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Reductive Addition of OH Radicals to Macrocyclic Complexes

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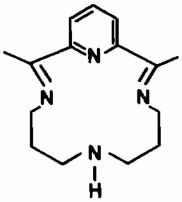
Abstract

The reactions of OH radicals with complexes of the macrocycle Me_2-3,4,5-pyo-[14]trieneN_4 and Cu(II), Co(II), Co(III) have been investigated by pulse radiolysis. The addition of the OH radical to the macrocycle leads to metal–ligand radical intermediates which achieve stability by reduction of the metal center. The mechanism of such reactions is discussed in terms of the redox potentials of the complexes and known mechanisms of addition to organic aromatic compounds.

Introduction

A considerable amount of work has dealt with reactions of radicals, *e.g.* OH, Cl_2^-, Br_2^-, $(SCN)_2^-$, and Ni(II) macrocyclic complexes [1–4]. In previous studies about the redox reactivity of Ni(Me_2-3,4,5-pyo-[14]trieneN_4)$^{2+}$ (I) [5]**, it has been established that OH radicals react with the ligand and the metal center [4]. The reaction at ligand sites produces reduced Ni(I) species while reaction at the metal center produces a Ni(III) complex. Since the large tendency of OH radicals to add to double bonds is well documented [6], the addition to the macrocycle must be a consequence of the extended π system in the ligand. Moreover, the formation of a Ni(I) center in such a reaction signals that, in this process, the complex must undergo a large electronic reorganization. Such a reorganization might be understood in terms of the aromatic character of the π system closed by the metal center. In this context, we have investigated the mechanism for the OH addition to the Me_2-3,4,5-pyo-[14]trieneN_4 ligand in complexes of Cu(II), Co(II), and Co(III).



I, Me_2-3,4,5-pyo-[14]trieneN_4

Experimental

Radiolytic Procedures

Optical pulse radiolysis measurements were made with a computerized system similar to that described earlier [1]. The apparatus makes use of the Notre Dame 10-MeV linear accelerator which has the capability of providing, at the limit, 5 ns pulses at currents of up to 7 A. Thiocyanate dosimetry was carried out at each session in order to calibrate the output signal of a secondary emission monitor against the concentration of $(SCN)_2^-$ generated in the radiolysis cell. Processes in the time domain of 3–200 ms were monitored with a quartz-halogen lamp while a Xe lamp, pulsed for less than 10 ms, was used for monitoring processes with lifetimes shorter than 3 ms.

Optical pulse radiolysis were carried out in N_2O saturated solutions in order to convert the hydrated electron to OH radicals via the reaction,

$$e_{aq}^- + N_2O \xrightarrow{H_2O} N_2 + OH^- + OH$$

Radicals Cl_2^- and Br_2^- were generated in acidic solutions by reactions of the OH radical with chloride and bromide ions respectively. Reactions of the hydrated electron were investigated in deaerated solutions containing various concentrations of methanol or 2-methyl-2-propanol for the removal of OH radicals.

Electrochemical Procedures

Cyclic voltammetric determinations were carried out in a Bioanalytical Systems apparatus with a glassy carbon working electrode and a reference calomel electrode. The solutions used for these experiments were deaerated with streams of O_2 free-nitrogen. Standard reduction potentials were calculated from the cathodic, E_c, and anodic, E_a, potentials according to the relationship, $(E_c + E_a)/2$, and these potentials, E_c and E_a, were estimated from the corresponding potentials for the maximum diffusion current, E_p, and half the maximum diffusion current, $E_{p/2}$, from the relationship, $(E_{p/2} + E_p)/2$ [7].

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**Abbreviations for ligands follow published rules.

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Extended Huckel Calculations

