

Syntheses and Characterization of Mn(III), Co(II), Zn(II) and Pd(II) Complexes of 5,7,12,14-Tetraphenyldibenzo[*b,i*][1,4,8,11]tetraaza[14]annulene: Electrochemical, Spectral Properties and the Effects of Axial Ligation

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Abstract

The syntheses and characterization of Co(II), Zn(II), Pd(II) and Mn(III) (with Cl^- as its counterion) complexes of the new ligand, 5,7,12,14-tetraphenyldibenzo[*b,i*][1,4,8,11]tetraaza[14]annulene, are reported. The UV–Vis spectra of the complexes along with a spectrometric titration of the Co(II) complex are presented. Cyclic voltammetry was used to determine the redox properties of these complexes. The results are compared to the analogous tetramethyltetraaza[14]annulene complexes. In addition, the effects of axial binding of F^- , CN^- , N_3^- and pyridine on the electrochemistry of Ni(II) and Cu(II) complexes of this new ligand were investigated. Both CN^- and N_3^- increased the oxidative current observed for the first oxidation wave. Pyridine increased the oxidative current observed for the second oxidation wave and decreased its reductive current on the reverse scan. A proposed EC mechanism between the complexes and the axial ligand was confirmed by a controlled oxidation of the Cu(II) complex at 0.90 V, followed by addition of N_3^- . A current increase was observed after the addition of N_3^- . The increase is due to reoxidation of the Cu(II) complex after the reduction by N_3^- . No current increase was observed for the addition of N_3^- in the absence of the Cu(II) complex. The Spin Hamiltonian parameters of the Co(II) complex as the O_2 adduct were determined. Various solvent systems (some containing axial ligands) were employed to compare their effects on the Spin Hamiltonian parameters of the Co(II) complex with the O_2 adduct. These results compared to similar Co(II) complexes show that the metal centers have approximately the same character even though the periphery is much different.

Introduction

A great deal of interest has focused on the study of transition element complexes of tetraazaannulenes

due to their ability to mimic some aspects of naturally occurring macrocycles [1] including some catalytic activity [2]. Many studies have been carried out in the hope of reproducing more closely the activities of metal sites present in biological systems [3]. The ultimate goal of these studies in our laboratories has been to develop a syn-enzyme which might be utilized in biological systems or in more demanding nonbiological systems as catalysts. For example, one area of particular interest has been cobalt(II) tetraazaannulenes [4] since they bind molecular oxygen [5], a property of the active metal sites in hemoglobin and myoglobin [6]. At the same time, the ability to bind small molecules other than oxygen has been of considerable interest [7], a prerequisite for innersphere oxidation or reduction [8, 9].

One area of electrochemical interest for these types of compounds is how electron transfer is effected by axial ligands. The effect of axial ligands on zinc(II) tetraphenylporphyrin films on SnO_2 electrodes has been investigated by Crouch and Langford [10]. They found when ZnTPP was 'doped' with pyridine, the rate of electron transfer is increased markedly. The rate constants reported for the SnO_2 –ZnTPP versus SnO_2 –ZnTPP 'doped' with pyridine were 9.10 and 11.8 ($\times 10^3 \text{ cm s}^{-1}$), respectively. The effect of various axial ligands on the cobalt(II) tetraaza[14]annulenes was first investigated by Pezeshk *et al.* [11, 12]. Their work clarified the effect of base strength of the axial ligand on the ESR magnetic parameters observed for the cobalt(II) tetraaza[14]annulenes. Lederman *et al.* [13] first reported the effect of axial bases on the ESR magnetic parameters of $[\text{Co}(\text{Me}_4\text{Bzo}_2[14]\text{-tetraeneN}_4)]\cdot\text{O}_2$. They also noted as the base strength increased, the isotropic splitting decreased as measured by electron spin resonance.

