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ELECTROCHEMICAL STUDIES OF MACROCYCLIC COMPLEXES AS SYNTHETIC P--ETC(U)

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Electrochemical Studies of Macrocyclic Complexes
as Synthetic Porphyrin Analogs

by

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metalloporphyrin complexes. Reduction potentials indicate that the LUMO is most affected by changes in central metal oxidation state and ligand planarity.

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The electrochemical generation of π anion and π cation radicals for several metalloporphyrin analogs was studied at a Pt electrode in nonaqueous media using cyclic voltammetry. The π -radical formation potentials were measured for the macrocyclic ligands TMTAA, TAA, TPP and OEP containing M(III) [Mn, Fe], M(II) [Pd, Ni, Co], and M(I) [Rh, Re] metal centers. M(I)TMTAA and M(I)TAA oxidation potentials were found to be inversely related to M(I) electronegativities, a trend opposite that previously observed for metalloporphyrin complexes. Reduction potentials indicate that the LUMO is most affected by changes in central metal oxidation state and ligand planarity.

Knowledge of biological and catalytic systems develops axiomatically with the associated state of knowledge of basic chemistry. The progress of the basic coordination chemistry of macrocyclic ligands has led to a better understanding of such biological systems as heme proteins, chlorophylls, and vitamin B₁₂ [1] and of catalysts such as fuel cells [2]. The presence of highly conjugated ligands in these systems implies that these ligands lend unusual properties to the coordinated metals.

Macrocycles such as porphyrins [3] and phthalocyanines [4] have been well studied as evidenced by the huge amount of material published on these ligands. There is a growing interest in synthetic macrocycles because of their unique nature in coordinating metals [5] as well as their electron transfer properties in transition metal complexes [6]. The aim of the electrochemical studies was to acquire an understanding of structure-reactivity relationships in synthetic systems and to apply this information to the electron transfer reactivity of naturally occurring macrocycles particularly metalloporphyrins.

In earlier papers [7-9] results for the electrochemical oxidation-reduction of dirhenium and dirhodium complexes with the macrocyclic ligands dibenzo [b,i] [1,4,8,11]tetraaza[14]annulene (TAA), 5,7,12,14-tetramethyldibenzo[b,i] [1,4,8,11] tetraaza[14]annulene (TMTAA) and tetraphenylporphine (TPP) have been reported. Cyclic voltammetry was used to probe energy levels of these macrocyclic complexes and comparisons were made between their half wave potentials and those obtained for oxidation-reduction of other synthetic metalloporphyrins.

The structures of octaethylporphyrin (H₂OEP), H₂TPP, H₂TAA, and H₂TMTAA are shown in Figure 1. Complexation with transition metals yield tetradentate N₄ coordinated complexes similar to those of metalloporphyrins. These ligands possess an extensively conjugated π system and for TMTAA complexes the resonance Raman spectra are dominated by in plane $\pi \rightarrow \pi^*$

electronic transitions [10]. Syntheses of TMTAA complexes with a wide variety of metal ions of different oxidation states have been reported [5b,c,g,i]. Metal ions of oxidation state +1, +2, or +3 may be incorporated into the ligand. For +2 and +3 metals both N-H protons are displaced from the

ligand and the metal is coordinated to the four donor nitrogens. M(I) will displace a single proton and is situated either above or below the plane of the four donor atoms.

Metal complexes with H_2TPP [11] and H_2TAA [12] are relatively planar. In contrast, almost all complexes with H_2TMTAA are saddle shaped [5f,h] with the o-phenylene rings and diimino framework displaced in opposite directions from the plane of the four nitrogens. This saddle shape differs dramatically from other metal ligand complexes reported in the literature and provides an interesting series of compounds for comparisons with the planar metalloporphyrin and TAA complexes.

Resonance Raman spectra of M(II) complexes where M=Mn, Fe, Co, Ni, Cu, and Zn have been published and comparisons made with similar metalloporphyrin systems [10,13]. Electrochemical oxidation and esr characterization of the Ni(II) [14] and Mn(III) [15] complexes with TMTAA show that the initial reaction at an electrode surface is a reversible one electron abstraction to yield a cation radical similar to the cation radicals observed for metalloporphyrin oxidation.

$[Ni(II)TMTAA]^+$ rapidly reacts in solution to form a dimeric NiTMTAA species consisting of a carbon-carbon bridge [14]. Potentials for these oxidations have been reported but no direct comparisons with the reversible metalloporphyrin reactions were made.

