

data obtained in this study and those from recent published reports of Pt(0) chemical shifts,<sup>18-22</sup> we conclude that Pt(0) resonances generally occur at higher fields than those for Pt(II) complexes. Although Pt(II) complexes have <sup>195</sup>Pt resonances as high as -5500 ppm<sup>1</sup> (range for Pt(II) complexes: -1600 to -5500 ppm), the resonances of Pt(0) complexes occur as high as -6596 ppm<sup>23</sup> for Pt[P(*i*-Pr)<sub>3</sub>]<sub>2</sub><sup>18</sup> (range for Pt(0) complexes: -4500 to -6600 ppm).

**Coupling Constants <sup>1</sup>J(Pt-P1), <sup>1</sup>J(Pt-P3), and <sup>2</sup>J(P1-P3).** Variation in the magnitudes of the Pt-P coupling constants for the tripod ligand, <sup>1</sup>J(Pt-P3), is relatively small as the monodentate phosphine ligand changes from PMe<sub>2</sub>Ph to P(OPh)<sub>3</sub>; however, the magnitude of the Pt-P coupling constant for the monodentate phosphine ligands, <sup>1</sup>J(Pt-P1), increases dramatically from 5342 to 9128 Hz. In addition, the magnitudes of <sup>1</sup>J(Pt-P3) are smaller than those observed for Pt(PR<sub>3</sub>)<sub>4</sub> compounds.<sup>24-26</sup> These changes reflect the increased p character of the Pt-P3 bonds to the tripod ligand due to the constricted P3-Pt-P3 bond angles (93-99°). This constrained C<sub>3v</sub> geometry of the tripod ligand allows a larger s character in the Pt-P1 bond; consequently, the P1 coupling constants are larger than for "T<sub>d</sub>" Pt(0) complexes. As mentioned previously, the magnitude of the one-bond phosphorus coupling constant depends primarily on α<sub>p</sub><sup>2</sup> and |ψ<sub>3s</sub>(P)|<sup>2</sup>. A change of the groups on one of the coupled phosphorus atoms (i.e., P1) can have a large effect on α<sub>p</sub><sup>2</sup> and |ψ<sub>3s</sub>(O)|<sup>2</sup> for that atom; however, it apparently has only a small effect on the corresponding terms of another phosphorus atom (i.e., P3).<sup>27</sup>

The magnitudes of <sup>1</sup>J(Pt-P) and <sup>2</sup>J(P-P) coupling constants for Pt(II) complexes are affected by the electronegativity of the phosphorus substituents.<sup>28</sup> This effect is observed also for the Pt(tripod)PR<sub>3</sub> complexes. A linear correlation (*p* = 0.978) is observed between <sup>2</sup>J(P1-P3) and Taft's constant<sup>29</sup>

$$\sigma^* = 1.57 \times 10^{-1} ({}^2J(\text{P1-P3})) - 7.10 \quad (4)$$

A similar relationship has been observed for the one-bond, metal-phosphorus coupling constants, <sup>1</sup>J(Pt-P1), in related Pt-(tripod)PR<sub>3</sub> complexes.<sup>15</sup> This similarity between <sup>2</sup>J(P1-P3) and <sup>1</sup>J(Pt-P1) is not surprising, since the two-bond, phosphorus-phosphorus coupling constants are transmitted through the metal center. In fact, a linear correlation (*p* = 0.993) exists between <sup>2</sup>J(P1-P3) and <sup>1</sup>J(Pt-P1) for the Pt(tripod)PR<sub>3</sub> complexes.

$${}^2J(\text{P1-P3}) = 9.02 \times 10^{-2} ({}^1J(\text{Pt-P1})) + 3.85 \quad (5)$$

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**Registry No.** 1, 112712-94-4; 2, 56261-12-2; 3, 56261-10-0; 4, 77933-86-9; 5, 112712-95-5; 6, 112712-96-6; 7, 112712-97-7; 8, 112712-98-8; 9, 112712-99-9; 10, 112713-00-5; 11, 56261-15-5; PtCl<sub>2</sub>-(tripod), 112712-93-3; <sup>195</sup>Pt, 14191-88-9.