Recently we reported the synthesis of a new macrocyclic ligand (see Fig. 1) that both better mimics the hydrophobic nature of a biological metal containing system [14] and may allow for the ultimate utility of complexes *in vivo*. We have

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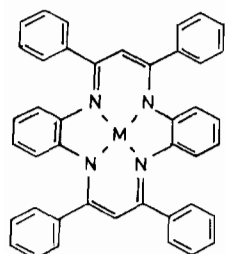


Fig. 1. $[M(\text{Ph}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]$.

extended the study of the properties of the 5,7,12,14-tetraphenyldibenzo[*b,i*][1,4,8,11]tetraaza[14]-annulene ligand by synthesizing various metal complexes. In order to more fully understand the potential catalytic properties of these metal complexes, we have also studied the effect of binding of various small molecules by examining the cyclic voltammograms of the Ni(II) and Cu(II) complexes. In addition, the effect of various ligands on the metal centers of these complexes was investigated by electron spin resonance spectroscopy.

Experimental

Materials

Tetraethylammonium perchlorate (TEAP) was purchased from Southwestern Chemicals, Inc., dried and used without further purification. Methylene chloride was purchased from Fisher Scientific. Gold label *N,N*-dimethylformamide, and all other chemicals were purchased from Aldrich Chemical Company. Solvents for electrochemistry were dried 48 h over 4A molecular sieves. Argon was obtained from National Welders Supply Company.

Physical Measurements

Electronic absorption spectra were obtained in methylene chloride solutions using matched 1 cm quartz cells and were recorded with a Cary 2300 spectrophotometer. ^1H NMR spectra were obtained in CDCl_3 employing a Varian EM-360 spectrometer. Elemental analyses were obtained from Atlantic Microlabs, Atlanta, GA, U.S.A.

Electrochemical properties were determined in methylene chloride or in *N,N*-dimethylformamide with 0.1 M tetraethylammonium perchlorate as the supporting electrolyte in conventional three compartment 'H' cells. Cyclic voltammograms were obtained using a BAS CV 27 potentiostat and recorded with a YEW Model 3022 A4 X-Y recorder. The measurements were made at a Bioanalytical System platinum electrode. Electrochemical potentials were recorded versus a saturated calomel electrode (SCE). Before use, the disk electrode was polished sequentially with 3, 1 and 0.25 μm diamond paste (Buehler) on a Buehler nylon disk followed by ultrasonic cleaning in deionized water (5 min) and in

gold label acetonitrile (5 min). Solutions were degassed for approximately 20 min with argon.

ESR spectra were recorded with a Varian E-3 spectrometer. The *g* values were measured relative to diphenylpicrylhydrazyl (DPPH), $g = 2.0036 \pm 0.0003$. The field sweep was calibrated utilizing the peak separation between the fourth and fifth lines of vanadyl acetylacetonate as 108.0 G ($g_{\text{apparent}} = 1.986$) [15].

ESR samples were prepared under anhydrous conditions in argon. The solid cobalt macrocyclic complex was dissolved in toluene, and varying amounts of substrate were added. The solution was transferred to a quartz ESR tube and the sample was degassed on a vacuum line using the usual freeze-pump-thaw method before the tube was sealed.

Syntheses

The macrocyclic ligand, $[\text{Ni}(\text{Ph}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]$ (an abbreviation for the nickel(II) complex of 5,7,12,14-tetraphenyldibenzo[*b,i*][1,4,8,11]tetraaza[14]annulene) and $[\text{Cu}(\text{Ph}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]$ were each prepared by modifying a procedure described by Hotz [16]. $[\text{Mn}(\text{III})(\text{Ph}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]\text{Cl}$ was prepared by modifying a procedure described for a general macrocyclic complex synthesis by Neves and Dabrowiak [17] starting with $\text{Mn}(\text{acac})_2\text{Cl}$ [18]. $[\text{Co}(\text{Ph}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]$ was prepared by modifying a general procedure described by Weiss and Goedken [19] starting with $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2$. $[\text{Zn}(\text{Ph}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]$ was prepared by modifying a procedure described in ref. 17 starting with $\text{Zn}(\text{SO}_3\text{CF}_3)_2$ [20]. $[\text{Pd}(\text{Ph}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]$ was prepared by a procedure described by Hochgesang and Bereman [21] starting with $\text{PdCl}_2(\text{CH}_3\text{SOCH}_3)_2$ [22]. The yields were between 30 and 50%.