Recently the synthesis and structural characterization of Pd(II) [16], Re(I) [17,18] and Rh(I) [19] complexes with cyclic ligands have been reported. These new compounds exhibit unusual coordination geometries.

The palladium complex of H_2TMTAA differs from other characterized metal complexes of H_2TMTAA in that the ligand has a "pseudo" planar configuration [16]. A side view illustrating this unique configuration is presented in Figure 2. The ligand accommodates for the strain produced in this geometry by expanding certain interior and exterior bond angles.

The coordination of $Re(I)$ and $Rh(I)$ carbonyls leads to some very interesting results in the geometry of these compounds. In $[Re(CO)_3]_2TAA$, the tricarbonyl rhenium(I) moieties are bound on opposite sides of the TAA ligand [17]. Figure 3 is a schematic picture of this compound. The rhenium-rhenium interatomic distance is $3.345\text{\AA}$. In this complex the TAA ligand, like the TPP ligand in the analogous $[Re(CO)_3]_2TPP$ compound shows an appreciable amount of twisting [20]. Ligation of tricarbonyl rhenium(I) and dicarbonyl rhodium(I) moieties to H_2TMTAA result in a uniquely different coordination geometry. The metal carbonyl moieties reside on the same side of the N_4 plane and are bound to two donor nitrogen atoms each. Figure 4 is a schematic representation of $[Rh(CO)_2]_2TMTAA$ ¹⁹. The dirhodium compound has very short rhodium-rhodium internuclear distance which is in the range of metal-metal interactions. The dirhenium compound has a rhenium-rhenium internuclear distance of $4.11\text{\AA}$ and is postulated to have a bridging H_2O molecule to fulfill the coordination number of six for rhenium(I).

In this paper we present a comparison between the electrooxidations and electroreductions of TMTAA, TAA, TPP, and OEP complexes containing the +3 metals Mn and Fe, the +2 metals Pd, Ni, and Co, and the +1 metals Rh and Re.

EXPERIMENTAL SECTION

Preparation of Compounds. H_2TAA , $CoTAA$, $NiTAA$, $PdTAA$, $[Re(CO)_3]_2TAA$, $[Re(CO)_2]_2TMTAA$ and $[Rh(CO)_2]_2TMTAA$ were prepared by literature methods [5]. $FeTPP(Br)$, $MnTPP(Br)$, $CoTPP$ and $NiTPP$ were synthesized by the methods of Adler, et. al. [22]. $MnTMTAA(SCN)$, $FeTMTAA(Br)$, and $NiTMTAA$ were generously provided to one of us (KMK) by Dr. William H. Woodruff. Physical

data for some compounds investigated are given Table I.

Chemicals. Dichloromethane (CH_2Cl_2) (Fisher, distilled from P_2O_5) and N,N-dimethylformamide (DMF) (Fisher reagent) were used as solvents for electrochemical studies. The supporting electrolyte, tetrabutylammonium fluoroborate (TBAT) (Fluka), was recrystallized from methanol and dried under reduced pressure prior to use.

Cyclic Voltammetry. Cyclic voltammograms were obtained either with a PAR 174 polarographic analyzer, in conjunction with a Houston Instruments 2000 X-Y recorder, or a PAR 173 potentiostat and 175 Universal Programmer on an oscilloscope. A three-electrode system was used, consisting of platinum working and counter electrodes and a commercial saturated lithium calomel electrode (SLCE) that was separated from the bulk of the solution by a bridge filled with solvent and supporting electrolyte. Solutions in the bridge were changed periodically to avoid aqueous contamination from entering the cell via the SLCE. All solutions were purged of oxygen by passing purified nitrogen through them for 10 min immediately prior to running cyclic voltammograms. For dichloromethane solutions, the nitrogen was solvent saturated prior to entering the cell. After degassing, a blanket of nitrogen was maintained over the solution.

For reversible electrode reactions, the $E_{1/2}$ values were measured as that potential lying midway between the oxidation and reduction peaks for a given couple. For several oxidations in DMF, no reverse cathodic peak was obtained. In these instances the potentials reported are the anodic peak potentials, E_p , recorded at 1V/sec. These potentials were scan rate dependent and shifted anodically by approximately $30/n$ mV for each tenfold increase in scan rate.