**Supplementary Material Available:** Sample <sup>31</sup>P{<sup>1</sup>H} and <sup>195</sup>Pt{<sup>1</sup>H} spectra and graphs corresponding to the least-squares equations (3)-(5) (5 pages). Ordering information is given on any current masthead page.

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## Kinetics of the Displacement of Gadolinium(III) from a Water-Soluble Porphyrin by EDTA

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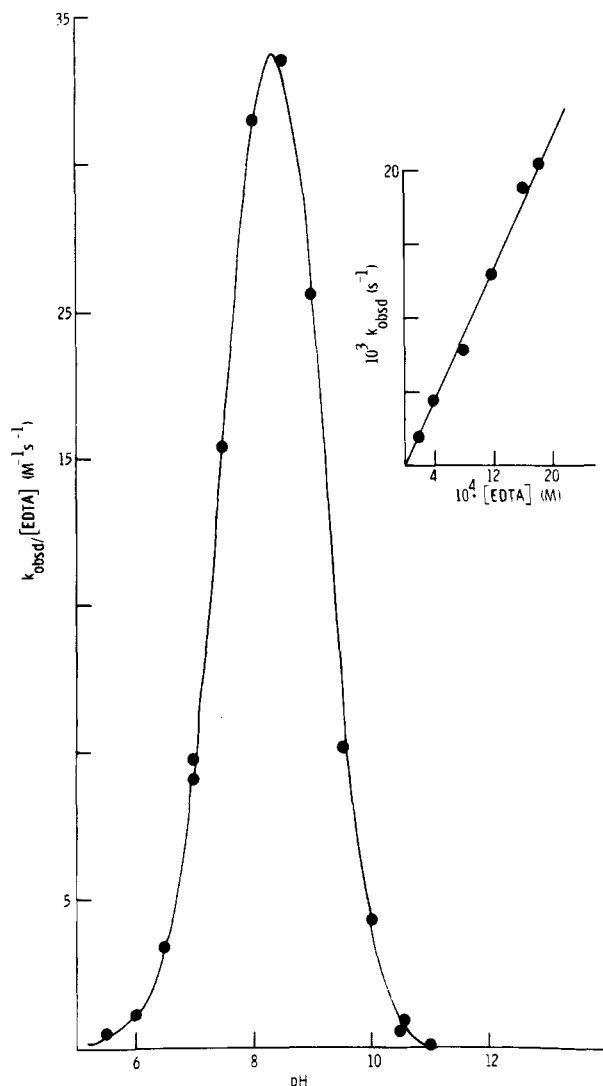
Paramagnetic water-soluble metalloporphyrins are being explored as tissue contrast agents in magnetic resonance imaging studies.<sup>1,2</sup> The tumor-concentrating ability<sup>3,4</sup> of tetrakis(4-sulfonatophenyl)porphyrin (H<sub>2</sub>TPPS) combined with the f<sup>7</sup> configuration of gadolinium(III) provides an impetus for the study of GdTPPS. Aside from reconstitution of Yb-mesoporphyrin into myoglobin<sup>5</sup> and applications as NMR shift reagents,<sup>6</sup> most work on the lanthanide derivatives has involved water-insoluble porphyrins.<sup>7-11</sup> We report the kinetics of displacement of Gd<sup>3+</sup> from GdTPPS by EDTA. This appears to be the first example of metal removal from a porphyrin by a chelating ligand.<sup>12</sup> The results parallel the kinetics of anion addition to certain cobalt(III) porphyrins.

