Electrochemical and Spectral Properties of the Ni(II) and Cu(II) Complexes of 5,7,12,14-tetraphenyldibenzo[b, i][1,4,8,11]tetraaza[14]annulene

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Abstract

A detailed electrochemical characterization of the Ni(II) and Cu(II) complexes of the new ligand, 5,7,12,14-tetraphenyldibenzo[b, i][1,4,8,11]tetraaza[14]annulene, has been carried out in an effort to more fully understand the mechanism of electropolymerization of the tetramethyl analog of the macrocycle. Evidence has been obtained to support a radical mechanism for the electropolymerization of the nickel(II) complex of 5,7,12,14-tetramethyldibenzo[b, i][1,4,8,11]tetraaza[14]annulene at the surface of an electrode at 0.97 V. The electrochemical properties of this new macrocyclic ligand system were also investigated. Metal complexes of a series of complexes with varying substituents were prepared and characterized. A linear relationship between the Hammett σ constants of the substituents and redox properties of the complexes was obtained. The redox potentials of the metal complexes of this new ligand were compared to those of the tetramethyl analog of the macrocycle. The new ligand system brings about a shift of the redox potentials by at least 0.3 V (in the positive direction). This shift is large in comparison to the shift in redox potential of tetraphenyl *versus* tetramethyl porphyrins. In order to determine of the nature of the redox shift is purely an inductive effect, the spin Hamiltonian parameters for the Cu(II) complexes of this new system are compared to that of the tetramethyl analog and it was determined that the inductive effect alone of the phenyl rings controls the large change in redox potentials of the ligand and the metal centers. The UV–Vis spectra of the copper(II) and the nickel(II) complexes, along with the free ligand, are also presented.

Introduction

The study of tetraaza[14]annulene macrocycles has been of considerable interest because of the utility of this ligand to model porphyrins and corrin rings in biological systems [1–5]. In addition, the

potential of metal complexes of these macrocycles as catalysts [6] has also fostered some attention. For example, the investigation of film formation on the surface of electrodes during routine cyclic voltametric studies, apparently formed through an electrochemical polymerization of the tetramethyldibenzo[b, i]tetraaza[14]annulene macrocycle, has recently been explored in some depth [7, 8]. This interest was increased when it was discovered that CO_2 can be electrocatalytically reduced to HCO_2^- by the Ni(II) containing film.

Our interest has been to explore the range of polymer films which might be possible, utilizing the basic tetraazaannulene framework. In order to better understand the mechanism of polymer formation as well as provide a macrocyclic ligand with which we might carry out electrochemical substrate binding studies, we designed a new macrocyclic molecule where we feel the proposed electrochemical coupling mechanism would be inhibited. The rather elusive ligand, 5,7,12,14-tetraphenyldibenzo[b, i][1,4,8,11]tetraaza[14]annulene [9, 10] (Fig. 1) satisfied those criteria. The four phenyl rings of the diiminate backbone would provide steric hindrance to the proposed electropolymerization scheme of metal complexes of the tetramethyldibenzo[b, i][1,4,8,11]tetraaza[14]annulene macrocycle, a mechanism which was postulated to proceed through the carbons of the diiminate backbone [7].

Even though the tetraaza[14]annulene ligand system was first reported by Jager [11] almost 20 years ago, to our knowledge no detailed electrochemical studies had been reported prior to our
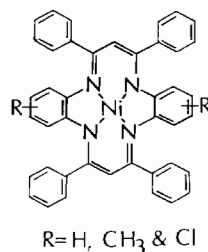

R= H, CH₃ & Cl

Fig. 1. [Ni(Ph₄(RBzo)₂[14]tetraeneN₄)].

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earlier observations of film formation. A series of compounds has been prepared with varied substituents on the two benzo rings that make up the backbone of the macrocycle ring. The effect of these substituents upon the redox behavior of the nickel(II) complexes are reported. The electrochemical properties as well as other spectral probes of the free ligand and the copper(II) complex ligand also yielded further insight into the coordination properties of this new macrocycle.

