

the product distribution will be dependent on the structure of L but independent on the concentration of L.<sup>30</sup>

The mechanism is also consistent with the results observed when CO is added. Increasing CO decreases 2 and increases 1. In CO-saturated solutions, the total quantum yield ( $\Phi_1 + \Phi_2$ ) does not decrease, within experimental error, and is the same as the yield previously obtained for substitution of Fe(CO)<sub>5</sub> by (E)-cyclooctene.<sup>2</sup> The independence of  $\Phi_1 + \Phi_2$  on [CO] suggests that  $k_1 \gg k_{CO}$  since in one experiment [CO]/[PEt<sub>3</sub>] = 9. Therefore PEt<sub>3</sub> adds to Fe(CO)<sub>4</sub> faster than does CO.

Further studies with other ligands and solvents are underway. We conclude that the formation of a disubstituted product is a single-photon process and that the relative rates of intersystem crossing and CO dissociation for <sup>3</sup>Fe(CO)<sub>4</sub>L may determine the relative yields of mono- and disubstituted products.

**Acknowledgment.** We thank Bob Squires for providing a copy of his manuscript prior to publication and David Rayner for helpful discussions. The donors of the Petroleum Research Fund, administered by the American Chemical Society, and a Memphis State University Faculty Research Grant are acknowledged for partial support of this research.

**Supplementary Material Available:** A figure showing IR spectra (1 page). Ordering information is given on any current masthead page.

(30) An alternative mechanism might involve Fe(CO)<sub>4</sub>(solvent) in equilibrium with Fe(CO)<sub>4</sub> where the different reactivities of the two intermediates determine the distribution of products. This alternative seems unlikely since at 20 K both Fe(CO)<sub>4</sub> and Fe(CO)<sub>4</sub>-methane are formed (Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* 1974, 2279). Since all the Fe(CO)<sub>4</sub> is not trapped, it may be that the Fe(CO)<sub>4</sub>-alkane interaction is very weak and at room temperature the formation of Fe(CO)<sub>4</sub>-alkane is not significant.

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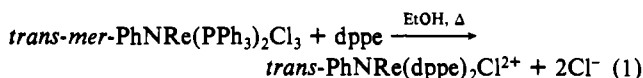
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### Unusual Stabilization of Trans 2,2'-Bipyridine Ligands in a Rhenium(V) Phenylimido Complex

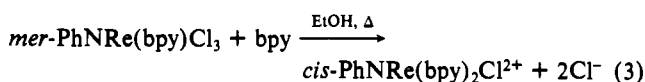
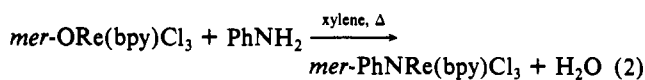
The majority of bis(2,2'-bipyridine) complexes possess cis geometries. In those few instances where the 2,2'-bipyridine (bpy) ligands are trans, extraordinary steric or electronic factors result in abnormal kinetic or thermodynamic stability. Some notable examples include Pd<sup>II</sup>(bpy)<sub>2</sub><sup>2+</sup>,<sup>1</sup> trans-Ru<sup>III</sup>(bpy)<sub>2</sub>(H<sub>2</sub>O)(OH)<sup>2+</sup>,<sup>2</sup> trans-Os<sup>II</sup>(bpy)<sub>2</sub>(PPh<sub>2</sub>Me)<sup>2+</sup>,<sup>3</sup> trans-Os<sup>VI</sup>(bpy)<sub>2</sub>O<sub>2</sub><sup>2+</sup>,<sup>4</sup> and trans-Ru<sup>II</sup>(bpy)<sub>2</sub><sup>2+</sup>.<sup>5</sup>

During our studies of the photochemistry of complexes with metal-nitrogen multiple bonds,<sup>6</sup> we have developed synthetic routes to new Re(V) imido complexes of the type [PhNRe(chelate)<sub>2</sub>X]<sup>2+</sup> where the chelate contains nitrogen or phosphorus donors. For example, a displacement reaction can be used to prepare the new complex trans-PhNRe(dppe)<sub>2</sub>Cl<sup>+</sup> as depicted in eq 1 (dppe =



1,2-bis(diphenylphosphino)ethane).<sup>7</sup> We also attempted to

prepare complexes containing two bipyridine ligands, with the expectation that they would adopt structures similar to that of the isoelectronic nitride cis-NRe(bpy)<sub>2</sub>Br<sup>+</sup>.<sup>8</sup> The synthesis was designed to follow the two-step procedure shown in eqs 2 and 3.