## Experimental Section

Gadolinium(III) was incorporated into H<sub>2</sub>TPPS by the imidazole melt method, which we later found was similar to that described by Horrocks.<sup>6</sup> Two hundred milligrams (0.16 mM) of the sodium salt of H<sub>2</sub>TPPS-12H<sub>2</sub>O was combined with 240 mg (0.65 mM) of GdCl<sub>3</sub>·6H<sub>2</sub>O and 5.0 g of imidazole. The mixture under N<sub>2</sub>(g) was placed in an oil bath at 200 °C. Samples of the melt were periodically withdrawn, dissolved in water, and the spectrum monitored, when the 637-nm free-base peak disappeared, the porphyrin was removed from the oil bath, the bath temperature was lowered to 120 °C, and the bulk of the imidazole was sublimed away. The sample was cooled, washed with CH<sub>2</sub>Cl<sub>2</sub>, dissolved in a minimum amount of methanol containing 1% water, and precipitated by the addition of acetone. After three such precipitations, the compound in methanol was spotted on SiC<sub>18</sub> Baker TLC plates, and developed with 90% methanol in water. Any free-base H<sub>2</sub>TPPS moves with the solvent front, and GdTPPS has R<sub>f</sub> 0.9. This band was cut from the plates, recovered in MeOH, evaporated under the hood, and finally dried at 40 °C. Anal. Calcd for GdC<sub>44</sub>N<sub>4</sub>S<sub>4</sub>O<sub>12</sub>H<sub>24</sub>Na<sub>3</sub>·20H<sub>2</sub>O: Gd, 10.3; C, 34.88;

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**Figure 1.** pH profile of the specific rate constants of the GdTPPS/EDTA reaction. The dots are the observed data, and the solid line was calculated from eq 7. The insert shows the first-order dependence of  $k_{\text{obsd}}$  on  $[\text{EDTA}]$  at pH 7.0.

N, 3.70; H, 4.25; S, 8.46; C:N:S:Gd, 44.4:4:1. Found: Gd, 9.87; C, 33.47; N, 3.70; H, 4.07; S, 8.32; C:N:S:Gd, 44.3:4.2:4.1:1. The absorption spectrum of GdTPPS in water at pH 7 shows bands (and molar extinction coefficients) at 587 nm ( $5.7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ), 552 nm ( $2.3 \times 10^4$ ), 514 nm ( $6.5 \times 10^3$ ) and 419 nm ( $5.5 \times 10^5$ ). The spectrum is similar to that of (acac)GdTPP (TPP = tetraphenylporphyrin) in acetone.<sup>8</sup>  $\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$  was standardized with zinc.<sup>13</sup>

For solution studies, the ionic strength was 0.1 M ( $\text{NaNO}_3$ ). The buffers at 10 mM levels were Tris [tris(hydroxymethyl)aminoethane,  $\text{pK}_a = 8.3$ , used between pH 7.5 and 9.5], Hepes [*N*-(2-hydroxyethyl)-piperazine-*N'*-ethanesulfonic acid,  $\text{pK}_a = 7.6$ , pH 7–8], and Pipes [piperazine-*N,N'*-bis(2-ethanesulfonic acid),  $\text{pK}_a = 6.8$ , pH 5.5–7.5].

## Results

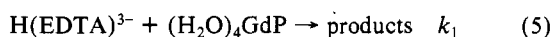
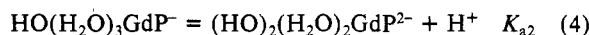
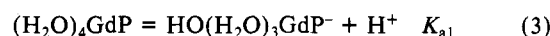
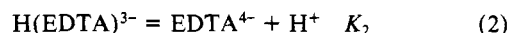
GdTPPS is stable for days at pH 7.4, and is rapidly transformed into the metal-free porphyrin by protons below pH 4. Beer's law (pH 8) was obeyed from  $8 \times 10^{-5}$  to  $4 \times 10^{-7}$  M. The kinetics were generally followed at  $6 \times 10^{-7}$  M porphyrin concentration, at 419 nm. In the presence of EDTA (pH 8), isosbestic points were found at 685, 605, 570, 535, 480, and 415 nm, as GdTPPS was cleanly transformed into the free base,<sup>14</sup>  $\text{H}_2\text{TPPS}$ . With at