RESULTS

Cyclic voltammograms were obtained at a platinum electrode in both DMF and CH_2Cl_2 , containing 0.1M TBAT as supporting electrolyte. For each complex

investigated, the scan rate was varied between 0.1 and 100 V/sec and the current-voltage curves recorded. Figure 5 illustrates a typical cyclic voltammogram of PdTAA, PdTMTAA, and NiTAA in DMF. Figure 6 is the cyclic voltammogram of $[\text{Re}(\text{CO})_3]_2\text{TAA}$, $[\text{Re}(\text{CO})_3]_2\text{TPP}$, and $[\text{Re}(\text{CO})_3]_2\text{TMTAA}$ in CH_2Cl_2 .

Homogeneous chemical reactions following a one electron electrooxidation were observed for H_2TAA and H_2TMTAA in both CH_2Cl_2 and DMF and for all of the TAA complexes in DMF. Likewise in DMF, NiTMTAA and PdTMTAA exhibited a rapid chemical reaction following electrooxidation. The rate constants for the homogeneous chemical reaction following electron transfer were largest in the absence of a metal ion. In both CH_2Cl_2 and DMF, coupled chemical reactions [23] of $[\text{H}_2\text{TAA}]^+$ and $[\text{H}_2\text{TMTAA}]^+$ were so rapid that even at scan rates of 100V/sec, no reverse reduction peaks were obtained. No attempt was made to ascertain the nature of these chemical reactions. For slow chemical reactions, reversible cyclic voltammograms could be obtained at rapid scan rates. In these cases $i_{p/v}^{1/2}$ was constant and $i_{p,a}/i_{p,c}$ was equal to unity.

Potentials for the electrooxidation-reduction of each ligand and its corresponding metal complex are listed in Tables II-IV. The halfwave potentials for the OEP complexes were taken from the data of Fuhrhop, Kadish, and Davis [24].

DISCUSSION

All of the compounds investigated were oxidized and/or reduced by single electron transfers. In nonaqueous media, porphyrins and metalloporphyrins are oxidized in two single-electron transfer steps to yield π cation radicals and dication. [25], or reduced in two single-electron transfer steps to yield π anion radicals and dianions [26]. The oxidations of NiTMTAA and MnTMTAA⁺ to yield π cation radicals similar to metalloporphyrins have been reported in the literature [14,15]. Based on these assignments, the product of the first

oxidation was assigned as a π cation reaction for complexes of Pd(II), Re(I), and Rh(I). Likewise, the product of the first reduction of Pd(II), Ni(II), Re(I), and Rh(I) complexes were designated as π anion radicals.

The oxidation and reduction potentials of the compounds investigated in CH_2Cl_2 are presented in Table II. Although the data is limited, changing the ligand from TPP to TAA has little effect on half wave potentials in CH_2Cl_2 . On the other hand, the oxidation potentials of TMTAA with respect to the TPP complexes are quite dissimilar. In fact, the oxidation potential differences between the metal complexes of TPP and TMTAA vary between 0.32 V (dirhenium central atoms) and 0.56V (iron central atoms) with the TMTAA complex being more easily oxidized in all cases.

The half wave potentials for oxidation of each complex in DMF is listed in Table III. Although the anodic peak potentials, E_p , are similar for the oxidations of TMTAA and TAA complexes in DMF, an absolute comparison of thermodynamic potentials cannot be made as was done in CH_2Cl_2 . The homogeneous chemical reaction following the electron transfer will shift the peak potential cathodically from the half wave potential. The rate constants are unknown quantities for the compounds investigated and thus $E^\circ(E_{1/2})$ cannot be determined.

Of special interest is a comparison of $[\text{Rh}(\text{CO})_2]_2\text{TMTAA}$ with $[\text{Re}(\text{CO})_3]_2\text{TMTAA}$. Both compounds are more easily oxidized than the uncomplexed ligand (Table III). In addition the potentials for the reversible oxidation of $[\text{Re}(\text{CO})_3]_2\text{TMTAA}$ are 0.32 to 0.36V cathodic of those for the oxidation of the $[\text{Re}(\text{CO})_3]_2\text{TPP}$ complex (Tables II and III). On the other hand, the reversible half wave potential for oxidation of $[\text{Rh}(\text{CO})_2]_2\text{TMTAA}$ is cathodic of $[\text{Re}(\text{CO})_3]_2\text{TMTAA}$ by 0.19V in both CH_2Cl_2 (Table II) and in DMF (Table III). This is opposite that predicted from the electronegativities of the two metal ions. For a series of M(II) to M(IV) metalloctaethylporphyrins, the difficulty of porphyrin ring oxidation is

directly proportional to the negative charge on the porphyrin ligand and, for a given metal oxidation state, the half wave potentials for cation radical formation can be linearly related to the electronegativities [24]. Since the potentials are reversed for the rhenium and rhodium complexes this would seem to imply that differences in metal-metal distance effect the interactions of the metal orbitals with those of the porphyrin ring.