Unexpectedly, the product was not cis-PhNRe(bpy)<sub>2</sub>Cl<sup>2+</sup>, as shown in eq 3, but trans-PhNRe(bpy)<sub>2</sub>(OEt)<sup>2+</sup>, where an ethoxide group had replaced chloride in the coordination sphere. The PF<sub>6</sub><sup>-</sup> salt was characterized by <sup>1</sup>H NMR and UV-visible spectroscopies, cyclic voltammetry, elemental analysis, and a structure determination by X-ray diffraction.<sup>9</sup>

The crystal structure of trans-PhNRe(bpy)<sub>2</sub>(OEt)<sup>2+</sup> shown in Figure 1 reveals a pseudooctahedral coordination sphere about Re with the bpy ligands distorted in a "concerted-canted" fashion so as to minimize steric interactions between the 6 and 6' protons on adjacent bpy ligands. The main distortions from ideal octahedral symmetry are due to the rather small bite angles of the bpy ligands (75.3 (2) and 74.9 (2)°) and to the asymmetric apical ligands. A closer look at the bond parameters shows the Re-N(bpy) lengths vary between 2.134 (6) and 2.163 (6) Å. These are notably shorter than the 2.210- and 2.203-Å Re-N(bpy) bond lengths found in the d<sup>2</sup> dioxo complex cis-Re<sup>V</sup>O<sub>2</sub>(bpy)(py)<sub>2</sub>.<sup>10</sup> The (Ph)N-Re-O(Et) angle is nearly, but not quite, linear (174.8 (3)°). Probably the most striking features are Re-N(Ph) and Re-O(Et) bond lengths of 1.740 (6) and 1.895 (5) Å, which are in the range of multiple bonds for both interactions. This is aptly illustrated by a Re-N distance of 1.726 (6) Å in mer-trans-

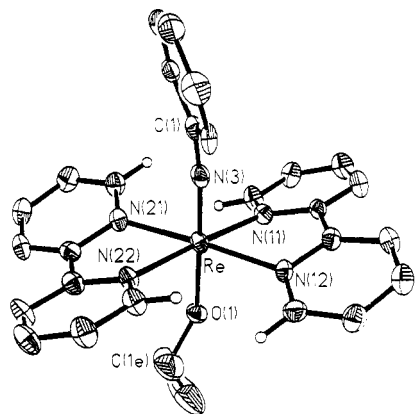
(7) Preparation of trans-[Re(NPh)(Cl)(dppe)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>: A mixture of ReNPhCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.2 g, 0.22 mmol), dppe (0.35 g, 0.88 mmol), and EtOH (200 mL) was refluxed for 2 days. The resulting reaction mixture was allowed to cool to room temperature and filtered. The yellow filtrate was evaporated to dryness. The resulting brown residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and the solution was loaded into a neutral alumina column. The column was washed with CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN, and finally a brown fraction was eluted with ethanol. The ethanol solution was reduced in volume, NH<sub>4</sub>PF<sub>6</sub> (0.3 g, 1.8 mmol) was added, and the mixture was stirred at room temperature for 1 h. A brown solid was filtered off, washed with ethanol, hexanes, and diethyl ether, and dried. Yield: 0.15 g (48%). Anal. Calcd for C<sub>38</sub>H<sub>33</sub>ClF<sub>12</sub>NP<sub>6</sub>: C, 49.78; H, 3.80; Cl, 2.54; N, 1.00. Found: C, 50.37; H, 3.72; Cl, 2.18; N, 0.77. UV-visible spectrum (CH<sub>2</sub>CN; λ, nm (ε)): 540 (160), 476 (2584), 339 (12488), 254 (50330), 236 (64516). <sup>13</sup>P NMR spectrum (CD<sub>3</sub>CN): a singlet at δ = +11.65 ppm due to the diphosphine and a septet at δ = -142 ppm due to the hexafluorophosphate anion.

