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Reactivity of Nickel(I) and Copper(I) Complexes Containing 14-Membered Macrocyclic Ligands in Aqueous Solution¹

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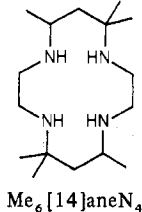
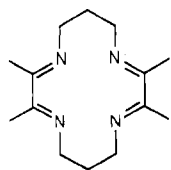
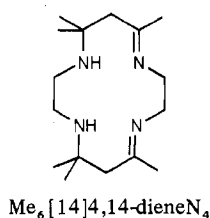
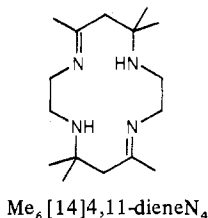
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The fast kinetics technique of pulse radiolysis has been used to generate and characterize, in aqueous solution, Ni(I) and Cu(I) complexes containing the tetradentate 14-membered macrocyclic ligands 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (\equiv 4,11-dieneN₄) and 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (\equiv aneN₄). Reduction of the corresponding divalent metal complexes by e_{aq}^- , H atoms, and CO_2^- radicals generates the M(I) species ($k = 10^8$ – $10^{10} M^{-1} s^{-1}$); $(CH_3)_2CO^-$ and $\cdot CH_2O^-$ radicals reduce $Cu^{II}(4,11\text{-diene}N_4)$ ($k = 9 \times 10^8 M^{-1} s^{-1}$). $Ni^{II}(4,11\text{-diene}N_4)$, $Ni^{II}(\text{ane}N_4)$, and $Cu^{II}(4,11\text{-diene}N_4)$ show intense absorption band maxima at 460 (ϵ 3900 $M^{-1} cm^{-1}$), 380 (ϵ 5150 $M^{-1} cm^{-1}$), and 410 nm (ϵ 4610 $M^{-1} cm^{-1}$), respectively. The decay kinetics of these species have been studied as a function of pH and in the presence of scavenging solutes. The M(I) complexes behave as bases, reacting with H_3O^+ , CH_3CO_2H , and $H_2PO_4^-$. They are also good reducing agents, transferring an electron to a variety of organic acceptors and one-electron oxidants such as cobalt(III)-, chromium(III)-, ruthenium(III)-, and iron(III)-amine-, -bipyridyl, and -macrocyclic ligand complexes. The M(I) complexes react rapidly with CH_3I , N_2O , and O_2 . In the latter reaction, the Ni(I) species produce O_2^- in solution, while the Cu(I) complex does not and appears to react with O_2 via an addition mechanism.

Introduction

Nickel(I) and copper(I) complexes containing the macrocyclic ligands 4,11-dieneN₄ and aneN₄³ are stable in CH_3CN solutions^{4,5} and have been isolated as solids from CH_3CN and other aprotic solvents.^{6–8} These low-valent macrocyclic species are short-lived in aqueous solution and reactive toward proton donor solutes.^{9,10} However, the details of their behavior in aqueous solution have not been resolved. Because of the instability of these species in water, fast kinetics techniques must be employed for their generation and characterization. Recently, we demonstrated¹¹ the use of pulse radiolysis to generate $Co^I(4,11\text{-diene}N_4)$, $Co^I(4,14\text{-diene}N_4)$, and $Co^I(1,3,8,10\text{-tetraene}N_4)$ by the reaction of the hydrated electron, e_{aq}^- , and other reducing radicals, such as CO_2^- and $(CH_3)_2COH$, with the corresponding Co(II) macrocyclic complexes. The low-valent Co(I) species were found to be powerful reducing agents, reacting rapidly with a variety of organic and metal complex oxidants. They also behave as bases, reacting with proton donors such as H_3O^+ , CH_3CO_2H , NH_4^+ , and H_2O .



In this paper we describe the generation of $Ni^I(4,11\text{-diene}N_4)$, $Ni^I(\text{ane}N_4)$, and $Cu^I(4,11\text{-diene}N_4)$ by the action of e_{aq}^- and reducing radicals on the corresponding divalent complexes and the reactivity of these low-valent species in aqueous solution.

Experimental Section

Preparation of Complexes. $[Ni(N\text{-rac-}(4,11\text{-diene}N_4))](ClO_4)_2$ ^{12,13} and $[Cu(N\text{-rac-}(4,11\text{-diene}N_4))](ClO_4)_2$ ¹⁰ were prepared by the

addition of the free ligand to the metal acetate in methanol as described in the literature. The free ligand salt was prepared from acetone and the monohydroperchlorate salt of ethylenediamine after the method of Curtis.¹⁴ $[Ni(C\text{-ms-}(\text{ane}N_4))](ClO_4)_2$ was prepared from nickel acetate and the free ligand in methanol solutions containing perchlorate.^{12,13,15} The free ligand was obtained by sodium borohydride reduction of $(4,11\text{-diene}N_4)(HClO_4)_2$ in methanol.^{13,16}

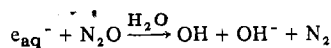
The other complexes were available from our laboratory reserves. The sample of $Cr(bpy)_3^{3+}$ was supplied to us by Professor J. F. Endicott (Wayne State University) and the $Ru(III)$ complexes were supplied by Professor J. N. Armor (Boston University).

Apparatus and Techniques. The pulse radiolysis apparatus with kinetics spectrophotometry has already been described in detail.^{17,18} Single pulses of 2.3-MeV electrons of ~ 30 -ns duration were generated (Febetron 705) and absorbed by the solution contained in a quartz cell with an optical path of 2 cm. Glass filters and a synchronized shutter were used to minimize the photolytic effects of the monitoring light.

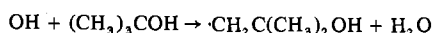
The pH of the solutions was adjusted by the use of $HClO_4$, KOH , phosphate (1 mM), or tetraborate (1 mM) buffer, except as otherwise indicated. Solutions were prepared from the solid just prior to use and were deoxygenated (except where indicated) by an Ar purge or saturated with N_2O at 1 atm partial pressure ($2.5 \times 10^{-2} M$). Extinction coefficients were evaluated by means of SCN^- dosimetry taking $\epsilon_{500} 7.6 \times 10^3 M^{-1} cm^{-1}$ for the $(SCN)_2^-$ radical.¹⁹ Rate constants with error limits of $\pm 10\%$ were determined by a least-squares computer fit of the kinetics data to the usual first- and second-order equations. In all cases, the spectra of the transient species produced initially were corrected for the equivalent amount of substrate destroyed in the pulse.