In contrast to the oxidations, the reduction behavior of the complexes may vary substantially with the ligand, but not necessarily with the central metal (Table IV). Formation of the anion radical is favored by 0.85V when the complex is H_2TPP compared to H_2TAA and by over 1.30V when compared to H_2TMTAA . This is not the case for complexes of Ni and Pd which have almost identical potentials independent of ligand. In the case of OEP one might predict identical potentials for radical formation when the central metal is Ni or Pd. However, this is totally unexpected for the TMTAA complexes of these metals since their geometries differ significantly, i.e. the Ni complex is saddle shaped while the Pd complex is pseudo planar [16].

It has been reported for octaethylporphyrin complexes [24], and verified with other metalloporphyrin complexes [27-29] that the potential difference between cation and anion radical formation, $|E_{1/2}(ox) - E_{1/2}(red)|$, is equal to $2.25 \pm 0.15V$. With several exceptions, this value is independent of metal ion electron transfers and holds true for a number of different natural and synthetic porphyrins containing metals of +2, +3, or +4 oxidation state. Recently, Louati, Gross, and Jordan [9] showed that this potential difference decreased to 1.83V for the $[Re(CO)_3]_2TPP$ oxidation-reduction and that the change was due almost entirely to changes associated with the lowest unoccupied molecular orbital (LUMO). Our results with H_2TMTAA , $[Re(CO)_3]_2TMTAA$ and $[Rh(CO)_2]_2TMTAA$ also indicate a change in the LUMO but in this case, in a direction opposite to that observed for the porphyrin complexes. Surprisingly, $[Re(CO)_3]_2$

TAA behaves very similarly to most metalloporphyrins [30]. The oxidation potential of 1.11V for $[\text{Re}(\text{CO})_3]_2\text{TAA}$ in CH_2Cl_2 is almost identical to that obtained for $[\text{Re}(\text{CO})_3]_2\text{TPP}$ (1.01V). When considering the reversible reduction potential of -1.09V for $[\text{Re}(\text{CO})_3]_2\text{TAA}$ in DMF, and the oxidation potential of +1.11V in CH_2Cl_2 , a combined $E_{1/2}(\text{ox}) - E_{1/2}(\text{red}) = 2.20 \text{ V}$ is obtained. Calculated values for $E_{1/2}(\text{ox}) - E_{1/2}(\text{red})$ are listed in Table V. For each TMTAA^{-2} and TAA^{-2} series only a lower estimate can be placed on the potential differences. However, the rough order of separation between the LUMO and HOMO appears to be as follows for the free base and the dirhenium complexes:



This order follows that of the reduction potentials (Table III) which seems to be the largest contributor to the differences in potential separation.

Work is presently underway to isolate complexes of TMTAA with other second and third row transition metals. The goal is to obtain other "pseudo-planar" complexes analogous to PdTMTAA to elucidate the dependence of changes in macrocyclic planarity on redox reactivity.

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Table I. Physical Data for Some of the Compounds Investigated

Compound	MP(°C)	Uv, $\nu_{\max}$, nm(log ϵ)	Ir, cm^{-1} (KBr pellet)
$[\text{Re}(\text{CO})_3]_2\text{TAA}^{\text{a}}$	278-279	455 (3.52)	2020 ($\nu(\text{M-CO})$) 1900 ($\nu(\text{M-CO})$)
$[\text{Re}(\text{CO})_3]_2\text{TMTAA}^{\text{b}}$	277°C	4.5 sh	1995 ($\nu(\text{M-CO})$) 1970 ($\nu(\text{M-CO})$) 1900 ($\nu(\text{M-CO})$) 1880 ($\nu(\text{M-CO})$)
$[\text{Re}(\text{CO})_3]_2\text{TPP}^{\text{c}}$	350 dec	408 (Soret) 485 sh 513	1900 ($\nu(\text{M-CO})$) 2025 ($\nu(\text{M-CO})$)
$[\text{Rh}(\text{CO})_2]_2\text{TMTAA}^{\text{d}}$	329 dec	375 488	2025 ($\nu(\text{M-CO})$) 1975 ($\nu(\text{M-CO})$)
$\text{PdTMTAA}^{\text{e}}$	150 dec	415 (4.5) 490 (4.2)	
PdTAA^{e}	7400	363, 402 ^{sh} , 424 455, 487	