Some MO calculations were carried out with a WOLFS program whose features have been extensively described by Zener and Gouterman [8–11]. For Cu(II) macrocycles, the reported 3d, 4s, and 4p VOIE values gave energies for the electronic transitions which, in comparison with experimental data, were too large. There was a better agreement between the experimental results of optical and ESR spectra and calculated values for the energies of electronic transitions and g-values when -18.9 eV and -8.73 were respectively used for the VOIE of 3d orbitals. Such values were obtained as linear extrapolations from plots of the known first row transition metal VOIE energies *vs.* nuclear charge [9–11]. The correctness of these MO calculations was judged from the agreement between calculated and experimental values of electronic transition energies and ESR g-values in a series of Ni(II) and Cu(II) complexes of the NH_3, Me_6-[14]aneN_4, Me_6-[14]-4,11-dieneN_4, Me_2-3,4,5-pyo-[14]trieneN_4, and phthalocyanine ligands [12]. A good agreement between calculated and experimental spectral data for these series of compounds was obtained in extended Huckel calculations with the Forticon 8 program, QCPE Program No. 344, based on Hoffman's work [13, 14]. In these calculations with double ζ-expanded radial d functions, the nondiagonal terms, H_{ij}, were expressed as weighted functions of the corresponding diagonal terms, H_{jj} and H_{ii}, and literature values of the VOIE were used for the diagonal elements [14].

Materials

Literature procedures were used for the synthesis of $[Co^{II}(Me_2\text{-}3,4,5\text{-pyo-}[14]\text{triene}N_4)](ClO_4)_2$ [15], $[Co^{III}(Me_2\text{-}3,4,5\text{-pyo-}[14]\text{triene}N_4)(H_2O)_2](ClO_4)_3$ [16], and $[Cu^{II}(Me_2\text{-}3,4,5\text{-pyo-}[14]\text{triene}N_4)](ClO_4)_2$ [17]. These complexes were recrystallized several times by the addition of 5 M $NaClO_4$. Two further recrystallizations were carried out from distilled water. The infrared and UV–Vis spectra agreed well with literature reports [12, 15–17].

Acetonitrile was zone distilled in an all glass apparatus with a fractionating column corresponding to 70 theoretical plates. Other materials were reagent grade and were used without further purification.

Results

The complexes of Me_2-3,4,5-pyo-[14]trieneN_4 react with OH radicals in a manner that is dictated by the metal center. Our observations on the reactivity of the Cu(II), Co(II), and Co(III) complexes and the corresponding reaction intermediates are described below while rate constants for the corresponding OH reactions are reported in Table I.

(1) $Cu^{II}(Me_2\text{-}3,4,5\text{-pyo-}[14]\text{triene}N_4)^{2+}$

The reaction of OH radicals with 10–3 $Cu^{II}(Me_2\text{-}3,4,5\text{-pyo-}[14]\text{triene}N_4)^{2+}$ in acidic solutions ($6.5 > pH > 4.0$) gives rise to transient spectra, Fig. 1, which at times shorter than 1.2 μs present an intense absorption band ($\lambda_{max} \sim 350$ nm) that is typical of

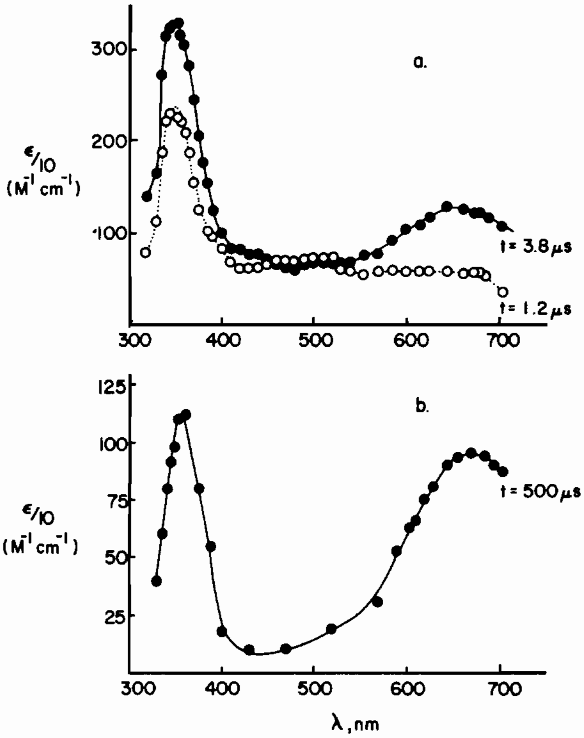

Fig. 1. Transient spectra following pulse radiolysis of 10^{-3} M $Cu(Me_2\text{-}3,4,5\text{-pyo-}[14]\text{triene}N_4)^{2+}$ solutions at pH 4.5: (a) N_2O saturated solutions and (b) N_2 saturated.