$[\text{Mn}(\text{III})(\text{Ph}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]\text{Cl} \cdot \text{CH}_3\text{CN}$:
Anal. Calc. for $\text{C}_{44}\text{H}_{33}\text{N}_5\text{ClMn}$: C, 73.18; H, 4.61; N, 9.70. Found: C, 73.00; H, 4.67; N, 9.59%.

$[\text{Co}(\text{Ph}_4\text{Bzo}_2[14]\text{tetraeneN}_4)] \cdot \text{H}_2\text{O}$: *Anal.* Calc. for $\text{C}_{42}\text{H}_{32}\text{N}_4\text{OCo}$: C, 75.56; H, 4.83; N, 8.39. Found: C, 75.77; H, 4.75; N, 8.40%.

$[\text{Zn}(\text{Ph}_4\text{Bzo}_2[14]\text{tetraeneN}_4)] \cdot 1/2(\text{CH}_3\text{CH}_2)_3\text{N}$:
 ^1H (60 MHz, ppm): 0.77(amine, CH_3); 1.99(amine, CH_2); 5.40(2H, s); 6.30, 6.50(8H, m); 7.23, 7.39-(20H, m). *Anal.* Calc. for $\text{C}_{42}\text{H}_{30}\text{N}_4\text{Zn} \cdot 1/2\text{C}_6\text{H}_{15}\text{N}$: C, 76.48; H, 5.35; N, 8.92. Found: C, 76.55; H, 5.23; N, 8.80%.

$[\text{Pd}(\text{Ph}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]$: *Anal.* Calc. for $\text{C}_{42}\text{H}_{30}\text{N}_4\text{Pd}$: C, 58.86; H, 4.95; N, 12.48. Found: C, 58.67; H, 4.98; N, 12.42%.

Results and Discussion

Electronic Spectra

Absorption spectra of all complexes were examined in the 700 to 250 nm range and the results

TABLE 1. Electronic absorption bands for $[M(\text{Ph}_4\text{Bzo}_2[14]\text{-tetraeneN}_4)]$ complexes^{a, b}

M	Position (nm)	$\epsilon \times 10^{-4} (\text{cm}^{-1} \text{M}^{-1}) (\log \epsilon)$
Mn	526	0.562 (3.75)
	379	1.93 (4.29)
	338	1.95 (4.29)
	271	2.82 (4.45)
Co	625	0.172 (3.24)
	575	0.227 (3.36)
	440	0.741 (3.87)
	385	1.98 (4.30)
	267	3.17 (4.50)
Zn	427	1.33 (4.13)
	380	2.93 (4.47)
	271	3.20 (4.51)
Pd	520	1.80 (4.26)
	446	2.76 (4.44)
	437	2.75 (4.44)
	308(Sh)	2.15 (4.33)
	269	4.84 (4.58)

^aSpectra were obtained for 10^{-4} M solutions in methylene chloride. ^b $22 \pm 2^\circ\text{C}$; position ± 0.5 nm; ϵ , $\pm 1\%$.

are summarized in Table 1. There were three major absorptions in the spectra of each of the metal complexes and each can be assigned as a ligand to ligand charge-transfer band [23]. In addition, the manganese(III), cobalt(II) and palladium(II) complexes each have bands in the visible region which exhibit energies between 440–630 nm, with molar absorptivities as high as $2.7 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$. These molar absorptivities are also indicative of charge-transfer absorptions, likely ligand to metal [24]. In the case of the zinc(II) complex there were only three broad absorptions as expected for the d^{10} system. This observation further supports the suggestion that the bands in the visible region of the other metal complexes are due to ligand to metal charge-transfers.