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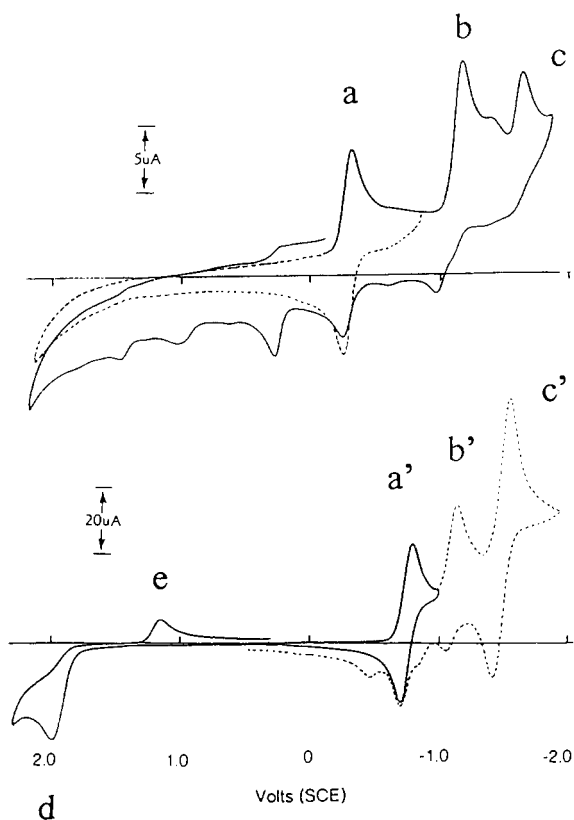
(9) Preparation of trans-[Re(NPh)(OEt)(bpy)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>: A mixture of ReNPhCl<sub>3</sub>(bpy) (0.2 g, 0.37 mmol), bpy (0.23 g, 1.48 mmol), and EtOH (200 mL) was refluxed for 4 days. The resulting reaction mixture was filtered. The brown filtrate was evaporated to dryness. The brown residue was dissolved in CH<sub>3</sub>CN, and the solution was loaded into a neutral alumina column. The column was washed with CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN, and finally a brown fraction was eluted with ethanol. The ethanol solution was reduced in volume, NH<sub>4</sub>PF<sub>6</sub> (0.3 g, 1.80 mmol) was added, and the mixture was stirred at room temperature for 1 h. A brown solid was filtered off, washed with ethanol, hexanes, and diethyl ether, and dried. Yield: 0.15 g (44%). Anal. Calcd for C<sub>28</sub>H<sub>26</sub>F<sub>12</sub>N<sub>5</sub>OP<sub>2</sub>Re: C, 36.37; H, 2.74; N, 7.57. Found: C, 36.42; H, 2.74; N, 7.53. UV-visible spectrum (CH<sub>2</sub>CN; λ, nm (ε)): 525 (424), 421 (3467 sh), 364 (9535 sh), 316 (23114), 221 (43339). <sup>1</sup>H NMR spectrum (CD<sub>3</sub>CN): δ 9.25 (d, bpy, 2 H), 8.70 (t, bpy, 2 H), 8.50 (t, bpy, 2 H), 7.95 (t, bpy, 2 H), 7.32 (t, Ph, 1 H), 7.18 (t, Ph, 2 H), 6.95 (t, Ph, 2 H), 3.25 (q, OEt, 2 H), 0.35 (t, OEt, 3 H). Crystal data for trans-[PhNRe(bpy)<sub>2</sub>(OEt)](PF<sub>6</sub>)<sub>2</sub> (C<sub>28</sub>H<sub>26</sub>F<sub>12</sub>N<sub>5</sub>OP<sub>2</sub>Re): M<sub>r</sub> = 924.7, monoclinic, space group P2<sub>1</sub>/n, with a = 11.032 (3) Å, b = 8.848 (2) Å, c = 34.642 (6) Å, β = 98.32 (2)°, V = 3208.6 (13) Å<sup>3</sup>, F(000) = 1800, Z = 4, and D<sub>c</sub> = 1.914 mg/m<sup>3</sup>. Final R = 0.0332 and R<sub>w</sub> = 0.0367 from 3704 observed reflections. The data were collected with a Siemens R3m/v diffractometer employing Mo Kα radiation and using ω scans. The structure was solved via Patterson methods and refined by least-squares techniques.

