, and simple phosphate monoesters. The ^{31}P NMR signal of phosphates shifts progressively downfield with increase in the number of Co(III)–phosphate oxygen bonds.[7] Typically, phosphates with one, two, and three Co(III)–phosphate oxygen bonds have ^{31}P NMR chemical shifts at about δ 10, δ 20, and δ 30 ppm, respectively, relative to trimethyl phosphate.[7] In general, addition of $[(\mathrm{N_4})\mathrm{Co}(\mathrm{OH_2})_2]^{3+}$ to a phosphate solution generates many new ^{31}P NMR signals due to the formation of a variety of Co(III)–phosphate complexes.[7,8] Surprisingly, the ^{31}P NMR spectrum is elegantly simple when $[(\mathrm{trpn})\mathrm{Co}(\mathrm{OH_2})_2]^{3+}$ is added to phosphate monoesters (Figure 1). Addition of 1 equiv of $[(\mathrm{trpn})\mathrm{Co}(\mathrm{OH_2})_2]^{3+}$ to AMP gave only one ^{31}P NMR signal (**1**, δ 18.5 ppm) corresponding to a phosphate with two Co(III)–phosphate oxygen bonds (Figure 1a). Four-membered ring Co(III)–inorganic phosphate complexes have been observed previously.[9] Four-membered ring Co(III)–phosphate monoester complex had been reported once; however it was later shown to be a phosphate ester bridged dimer consisting of three ^{31}P NMR signals.[8] Addition of 2 equiv of $[(\mathrm{trpn})\mathrm{Co}(\mathrm{OH_2})_2]^{3+}$ to inorganic phosphate or phosphate monoesters gave only one major peak with the greatest ^{31}P NMR chemical shift reported to date (**2**, δ 40.5 ppm (Figure 1d)). The binuclear complex **2** represents the first case where all four phosphate oxygens are bound to the cobalt.

The mechanism of cobalt(III) complex promoted hydrolysis of *p*-nitrophenyl phosphate involves intramolecular metal–hydroxide attack on the metal coordinated phosphate monoester.[2] Addition of 1 equiv of $[(\mathrm{trpn})\mathrm{Co}(\mathrm{OH_2})(\mathrm{OH})]^{2+}$ to *p*-nitrophenyl phosphate in neutral water rapidly produced *p*-nitrophenol. In contrast, phosphate monoesters with poor leaving groups initially formed stable cobalt complexes (**1**) that subsequently hydrolyzed to **2** upon further addition of $[(\mathrm{trpn})\mathrm{Co}(\mathrm{OH_2})(\mathrm{OH})]^{2+}$. We propose that the mechanism of hydrolysis of **1** involves complexation of **1** to $[(\mathrm{trpn})\mathrm{Co}(\mathrm{OH_2})(\mathrm{OH})]^{2+}$ followed by cleavage of the ester bond (**3**). Cobalt(III) complex promoted hydrolysis of phosphate monoesters with good leaving groups[2] or phosphate diesters[10] involves a 1:1 complex between the metal and the substrate. In contrast, a 2:1 $[(\mathrm{trpn})\mathrm{Co}(\mathrm{OH_2})(\mathrm{OH})]^{2+}$ to substrate ratio is observed for the hydrolysis of phosphate monoesters with poor leaving groups. Cobalt(III) complex promoted hydrolysis of ATP also involves the formation of a 2:1 metal to substrate ratio.[2] However in the case of ATP hydrolysis, oxygen atoms from more than one phosphorus are bound to the metal.