A spectrometric titration of $[\text{Co}(\text{Ph}_4\text{Bzo}_2[14]\text{-tetraeneN}_4)] \cdot \text{O}_2$ with pyridine is shown in Fig. 2. As pyridine is added, the ligand to metal charge-transfer bands decreased. The solution changed color from a greenish-brown to a deep red. Two isosbestic points emerged with the increased amount of pyridine corresponding to 1:1 axial base to complex, as expected for cobalt(II) tetraazaannulenes [12].

Electrochemistry

Cyclic voltammograms of the $[\text{Pd}(\text{Ph}_4\text{Bzo}_2[14]\text{-tetraeneN}_4)]$ and $[\text{Mn}(\text{III})(\text{Ph}_4\text{Bzo}_2[14]\text{-tetraeneN}_4)]\text{-Cl}$ are displayed in Figs. 3 and 4, respectively. The redox properties of the manganese(III), cobalt(II), zinc(II) and palladium(II) complexes of the tetraphenyl ligand have been determined (see Table 2). The zinc(II) complex had approximately the same properties as those of the ligand [23]. A comparison

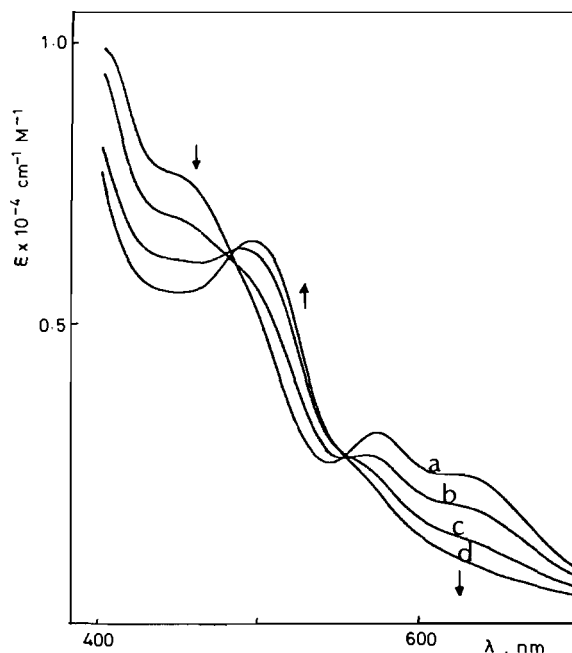


Fig. 2. Electronic spectra of $[\text{Co}(\text{Ph}_4\text{Bzo}_2[14]\text{-tetraeneN}_4)]$ with pyridine added: (a) Co(II) complex only; (b) Co(II) complex and pyridine, 1:<1 ratio; (c) Co(II) complex and pyridine, $\sim 1:1$ ratio; (d) Co(II) complex and pyridine, 1:>1 ratio.

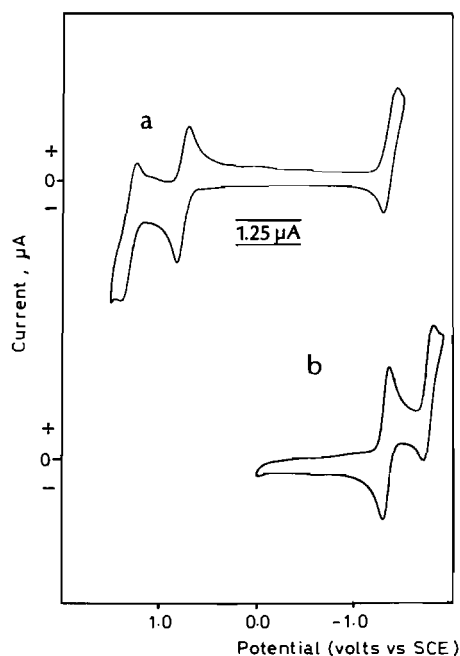


Fig. 3. Cyclic voltammograms of $[\text{Pd}(\text{Ph}_4\text{Bzo}_2[14]\text{-tetraeneN}_4)]$ in solutions containing 0.1 M TEAP and 1.0×10^{-3} M complex (sweep rate 200 mV/s): (a) in methylene chloride (limits of +1.50 to -1.50 V vs. SCE), (b) in DMF (limits of 0.00 to -1.90 V vs. SCE).