Results and Discussion

The radiolysis of water and aqueous solutions can be represented by $H_2O \rightarrow e_{aq}^-$ (2.8), OH (2.8), H (0.55), where the numbers in parentheses represent the G values (number of radicals formed per 100 eV of energy absorbed by the solvent). The hydrated electron, e_{aq}^- , is a powerful reducing agent ($E^\circ_{ox} = 2.8 V$)²⁰ and can be scavenged rapidly ($k = 8.7 \times 10^9 M^{-1} s^{-1}$)²¹ by N_2O , i.e.



In acidic solution, e_{aq}^- species are effectively ($k = 2.2 \times 10^{10} M^{-1} s^{-1}$)²¹ converted into H atoms. The scavenging of OH radicals by *tert*-butyl alcohol ($k = 5.2 \times 10^8 M^{-1} s^{-1}$)²² generates a relatively inert and weakly absorbing radical¹⁷



Scavenging by HCO_2^- and 2-propanol generates ($k = 2.5 \times 10^8$ and $1.3 \times 10^9 M^{-1} s^{-1}$, respectively)²² the strongly reducing

Table I. Rate Constants for the Reaction of Reducing Radicals with Divalent Nickel and Copper Macrocyclic Complexes

Reductant, R	pH of expt	$k(\text{M(II)} + \text{R}), \text{M}^{-1} \text{s}^{-1}$		
		Ni ^{II} (4,11-dieneN ₄)	Ni ^{II} (aneN ₄)	Cu ^{II} (4,11-dieneN ₄)
e _{aq} ⁻ ^a	6-10	7.8×10^{10}	5.6×10^{10}	5.0×10^{10}
CO ₂ ⁻ ^b	7.0	6.7×10^9	5.7×10^9	2.3×10^9
H ^c	1.0	8.7×10^8	3.2×10^8	$>5 \times 10^9$
(CH ₃) ₂ CO ^{-d}	12.5			9.0×10^8
·CH ₂ O ^{-e}	12.0			9.0×10^8

^a Determined in the presence of $(1.25-2.5) \times 10^{-5}$ M M(II), 1 M *tert*-butyl alcohol, and 1 mM phosphate or tetraborate buffer in Ar-purged solutions; monitored at 700 nm. ^b Determined in the presence of $(2-5) \times 10^{-4}$ M M(II), 0.1 M HCO₂⁻, and 1 mM phosphate buffer in Ar-purged solutions; monitored at λ_{max} of M(I). ^c Determined in the presence of 1×10^{-3} M M(II) and 1 M *tert*-butyl alcohol in Ar-purged solutions; monitored at λ_{max} of M(I). ^d Determined in the presence of 1×10^{-3} M M(II), in Ar-purged solutions containing 1 M 2-propanol; monitored at λ_{max} of M(I). ^e Determined in the presence of 1×10^{-3} M M(II) in Ar-purged solutions containing 1 M CH₃OH; monitored at λ_{max} of M(I).

CO₂⁻ and (CH₃)₂COH radicals. Hydrogen atoms are also scavenged by HCO₂⁻ and 2-propanol ($k = 2.5 \times 10^8$ and $5.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, respectively)²³ to yield the above named reducing radicals. Thus, by the judicious choice of scavenger solute, a selected radical species can be made the principal reactant in solution. The secondary reactions of the radicals with the metal complex solutes can be observed using the fast kinetics technique of pulse radiolysis with absorption spectrophotometry (time resolution $\sim 0.1 \mu\text{s}$).

The macrocyclic complexes used in this study are known to exist in a number of isomeric modifications.^{15,24} Briefly, isomerism in the Ni^{II}(4,11-dieneN₄) and Cu^{II}(4,11-dieneN₄) systems is due to the presence of two asymmetric secondary amine nitrogens, N-meso or N-racemic, corresponding to the two amine protons being on the same or opposite sides of the N₄-coordination plane, respectively. The reaction of nickel acetate with (4,11-dieneN₄)(HClO₄)₂ produces only the pure N-racemic isomer,¹² whereas the analogous reaction with copper acetate produces a mixture of the N-racemic (80%) and N-meso (20%) isomers.¹⁰ The racemic and meso isomers are interconvertible in solution, the rate of hydrogen exchange depending upon pH and temperature. Extensive work on the Ni system²⁵ has shown that both isomers retain their configuration at pH < 2 whereas dissolution of either pure isomer in neutral aqueous solution leads to the same equilibrium mixture. Little is known about the copper system but it is likely that similar changes occur in solution.

Isomerism in the Ni^{II}(aneN₄) system is due to the presence of two asymmetric carbon atoms (noninterconvertible C-meso and C-racemic) and the four asymmetric coordinated secondary amine nitrogens.²⁶ However, no evidence for the existence of diastereoisomers relating to N-H inversion has been found for the C-meso isomer in aqueous solution, the observed N-H configurations being retained over a wide pH range.

Reactions of the Divalent Metal Complexes. With e_{aq}⁻. The rate constants for the reaction of e_{aq}⁻ with the Ni(II) and Cu(II) complexes were determined from the pseudo-first-order decay of e_{aq}⁻ monitored at 700 nm (Table I). Reduction of these square-planar complexes occurs at diffusion-controlled rates, similar to those found for the analogous Co(II) and Co(III) complexes.^{11,27} The rates are independent of pH (6-10) suggesting that there is no dependence of reactivity with e_{aq}⁻ on changes in the isomeric composition (racemic ↔ meso) for the 4,11-dieneN₄ complexes. The electrochemistry of these complexes in acetonitrile solution is also independent of the type of isomer present.⁶