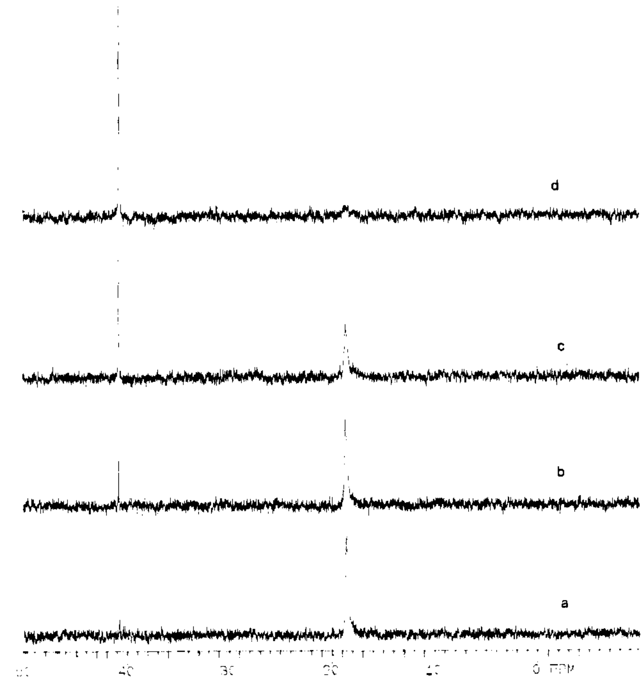
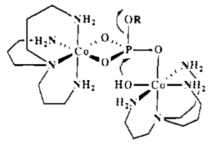


Figure 1. ^{31}P NMR of **1** (0.025 M) after adding $(\mathrm{trpn})\mathrm{Co}(\mathrm{OH})(\mathrm{OH_2})]^{2+}$ (0.075 M) pD 5.0, 25 °C. Elapsed time: (a) 0 min, (b) 10 min, (c) 40 min, (d) 240 min.



3

Interestingly, $[(\mathrm{tren})\mathrm{Co}(\mathrm{OH_2})(\mathrm{OH})]^{2+}$ did not hydrolyze phosphate monoesters with poor leaving groups under the same conditions used to hydrolyze the esters with $[(\mathrm{trpn})\mathrm{Co}(\mathrm{OH_2})(\mathrm{OH})]^{2+}$.[11] Furthermore, in contrast to the ease of formation of $[((\mathrm{trpn})\mathrm{Co})_2\mathrm{PO_4}]^{3+}$ (**2**), the corresponding cobalt complex with the tren ligand, $[((\mathrm{tren})\mathrm{Co})_2\mathrm{PO_4}]^{3+}$, could not be synthesized. Whereas addition of 2 equiv of $[(\mathrm{trpn})\mathrm{Co}(\mathrm{OH_2})_2]^{3+}$ to inorganic phosphate gave only one major ^{31}P NMR signal (δ 40.5 ppm), addition of 2 equiv of $[(\mathrm{tren})\mathrm{Co}(\mathrm{OH_2})_2]^{3+}$ to inorganic phosphate gave numerous ^{31}P NMR signals between δ 10 and δ 30 ppm. The contrast in the ^{31}P NMR is striking considering that the structures of $[(\mathrm{tren})\mathrm{Co}(\mathrm{OH_2})_2]^{3+}$ and $[(\mathrm{trpn})\mathrm{Co}(\mathrm{OH_2})_2]^{3+}$ are so closely related. Clearly, the stability of the spiro four-membered ring

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(5) ^{31}P NMR were taken on a Varian XL-300 spectrometer. Compound **1**: ^{31}P NMR, D_2O (trimethylphosphate) δ 18.5 ppm. Although **1** could not be isolated in pure form, the corresponding adduct with phenylphosphonate ($[(\mathrm{trpn})\mathrm{Co}(\mathrm{PO_3Ar})]^{+}$) was recrystallized in water and characterized: ^{31}P NMR, D_2O (phenylphosphonic acid) δ 25.86 ppm. Anal. Calcd for $C_{15}H_{29}N_4O_7ClCoP{\cdot}ClO_4{\cdot}H_2O$: C, 34.59; H, 6.00; N, 10.76; Cl, 6.81; P, 5.95. Found: C, 34.94; H, 6.02; N, 10.86; Cl, 6.48; P, 5.97.