least a 30-fold or greater excess of EDTA to porphyrin, the reactions were found to be first order in porphyrin over more than 2 half-lives, with an observed pseudo-first-order rate constant,  $k_{\text{obsd}}$ . Figure 1 indicates that at constant pH, the reaction is also first order in total EDTA, over a 9-fold range. The kinetics were followed from pH 5.5 to 11, and a plot of  $k_{\text{obsd}}/[\text{EDTA}]$  vs pH is shown in Figure 1. The data are given in Table I of the supplementary material.

Experiments done at a 10-fold lower buffer concentration, and at the same ionic strength showed no significant buffer effect on  $k_{\text{obsd}}$ . A spectrophotometric study between pH 6.6 and 11 in both the visible and the Soret regions gave little variation in absorbance ( $\pm 5\%$ ) with pH.

## Discussion

The following reactions can be used to explain the kinetics of removal of  $\text{Gd}^{3+}$  from GdTPPS (GdP) by EDTA:



The main products are  $\text{GdEDTA}^-$  and  $\text{H}_2\text{TPPS}$ .  $K_1$ ,  $K_2$ ,  $K_{a1}$ , and  $K_{a2}$  are rapid preequilibria, and  $k_1$  and  $k_2$  are the rate-determining steps. The observed rate law is of the form

$$k_{\text{obsd}}/[\text{EDTA}] = Q_1 Q_2 (k_1 + k_2 K_{a1}/[\text{H}^+]) \quad (7)$$

where  $Q_1 = [1 + K_{a1}/[\text{H}^+] + K_{a1}K_{a2}/[\text{H}^+]^2]^{-1}$  and  $Q_2 = [1 + [\text{H}^+]/K_1 + K_2/[\text{H}^+]]^{-1}$ . From the literature,<sup>15</sup>  $\text{pK}_1 = 6.16$  and  $\text{pK}_2 = 10.26$ . With reference to Figure 1,  $k_1$  and  $\text{pK}_{a1}$  were determined in the low-pH region, and these constants were used to calculate  $k_2$  and  $\text{pK}_{a2}$  at higher pH values. We find  $k_1 = 1.2 \pm 0.2 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_2 = 44 \pm 5 \text{ M}^{-1} \text{ s}^{-1}$ ,  $\text{pK}_{a1} = 7.5 \pm 0.1$  and  $\text{pK}_{a2} = 9.2 \pm 0.1$ . By the use of these parameters in eq 7, Figure 1 (and Table I, supplementary material) shows the excellent agreement between the observed and calculated  $k_{\text{obsd}}/[\text{EDTA}]$  values as a function of pH.

We would have more confidence in the mechanism if independent spectrophotometric evidence had been found for  $\text{pK}_{a1}$  and  $\text{pK}_{a2}$ . However, no significant variation in the absorption spectra of  $\text{Gd}^{\text{III}}$ TPPS with pH was found from pH 6 to 11. The  $\text{Gd}^{3+}$  ion probably sits well above the porphyrin plane. In TmTPPS, the metal could be 1.6 Å above the plane,<sup>6</sup> and Ce(IV) in Ce-(OEP)<sub>2</sub> (OEP = octaethylporphyrin) is 1.37 Å out of the mean plane.<sup>10</sup> It has been suggested<sup>10</sup> than lanthanide ions are octa-coordinated in porphyrin complexes, and this is reflected in eq 3–6. Both hydroxides might be coordinated to  $\text{Gd}^{3+}$  on the same side of the porphyrin, as in  $(\text{OAc})_2\text{HfOEP}$ .<sup>10</sup> The large out-of-plane distance of the metal ion and its high coordination number might rationalize the similarity in spectra of the aquo and hydroxy forms of GdTPPS. In several Co(III), Rh(III), and Mn(III) porphyrins, the absorbance changes with pH ascribed to protonations (where the metalloporphyrin is in the micromolar concentration range) either are small<sup>16,17</sup> or are too small to detect.<sup>18</sup> Reduction potentials of  $\text{Mn}^{\text{III}}$ TPPS are the same<sup>19</sup> between pH 5 and 10, in the regions where  $\text{pK}_a$ s have been assigned from spectral changes. The kinetics of the  $\text{Rh}^{\text{III}}$ TPPS/ $\text{CN}^-$  reaction<sup>20</sup>