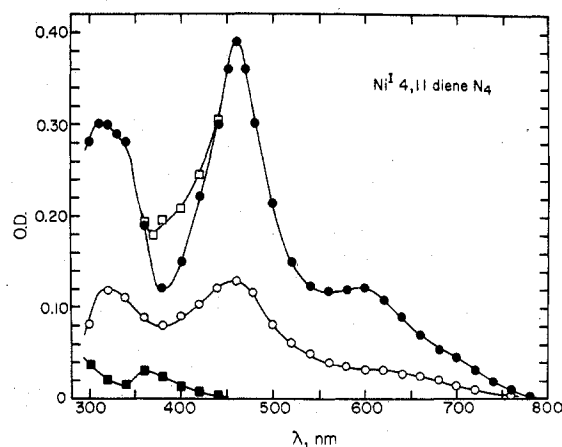


Figure 1. Absorption spectra generated from the reaction of e_{aq}⁻ with Ni^{II}(4,11-dieneN₄) in Ar-purged solutions containing 1 M *tert*-butyl alcohol and 1 mM phosphate buffer at pH 7.0. Spectra recorded at the following times after the pulse: $\sim 0.1 \mu\text{s}$, ●; 30 μs , ○; 400 μs , □; 20 s, ■. The same initial transient spectrum is also produced upon the reaction of the Ni(II) substrate with H atoms at pH 1.0 or with CO₂⁻ radicals at pH 7.0.

With CO₂⁻ and (CH₃)₂COH Radicals. In Ar-purged solutions containing HCO₂⁻ at pH 7.0, the reactive species are e_{aq}⁻ ($G = 2.8$) and CO₂⁻ radicals ($G = 3.4$). In the presence of M(II) complex, the reaction of e_{aq}⁻ to form the M(I) species (see following section) is very fast ($t_{1/2} \approx 10^{-7}$ s) occurring within the time resolution of the apparatus. The slower reaction of CO₂⁻ with M(II) can be discerned from the formation kinetics of the additional M(I) absorption. The rate constants for these reactions are given in Table I. They are of the same magnitude shown by Co^{II}(1,3,8,10-tetraeneN₄)¹¹ and Co(III) complexes containing macrocyclic²⁷ and aromatic²⁸ ligands. In contrast, under identical conditions, no reaction with CO₂⁻ was observed for Co^{II}(4,11-dieneN₄);¹¹ this latter compound has a more negative reduction potential (measured in CH₃CN) than the Ni(II) and Cu(II) complexes.⁶⁻⁸

No formation of any M(I) absorption from the reaction of (CH₃)₂COH radicals with the Ni(II) or Cu(II) complexes ($(3-4) \times 10^{-4}$ M) could be discerned. Under similar circumstances we had observed¹¹ that the (CH₃)₂COH radical reduces Co^{II}(1,3,8,10-tetraeneN₄) ($k = 5.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) but not the Co^{II}(dieneN₄) complexes.

With H Atoms. The formation of the absorption of M(I) was observed under conditions where H atoms are the only reactive radicals (Table I). In the case of the copper complex, the value of k is only a lower limit inasmuch as the spectrum of the Cu(I) species was formed within the time resolution of the apparatus. A slower formation rate achieved by using a lower concentration of complex interfered with the initial rapid spectral changes shown by the Cu(I) in acidic solution. Inasmuch as the reaction of H with Ni^{II}(aneN₄) has a rate constant that is similar to that of the other complexes containing unsaturated ligands and k is significantly higher than that shown by reaction of H atoms with saturated hydrocarbons,²³ the conclusion can be drawn that H atom attack does not occur at a macrocyclic ligand site. The direct rapid formation of M(I) suggests that the reaction occurs via highly energetic electron transfer; E°_{ox} for H = 2.1 V.²⁹ The M(I) and H⁺ products would be expected to diffuse apart rather than back-react in the solvent cage because of the extremely high mobility of H⁺: $\text{M(II)} + \text{H} \rightarrow \text{M(I)} + \text{H}^+$.

Spectra and Decay Kinetics of the Reduced Species. Ni^I(4,11-dieneN₄). The reaction of e_{aq}⁻, CO₂⁻ radicals, or H atoms with Ni^{II}(4,11-dieneN₄), either as the pure racemic isomer (pH 1) or as a mixture of isomers (neutral solution),

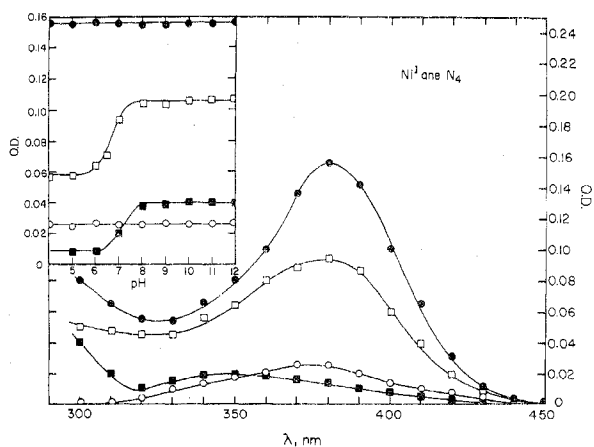


Figure 2. Absorption spectra generated from the reaction of e_{aq}^- with $Ni^{II}(\text{ane}N_4)$ in Ar-purged solutions containing 1 M *tert*-butyl alcohol and 1 mM phosphate buffer at pH 7.0. Spectra recorded at the following times after the pulse: $\sim 0.1 \mu\text{s}$, \bullet ; 600 μs , \blacksquare ; 20 ms, \circ ; 20 s, \square . The same initial transient spectrum is also produced upon reaction of the Ni(II) substrate with H atoms at pH 1.0 or with CO_2^- radicals at pH 7.0. Insert: dependence of the spectral absorbance on pH; monitoring wavelength 380 nm for \bullet , \square , and \circ and 350 nm for \blacksquare .

produces the identical initial transient spectrum, independent of pH (1–10), shown in Figure 1. The initial transient spectrum is in good agreement with the spectrum of $Ni^{II}(\text{4,11-diene}N_4)$ obtained electrochemically in CH_3CN .^{6,9} The spectral bands are considered to be charge transfer in nature with the one at 460 nm arising from a metal–ligand transition involving the azomethine (C=N) group.^{6,9,10}

The decay of the transient absorbance was very complex and wavelength dependent (Figure 1). The spectral changes observed in the 360–400-nm region were not observed when $Ni^{II}(\text{4,11-diene}N_4)$ reacted with H atoms at pH 1. This observation suggests that these spectral changes may be due to changes in the equilibrium isomeric composition of the Ni(I) species inasmuch as the Ni(II) substrate exists purely in the racemic form at pH 1 and presumably would produce racemic Ni(I) species upon reduction. On the other hand, the neutral aqueous solution contains about 17% meso isomer with the exact composition of the solution varying with pH.²⁵ Olson and Vasilevskis⁶ have suggested that there are larger conformational differences between the Ni(I) isomers than between those of Ni(II). Hence, the equilibrium isomeric composition of the Ni(I) substrate may be different from that of the Ni(II) substrate from which it is derived, possibly accounting for some of the small spectral changes observed.