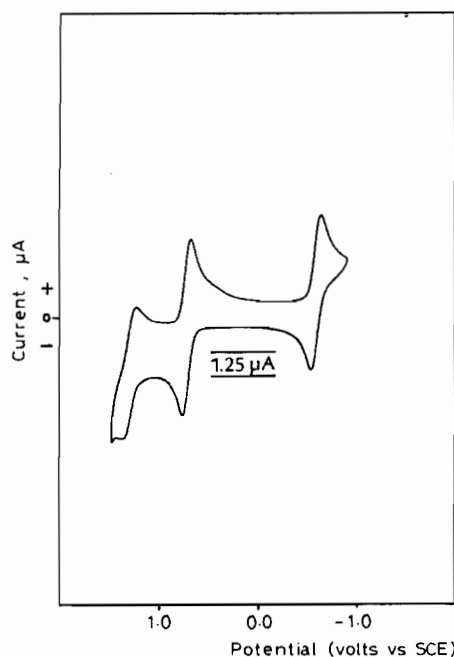


Fig. 4. Cyclic voltammogram of $[\text{Mn(III)(Ph}_4\text{Bzo}_2[14]\text{-tetraeneN}_4)]$ in methylene chloride containing 0.1 M TEAP and 1.0×10^{-3} M complex (sweep rate 200 mV/s, limits of +1.50 to -0.90 V vs. SCE).

of the oxidation waves and reduction waves of $[\text{Mn(III)(Ph}_4\text{Bzo}_2[14]\text{-tetraeneN}_4)]\text{Cl}$ to $[\text{Mn(III)(Me}_4\text{Bzo}_2[14]\text{-tetraeneN}_4)]\text{Cl}$ shows that the tetraphenyl substituents shift both the oxidations and the reductions to more positive values than those of the tetramethyl analog (0.74, 1.30 and -0.51 V versus 0.52, 1.24 and -0.73 V [25], respectively). This effect occurs in a comparison of the palladium(II) complexes [21] and the cobalt(II) complexes [26] as well. The shifts were largest in the case of the palladium(II) complexes (~ 0.4 V difference). This behavior had been observed earlier in the cases of nickel(II) and copper(II) complexes [23]. The shift is believed to be due solely to the electron withdrawing nature of the four phenyl rings and is

apparently unrelated to any structural differences of the macrocyclic ligand.

Effects of Axial Ligands on Redox Properties

We examined the effect of axial ligands on the redox properties of several of the new complexes. We were surprised to see a large increase in current in the second oxidation wave of $[\text{Cu(Ph}_4\text{Bzo}_2[14]\text{-tetraeneN}_4)]$ in the presence of pyridine (see Fig. 5a) when scanned through the oxidation portion of the cyclic voltammogram. Upon reversal of scan direction (through the reduction of the second oxidation wave) no current was observed. This can best be explained by an EC mechanism. As the Cu(II) complex is oxidized at the electrode (E or electrochemical reaction), it is reduced by the pyridine (C or chemical reaction). This caused an increase in current due to the reoxidation of some of the Cu(II) complex. On the reverse scan, there is no observed reduction of the Cu(II) complex because it has already been reduced by the pyridine that was in solution. The same effect can be seen in the case of pyridine added to a solution of $[\text{Ni(Ph}_4\text{Bzo}_2[14]\text{-tetraeneN}_4)]$ (see Fig. 5b), even though this effect was much smaller than that observed for the Cu(II) complex.