Experimental

Materials

Tetraethylammonium perchlorate (TEAP) was purchased from Southwestern Chemicals, Inc., dried overnight at 70 °C under vacuum and used without further purification. Methylene chloride was purchased from EM Science. 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, used for degassing solvents, 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. NMR spectra were obtained in $CDCl_3$ employing a Varian EM-360 spectrometer for 60 MHz ^1H NMR. Elemental analyses were obtained from Atlantic Microlabs, Atlanta, GA, U.S.A.

Electrochemical properties were determined in methylene chloride 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 in gauss by assigning the peak separation between the fourth and fifth lines of the vanadyl acetylacetonate as 108.0 G ($g_{apparent} = 1.986$) [12]. Solution spectra

were obtained in benzene, and frozen glass spectra were obtained in a 1:1 v/v mixture of methylene chloride and DMF.

Syntheses

The ligands were prepared by either a modified method of Jager [11] or, in the case of the new tetraphenyl ligand, a modified procedure of Hotz [10] [Ni(Ph$_4$Bzo$_2$[14]tetraeneN$_4$], (an abbreviation for the nickel(II) complex of 5,7,12,14-tetraphenyl-dibenzo[b, i][1,4,8,11]tetraaza[14]annulene), [Ni(Ph$_4$(CH$_3$Bzo)$_2$[14]tetraeneN$_4$], [Ni(Ph$_4$(ClBzo)$_2$-[14]tetraeneN$_4$], [H$_2$(Ph$_4$Bzo$_2$[14]tetraeneN$_4$)] and [Cu(Ph$_4$Bzo$_2$[14]tetraeneN$_4$)] were prepared by methods described by Hotz [10]. The reactions were carried out under a slight flow of argon to remove water as it formed. The synthesis of [Ni(Ph$_4$(ClBzo)$_2$[14]tetraeneN$_4$)] was carried out for 240 min (as compared to 90 min previously) at lower temperature due. to the volatility of the 4-chloro-*o*-phenylenediamine. The yields were also lowered somewhat due to the changes in reaction conditions. [Ni(Ph$_4$(CH$_3$Bzo)$_2$[14]tetraeneN$_4$)]: ^1H(60 MHz, ppm): 2.33(6H, s); 5.13(2H, s); 5.50, 5.63, 5.73(6H, m); 7.15, 7.31(20H, m). *Anal.* Calc. for C$_{44}$H$_{34}$N$_4$Ni: C, 78.01; H, 5.06; N, 8.27. Found: C, 77.90; H, 5.08; N, 8.20%. [Ni(Ph$_4$(ClBzo)$_2$[14]-tetraeneN$_4$)]: ^1H(60 MHz, ppm): 5.23(2H, s); 5.67, 5.83, 5.95(6H, m); 7.25, 7.38(20H, m).

Results and Discussion

Electronic Spectra

Absorption spectra of these complexes and the neutral ligand were examined over the 700 to 250 nm range and the results are summarized in Table 1. There are three major absorptions in the spectrum of the ligand and each can be assigned as a ligand to ligand charge-transfer band. These same bands are present in the metal complexes along with additional absorption bands in the visible region which are responsible for the intense color of the metal complexes. The bands in the visible region of the metal complexes exhibit energies between 460–670 nm, with molar absorptivities as high as 1.3×10^4 cm^{-1} M^{-1}. The molar absorptivities are indicative of charge-transfer absorptions, likely ligand to metal [13].

Electrochemistry

We have shown that solutions of complexes of the form [M(Me$_4$Bzo$_2$[14]tetraeneN$_4$)] form films on electrode surfaces during repetitive cyclic scanning thru the oxidation waves of the ligand itself [7, 8]. Since it had been proposed [7] that the electropolymerization takes place thru the diiminate backbone of these compounds, we felt further

TABLE 1. Electronic Absorption Bands for [M(Ph$_4$(Bzo)$_2$-[14]tetraeneN$_4$)] Complexes[a,b]

