data obtained in this study and those from recent published reports of Pt(0) chemical shifts,[18-22] we conclude that Pt(0) resonances generally occur at higher fields than those for Pt(II) complexes. Although Pt(II) complexes have ^{195}Pt resonances as high as -5500 ppm[1] (range for Pt(II) complexes: -1600 to -5500 ppm), the resonances of Pt(0) complexes occur as high as -6596 ppm[23] for $Pt[P(i\text{-}Pr)_3]_2$[18] (range for Pt(0) complexes: -4500 to -6600 ppm).

Coupling Constants ^1J(Pt-P1), ^1J(Pt-P3), and ^2J(P1-P3). Variation in the magnitudes of the Pt-P coupling constants for the tripod ligand, ^1J(Pt-P3), is relatively small as the monodentate phosphine ligand changes from PMe_2Ph to $P(OPh)_3$; however, the magnitude of the Pt-P coupling constant for the monodentate phosphine ligands, ^1J(Pt-P1), increases dramatically from 5342 to 9128 Hz. In addition, the magnitudes of ^1J(Pt-P3) are smaller than those observed for $Pt(PR_3)_4$ compounds.[24-26] 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_{3v} 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_d" Pt(0) complexes. As mentioned previously, the magnitude of the one-bond phosphorus coupling constant depends primarily on $\alpha_p{}^2$ and $|\psi_{3s}(P)|^2$. A change of the groups on one of the coupled phosphorus atoms (i.e., P1) can have a large effect on $\alpha_p{}^2$ and $|\psi_{3s}(0)|^2$ for that atom; however, it apparently has only a small effect on the corresponding terms of another phosphorus atom (i.e., P3).[27]

The magnitudes of ^1J(Pt-P) and ^2J(P-P) coupling constants for Pt(II) complexes are affected by the electronegativity of the phosphorus substituents.[28] This effect is observed also for the Pt(tripod)PR_3 complexes. A linear correlation ($\rho = 0.978$) is observed between ^2J(P1-P3) and Taft's constant[29]

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

A similar relationship has been observed for the one-bond, metal-phosphorus coupling constants, ^1J(Pt-P1), in related Pt(tripod)PR_3 complexes.[15] This similarity between ^2J(P1-P3) and ^1J(Pt-P1) is not surprising, since the two-bond, phosphorus-phosphorus coupling constants are transmitted through the metal center. In fact, a linear correlation ($\rho = 0.993$) exists between ^2J(P1-P3) and ^1J(Pt-P1) for the Pt(tripod)PR_3 complexes.

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

Acknowledgment. The authors are grateful to the Amoco Foundation for a Graduate Fellowship to L.M.G. during 1986-1987, to Dr. Charles Cottrell for collecting the ^{195}Pt NMR spectra, and to The Ohio State University for a University Fellowship to L.M.G. and for purchase of the Bruker MSL-300 NMR spectrometer.

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; $PtCl_2$(tripod), 112712-93-3; ^{195}Pt, 14191-88-9.

Supplementary Material Available: Sample $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ 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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Received October 2, 1986

Paramagnetic water-soluble metalloporphyrins are being explored as tissue contrast agents in magnetic resonance imaging studies.[1,2] The tumor-concentrating ability[3,4] of tetrakis(4-sulfonatophenyl)porphyrin (H_2TPPS) combined with the f^7 configuration of gadolinium(III) provides an impetus for the study of GdTPPS. Aside from reconstitution of Yb-mesoporphyrin into myoglobin[5] and applications as NMR shift reagents,[6] most work on the lanthanide derivatives has involved water-insoluble porphyrins.[7-11] We report the kinetics of displacement of Gd^{3+} from GdTPPS by EDTA. This appears to be the first example of metal removal from a porphyrin by a chelating ligand.[12] The results parallel the kinetics of anion addition to certain cobalt(III) porphyrins.