$Ni^{II}(\text{ane}N_4)$. The reaction of e_{aq}^- , CO_2^- radicals, or H atoms with $Ni^{II}(\text{ane}N_4)$, in its C-meso isomeric form, produced the identical initial transient absorption independent of pH (Figure 2). This spectrum is almost identical with that of $Ni^{II}(\text{ane}N_4)$ generated electrochemically in CH_3CN .⁶ At pH 7.0, using e_{aq}^- as the reducing species, a series of spectral changes with associated complex kinetics was observed. The insert of Figure 2 shows the changes in absorbance experienced by the various intermediates and the final product as a function of pH.

$\text{Cu}^{II}(\text{4,11-diene}N_4)$. The reaction of e_{aq}^- (in the presence of *tert*-butyl alcohol or 2-propanol) and CO_2^- with $\text{Cu}^{II}(\text{4,11-diene}N_4)$ at pH 7.0 produces the identical initial transient absorption with a band at 410 nm (ϵ 4610 $\text{M}^{-1} \text{cm}^{-1}$) shown in Figure 3. The spectrum is very similar to that of the Cu(I) species produced electrochemically in CH_3CN .⁸ At pH ≥ 7.0 , the initial absorbance from the e_{aq}^- reduction in *tert*-butyl alcohol decayed in an apparently stepwise manner producing subsequent transient absorptions and a final absorption spectrum. All of the transient species and the final absorption showed a spectral maximum at ~ 410 nm. Some of the species

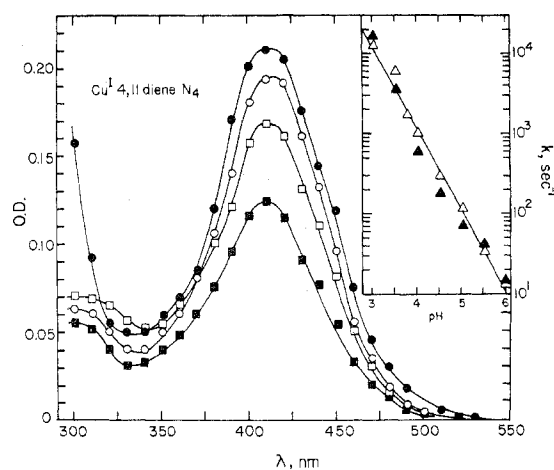


Figure 3. Absorption spectra generated from the reaction of e_{aq}^- with $\text{Cu}^{II}(\text{4,11-diene}N_4)$ in Ar-purged solutions containing 1 M *tert*-butyl alcohol and 1 mM phosphate buffer at pH 7.0. Spectra recorded at the following times after the pulse: $\sim 0.1 \mu\text{s}$, \bullet ; 8 μs , \circ ; 6 ms, \square ; 20 s, \blacksquare . The same initial transient spectra are also produced upon reaction of the Cu(II) substrate with CO_2^- radicals at pH 7.0. Insert: dependence on pH of the first-order rate constant for the decay of T_2 in the presence of 1 M *tert*-butyl alcohol (\blacktriangle) and 1 M 2-propanol (\triangle).

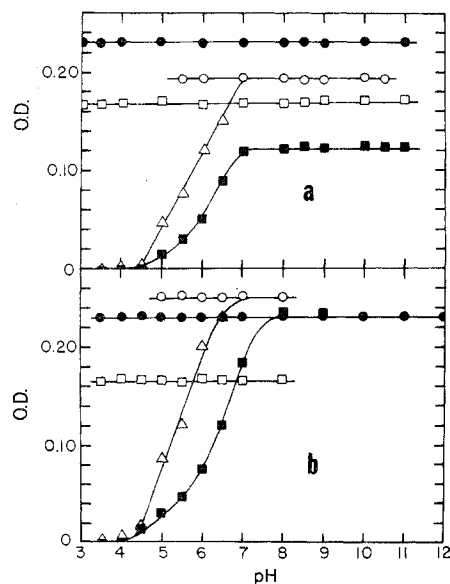


Figure 4. (a) Dependence on pH of the absorbance of the transient spectra generated from the reaction of e_{aq}^- with $\text{Cu}^{II}(\text{4,11-diene}N_4)$ in Ar-purged solution containing 1 M *tert*-butyl alcohol. Spectra monitored at 410 nm and recorded at the following times after the pulse: $\sim 0.1 \mu\text{s}$, \bullet ; 8 μs , \circ ; 6 ms, \square ; 0.4 s, \triangle ; 20 s, \blacksquare . (b) The same as part (a) except the solution contained 1 M 2-propanol instead of *tert*-butyl alcohol.

showed acid–base behavior as evidenced by the variation of absorbance as a function of pH (Figure 4a). At pH < 1 , with H atoms as the reactive radical, only the initial species was observed decaying via reaction with H_3O^+ to produce a final product which did not show any absorption at 410 nm.