M	R	Position (nm)	ϵ (cm^{-1} M^{-1}) (log ϵ)
Ni	H	622	4.44×10^3(3.04)
		462	1.30×10^4(4.11)
		406	2.00×10^4(4.30)
		356	7.64×10^3(3.88)
		266	3.34×10^4(4.52)
	CH$_3$	621	4.80×10^3(3.68)
		466	1.49×10^4(4.17)
		408	2.19×10^4(4.34)
		354	8.68×10^3(3.94)
		264	4.01×10^4(4.60)
	Cl	620	3.86×10^3(3.59)
		465	1.16×10^4(4.06)
		408	1.78×10^4(4.25)
		354	6.71×10^3(3.83)
		250	3.65×10^4(4.56)
Cu	H	672	4.00×10^2(2.60)
		544	$\sim 1.36 \times 10^3$(3.13)
		461	1.34×10^4(4.13)
		406	2.81×10^4(4.45)
		275	3.03×10^4(4.48)
H$_2$	H	427(Sh)[c]	7.60×10^3(3.88)
		379	3.54×10^4(4.55)
		272	2.14×10^4(4.33)

[a]Spectra were obtained for 10^{-4} M solutions in methylene chloride. [b]22 ± 2 °C; Position ± 0.5 nm; ϵ, $\pm 1\%$. [c]sh, shoulder peak.

Fig. 2. Cyclic voltammograms of [Ni(Ph$_4$(Bzo)$_2$[14]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. 3. Cyclic voltammograms of [Cu(Ph$_4$(Bzo)$_2$[14]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 −1.75 V *vs.* SCE).

evidence of this mechanism might be obtained by considering the electrochemical properties of systems where a sterically constrained coupling was required for film formation. The new ligand system, [M(Ph$_4$-Bzo$_2$[14]tetraeneN$_4$)], which has phenyl rings instead of the methyl groups on the diiminate backbone provides just such an opportunity. The repetitive scans of [Ni(Ph$_4$Bzo$_2$[14]tetraeneN$_4$)] (see Fig. 2a) and of [Cu(Ph$_4$Bzo$_2$[14]tetraeneN$_4$)] (see Fig. 3a) thru the oxidation part of the cyclic yield fairly reversible waves, an observation much different from the irreversible waves of the tetramethyl derivatives. Also, there was no film formation upon repetitive scans.

These new compounds, [M(Ph$_4$Bzo$_2$[14]tetraeneN$_4$)], are more easily reduced and less easily oxidized than the analog with the four methyl groups. For example, the nickel complex of the tetraphenyl ligand exhibits a reduction at −1.28 V (see Table 2) as compared with the tetramethyl analog which shows a reduction at −1.76 V *versus* SCE [8]. A comparison of the oxidation waves of the new nickel compound to the oxidation peaks of the tetramethyl analog yields the same observation
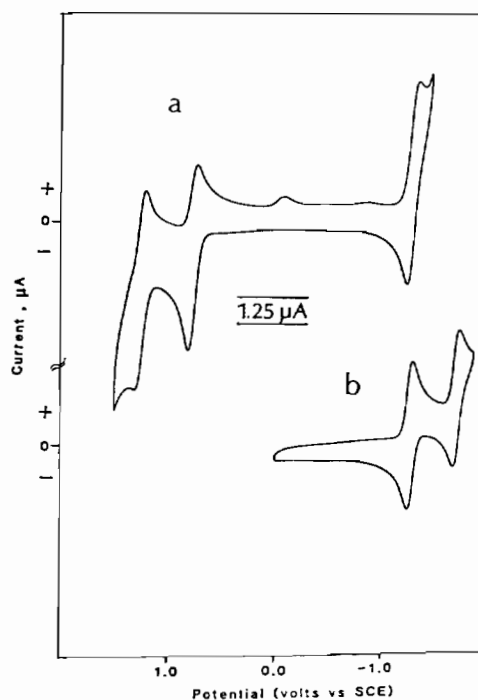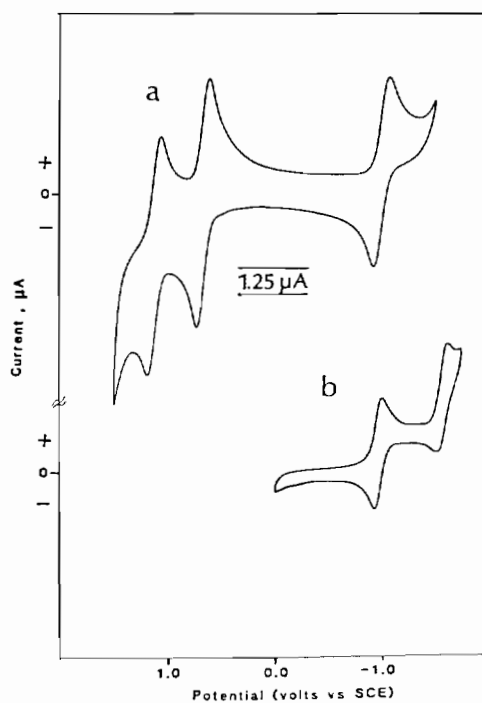
TABLE 2. Redox Properties of $[M(Ph_4(Bzo)_2[14]tetra-eneN_4)]$ Complexes