Three other axial ligands were investigated to determine the possible effects on these metal complexes. They were azide, cyanide and fluoride. In the case of fluoride, there was no change in the cyclic voltammograms of the copper(II) and nickel(II) complexes. Cyanide increased the current of the first oxidation wave of $[\text{Cu(Ph}_4\text{Bzo}_2[14]\text{-tetraeneN}_4)]$ (see Fig. 6a) when scanned through the oxidation part of the cyclic voltammogram. Cyanide effected the redox properties of $[\text{Ni(Ph}_4\text{Bzo}_2[14]\text{-tetraeneN}_4)]$ in much the same way (see Fig. 6b). The first oxidation wave displayed an increase in current as compared to a solution without cyanide added. The increase in current observed for these complexes could once again suggest possible EC mechanism with the axial ligand. There were no oxidation waves due to pyridine or cyanide in neat solutions over this

TABLE 2. Redox properties of $[\text{M(Ph}_4\text{Bzo}_2[14]\text{-tetraeneN}_4)]$ complexes

M	$E_{1/2}\text{Oxid(1)} \text{ (V)}^{\text{a, c}}$	$E_{1/2}\text{Oxid(2)} \text{ (V)}^{\text{a, c}}$	$E_{1/2}\text{Oxid(3)} \text{ (V)}^{\text{a, c}}$	$E_{1/2}\text{Red(1)} \text{ (V)}^{\text{a, b}}$	$E_{1/2}\text{Red(2)} \text{ (V)}^{\text{a, b}}$
Mn ^e	0.74	1.30		-0.51	-1.54
Co	0.51	0.88	1.16	-1.25	-1.77
Ni ^d	0.76	1.26		-1.28	-1.73
Cu ^d	0.68	1.13		-0.96	-1.55
Zn	0.95(irr)	1.37(irr)		-1.56	
Pd	0.74	1.31		-1.31	-1.74

^a0.1 M TEAP–methylene chloride solutions; $T = 22 \pm 2$ °C. ^b0.1 M TEAP–DMF solutions; $T = 22 \pm 2$ °C. ^cVolts vs. SCE, ± 0.01 V; sweep rates 200 mV/s. ^dSee ref. 23. ^eMn is $[\text{Mn(III)(Ph}_4\text{Bzo}_2[14]\text{-tetraeneN}_4)]\text{Cl}$.

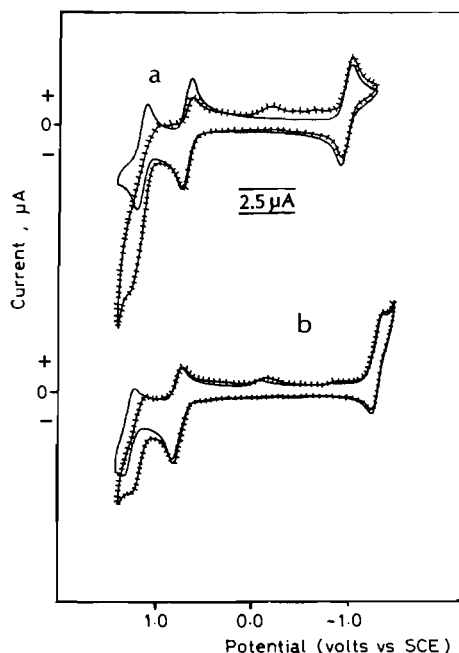


Fig. 5. Cyclic voltammograms in solutions containing 0.1 M TEAP and 1.0×10^{-3} M complex without pyridine (—) and with pyridine (---) (sweep rate 200 mV/s): (a) complex was $[\text{Cu}(\text{Ph}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]$ (limits of +1.40 to -1.30 V vs. SCE), (b) complex was $[\text{Ni}(\text{Ph}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]$ (limits of +1.40 to -1.50 V vs. SCE).