Experiments were conducted on Ar-purged solutions containing 1 M 2-propanol as an OH and H scavenger so the e_{aq}^- was the only effective reducing agent. In the presence of 2-propanol at pH < 8.0 , the same initial (T_1) and secondary (T_2) absorbances and their decay kinetics were observed as seen in the presence of *tert*-butyl alcohol (insert to Figure 3 and Figure 4b). At pH > 8 , the initial absorbance increased with increasing pH until at pH > 13 the absorbance was twice that at pH < 8 . In addition, this incremental absorbance was

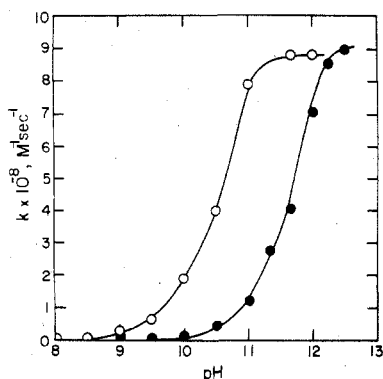
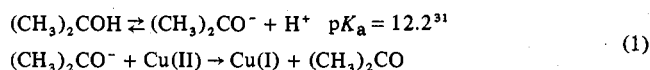


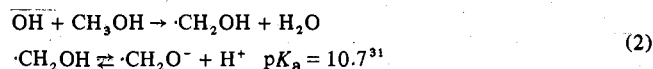
Figure 5. Dependence on pH of the rate constants for the reactions of $(\text{CH}_3)_2\text{COH}$ or $(\text{CH}_3)_2\text{CO}^\bullet$ radicals (\bullet) and $\cdot\text{CH}_2\text{OH}$ or $\cdot\text{CH}_2\text{O}^\bullet$ radicals (\circ) with $\text{Cu}^{\text{II}}(4,11\text{-dieneN}_4)$ in Ar-purged solutions containing 1 M 2-propanol or 1 M methanol.

accompanied by the formation of T_1 via pseudo-first-order kinetics (Figure 5). The conclusion must be made that although $(\text{CH}_3)_2\text{COH}$ is unable to reduce $\text{Cu}(\text{II})$ to $\text{Cu}(\text{I})$, the conjugate base of the radical, $(\text{CH}_3)_2\text{CO}^\bullet$, being a stronger reducing agent,³⁰ is capable of that reaction.



As the solution is made more basic, the extent of deprotonation of the radical increases, the amount of T_1 increases, and the rate at which reaction 1 occurs increases. Thus, the dependence of k_1 on pH in Figure 5 follows the equilibrium involving the radical.

A similar effect was seen in solutions containing 1 M CH_3OH as an OH scavenger with $k_2 = 5.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.²²



In neutral solution, no $\text{Cu}(\text{I})$ could be detected from the reaction of $\cdot\text{CH}_2\text{OH}$ with $\text{Cu}(\text{II})$. However, in more basic solution, $\text{Cu}(\text{I})$ appeared due to reaction 3 and the rate

$$\cdot\text{CH}_2\text{O}^\bullet + \text{Cu}(\text{II}) \rightarrow \text{Cu}(\text{I}) + \text{CH}_2\text{O} \quad (3)$$

constant increased to a plateau value (Figure 5). From these data, the values of k_1 and $k_3 \approx 9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ are obtained. Reactions corresponding to (1) and (3) were not observed in the $\text{Ni}(\text{II})$ systems.

The $\text{Cu}^{\text{I}}(4,11\text{-dieneN}_4)$ system is characterized by the fact that all transient species and the final product (at $\text{pH} > 4$) have extremely similar absorption spectra with λ_{max} 410 nm. This suggests that the various intermediates can be designed as $\text{Cu}(\text{I})$ species with their spectral and kinetic properties attributable to differences in molecular geometry or isomeric composition. The $\text{Cu}(\text{I})$ complex may be susceptible to axial coordination by water, proton donors, radiation-generated species, or the alcohol solute, all of which may affect its spectral and kinetic properties.

Reactions of the $\text{M}(\text{I})$ Species. Although the natural decays of the $\text{M}(\text{I})$ species are complex and the detailed structure of each observed transient intermediate cannot be ascertained by the pulse radiolysis technique, the reactivity of the initially produced $\text{M}(\text{I})$ species toward scavenger solutes can be examined if the rate of the $\text{M}(\text{I})$ -scavenger reaction is greater than that of the natural disappearance of the $\text{M}(\text{I})$ species. Scavenger solutes were added to the solutions so that the disappearance of the absorption attributable to the initial $\text{M}(\text{I})$ species occurred via pseudo-first-order kinetics; concentrations of solutes and $\text{M}(\text{II})$ substrates were adjusted so that the predominant reaction of e_{aq}^- or other reducing radicals was with $\text{M}(\text{II})$.

Table II. Rate Constants for the Reaction of $\text{M}(\text{I})$ with Proton Donors

Proton donor, HX	pH of expt	$k(\text{M}(\text{I}) + \text{HX}),^a \text{ M}^{-1} \text{ s}^{-1}$		
		$\text{Ni}^{\text{I}}(4,11\text{-dieneN}_4)$	$\text{Ni}^{\text{I}}(\text{aneN}_4)$	$\text{Cu}^{\text{I}}(4,11\text{-dieneN}_4)$
H_3O^+ ^b	0.5–1.25	1.3×10^6	1.1×10^5	5.0×10^6
$\text{CH}_3\text{CO}_2\text{H}^c$	4.85	1.9×10^5	1.2×10^4	$< 10^4$
H_2PO_4^- ^d	5.50	2.4×10^5	$< 10^4$	$< 10^4$

^a Determined in Ar-purged solutions containing $3 \times 10^{-3} \text{ M}$ $\text{M}(\text{II})$ and 1 M *tert*-butyl alcohol; monitored at λ_{max} of $\text{M}(\text{I})$.
^b Ionic strength range 0.06–0.3 M. ^c $[\text{CH}_3\text{CO}_2\text{H}] = [\text{CH}_3\text{CO}_2^-] = (0.5\text{--}5) \times 10^{-2} \text{ M}$; ionic strength range 0.015–0.06 M. ^d $[\text{H}_2\text{-PO}_4^-] = (1\text{--}10) \times 10^{-2} \text{ M}$; ionic strength range 0.01–0.1 M.

Table III. Rate Constants for the Reaction of $\text{M}(\text{I})$ with Organic Electron Acceptors

Compd A	$k(\text{M}(\text{I}) + \text{A}),^a \text{ M}^{-1} \text{ s}^{-1}$		
	$\text{Ni}^{\text{I}}(4,11\text{-dieneN}_4)$	$\text{Ni}^{\text{I}}(\text{aneN}_4)$	$\text{Cu}^{\text{I}}(4,11\text{-dieneN}_4)$
<i>p</i> -Benzoquinone	3.8×10^9	4.8×10^9	2.6×10^9
9,10-Anthraquinone-2,6-disulfonate	5.0×10^9	4.8×10^9	4.3×10^9
9,10-Anthraquinone-2-sulfonate	<i>b</i>	<i>b</i>	1.1×10^9
Eosin Y	2.7×10^9	<i>b</i>	<i>c</i>
Fluorescein	3.3×10^9	3.2×10^9	<i>c</i>
3-Benzoylpyridine	7.5×10^8	2.5×10^8	<i>c</i>

^a Determined in Ar-purged solutions at pH 7.0 containing $1 \times 10^{-3} \text{ M}$ $\text{M}(\text{II})$, $(2.5\text{--}5) \times 10^{-5} \text{ M}$ A, 1 M *tert*-butyl alcohol, and 1 mM phosphate buffer; ionic strength 0.004 M. ^b Value not determined. ^c No observed reaction.