M	R	$E_{1/2}$ Ox(1) $(V)^{a,c}$	$E_{1/2}$ Ox(2) $(V)^{a,c}$	$E_{1/2}$ Red(1) $(V)^{b,c}$	$E_{1/2}$ Red(2) $(V)^{b,c}$
Ni	CH_3	0.67	1.19	−1.34	−1.78
	H	0.76	1.26	−1.28	−1.73
	Cl	0.87	1.31	−1.17	−1.64
Cu	H	0.68	1.13	−0.96	−1.55
H_2	H	0.94(irr)	1.33(irr)	−1.57(irr)	

[a]0.1 M TEAP–methylene chloride solutions; T = 22 ± 2 °C.
[b]0.1 M TEAP–DMF solutions; T = 22 ± 2 °C. [c]Volts vs. SCE, ±0.01 V; sweep rates 200 mV/s.

(0.76 and 1.26 V versus 0.42 and 0.97 V [8], respectively). The same trend occurs in the copper(II) complexes. In $[Cu(Ph_4Bzo_2[14]tetraeneN_4)]$ the reduction wave is at −0.96 versus −1.39 V [15] for the tetramethyl analog. In a comparison of the oxidation waves of the former to the oxidation peaks of the latter, the same trend is seen (0.68 and 1.13 V versus 0.37 and 0.87 V [15], respectively). Evidently, the electron withdrawing nature of the phenyl ring better supports the reduction of not only the new macrocyclic ligand but also the metal center.

A comparison of the half-wave potentials of the tetramethyl/tetraphenyl macrocycles to those of the tetramethyl/tetraphenyl porphyrins is interesting. The reduction half-wave potential of (tetraphenylporphinato)nickel(II), (TPP)Ni, as compared to (tetramethylporphinato)nickel(II), (TMeP)Ni, shows the same trend as with these macrocyclic complexes (−1.28 versus −1.36 V [14], respectively). However, this latter difference is rather small in comparison to the macrocyclic systems.

We also observed a new, second reduction wave in these complexes which has not been observed before (see Figs. 2b and 3b). It is apparent that the phenyl substituent effect has moved this reduction within the 'solvent window'. The potential difference between the first and second reductions is approximately 0.5 V. The second reduction observed in the metal complexes is believed to be a reduction of the ligand itself. The reduction of the ligand is not as reversible as the second reduction of the metal complexes (see Figs. 2b and 4b). The nature of the reduction wave becomes more reversible when a metal ion is complexed to the ligand. Clearly, this ligand orbital into which the second reduction occurs must gain some metal character.

The free base ligand exhibits two irreversible oxidations (see Fig. 4a). It had been noted by Kadish et al. [16] that $[H_2(Me_4Bzo_2[14]tetraeneN_4)]$ exhibited no reduction as far negative as −2.20 V
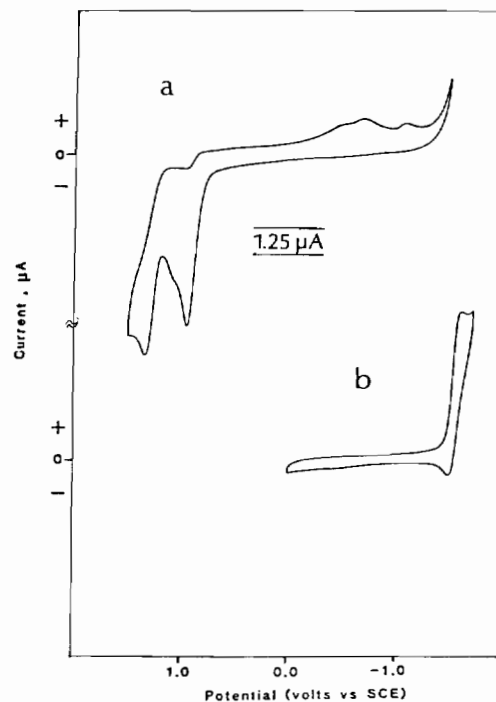