Experimental Section

Gadolinium(III) was incorporated into H_2TPPS by the imidazole melt method, which we later found was similar to that described by Horrocks.[6] Two hundred milligrams (0.16 mM) of the sodium salt of $H_2TPPS\cdot 12H_2O$ was combined with 240 mg (0.65 mM) of $GdCl_3\cdot 6H_2O$ and 5.0 g of imidazole. The mixture under $N_2(g)$ 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_2Cl_2, 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_{18} Baker TLC plates, and developed with 90% methanol in water. Any free-base H_2TPPS moves with the solvent front, and GdTPPS has R_f 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 $GdC_{44}N_4S_4O_{12}H_{24}Na_3\cdot 20H_2O$: Gd, 10.3; C, 34.88;

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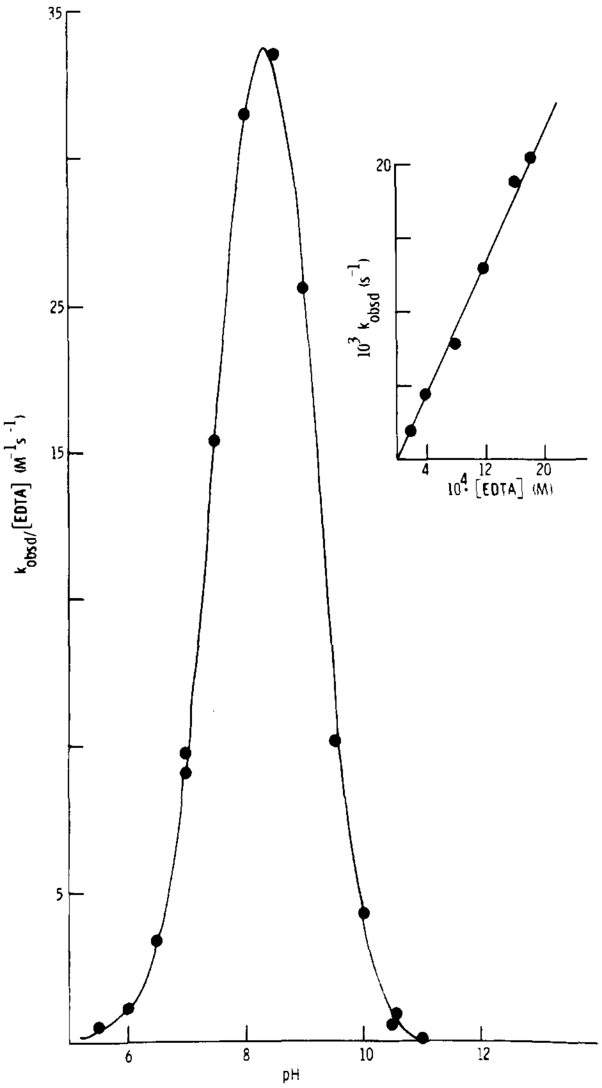

Figure 1. pH profile of the specific rate constants of the GdTPPS/EDTA reaction. The dots are the observed data, and the solid line was calculated from eq 7. The insert shows the first-order dependence of k_{obsd} on [EDTA] at pH 7.0.

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 (5.7×10^3 M^{-1} cm^{-1}), 552 nm (2.3×10^4), 514 nm (6.5×10^3) and 419 nm (5.5×10^5). The spectrum is similar to that of (acac)GdTPP (TPP = tetraphenylporphyrin) in acetone.[8] $Na_2EDTA \cdot 2H_2O$ was standardized with zinc.[13]

For solution studies, the ionic strength was 0.1 M ($NaNO_3$). The buffers at 10 mM levels were Tris [tris(hydroxymethyl)aminoethane, pK_a = 8.3, used between pH 7.5 and 9.5], Hepes [*N*-(2-hydroxyethyl)-piperazine-*N'*-ethanesulfonic acid, pK_a = 7.6, pH 7–8], and Pipes [piperazine-*N*-*N'*-bis(2-ethanesulfonic acid), 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 8×10^{-5} to 4×10^{-7} M. The kinetics were generally followed at 6×10^{-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,[14] H_2TPPS. 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_{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_{obsd}/[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_{obsd}. A spectrophotometric study between pH 6.6 and 11 in both the visible and the Soret regions gave little variation in absorbance (±5%) with pH.