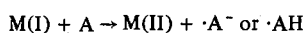
With Acids. Generation of the $\text{M}(\text{I})$ species by reaction of H atoms with $\text{M}(\text{II})$ in Ar-purged solutions at $\text{pH} < 1.25$ resulted in the rapid decay of $\text{M}(\text{I})$ with a pseudo-first-order rate constant that depended linearly on $[\text{H}_3\text{O}^+]$. The resulting second-order rate constants are given in Table II. Similarly, the rate constants for the reaction of $\text{M}(\text{I})$ with $\text{CH}_3\text{CO}_2\text{H}$ and H_2PO_4^- , determined at pH 4.85 and 5.50, respectively, are also shown in Table II. Upper limits can only be given for $k < 10^4 \text{ M}^{-1} \text{ s}^{-1}$ because of the slowness of these scavenger reactions.

The rate constants for the reaction of $\text{Ni}(\text{I})$ and $\text{Cu}(\text{I})$ species with proton donors are 3–4 orders of the magnitude lower than those of $\text{Co}^{\text{I}}(4,11\text{-dieneN}_4)$ and are of the same order as those of $\text{Co}^{\text{I}}(1,3,8,10\text{-tetraeneN}_4)$.¹¹ The fact that proton transfer takes place to a complex containing a fully saturated macrocyclic ligand would seem to rule out proton attack on the imine functional groups as a requirement for this reaction. The $\text{Ni}(\text{I})$ and $\text{Cu}(\text{I})$ species appear to be much weaker bases than their $\text{Co}(\text{I})$ analogue. Proton transfer to the metal center could generate hydrido complexes which have been proposed as intermediates or products in other metal systems;³² stable hydriocobaloximes and $\text{Co}^{\text{III}}(\text{CN})_5\text{H}^{3-}$ have been isolated as solids.³³



Further pulse radiolytic characterization of the products of the reaction of the low-valent complexes with proton donors was not attempted because of the low final absorbances of the solutions at $\lambda > 350 \text{ nm}$.

With Organic Electron Acceptors. The kinetics of the reaction of $\text{M}(\text{I})$ with organic acceptors (A) were determined by monitoring the decay of $\text{M}(\text{I})$, the disappearance of A, or the formation of the reduced species ($\cdot\text{A}^-$ or $\cdot\text{AH}$) at a suitable wavelength.³⁴ The observed rate constants are given in Table



III, which show the $\text{M}(\text{I})$ species to be facile reducing agents toward these acceptors.

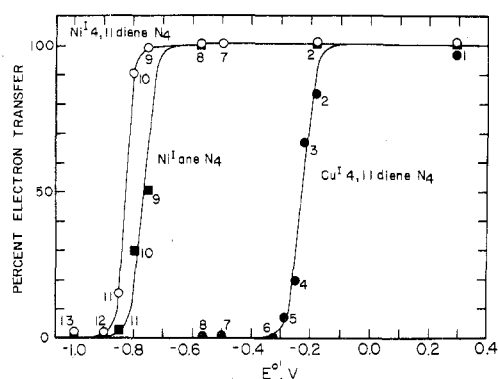


Figure 6. Dependence of the efficiency of electron transfer (expressed as percent) in the reaction of M(I) with organic electron acceptors as a function of the standard reduction potential of the acceptors at pH 7.0 (E°). Solutions were Ar purged and contained 1 M *tert*-butyl alcohol and 1 mM phosphate buffer. Acceptors used: 1, *p*-benzoquinone; 2, 9,10-anthraquinone-2,6-disulfonate; 3, 9,10-anthraquinone-2-sulfonate; 4, phenosafranine; 5, safranin T; 6, neutral red; 7, eosin Y; 8, fluorescein; 9, 3-benzoylpyridine; 10, *p*-cyanoacetophenone; 11, 4,4'-bipyridine; 12, benzalacetone; 13, benzophenone. Experimental conditions are given in Table III for $\text{Ni}^{\text{I}}(4,11\text{-dieneN}_4)$ (○), $\text{Ni}^{\text{I}}(\text{aneN}_4)$ (□), and $\text{Cu}^{\text{I}}(4,11\text{-dieneN}_4)$ (●).

The extent of electron transfer from M(I) to A was determined by comparing the quantitative absorbance due to $\cdot\text{A}^-$ formed from the reaction of M(I) with A with that obtained directly from the very rapid reaction of e_{aq}^- with A.³⁴ Figure 6 shows the percent of electron transfer as a function of the known standard two-electron reduction potentials of A at pH 7.0, E° . The apparent oxidation potentials of M(I) at pH 7, evaluated from the midpoint of the "titration" curve, are +0.83, +0.75, and +0.23 V for $\text{Ni}^{\text{I}}(4,11\text{-dieneN}_4)$, $\text{Ni}^{\text{I}}(\text{aneN}_4)$, and $\text{Cu}^{\text{I}}(4,11\text{-dieneN}_4)$, respectively.