Fig. 4. Cyclic voltammograms of $[H_2(Ph_4(Bzo)_2[14]tetra-eneN_4)]$ in solutions containing 0.1 M TEAP and 1.0 × 10^{-3} M complex (sweep rate 200 mV/s): (a) in methyl chloride (limits of +1.50 to −1.50 V vs. SCE); (b) in DMF (limits of 0.00 to −1.75 V vs. SCE).

versus SLCE (saturated lithium calomel electrode), it was surprising to find that the tetraphenyl analog showed a reduction wave (see Fig. 4b) at −1.57 V.

The electrochemical data obtained on the series $[Ni(Ph_4(RBzo)_2[14]tetraeneN_4)]$, where R = CH_3, H and Cl, are given in Table 2. Potentials are listed for the four redox waves of this series, one which contains an electron withdrawing and an electron donating group. A plot of Ox(1) versus $2\sigma_p$ [17] is given in Fig. 5 and it can be seen that the plot is linear (correlations for these are 0.9997, 0.983,
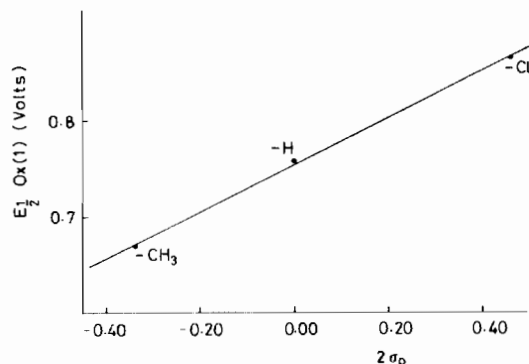

Fig. 5. Hammett plot of $E_{1/2}Ox(1)$ vs. $2\sigma_p$ for $[Ni(Ph_4(RBzo)_2[14]tetraeneN_4)]$ macrocycles.

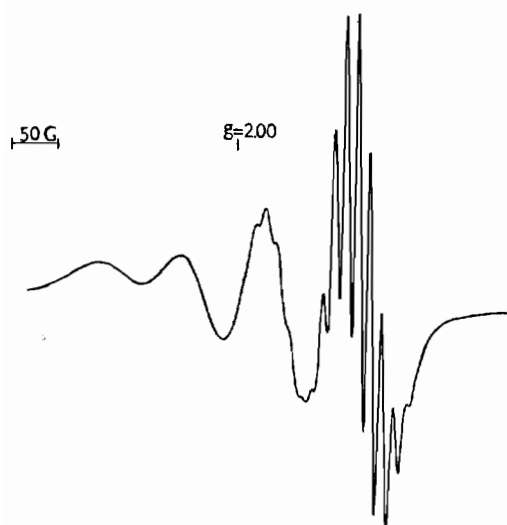Fig. 6. Solution ESR spectrum of [Cu(Ph$_4$Bzo$_2$[14]tetra-eneN$_4$)] in benzene.

0.997 and 0.997 for the respective redox waves of $E_{1/2}$ Ox(1), $E_{1/2}$ Ox(2), $E_{1/2}$ Red(1) and $E_{1/2}$ Red(2)). The slopes of these plots range from 0.148 to 0.249 (0.249, 0.148, 0.214 and 0.176, respectively) which fall between the values of 0.07 V [18] for remote substitution effect and 0.50 V [19] for direct substitution effect of porphyrins. These values also fall between the remote and direct substitution range for macrocycles (0.064 and 0.52 V [20] respectively). The value for the slopes more closely correspond with those found by Giraudeau *et al.* [21] for β-pyrrole substituents. A larger range of substituents might better define these effects, but our attempts to prepare molecules with –COOH and –NO$_2$ substituents were unsuccessful.