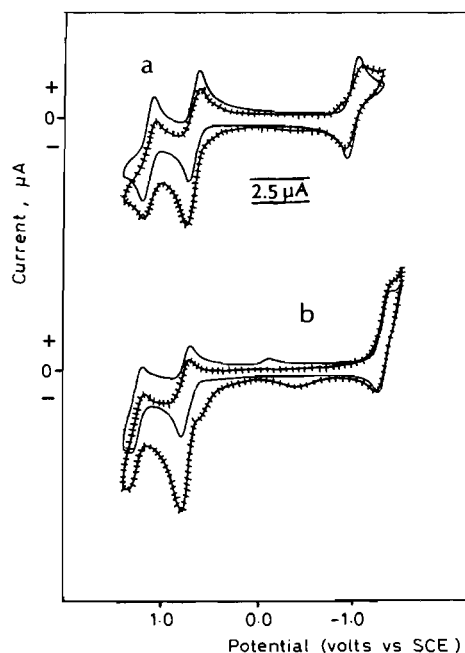


Fig. 6. Cyclic voltammograms in solutions containing 0.1 M TEAP and 1.0×10^{-3} M complex without CN^- (—) and with CN^- (---) (sweep rate 200 mV/s): (a) complex was $[\text{Cu}(\text{Ph}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]$ (limits of +1.40 to -1.30 V vs. SCE), (b) complex was $[\text{Ni}(\text{Ph}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]$ (limits of +1.40 to -1.50 V vs. SCE).

scan range. Azide had approximately the same effect on the redox properties of these complexes as did cyanide. There was an increase of current in the first oxidation like those seen for cyanide.

To further verify the proposed EC mechanism observed, a controlled step oxidation of $[\text{Cu}(\text{Ph}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]$, followed by addition of azide, was examined. The Cu(II) complex was oxidized at a potential of 0.90 V versus SCE until a steady-state current was obtained. Azide ($E^\circ = 1.08$ V versus SCE [27]) was added to the oxidized solution. An increase in current was observed due to the addition of azide to the solution. The increase in current was attributed to the reoxidation of the Cu(II) complex after its reduction by azide. The same experiment in the absence of Cu(II) complex showed no increase when azide was added to the solution. In order to more fully understand this process, the above experiment was repeated pyridine. Upon first addition of an excess of pyridine to the solution there was an increase in current, which decreased with time. Addition of more pyridine increased the current again. This demonstrates the complex can be used through several EC cycles.

Electron Spin Resonance

We also investigated the effect of axial ligands on metal centers by the use of ESR, a technique which has been shown to be very sensitive in these systems. A comparison of the spectrum of $[\text{Co}(\text{Ph}_4\text{Bzo}_2[14]\text{tetraeneN}_4)] \cdot \text{O}_2$ in toluene (see Fig. 7) versus DMF/ CCl_2H_2 (see Fig. 8) can help to illustrate this point. In comparing the two Figures it can be seen that there are differences in the hyperfine values for these two different solvent systems. The spectrum in

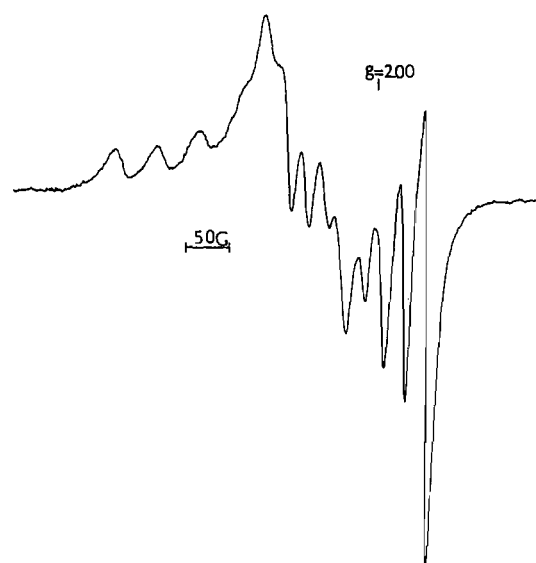


Fig. 7. Frozen glass ESR spectrum of $[\text{Co}(\text{Ph}_4\text{Bzo}_2[14]\text{tetraeneN}_4)] \cdot \text{O}_2$ in toluene ($T = 100$ K).