The reaction of M(I) with A is not reversible under these experimental conditions and the $\cdot\text{A}^-$ radicals undergo irreversible bimolecular decay.^{34a,b} In addition, the reduction potentials used for the acceptors are two-electron potentials so that the apparent oxidation potentials for the M(I) species differ from the thermodynamic potential.^{34f} In our work with Co(I) complexes,¹¹ we obtained apparent oxidation potentials for $\text{Co}^{\text{I}}(4,11\text{-dieneN}_4)$ and $\text{Co}^{\text{I}}(1,3,8,10\text{-tetraeneN}_4)$ of +0.86 and +0.28 V, respectively. These latter potentials are to be compared with literature E°_{ox} values of +0.7 and +0.48 V, respectively.³⁵

With Metal Complexes. The M(I) species were generated by the reaction of e_{aq}^- with the corresponding M(II) complex in the presence of metal ion oxidant. Under the experimental conditions, >80% of e_{aq}^- reacted with the M(II) substrates with the remainder reacting directly with the M(III) complexes. However, low doses of e_{aq}^- ($<2 \times 10^{-5}$ M) were used so that loss of M(III) via reaction with e_{aq}^- was not significant. M(I) decayed via pseudo-first-order kinetics from which, for two to four different oxidant concentrations, the second-order rate constants given in Table IV were calculated. Upper limits are given in the cases where the maximum concentration of M(III) used did not produce enhanced decay of M(I).

The rate constants for the Ni(I) complexes are very similar to those of $\text{Co}^{\text{I}}(1,3,8,10\text{-tetraeneN}_4)$.¹¹ These sets of complexes also show similar redox properties. On the other hand, the values of k given in Table IV, measured at low and constant ionic strength, do not correlate with the known E° values of the metal complex acceptors; the same apparent lack of correlation was noted for Co(I).¹¹ The highest reactivity is shown by the bipyridyl complexes where involvement of the ligand orbitals in the necessarily outer-sphere electron-transfer process may occur; the behavior of $\text{Fe}(\text{bpy})_3^{3+}$, with its highly

Table IV. Rate Constants for the Reaction of M(I) with Trivalent Metal Complexes

Compd S	$k(\text{M(I)} + \text{S}),^a \text{M}^{-1} \text{s}^{-1}$		
	$\text{Ni}^{\text{I}}(4,11\text{-dieneN}_4)$	$\text{Ni}^{\text{I}}(\text{aneN}_4)$	$\text{Cu}^{\text{I}}(4,11\text{-dieneN}_4)$
$\text{Co}(\text{bpy})_3^{3+}$	1.3×10^9	1.3×10^9	1.2×10^7
$\text{Cr}(\text{bpy})_3^{3+}$	1.1×10^8	7.7×10^8	3.7×10^6
$\text{Fe}(\text{bpy})_3^{3+}$	2.2×10^6	6.4×10^7	$<10^3$
$\text{Ru}(\text{NH}_3)_6^{3+}$	4.5×10^8	3.8×10^8	7.2×10^4
$\text{Ru}(\text{NH}_3)_5\text{NO}^{3+}$	3.5×10^7	7.4×10^7	$<10^3$
$\text{Co}(\text{en})_3^{3+}$	1.1×10^6	1.1×10^5	$<10^3$
$\text{Co}(\text{NH}_3)_6^{3+}$	1.9×10^6	1.9×10^5	$<10^3$
$[\text{Co}(4,11\text{-dieneN}_4)(\text{OH}_2)_2\text{OH}]^{2+}$	2.6×10^6	1.1×10^6	$<10^3$
$[\text{Co}(1,3,8,10\text{-tetraeneN}_4)(\text{OH}_2)_2]^{+}$	3.6×10^7	1.7×10^7	$<10^3$

^a Determined in Ar-purged solutions at pH 7.0 containing $(2.5\text{--}5.0) \times 10^{-3}$ M M(II), 1 M *tert*-butyl alcohol, 1 mM phosphate buffer, and $(2.5\text{--}10) \times 10^{-4}$ M S; ionic strength range 0.016–0.028 M; monitored at λ_{max} of M(I).

Table V. Rate Constants for the Reaction of M(I) with O_2 , N_2O , and CH_3I

Compd S	$k(\text{M(I)} + \text{S}),^a \text{M}^{-1} \text{s}^{-1}$		
	$\text{Ni}^{\text{I}}(4,11\text{-dieneN}_4)$	$\text{Ni}^{\text{I}}(\text{aneN}_4)$	$\text{Cu}^{\text{I}}(4,11\text{-dieneN}_4)$
O_2^b	1.7×10^9	1.6×10^9	2.6×10^7
N_2O^c	1.8×10^7	3.9×10^7	1.7×10^6
CH_3I^d	1.3×10^8	4.6×10^8	3.1×10^6

^a Determined in solutions containing 3×10^{-3} M M(II), 1 mM phosphate or tetraborate buffer, and 1 M *tert*-butyl alcohol; ionic strength 0.01 M; monitored at λ_{max} of M(I). ^b $[\text{O}_2] = (7.5\text{--}25) \times 10^{-5}$ M; pH 7.0. ^c $[\text{N}_2\text{O}] = (7.5\text{--}25) \times 10^{-4}$ M; pH 7.0. ^d $[\text{CH}_3\text{I}] = (2.5\text{--}5.0) \times 10^{-4}$ M; pH 9.2.

positive reduction potential, is not easily rationalized. The cobalt(III)-amine and -macrocyclic ligand complexes have similar rates which are generally lower than those of the Ru(III) complexes. In evaluating the rate constants, it must be noted that the Co(III) macrocyclic complexes possess different redox potentials and different overall charges at pH 7.0 due to the deprotonation of the axial aquo ligands.³⁶

With O_2 , N_2O , and CH_3I . The rate constants for the reaction of CH_3I with M(I) are given in Table V. The values of k for the Ni(I) complexes are of the same magnitude as that of $\text{Co}^{\text{I}}(4,11\text{-dieneN}_4)$ ¹¹ and are 4 orders of magnitude larger than for the reaction of CH_3I with vitamin B₁₂s.³² The latter reaction, proposed to occur via an S_N2 mechanism, produces a Co–C bond. Hydrated Ni⁺ ions react with organic molecules to produce complexes containing a Ni–C bond³⁷ and such a mechanism may be operative here. Because of the high concentrations of M(II) used, we were unable to make spectral observations below 370 nm where the products of the reaction would be expected to absorb.

The decay of the M(I) absorption was monitored as a function of $[\text{N}_2\text{O}]$ from which the second-order rate constants given in Table V were obtained. The rate constants are similar to those found for Co(I) complexes¹¹ where the reaction is presumed to proceed via the simple two-electron reduction of N_2O to N_2 with the concomitant formation of Co(III). Again, the high concentrations of M(II) required to react with all e_{aq}^- did not make it possible to analyze spectrally for the products of this reaction.