Electron Spin Resonance

In an effort to determine if the shifts of the redox potentials are totally inductive or possibly partly due to structural changes, we compared the electron spin resonance parameters for the copper(II)tetramethyl and tetraphenyl macrocyclic complexes. The ESR spectra for [Cu(Me$_4$Bzo$_2$[14]tetraeneN$_4$)] looked approximately the same as that of the [Cu-(Ph$_4$Bzo$_2$[14]tetraeneN$_4$)] (Figs. 6 and 7). Only slight differences were observed in a comparison of the *g* values and *A* values (Table 3). The method described by Maki *et al.* [22] was used to determine the covalence of the σ bonding. For the ground state in a tetragonal environment (where $g_{xx} = g_{yy} = g_\perp$, $g_{zz} = g_\parallel$, $A_{xx} = A_{yy} = A_\perp$ and $A_{zz} = A_\parallel$), the expressions for the spin Hamiltonian parameters are

$$g_\parallel = 2 - 8\alpha_1$$

$$g_\perp = 2 - 2\alpha_2$$

and

$$A_\parallel = P[-8\alpha_1 - \kappa - 4/7 - 3/7(2\alpha_2)]$$

$$A_\perp = P[-2\alpha_2 - \kappa + 2/7 + 3/7\alpha_2]$$

where α_1 and α_2 are mixing parameters and $P = g_N\beta_e\beta_N r^{-3}$ and refers to the Fermi hyperfine coupling energy in units of P. The observed hyperfine coupling constant in solution, $\langle a \rangle = 1/3(2A_\perp + A_\parallel) \sim$ 90 gauss, is consistent only with $A_\perp$ and $A_\parallel$ of the same sign, and since $|A_\parallel| \gg |A_\perp|$, the sign of each must be negative (P is positive for ^{63,65}Cu). Solving for P and κ, we obtained $P = 0.023$ and 0.026 cm^{-1} and $\kappa = 0.47$ and 0.41 (for [Cu(Me$_4$Bzo$_2$[14]tetra-eneN$_4$)] and [Cu(Ph$_4$Bzo$_2$[14]tetraeneN$_4$)], respectively). For the free ion, $P_0 \sim 0.035$ cm^{-1} [23], so in these complexes r^{-3} has been roughly reduced
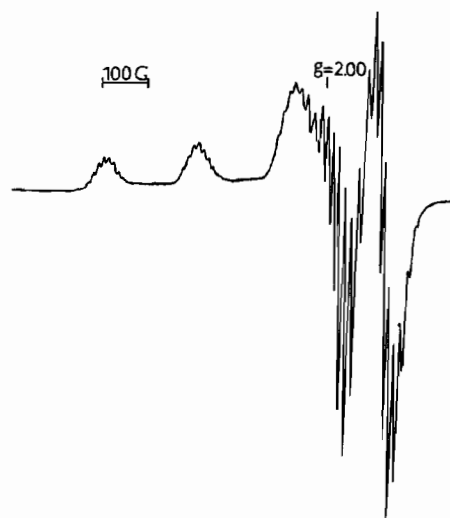

Fig. 7. Frozen glass ESR spectrum of [Cu(Ph$_4$Bzo$_2$[14]-tetraeneN$_4$)] in a (1:1 *v*/*v*) methylene chloride: DMF solution.

TABLE 3. Magnetic Parameters for [Cu(Me$_4$Bzo$_2$[14]-tetraeneN$_4$)] and [Cu(Ph$_4$Bzo$_2$[14]tetraeneN$_4$)][a,b]

R	g^c	A_{Cu}^d (gauss)	A_N^d (gauss)
Me	2.091	89.25	25.75
Ph	2.076	89.56	25.75
Me$_\parallel$	2.162	197.91	10.91
Ph$_\parallel$	2.174	208.45	10.07
Me$_\perp$	2.056	34.92	14.19
Ph$_\perp$	2.027	30.14	14.37
Me$_0$	1.965		12.81
Ph$_0$	1.963		12.84

[a]Solution spectra were recorded in benzene using 1×10^{-4} M [Cu(Ph$_4$Bzo$_2$[14]tetraeneN$_4$)] at 22 ± 2 °C. [b]Frozen glass spectra were recorded in methylene chloride:DMF (1:1 *v*/*v*) using 1×10^{-4} M [Cu(Ph$_4$Bzo$_2$[14]tetraeneN$_4$)] at ~ 77 K. [c]Error is ± 0.002. [d]Error is ± 0.5 gauss.