TABLE I. Rate Constants for Reactions of OH Radicals with Pyridynium Ions and Me_2-3,4,5-pyo-[14]trieneN_4 Complexes

Substrate	k_1 $(10^9, M^{-1} s^{-1})^a$	k_2 $(10^5, s^{-1})^a$	Conditions^b
Pyridynium ions	0.020 [18]		
$Co(Me_2\text{-}3,4,5\text{-pyo-}[14]\text{triene}N_4)(OH_2)_2{}^{3+}$	1.2		
$Cu(Me_2\text{-}3,4,5\text{-pyo-}[14]\text{triene}N_4)^{2+}$	3.5	6.3	pH = 3.5, 4.5
$Ni(Me_2\text{-}3,4,5\text{-pyo-}[14]\text{triene}N_4)^{2+}$	4.5 [4]		$3.5 \geqslant pH \geqslant 7$
$Co(Me_2\text{-}3,4,5\text{-pyo-}[14]\text{triene}N_4)^{2+}$	11.0	1.1	

[a] Rate constant for the formation of the radical adduct, k_1, and the intramolecular reduction of the metal center, k_2. [b] Determined at pH = 4.0 and ionic strength, I = 0.1 M $NaClO_4$, except where noted.

TABLE II. Selected Redox Potentials of Me_2-3,4,5-pyo-[14]trieneN$_4$ Complexes

Metal center	$E_{1/2}$ (V)[a]	Δ (V)[b]	Solvent (electrolyte)
Cu(II)	−0.275	0.065	MeOH (0.1 M $NaClO_4$)
	−0.269	0.074	MeCN (0.1 M $NaClO_4$)
	−0.249	0.062	MeOH (0.05 M Et_4NClO_4)[c,d]
Co(II)	0.534	0.065	H_2O (0.1 M $HClO_4$)
	0.509	0.115	H_2O (0.1 M $NaClO_4$)
	∼−0.53	0.20	
	∼0.50	0.38	MeOH (0.1 M $NaClO_4$)
	−0.407	0.085	
	0.682	0.176	MeCN (0.1 M $NaClO_4$)[e]
	−0.534	0.088	
	0.570	0.087	H_2O (0.1 M $HClO_4$)
Ni(II)	1.532	0.076	MeCN (0.1 M $NaClO_4$)[e]
	−0.434	0.055	
	−0.980	0.061	

[a] $E_{1/2}$ *vs.* NHE; a GCE working electrode was used in all cases except where noted. [b] $\Delta = |E_a - E_c|$ or the slope of $\log(i/i_d - i)$ *vs.* $-E$ [7]. [c] HMDE working electrode. [d] Values from ref. 17. [e] Pt working electrode.

pyridine–OH radical adducts [18, 19]. Further spectral changes, namely an increase in the intensity of the 350 nm band and the appearance of a new absorption band with $\lambda_{max} \sim 650$ nm, take place after the reaction between OH and $Cu^{II}(Me_2$-3,4,5-pyo-[14]trieneN$_4)^{2+}$ has ended, *i.e.* at times longer than 1.2 μs. Such a process obeys a first order kinetics, $k = 6.5 \times 10^5$ s^{-1} at pH 4.5, and yields a difference in spectrum which, at the end of the reaction, bears a strong resemblance with the spectrum of the $Cu^{I}(Me_2$-3,4,5-pyo-[14]trieneN$_4)^{+}$ produced by radiolytic, Fig. 1b, or photolytic procedures [20]. Despite the spectral similarities between the products of the reactions with OH and e_{aq}^-, their respective stabilities are considerably different. Indeed the $Cu^{I}(Me_2$-3,4,5-pyo-[14]trieneN$_4)^{+}$ obtained in the absence of oxidants, e.g. O_2, is stable at pH > 3 while the Cu(I) species generated with OH is unstable and disappears with a first order kinetics, $k = 1.6 \times 10^3$ s^{-1}, independent of acid concentration in a pH range, $4 < pH < 7$. Continuous radiolysis of $Cu^{II}(Me_2$-3,4,5-pyo-[14]trieneN$_4)^{2+}$ in acidic solutions, pH 4, saturated with N_2O reveal the formation of free copper ions as a reaction product.

Despite the reactivity shown by OH radicals, the halide anion radicals, Cl_2^- or Br_2^-, proved to be unreactive toward $Cu^{II}(Me_2$-3,4,5-pyo-[14]trieneN$_4)^{2+}$ as expected from the highly unfavorable electrochemical potential that seems to be required for the oxidation of the complex, Table II.