The reaction of O_2 with M(I) was very rapid (Table V). The reaction can be viewed as proceeding via outer-sphere electron transfer ($\text{M}^{\text{I}} + \text{O}_2 \rightarrow \text{M}^{\text{II}} + \text{O}_2^-$) or addition ($\text{M}^{\text{I}} + \text{O}_2 \rightarrow [\text{M}^{\text{I}}\text{--O}_2] \leftrightarrow [\text{M}^{\text{II}}\text{--O}_2^-]$). Therefore, tests were performed to distinguish between these mechanisms. Although the optical spectrum of O_2^- is known,³⁸ its short-wavelength absorption and the high absorptivity of M(II) in the 250-nm

spectral region made direct observation impossible under the conditions given above. Instead, it is known that O₂⁻ reacts via electron transfer ($k = 5.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) with *p*-benzoquinone (BQ)^{39,40} to produce $\cdot\text{BQ}^-$ but does not react with menaquinone (MQ).^{34b,39} Experiments were performed using $7 \times 10^{-3} \text{ M M(II)}$, $1.3 \times 10^{-3} \text{ M O}_2$ (O₂ saturated at 1 atm), $3 \times 10^{-5} \text{ M BQ}$ or MQ, and 1 M *tert*-butyl alcohol buffered at pH 7.0. Under these conditions, all e_{aq}⁻ react with M(II) and none with O₂, BQ, or MQ. All OH react with alcohol and the resultant radical is rapidly scavenged by O₂ to give a peroxy radical that is not capable of reducing BQ or MQ. Any O₂⁻ generated by the reaction of M(I) with O₂ not scavenged by M(II) would produce $\cdot\text{BQ}^-$ but not $\cdot\text{MQ}^-$. For the two Ni(I) complexes, $\cdot\text{BQ}^-$ was observed and $\cdot\text{MQ}^-$ was not indicating that the reaction of Ni(I) with O₂ proceeds via the electron-transfer path generating O₂⁻. The results further demonstrate that any reaction of O₂⁻ with Ni(II) is not competitive and would have a rate constant of $<10^6 \text{ M}^{-1} \text{ s}^{-1}$.

The failure of the presence of free O₂⁻ to be detected in the reaction of the Cu(I) species with O₂ can be due to a Cu–O₂ addition reaction or to a competitive reaction of free O₂⁻ radicals with the Cu(II) substrate. O₂⁻ radicals reduce Cu²⁺ ($k = 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)⁴¹ in aqueous solution and Cu(phen)₂²⁺ in DMSO solution.⁴² We tested the Cu(II) + O₂⁻ reaction in an O₂-saturated solution containing $4 \times 10^{-5} \text{ M Cu(II)}$ and 1 M *tert*-butyl alcohol buffered at pH 7.2. Under such conditions, all e_{aq}⁻ are scavenged by O₂ to form O₂⁻ ($k = 2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).²¹ No depletion of Cu(II) at 300 nm nor formation of Cu(I) at 410 nm was observed. Absorption due to O₂⁻ was observed at 280 nm which did not diminish in intensity within 0.5 ms. The conclusion is drawn that for Cu^{II}(4,11-dieneN₄), $k(\text{Cu(II)} + \text{O}_2^-) < 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Therefore, reaction of O₂⁻ with Cu(II) would not be competitive with reaction of O₂⁻ with BQ. The failure to observe $\cdot\text{BQ}^-$ must indicate that the reaction of O₂ with the Cu(I) macrocyclic species proceeds via an addition mechanism. The final products of the reaction could not be determined by the pulse radiolytic technique.

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Registry No. Ni^{II}(4,11-dieneN₄), 15079-52-4; Ni^{II}(aneN₄), 47105-35-1; Cu^{II}(4,11-dieneN₄), 48186-22-7; CO₂, 14485-07-5; H, 12385-13-6; (CH₃)₂CO⁻, 17836-38-3; $\cdot\text{CH}_2\text{O}^-$, 27837-46-3; Ni^I(4,11-dieneN₄), 57719-35-4; Ni^I(aneN₄), 57719-34-3; Cu^I(4,11-dieneN₄), 57793-30-3; H₃O⁺, 13968-08-6; CH₃CO₂H, 64-19-7; H₂PO₄⁻, 14066-20-7; *p*-benzoquinone, 106-51-4; 9,10-anthraquinone-2,6-disulfonate, 84-50-4; 9,10-anthraquinone-2-sulfonate, 84-48-0; eosin Y, 548-26-5; fluorescein, 518-47-8; 3-benzoylpyridine, 5424-19-1; Co(bpy)₃³⁺, 19052-39-2; Cr(bpy)₃³⁺, 15276-15-0; Fe(bpy)₃³⁺, 18661-69-3; Ru(NH₃)₆³⁺, 18943-33-4; Ru(NH₃)₅NO³⁺, 37874-79-6; Co(en)₃³⁺, 14878-41-2; Co(NH₃)₆³⁺, 14695-95-5; [Co(4,11-dieneN₄)(OH₂)OH]²⁺, 33337-47-2; [Co(1,3,8,10-tetraeneN₄)(OH)₂]⁺, 57719-36-5; O₂, 7782-44-7; N₂O, 10024-97-2; CH₃I, 74-88-4; phenosafranin, 81-93-6; safranin T, 477-73-6; *p*-cyanoacetophenone, 1443-80-7; 4,4'-bipyridine, 553-26-4.

References and Notes

- (1) Presented in part at the XVIth International Conference on Coordination Chemistry, Dublin, Ireland, Aug 1974; see Abstracts, No. 3.44.

- (2) (a) Boston University. (b) U.S. Army Natick Laboratories.
- (3) The abbreviations used for the macrocyclic ligands are based on the suggestions of Busch and co-workers^{4,5} and will be used in their simplest form: 4,11-dieneN₄ ≡ Me₆[14]4,11-dieneN₄ = 5,7,7,12,14,14-hexamethyl-1,4,3,11-tetraazacyclotetradeca-4,11-diene; 4,14-dieneN₄ ≡ Me₆[14]4,14-dieneN₄ = 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene; aneN₄ ≡ Me₆[14]aneN₄ = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; 1,3,8,10-tetraeneN₄ ≡ Me₄[14]1,3,8,10-tetraeneN₄ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene.
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