Discussion

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

$$H_2(EDTA)^{2-} = H(EDTA)^{3-} + H^+ \quad K_1 \tag{1}$$

$$H(EDTA)^{3-} = EDTA^{4-} + H^+ \quad K_2 \tag{2}$$

$$(H_2O)_4GdP = HO(H_2O)_3GdP^- + H^+ \quad K_{a1} \tag{3}$$

$$HO(H_2O)_3GdP^- = (HO)_2(H_2O)_2GdP^{2-} + H^+ \quad K_{a2} \tag{4}$$

$$H(EDTA)^{3-} + (H_2O)_4GdP \rightarrow \text{products} \quad k_1 \tag{5}$$

$$H(EDTA)^{3-} + HO(H_2O)_3GdP^- \rightarrow \text{products} \quad k_2 \tag{6}$$

The main products are $GdEDTA^-$ and H_2TPPS. 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

$$k_{obsd}/[EDTA] = Q_1Q_2(k_1 + k_2K_{a1}/[H^+]) \tag{7}$$

where $Q_1 = [1 + K_{a1}/[H^+] + K_{a1}K_{a2}/[H^+]^2]^{-1}$ and $Q_2 = (1 + [H^+]/K_1 + K_2/[H^+])^{-1}$. From the literature,[15] pK_1 = 6.16 and pK_2 = 10.26. With reference to Figure 1, k_1 and pK_{a1} were determined in the low-pH region, and these constants were used to calculate k_2 and pK_{a2} at higher pH values. We find $k_1 = 1.2 \pm 0.2$ M^{-1} s^{-1}, $k_2 = 44 \pm 5$ M^{-1} s^{-1}, $pK_{a1} = 7.5 \pm 0.1$ and $pK_{a2} = 9.2 \pm 0.1$. 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_{obsd}/[EDTA] values as a function of pH.

We would have more confidence in the mechanism if independent spectrophotometric evidence had been found for pK_{a1} and pK_{a2}. However, no significant variation in the absorption spectra of Gd^{III}TPPS with pH was found from pH 6 to 11. The Gd^{3+} ion probably sits well above the porphyrin plane. In TmTPPS, the metal could be 1.6 Å above the plane,[6] and Ce(IV) in Ce-$(OEP)_2$ (OEP = octaethylporphyrin) is 1.37 Å out of the mean plane.[10] It has been suggested[10] than lanthanide ions are octacoordinated in porphyrin complexes, and this is reflected in eq 3–6. Both hydroxides might be coordinated to Gd^{3+} on the same side of the porphyrin, as in $(OAc)_2$HfOEP.[10] 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[16,17] or are too small to detect.[18] Reduction potentials of Mn^{III}TPPS are the same[19] between pH 5 and 10, in the regions where pK_as have been assigned from spectral changes. The kinetics of the $Rh^{III}TPPS/CN^-$ reaction[20]

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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.[17,21,22] Our kinetically determined pK_as of Gd^{III}TPPS (7.5 and 9.2) are similar[21] 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.[23] In agreement with Srivastava,[9] no evidence for GdTPPS self-association was found.

Solutions containing 10 μM 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.[24] As expected, the labile CdTPPS was demetallated, since the equilibrium constant[25] for reaction 8 is ca. 10^{16}. It appears that the weak metal to

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

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,[26] 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[27] 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.[27] The rate constants of $H(EDTA)^{3-}$ with $HO(H_2O)_3GdP^-$ and $(H_2O)_4GdP$ 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[28] is 4.2:1, whereas with CN^-, the ratio[20] 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[21,28,29] 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 $HO(H_2O)_3GdTPPS^-$ is in high concentration at pH 7.5. The fact that GdTPPS (but not Mn^{III}TPPS] was demetalated[2] 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.

Acknowledgment. This work was supported by Howard University NIH Biomedical Research Grant 5-SO-6-RR-08019-9.

Registry No. EDTA, 60-00-4; Gd-TPPS, 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.

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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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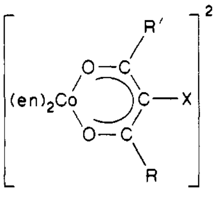
Received August 6, 1987

We have synthesized and studied the redox chemistry of a number of bis(ethylenediamine)cobalt(III) complexes of β-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.[1-3]



A

The presence of phenyl substituents on the β-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.[4] 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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