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gives strong evidence for  $pK_{a1}$ , while there is disagreement as to the magnitude of this  $pK_a$  or even the existence of  $pK_{a2}$  in this system due to the minor absorbance variations found.<sup>17,21,22</sup> Our kinetically determined  $pK_a$ s of  $Gd^{III}TPPS$  (7.5 and 9.2) are similar<sup>21</sup> to those of  $Co^{III}TPPS$  (7.02 and 9.76) and other trivalent porphyrins. It has been noted that the ligand TPPS has more influence on  $pK_{a1}$  than does the identity of the metal ion itself.<sup>23</sup> In agreement with Srivastava,<sup>9</sup> no evidence for  $GdTPPS$  self-association was found.

Solutions containing 10  $\mu M$  metalloporphyrin and 25 mM EDTA at pH 8 were allowed to stand overnight in the dark. The  $Ni(II)$ ,  $Mn(III)$ ,  $Cu(II)$ ,  $Rh(III)$ ,  $In(III)$ ,  $Zn(II)$ ,  $Co(III)$ ,  $V^{IV}O$ ,  $Fe(III)$ ,  $Al(III)$ ,  $Cr(III)$ , and  $Sn(IV)$  complexes of TPPS were not demetalated.  $Pd(TMPyP)$  [ $TMPyP$  = tetrakis(1-methylpyridium-4-yl)porphyrin] was photoreduced in dim light in the presence of EDTA to the palladium chlorin.<sup>24</sup> As expected, the labile  $CdTPPS$  was demetalated, since the equilibrium constant<sup>25</sup> for reaction 8 is ca.  $10^{16}$ . It appears that the weak metal to

$$H(EDTA)^{3-} + H^+ + CdTPPS = H_2TPPS + CdEDTA^{2-} \quad (8)$$

porphyrin bonding of the large  $Gd^{3+}$  ion in  $GdTPPS$  favors metal removal by EDTA.

In the reaction of  $FeEDTA^{2-}$  with cobalt(III) porphyrins,<sup>26</sup> the rate law indicated that a complex formed between the negatively charged reductant and positively charged porphyrin. No evidence for such complexation was found with negatively charged metalloporphyrins, and such is the case in the present study where both reactants are negatively charged.

The area of metal exchange between two ligands has been reviewed<sup>27</sup> and much of this work involves EDTA chelates. Postulation of initial solvent displacement from the metal ion followed by EDTA oxygen atom coordination with subsequent chelation-dechelation steps in the mixed complex is applicable both to classical complexes and to the  $GdTPPS/EDTA$  reaction. Our data indicate that  $H(EDTA)^{3-}$  is substantially more reactive than both  $H_2(EDTA)^{2-}$  and  $EDTA^{4-}$ , and the protonated forms of EDTA generally exhibit differing reactivities, where the relative contributions of each depend on the nature of the substrate.<sup>27</sup> The rate constants of  $H(EDTA)^{3-}$  with  $HO(H_2O)_3GdP^{2-}$  and  $(H_2-O)_4GdP$  and are in the ratio of 36:1, and the same trend is found in certain anation reactions of cobalt(III)-porphyrins. With  $Co^{III}TPPS$  and  $SCN^-$ , the diaquo to monohydroxy ratio<sup>28</sup> is 4.2:1, whereas with  $CN^-$ , the ratio<sup>20</sup> is 7.7:1. For  $Gd^{III}$ ,  $Rh^{III}$ , and  $Co^{III}TPPS$  [also  $Co^{III}TMPyP^{28}$ ], the dihydroxy forms are at least several orders of magnitude less reactive as compared to species containing at least one coordinated water molecule. The cobalt(III) porphyrin reactions are considered dissociative in character<sup>21,28,29</sup> where the coordinated hydroxide labilizes a water molecule, facilitating dissociation to provide a position for the entering ligand. Thus, the  $GdTPPS/EDTA$  reaction also appears dissociative, with a rate determining step similar to that of simpler monoanations.