35% and 25%. This indicates a somewhat more co-valent σ bond in $[Cu(Me_4Bzo_2[14]tetraeneN_4)]$ complex.

Evaluation of the parameters α_1 from the expression for g would allow for an estimate of configurational excitation energies. Estimates were made assuming ζ to be about 0.5 to 0.7 of the free ion value, $\zeta_0 = 828$ cm^{-1}. However, charge transfer bands of these complexes mask areas where these transitions should take place. Therefore, no true comparison of the calculated values to the actual values could be made.

Conclusion

To more fully understand the electropolymerization of $[M(Me_4Bzo_2[14]tetraeneN_4)]$, an electrochemical study of the tetraphenyl analog was undertaken. This study further supports the electropolymerization scheme which we had proposed. We not only found that electropolymerization was prevented, but also that the oxidations became reversible. Varying the substituents on the benzo rings of the macrocycle did change the electrochemistry of the macrocycle as would be expected. A shift in the electrochemical properties of the macrocycle allowed for the identification of a second reduction. The large change in overall ease of reduction prompted investigation. This ease in reduction could be solely due to an inductive effect of the phenyl rings alone. A study of the spin Hamiltonian parameters comparing the copper tetramethyl and tetraphenyl macrocycles showed a slight difference in the covalency in σ bonding. The optical bands are not well enough resolved to allow any molecular orbital calculations but it would be surprising if these calculations lead to any meaningful difference in MO type. Therefore, it was concluded that the large change in overall reduction must be due in large part to the inductive effects of the phenyl rings.