^aRef. 17. ^bRef. 18. ^cRef. 20. ^dRef. 19. ^eRef. 16.

Table II. Half Wave Potentials for First Oxidation in CH_2Cl_2

Central ion	TMTAA	ligand	
		TAA	TPP
2H^+	—	—	1.10
Mn(III) SCN^-	0.74	—	1.24
$\text{Fe(III) (Br}^-)$	0.58	—	1.14
Co(II)	—	0.82 ^a	0.82 ^a
2 Re(I) (CO)_3	0.69	1.11	1.01
2 Rh(I) (CO)_2	0.50	—	—

a. Metal centered reaction $\text{Co(II)} \rightarrow \text{Co(III)}$.

Table III. Half Wave Potentials for Cation Radical Formation in DMF^a

Central ion	Ligand			
	TMTAA	TAA	OEP ^b	TPP
2H ⁺	(0.96)	(0.85)	0.81	1.25
Pd(II)	(0.70)	(0.80)	0.82	—
Ni(II)	(0.75)	(0.83)	0.73	—
Re(I)(CO) ₃	0.80	(1.28)	—	1.16 ^c
[†] , Re(I) (CO) ₃	—	(0.82)	—	(1.06)
Rh(I) (CO) ₂	0.61	—	—	—

a. Values listed in parentheses are anodic peak potentials for chemically coupled oxidations measured at a scan rate of 1V/s.

b. Ref. 24.

c. Ref. 9.

Table IV. Half Wave Potentials for Anion Radical Formation in DMF

Central ion	TMTAA	Ligand		
		TAA	OEP ^a	TPP
2H ⁺	>-2.20	-1.75	-1.46	-0.90
Pd(II)	-1.58	-1.46	-1.53	—
Ni(II)	-1.56	-1.54	-1.59	-1.18 ^b
2Re(I) (CO) ₃	>-2.20	-1.09	—	-0.66 ^c
H ⁺ , Re(I) (CO) ₃	—	—	—	-0.75

a. Ref. 24.

b. Ref. 26a.

c. Ref. 9.

Table V. Potential Difference Between Cation and Anion Radical Formation
in DMF^a

Central ion	TMTAA	Ligand		
		TAA	OEP ^b	TPP
2H ⁺	>3.16	(2.60)	2.27	2.15
Pd(II)	(2.28)	(2.26)	2.35	—
Ni(II)	(2.31)	(2.37)	2.23	—
2Re(I) (CO) ₃	>3.00	(2.37)	—	1.82 ^c
H ⁺ , Re(I) (CO) ₃	—	—	—	(1.81)

a. All values in parentheses are differences computed from a chemically coupled oxidation and as such, represent the minimum potential difference.

b. Ref. 24.

c. Ref. 9.

Figures

Figure 1. The Structures of (a) H_2OEP , (b) H_2TPP , (c) H_2TAA , and (d) H_2TMTAA

Figure 2. An ORTEP sideview of $PdTMTAA$ illustrating the "Psuedo" planarity of the complex

Figure 3. Schematic representation of $[Re(CO)_3]_2TAA$

Figure 4. Schematic representation of $[Rh(CO)_2]_2TMTAA$

Figure 5. Cyclic voltammograms of (a) N_1TAA , (b) $PdTAA$, (c) $PdTMTAA$ in DMF, 0.1M TBAT. Concentrations were between 1.0 to 2.0mM. Scan Rate = 0.20v/s

Figure 6. Cyclic voltammograms of (a) $[Re(CO)_3]_2TAA$, (b) $[Re(CO)_3]_2TMTAA$, (c) $[Re(CO)_3]_2TPP$ in CH_2Cl_2 , 0.1M TBAT. Concentrations were between 1.0 to 2.0mM. Scan rate = 0.20v/s