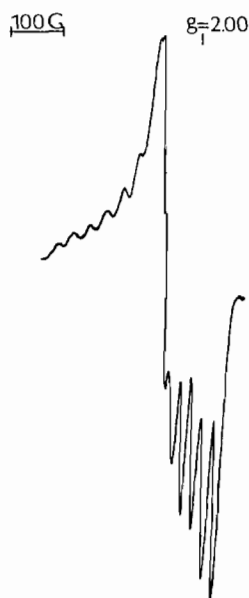


Fig. 8. Frozen glass ESR spectrum of $[\text{Co}(\text{Ph}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]\cdot\text{O}_2$ in a (1:1 vol./vol.) methylene chloride:DMF solution ($T = 100$ K).

toluene, a solvent which has no coordination properties, is quite different from that in DMF/ CCl_2H_2 (see Table 3). Further, in comparing the metal hyperfine values for $[\text{Co}(\text{Ph}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]\cdot\text{O}_2$ in toluene versus those after the addition of an axial ligand to toluene, it was found that the A values were approximately one half as large as in toluene alone. Table 3 also lists other examples of Spin Hamiltonian parameters of similar systems and the comparisons are clearly similar.

Conclusions

Clearly, these tetraazaannulene complexes have much to offer. The effects of axial ligands on the cyclic voltammograms of copper(II) and nickel(II) tetraphenyltetraazaannulene were studied. These axial ligands were found to increase the current observed in the oxidation cycle and decrease the reduction current on the reverse scan. This implies an EC mechanism between the complex and a substrate, likely an axial ligand. A controlled oxidation of copper(II) complex followed by addition of azide confirmed the EC mechanism. An increase in current observed after the addition of azide was attributed to the reoxidation of copper(II) complex after its reduction by azide. This work suggests the possible application of axial binding to other comparable systems. Electrodes coated with films of this type of complex could be used as a mediator for electron transfer through an EC mechanism like that observed here. This would allow these modified electrodes to serve as an electron source for possible catalytic applications.

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TABLE 3. Magnetic parameters for $[\text{Co}(\text{Ph}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]\cdot\text{O}_2$ ^a

Solvent system	g_{\parallel}	g_{\perp}	A_{\parallel} (gauss)	A_{\perp} (gauss)	$\langle A \rangle$ (gauss)
$[\text{Co}(\text{Ph}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]\cdot\text{O}_2$					
Toluene	2.056	1.998	45.6	22.8	30.4
DMF/ CCl_2H_2	2.093	2.004	27.5	20.8	23.0
Toluene/HMPA ^b	2.052	1.998	25.1	10.2	15.2
Toluene/thiophene	2.061	1.999	22.1	10.5	14.4
Toluene/pyridine	2.064	2.000	21.3	10.4	14.1
$[\text{Co}(\text{Bzo}_2[14]\text{tetraeneN}_4)]\cdot\text{O}_2$ ^c					
DMF/pyridine	2.088	1.993	19.7	13.7	15.7
DMF/imidazole	2.086	2.002	18.6	11.2	13.7
$[\text{Co}(\text{Et}_2\text{Py}_2[14]\text{tetraeneN}_4)]\cdot\text{O}_2$ ^d					
Pyridine	2.076	1.999	18.7	13.3	15.1
4-Mepyrindine	2.076	1.999	18.2	13.0	14.7

^aMaximum possible errors: $g, \pm 0.005$; $A \pm 0.5$ gauss.

^bHexamethylphosphoramide.

^cSee ref. 13.

^dSee ref. 28.

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