(2) $Co^{III}(Me_2$-3,4,5-pyo-[14]trieneN$_4)(H_2O)_2^{3+}$

The transient spectra generated when OH radicals react with $Co^{III}(Me_2$-3,4,5-pyo-[14]trieneN$_4)(H_2O)_2^{3+}$ in acidic solutions has some of the features of the $Co^{II}(Me_2$-3,4,5-pyo-[14]trieneN$_4)^{2+}$ spectrum, Fig. 2. The species generated in this reaction is considerable stable, $t_{1/2} > 1.0$ s, in the absence of O_2.

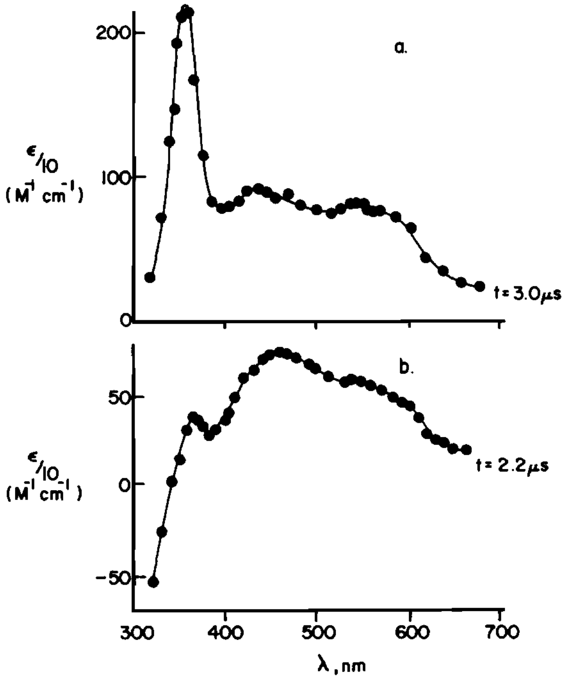

Fig. 2. Transients following pulse radiolysis of 10^{-3} M $Co(Me_2$-3,4,5-pyo-[14]trieneN$_4)(OH_2)_2^{3+}$ at pH 5.0: (a) N_2O saturated and (b) N_2 saturated solutions.

(3) $Co^{II}(Me_2$-3,4,5-pyo-[14]trieneN$_4)^{2+}$

The reaction of $Co^{II}(Me_2$-3,4,5-pyo-[14]-trieneN$_4)^{2+}$ with OH radicals generates transient spectra which at long times bear a strong resemblance

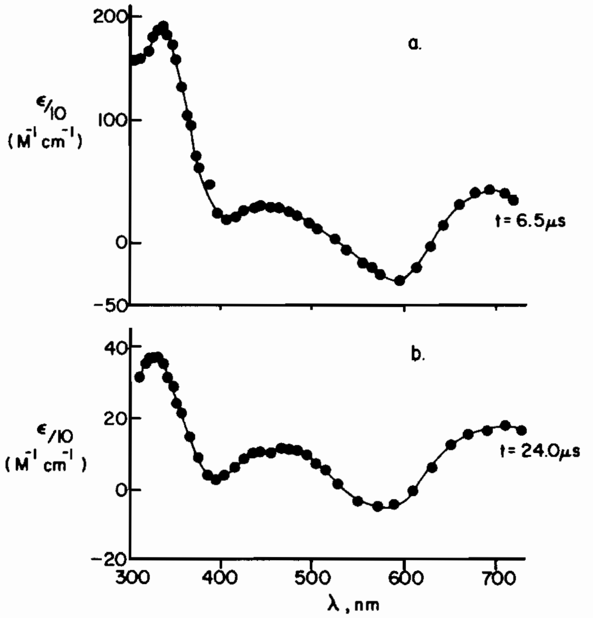

Fig. 3. Pulse radiolysis of 10^{-3} M Co(Me_2-3,4,5-pyo-[14]-trieneN_4)$^{2+}$ in (a) N_2O and (b) N_2 saturated solutions.

with the spectrum obtained in the reduction of the same complex with solvated electrons, Fig. 3. However, the species produced by the solvated electron, probably a Co(I) complex, is considerably more stable, $t_{1/2} \geqslant 20$ ms, than the species generated with OH radicals, *i.e.* $t_{1/2} \leqslant 1$ ms, in solutions containing excess Co(II) complex and an initial concentration of radicals, [OH] ~ 10^{-5} M. The spectra determined after the decay of the Co(I) intermediates suggests the formation of Co(III) macrocycles [4]*.