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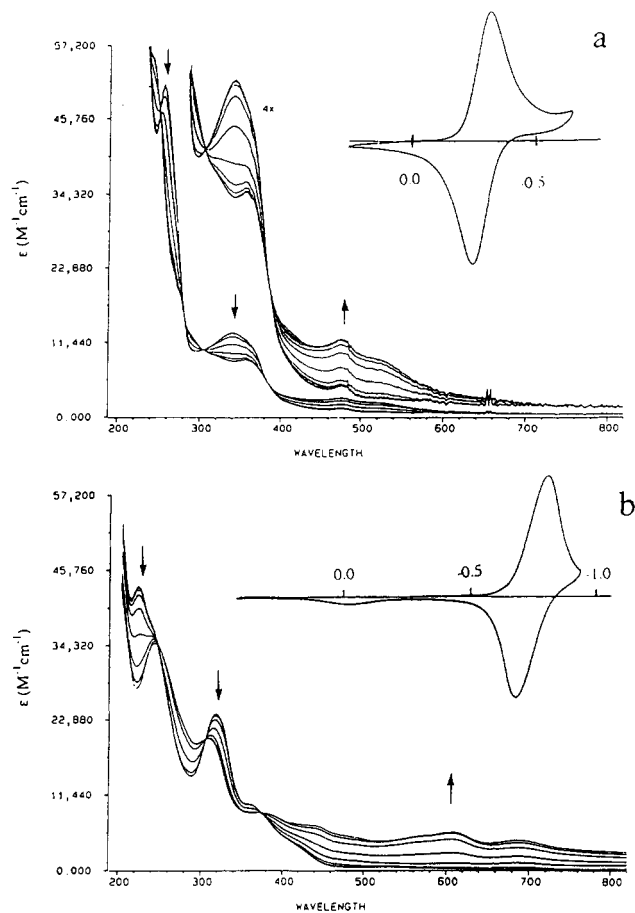


**Figure 1.** ORTEP view of the X-ray crystal structure of *trans*-PhNRe(bpy)<sub>2</sub>(OEt)<sub>2</sub><sup>+</sup>. The thermal ellipsoids are drawn at the 45% probability level. Important bond lengths (Å) and angles (deg): Re–N(3), 1.740 (6); Re–O(1), 1.895 (5); C(1)–N(3)–Re, 167.4 (6); Re–O(1)–C(1e), 145.7 (6); N(11)–Re–N(12), 75.3 (2); N(21)–Re–N(22), 74.9 (2); O(1)–Re–N(3), 174.8 (3).



**Figure 2.** Cyclic voltammetry of *trans*-PhNRe(dppe)<sub>2</sub>Cl<sub>2</sub><sup>2+</sup> (top) and *trans*-PhNRe(bpy)<sub>2</sub>(OEt)<sub>2</sub><sup>2+</sup> (bottom) in CH<sub>3</sub>CN with 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte at a Pt button working electrode and a scan rate of 100 mV/s. The reductive redox processes labeled a–c and a'–c' are inherent to the complexes. The processes labeled a and a' are reversible or quasi-reversible (see text) reductions to a formal Re<sup>IV</sup> form. The process labeled d is a chemically irreversible oxidation to a Re<sup>VI</sup> complex that is coupled to the formation of a new product (e).

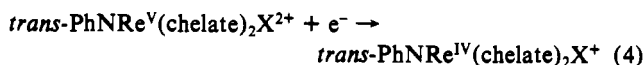
PhNReCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub><sup>11</sup> and 1.880 (9) Å for the Re–O(Et) bond length in *trans,trans*-OREI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>OEt.<sup>10</sup> Another indication of the multiple-bond nature of Re–O(Et) is that the Re–O–C angle of the grouping is splayed to 145.7 (6)° when no apparent intramolecular nonbonding contacts exist (perhaps due to the planar



**Figure 3.** Spectroelectrochemical studies of (a) 1.2 mM *trans*-PhNRe(dppe)<sub>2</sub>Cl<sub>2</sub><sup>2+</sup> and (b) 1.3 mM *trans*-PhNRe(bpy)<sub>2</sub>(OEt)<sub>2</sub><sup>2+</sup> through the first reduction, which corresponds to the Re<sup>V/IV</sup> couple. The arrows show the direction of growth or disappearance of the spectral features as the potential was scanned cathodically (see text).

nature of the *trans* bpy ligands). This is analogous to the cases of (*p*-MeC<sub>6</sub>H<sub>4</sub>)NRe(S<sub>2</sub>CNMe<sub>2</sub>)<sub>2</sub>OEt,<sup>13</sup> where the angle is 131.7 (4)° and multiple bonding minimal, and ONbCl<sub>2</sub>(bpy)OEt,<sup>14</sup> where the angle is 149° and multiple bonding profound.