(6) pD of the reaction solution decreased by less than 0.4 units during the course of the reaction. Buffers could not be used since they catalyze the dimerization of the cobalt complex.

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(11) Tren: tris(aminoethyl)amine.

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

In conclusion, we have shown that [(trpn)Co(OH_2)(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 [(trpn)Co(OH_2)(OH)]$^{2+}$ are highly sensitive to the tetraamine ligand structure.

Acknowledgment. We thank summer undergraduate student Normand Cloutier for his contributions in the preliminary stage of this project. This work was supported by the Natural Sciences and Engineering Research Council of Canada.

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Mixed-Valence, Conjugated Semiquinones

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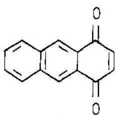
On inspection, the semiquinone **4**$^{\bullet-}$ is expected to have a delocalized π-electronic structure. Indeed, it has been shown that the three-ringed analogue **3**$^{\bullet-}$ is delocalized.[1] We now report evidence that **4**$^{\bullet-}$ and **5**$^{\bullet-}$ are not delocalized and propose 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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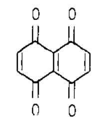
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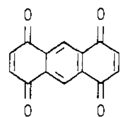
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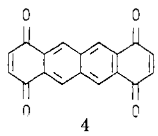
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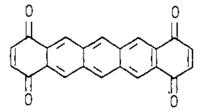
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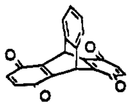
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The neutral quinones **1** and **2** were prepared using literature methods.[2,3] Quinones **3**–**5** were prepared as follows: **3** (**7**[5] plus benzoquinone and then Ce(NH_4)$_2$(NO_3)$_6$), **4** (see below), **5** (pyromellitic dianhydride plus hydroquinone[6] and then $NaBH_4$).

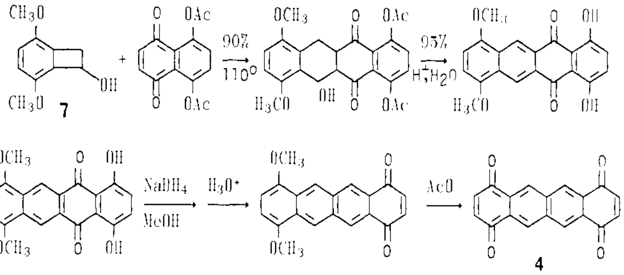

Table I. Electrochemical $E^{\circ\prime}$ and Computed Dipole Moments

compd	$-E^{\circ\prime}$[a] (V, SCE)	μ(D)[b]	μ(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 $Bu_4N(BF_4)$ at 100 mV 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).

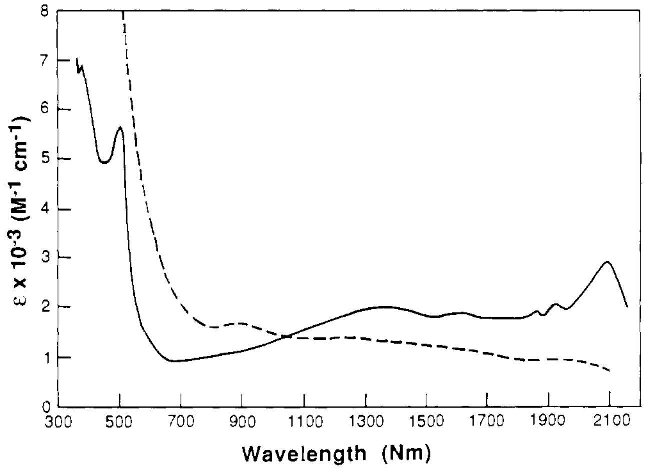

Figure 1. Vis NIR spectra of **4**$^{\bullet-}$ (—) and **5**$^{\bullet-}$ (– –) in DMF, $Bu_4N(BF_4)$.

The semiquinones were prepared electrochemically in DMF, 0.1 M $Bu_4N(BF_4)$ 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.

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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