Discussion

In the reaction of OH with Me_2-3,4,5-pyo-[14]-trieneN_4 complexes of Cu(II) and Co(III), the OH radicals react with the macrocyclic ligand without a competitive oxidation of the metal center; a behavior that departs from the reported for related macrocycles. Such a lack of reactivity at the metal center can be related to the large negative potentials that are associated with the oxidation of Cu(II) and Co(III) in Me_2-3,4,5-pyo-[14]trieneN_4 complexes. Indeed, couples with less negative potentials, e.g. for the oxidation of Ni(II) to Ni(III), undergo parallel transformations at the metal center and the ligand. It is also possible that the short life of the OH radicals may also prevent them from reacting at the metal center when axial positions are insufficiently labile, e.g. in Co(III) complexes, for oxidations that, as in the case of Ni(II) macrocycles, must proceed through an inner sphere mechanism [1–3].

According to the known reactivity of the OH radical with organic unsaturated molecules, the abstraction of hydrogen or electrons from the macrocycle and the addition to aromatic rings represent three possible modes of reaction. One can, however, dismiss the electron abstraction in the Me_2-3,4,5-pyo-[14]trieneN_4 complexes of Cu(II) and Co(III) since such a reaction is expected to have a small driving force. Indeed, the potentials determined by cyclic voltammetry, Table II, and the lack of reactivity toward Cl_2^- and Br_2^- show that the removal of an electron from the HOMO is a highly endoergonic process requiring more than 1.5 V. Such observation is in agreement with MO calculations which, in addition, show that the HOMO has mixed character with a large contribution, *ca.* 60% character, from the d metal orbital, while the occupied ligand centered orbitals, *i.e.* with *ca.* 100% ligand character, are placed at lower energies than the HOMO. Moreover, values of the standard free energy for the abstraction of hydrogen, estimated from either the binding energies of the reactants and products and/or thermochemical data, show that such a reaction must be exoergonic by less than −10 kJ; a value that is incompatible with the fast reaction rates that were experimentally determined for such reactions. By contrast, the known mechanism of association of OH radicals to aromatic compounds can be expected to be largely exoergonic, *ca.* −64.2 kJ [19, 20].** Henceforth, provided that OH radicals add to the macrocyclic ligand, it is possible to find several positions where such an addition takes place.† The results presented above suggest that the largest fraction of the OH radicals react at the pyridine site, and that the

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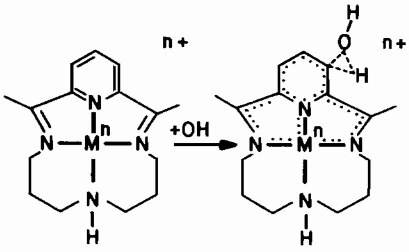
*An uncertain reaction stoichiometry prevented an accurate determination of the reaction rate constants.

For the overall reaction, Cu^{II}(Me_2-3,4,5-pyo-[14]triene-N_4)$^{2+}$ + OH → **III + H^+, we have estimated a free energy of reaction of *ca.* −138 kJ/mol by considering that the reduction of Cu^{II}(Me_2-3,4,5-pyo-[14]trieneN_4) to Cu^I(Me_2-3,4,5-pyo-[14]trieneN_4)$^+$ and the dissociation of a C–H bond from the pyridine ring of Cu^I(Me_2-3,4,5-pyo-[14]trieneN_4)$^+$ are endoergonic by 26.7 kJ/mol and 411.7 kJ/mol respectively while the formation of a C–O bond, *i.e.* in the OH addition to the dehydrogenated Cu(I)–ligand radical complex, is exoergonic in −356.7 kJ/mol. For the step corresponding to the formation of the species **II**, MO calculations for an OH adduct with a three center orbital show that such a species is more stable than the reactants, Cu^{II}(Me_2-3,4,5-pyo-[14]-trieneN_4)$^{2+}$ + OH, by *ca.* 90 kJ/mol. This result leads to the conclusion that the formation of the adduct (**II**), must be exoergonic by *ca.* −64.2 kJ/mol and the formation of Cu(I) product (**III**) from the adduct must liberate *ca.* 74 kJ/mol.