The redox chemistry of both *trans*-PhNRe(dppe)<sub>2</sub>Cl<sub>2</sub><sup>2+</sup> and *trans*-PhNRe(bpy)<sub>2</sub>(OEt)<sub>2</sub><sup>2+</sup> is rich and promises to yield further insight into the nature of rhenium–phenylimido bonding. Cyclic voltammetry of each complex in CH<sub>3</sub>CN, with 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte (Figure 2), exhibits complex electrochemistry during a reductive potential sweep. Both complexes exhibit three reductive waves (labeled a–c and a'–c' in Figure 2) that variable scan rate studies indicate are inherent to the complexes. For both complexes, the first reduction wave shows reversible behavior during the time scale of the voltage sweep (50–200 mV/s). Comparison with the ferrocenium/ferrocene couple as an internal standard demonstrates that they are one-electron processes, consistent with reduction to a d<sup>3</sup> Re<sup>IV</sup> complex (eq 4). That the reversible potential for



*trans*-PhNRe(bpy)<sub>2</sub>(OEt)<sub>2</sub><sup>2+</sup> is more negative than that for *trans*-PhNRe(dppe)<sub>2</sub>Cl<sub>2</sub><sup>2+</sup> is an indication of the pronounced donor ability of the {bpy, OEt} ligand set relative to {dppe, Cl}.

Spectroelectrochemical experiments<sup>15</sup> demonstrate the reversibility of the Re<sup>V</sup>/Re<sup>IV</sup> couple for PhNRe(dppe)<sub>2</sub>Cl<sub>2</sub><sup>2+</sup> in that a

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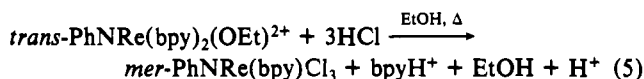
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limiting spectrum of the reduced form (Figure 3a) can be produced and then quantitatively oxidized back to  $\text{Re}^{\text{V}}$ . For  $\text{trans-PhNRe}^{\text{V}}(\text{bpy})_2(\text{OEt})^{2+}$ , reduction on our spectroelectrochemical time scale (each scan in Figure 3a is made in ca. 5 s) produces predominantly  $\text{trans-PhNRe}^{\text{IV}}(\text{bpy})_2(\text{OEt})^+$ ; however, a slow chemical process drains this away to product. This is evidenced by the appearance of a new oxidative process at  $-0.05$  V (Figure 3b) and the observation that reoxidation of  $\text{PhNRe}^{\text{IV}}(\text{bpy})_2(\text{OEt})^+$  immediately after spectroelectrochemical reduction regenerates the limiting spectrum of  $\text{trans-PhNRe}^{\text{V}}(\text{bpy})_2(\text{OEt})^{2+}$  mixed with the spectral signature of a new complex (not shown in Figure 3b). In the oxidative branch of the cyclic voltammogram, only  $\text{trans-PhNRe}^{\text{V}}(\text{bpy})_2(\text{OEt})^{2+}$  is observed to be redox-active, exhibiting a single-electron oxidation ( $E_p = \text{ca. } +1.95$  V; feature d in Figure 3b), which generates a transiently stable  $\text{trans-PhNRe}(\text{bpy})_2(\text{OEt})^{3+}$  species that is coupled to the rapid formation of a new complex ( $E_p = \text{ca. } +1.02$  V; feature e in Figure 3b).

The observation of trans bpy ligands which are apparently stabilized by strong multiple bonding in a  $\text{Re}^{\text{V}}$ -imido complex, coupled with a rich redox chemistry of a presumed  $\text{Re}^{\text{VI}}$  state and an observed  $\text{Re}^{\text{IV}}$  state, will enable us to define the interplay of steric and electronic requirements that exist in the high-valent polypyridine chemistry of rhenium.

We have been unsuccessful in our attempts to convert  $\text{trans-PhNRe}(\text{bpy})_2(\text{OEt})^{2+}$  to its cis isomer. Extended heating at reflux (48 h) in EtOH results in no apparent reaction. This is consistent with either the trans form being the thermodynamic product or an abnormally high activation free energy for trans to cis isomerization. Protonation under mild conditions proceeds through a green intermediate, which eventually loses bpy and generates  $\text{mer-PhNRe}(\text{bpy})\text{Cl}_3$  in quantitative yield, presumably as depicted in eq 5.



The unusual stability of  $\text{trans-PhNRe}(\text{bpy})_2(\text{OEt})^{2+}$  can be rationalized in terms of a qualitative molecular orbital argument,<sup>16</sup> which predicts enhanced stability of the 18- $e^-$  trans isomer for the model complex  $\text{trans-O}_2\text{Mo}(\text{PH}_3)_4$ , relative to the cis form. In our example, the electronic stabilization of multiple bonding apparently overcomes the steric hindrance imposed by the "bumping" of the 6, 6' protons on the bpy ligand. Because of this electronic stabilization, it seems likely that an extended series of abnormally stable trans complexes with axial metal-ligand multiple bonds can be prepared: for example,  $\text{trans-O}_2\text{Re}(\text{bpy})_2^+$ ,  $\text{trans-NRe}(\text{bpy})_2(\text{OR})^+$ , and  $\text{trans-ORe}(\text{bpy})_2(\text{OR})^{2+}$ .