Acknowledgements

References

1 (a) M. C. Weiss, G. C. Gordon and V. L. Goedken, *J. Am. Chem. Soc., 101* (1979) 857; (b) M. C. Weiss and V. L. Goedken, *J. Am. Chem. Soc., 98* (1976) 3389; (c) F. A. L'Eplattenier and A. Pugin, *Helv. Chem. Acta, 58* (1975) 917; (d) T. J. Truex and R. H. Holm, *J. Am. Chem. Soc., 93* (1971) 285; (e) D. A. Place, G. P. Ferrara, J. J. Harland and J. C. Dabrowiak, *J. Heterocyclic Chem., 17* (1980) 439; (f) G. P. Ferrara and J. C. Dabrowiak, *Inorg. Nucl. Chem. Lett.*, (1978) 1431; (g) R. Hanki and E. Breitmaier, *Chem. Ber., 115* (1982) 1657; (h) D. R. Neves and J. C. Dabrowiak, *Inorg. Chem., 15* (1976) 129; (i) T. J. Truex and R. H. Holm, *J. Am. Chem. Soc., 94* (1972) 4529; (j) M. C. Weiss, G. Gordon and V. L. Goedken, *Inorg. Chem., 16* (1977) 305; (k) F. Hanic, M. Handlovic and O. Lindgren, *Coll. Czech. Chem. Commun., 37* (1972) 2119; (l) J. C. Dabrowiak, D. P. Fisher, F. C. McElroy and D. Macero, *Inorg. Chem., 18* (1979) 2304.
2 (a) M. Tsutsui, R. L. Bobsein, G. Cash and R. Pettersen, *J. Am. Chem. Soc., 98* (1976) 8014; (b) V. L. Goedken, J. J. Pluth, S-M. Peng and B. Bursetn, *J. Am. Chem. Soc., 98* (1976) 8014; (c) K. M. Kadish, D. Schaefer, L. A. Bottomley, M. Tsutsui and R. L. Bobsein, *Inorg. Nucl. Chem., 42* (1980) 469.
3 (a) T. Matsushita, N. Kubota, M. Fujara and T. Shono, *Chem. Lett.*, (1984) 657; (b) K. Sakata, H. Nakanura and M. Hashimoto, *Inorg. Chim. Acta, 83* (1984) L67.
4 (a) S. Ciurli, E. M. Meyer, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Chem. Commun.*, (1987) 281; (b) A. J. Blake, A. J. Holder, M. Schroder and T. A. Stephenson, *Acta Crystallogr., Sect. C, 43* (1987) 847; (c) D. Mandow, J.-M. Girandon, L. Toupet, Jr Sola-Pala and J. E. Guerchais, *J. Am. Chem. Soc., 26* (1987) 3490.
5 (a) M. K. Moi, M. Yanuck, S. V. Deshpande, H. Hope and S. J. DeNardo, *Inorg. Chem., 26* (1987) 3458; (b) H. Nishihara, M. Noguchi and K. Armaki, *Inorg. Chem., 26* (1987) 2862; (c) M. Himmelsbach, R. L. Lintvedt, J. K. Zehetmair, M. Nanny and M. J. Heeg, *J. Am. Chem. Soc., 109* (1987) 8003.
6 (a) D. A. Gangi and R. R. Durand, Jr., *J. Chem. Soc., Chem. Commun.*, (1986) 697; (b) C. L. Bailey, R. D. Bereman, D. P. Rillema and R. Nowak, *Inorg. Acta, 116* (1986) 245; (c) D. P. Fisher, V. Piermattie and J. C. Dabrowiak, *J. Am. Chem. Soc., 99* (1977) 2811; (d) J. S. Miller (ed.), *Chemically Modified Surfaces in Catalysis and Electrocatalysis*, ACS Symposium Series, Washington, 1982, p. 159; (e) B. W. Clauberg and G. Sandsteded, *J. Electroanal. Chem., 74* (1976) 393; (f) C. M. Lieber and N. S. Lewis, *J. Am. Chem. Soc., 106* (1984) 5033; (g) S. Kapusta and N. J. Hackerman, *Electrochem. Soc., 131* (1984) 1511; (h) G. De-Grand and L. R. Miller, *J. Am. Chem. Soc., 102* (1980) 5728; (i) S. Meshitsuka, M. Ichikawa and K. Tamaru, *J. Chem. Soc., Chem. Commun.*, (1974) 158.
7 C. L. Bailey, R. D. Bereman, D. P. Rillema and R. Nowak, *Inorg. Chem., 25* (1986) 933.
8 P. J. Hochgesang and R. D. Bereman, *Inorg. Chim. Acta, 149* (1988) 69.
9 R. P. Hotz, S. T. Purrington, P. Singh and R. D. Bereman, *Inorg. Chim. Acta, 130* (1987) 195.
10 R. P. Hotz, *Ph.D. Dissertation*, NCSU, Raleigh, NC, 1987.
11 E. G. Jager, *Z. Anorg. Allg. Chem., 364* (1969) 177.
12 R. S. Giordana, *Ph.D. Dissertation*, SUNY, Buffalo, 1976.
13 C. L. Bailey, R. D. Bereman, D. P. Rillema and R. Nowak, *Inorg. Chem., 23* (1984) 3956.
14 D. Chang, T. Malinski, A. Ulman and K. M. Kadish, *Inorg. Chem., 23* (1984) 817.
15 C. L. Bailey, R. D. Bereman and D. P. Rillema, *Inorg. Chem., 25* (1986) 3149.
16 K. M. Kadish, L. A. Bottomley, D. Schaeper, M. Tsutsui and R. L. Bobsein, *Inorg. Chim. Acta, 36* (1979) 219.

17 C. G. Swain and E. C. Lupton, Jr., *J. Am. Chem. Soc., 90* (1968) 4329.
18 K. M. Kadish and M. M. Morrison, *Bioinorg. Chem., 7* (1977) 107.
19 (a) K. M. Kadish and M. M. Morrison, *J. Am. Chem. Soc., 98* (1976) 3326; (b) K. M. Kadish and M. M. Morrison, *Inorg. Chem., 15* (1976) 980; (c) F. A. Walker, D. Beroiz and K. M. Kadish, *J. Am. Chem. Soc., 98* (1976) 3484.

20 J. A. Streeky, D. G. Pillsbury and D. H. Busch, *Inorg. Chem., 19* (1980) 3148.
21 A. Giraudeau, H. J. Callot and M. Gross, *Inorg. Chem., 18* (1979) 201.
22 A. H. Maki, N. Edelstein, A. Davison and R. H. Holm, *J. Am. Chem. Soc., 86* (1964) 4580.
23 A. Abragam and M. H. L. Pryce, *Proc. R. Soc. London, Ser. A, 206* (1951) 164.