†Although the OH radical might attack in several positions of the aromatic ring, e.g. positions numbered 15 through 17 in **I**, for the sake of simplicity only reaction at position 15 is considered in the following equations.

spectral transformations observed with complexes of Cu(II) and Co(III) are the result of the reductive addition initiated by the attachment of the OH radical to the ligand.

In the reaction of OH radicals with $Cu^{II}(Me_2$-3,4,5-pyo-[14]triene$N_4)^{2+}$, the first step, Fig. 1 and eqn. (1), can be assigned to the formation of the OH adduct (**II**), while the second step can be related to the reorganization of such an adduct into a more stable Cu(I) complex, Fig. 1 and eqn. (2). Thermochemical data suggest that the second step, eqn. (2), must be as exoergonic as is required by the observed reaction rates. Moreover, the fast rate of OH addition to $Cu^{II}(Me_2$-3,4,5-pyo-[14]triene$N_4)^{2+}$, *i.e.* with respect to the rate of addition to pyridinium ions, signals that the metal center does not function with the same efficiency of the proton (in pyridinium ions) withdrawing electronic density from the aromatic π-system. This reduction on the electron withdrawing character of the metal center can probably be associated with an intrinsic back electronic donation from filled d(π)-metal orbitals.

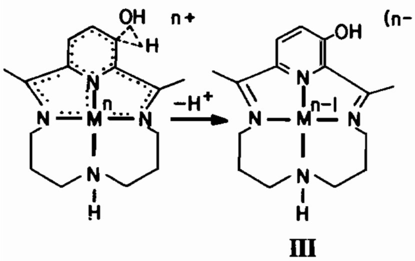


(1)

II

($M^n = Cu^{II}, Co^{II}, Co^{III}$)

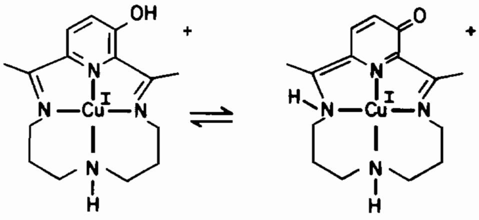
The mechanism proposed above can also explain the results obtained in the reaction OH radicals with $Co^{III}(Me_2$-3,4,5-pyo-[14]triene$N_4)(H_2O)_2{}^{3+}$ or Co^{II}-$(Me_2$-3,4.5-pyo-[14]triene$N_4)^{2+}$. In this regard, the spectrum in Fig. 2 can be associated with the addition of OH to the macrocycle, *i.e.* to the formation of a species similar to the intermediate **III** of the OH reaction with $Cu^{II}(Me_2$-3,4,5-pyo-[14]triene$N_4)^{2+}$, eqn. (2).



(2)

III

The rapid decay of the Cu(I) intermediate **III**, eqn. (2), stands in contrast, however, with stability shown by the similar complex of Co(III) and $Cu^{I}(Me_2$-3,4,5-pyo-[14]triene$N_4)^{+}$, and exhibits a rate that is inconsistent with the known rates reported for the demetallation of macrocycles [20, 21, 22]. The detection of free copper ions suggests that copper is liberated through a process that involves the hydrolytic degradation of the ligand [23]. In this regard, the reactivity of these species can be attributed to differences between Me_2-3,4,5-pyo-[14]-trieneN_4 and the ligand in **III** and to intrinsical metal effects. Indeed, it must be noticed that these hydroxo derivatives can exist as isomers with a quinonic structure, **IV** in eqn. (3), which are expected to be largely reactive toward hydrolysis. Metals that favor structures with a folded ligand, e.g. Cu(I), must stabilize such quinonic moieties and present, therefore, a large tendency to decompose.



(3)

IV

The reactions described above emphasize that the chemical reactivity of the Me_2-3,4,5-pyo-[14]-trieneN_4 complexes is in many aspects similar to the reactivity of organic aromatic compounds [24]. In this regard, the existence of some aromatic character in complexes of such a ligand can be assessed from experimental data, e.g. ESR spectra, and theoretical calculations. For example, the ESR spectra of the $Cu^{II}(Me_2$-3,4,5-pyo-[14]triene$N_4)^{2+}$ [25], and the Cu(phthalocyanine) [26], show similar features which, in case of the phthalocyanine, have been equated with the existence of a strong out-of-plane π-bonding that includes d(π) orbitals of the metal center. Such electronic delocalization is expected to exist also in the radical intermediates described above and determine, to a certain extent, their reactivity.

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