**Acknowledgment.** We thank the National Science Foundation for support under the EPSCoR Program and the University of Wyoming for a Basic Research Grant.

**Registry No.** *trans,mer-PhNRe*(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub>, 62192-31-8; *mer-PhNRe*(bpy)Cl<sub>3</sub>, 139199-31-8; *trans-[Re(NPh)(Cl)(dppe)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>*, 139199-33-0; *trans-[Re(NPh)(OEt)(bpy)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>*, 139199-35-2; *trans-[PhNRe(dppe)<sub>2</sub>Cl]<sup>+</sup>*, 139199-36-3; *trans-[PhNRe(bpy)<sub>2</sub>(OEt)]<sup>+</sup>*, 139199-37-4.

**Supplementary Material Available:** For *trans-[PhNRe(bpy)<sub>2</sub>(OEt)](PF<sub>6</sub>)<sub>2</sub>*, tables of atomic coordinates and isotropic displacement coefficients (Table 1), bond lengths (Table 2), bond angles (Table 3), anisotropic displacement coefficients (Table 4), hydrogen coordinates and isotropic displacement coefficients (Table 5), crystallographic data collection parameters (Table 6), and solution and refinement parameters (Table 7) (7 pages); a listing of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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## Articles

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### Electrochemical Investigation of the Association of Distamycin A with the Manganese(III) Complex of *meso*-Tetrakis(*N*-methyl-4-pyridiniumyl)porphine and the Interaction of This Complex with DNA

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Differential pulse voltammetry (DPV) was used to study the interaction of distamycin A (Dis) with the manganese(III) complex of *meso*-tetrakis(*N*-methyl-4-pyridiniumyl)porphine ( $\text{Mn}^{\text{III}}\text{P}$ ) and that of this complex with calf thymus (CT) DNA. The addition of distamycin to  $\text{Mn}^{\text{III}}$  caused a diminution in the peak current and a positive shift in the peak potential of the DPV wave for the reduction of  $\text{Mn}^{\text{III}}\text{P}$ . This effect on the peak current is a result of a decrease in the diffusion coefficient ( $D$ ) of  $\text{Mn}^{\text{III}}\text{P}$  from  $D_1 = 1.2 (\pm 0.3) \times 10^{-6} \text{ cm}^2/\text{s}$  to  $D_2 = 7.2 (\pm 0.2) \times 10^{-8} \text{ cm}^2/\text{s}$ . An amperometric titration was used to show that two distamycins bind to one  $\text{Mn}^{\text{III}}\text{P}$  with an overall binding constant of  $K = 5 (\pm 3) \times 10^8 \text{ M}^{-2}$ , assuming a static equilibrium model, probably by axial coordination of the oxygen atom of the formyl end of Dis to  $\text{Mn}^{\text{III}}$ . The 23-mV positive shift in the DPV peak potential of  $\text{Mn}^{\text{III}}\text{P}$  indicates that distamycin binds 2.5 times more strongly to  $\text{Mn}^{\text{II}}\text{P}$  than to  $\text{Mn}^{\text{III}}\text{P}$ . The  $\text{Mn}^{\text{III}}\text{P}(\text{Dis})_2$  complex interacts with sonicated CT DNA; DPV and amperometric titration were also used to investigate this interaction.

#### Introduction

In this work we describe the association of the manganese(III) complex of *meso*-tetrakis(*N*-methyl-4-pyridiniumyl)porphine ( $\text{Mn}^{\text{III}}\text{P}$ ) and distamycin A (Dis) (Figure 1) in the absence and in the presence of sonicated calf thymus (CT) DNA. Both  $\text{Mn}^{\text{III}}\text{P}$  and Dis are known to bind individually to DNA. We originally intended to study the interaction of DNA with Dis by electro-

chemical competition experiments with electroactive  $\text{Mn}^{\text{III}}\text{P}$  using differential pulse voltammetry (DPV).<sup>1</sup> Dis is not electroactive in the potential range where  $\text{Mn}^{\text{III}}$  is reduced, but it can be irreversibly oxidized at 0.8 V vs SCE. However, we found that

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