Work is in progress with other water-soluble lanthanide porphyrins. It is noted that the reactive  $HO(H_2O)_3GdTPPS^{2-}$  is in high concentration at pH 7.5. The fact that  $GdTPPS$  (but not  $Mn^{III}TPPS$ ) was demetalated<sup>2</sup> when equilibrated for several days

with human plasma at this pH could be due to a biological chelating agent acting in a manner similar to EDTA.

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**Registry No.** EDTA, 60-00-4;  $GdTPPS$ , 107283-78-3.

**Supplementary Material Available:** Table I, giving pH, [EDTA], and observed and calculated  $k_{obsd}/[EDTA]$  values (1 page). Ordering information is given on any current masthead page.

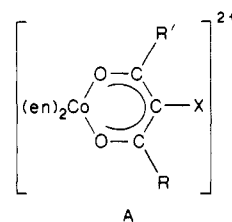
Contribution from the Department of Chemistry, University of Miami, Coral Gables, Florida 33124, Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 6E2, and Department of Chemistry and Biochemistry, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Guelph, Guelph, Ontario, Canada N1H 5W1

# Use of Extended Hückel Molecular Orbital Calculations in Determining the Position of Attack in Inner-Sphere Electron-Transfer Reactions: X-ray Crystal Structure of (1,3-Diphenylpropane-1,3-dionato)bis(ethylenediamine)cobalt(III)

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We have synthesized and studied the redox chemistry of a number of bis(ethylenediamine)cobalt(III) complexes of  $\beta$ -diketones having the general formula given in A where  $R = R' =$



$CH_3$  and  $X = H, CHO, COCH_3, Cl, Br$ , and  $I$ ;  $R = CH_3$ ,  $R' = H$ , and  $X = COCH_3$ ;  $R = R' = C_6H_5$  and  $X = H$ . With the exception of the last complex, all of these were thought to involve at least partial inner-sphere attack of the reductant,  $Cr(II)$ , either at the coordinated oxygen or at the X substituent.<sup>1-3</sup>

The presence of phenyl substituents on the  $\beta$ -diketone ring resulted in a complex having very peculiar reduction properties. The most noticeable effect was that the reaction with  $Cr(II)$  was autocatalytic and was inversely related to the acidity of the medium.<sup>4</sup> Further, the perchlorate salt of A crystallized from triply distilled water always contained an extra  $HClO_4$  upon analysis. The location of this additional proton was of interest considering the inverse acid dependency observed in the kinetics. The perchlorate crystals were thin plates that were unsuitable for a crystal study. After several other counterions were tried, a suitable crystal was grown in a neutral nitrate medium. The crystals were rectangular and the structure, reported in this work, indicated that the complex was unprotonated. If the crystals were grown in nitric acid, they formed long needles initially, which were crystallographically identical with the rectangular crystals obtained from neutral solutions. After some time, thin plates began to appear in the acidic nitrate medium. These were by analysis also a protonated form of the complex but as was true when the counterion was perchlorate, they were unsuitable for X-ray analysis.

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