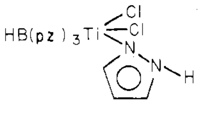
A deep purple component, isolated in minor amounts, corresponds to $HB(pz)_3TiCl_2(C_3H_3N_2H)$ (**4**) on the basis of



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analytical data. The presence of an N–H stretch implies an N-coordinated pyrazole unit.

The addition of a large excess of $K[HB(pz)_3]$ did not give disubstitution products, consistent with the chemistry found for Ti(IV).

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Registry No. 1, 58097-69-1; **2**, 59710-48-4; **3**, 59710-49-5; **4**, 59710-50-8.

References and Notes

(1) (a) S. Trofimenko, *Acc. Chem. Res.*, **4**, 17 (1971); (b) S. Trofimenko, *Chem. Rev.*, **72**, 497 (1972).
(2) For examples see (a) C. S. Arcus, J. L. Wilkinson, C. Mealli, T. J. Marks, and J. A. Ibers, *J. Am. Chem. Soc.*, **96**, 7564 (1974); (b) D. H. Williamson, C. Santini-Scampucci, and G. Wilkinson, *J. Organomet. Chem.*, **77**, C25 (1974); (c) H. C. Clark and L. Manzer, *Inorg. Chem.*, **13**, 1996 (1974); (d) F. A. Cotton and A. G. Stanislowsky, *J. Am. Chem. Soc.*, **96**, 5074 (1974).
(3) (a) F. Calderazzo, *J. Organomet. Chem.*, **53**, 179 (1973); (b) G. A. Razuvaev and V. N. Latyaeva, *Organomet. Chem. Rev.*, **2**, 349 (1967); (c) R. S. P. Coutts and P. C. Wailes, *Adv. Organomet. Chem.*, **10**, 135 (1970); (d) R. J. H. Clark, "The Chemistry of Titanium and Vanadium", Elsevier, Amsterdam, 1968.
(4) L. Manzer, *J. Organomet. Chem.*, **102**, 167 (1975).
(5) (a) S. Trofimenko, *J. Am. Chem. Soc.*, **89**, 3170 (1967); (b) *ibid.*, **89**, 6288 (1967).
(6) Prepared by treatment of aqueous solution of Tl(acac) with aqueous $K[HB(pz)_3]$ and recrystallization of the precipitate from hexane. Anal. Calcd for $C_9H_{10}BTlN_6$: C, 25.90; H, 2.42; N, 20.12. Found: C, 25.88; H, 2.40; N, 20.11.
(7) (a) C. S. Sloan and W. A. Barber, *J. Am. Chem. Soc.*, **81**, 1364 (1959); (b) A. F. Reid and P. C. Wailes, *J. Organomet. Chem.*, **2**, 329 (1964).

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Synthesis and Characterization of New Isomeric Water-Soluble Porphyrins. Tetra(2-*N*-methylpyridyl)porphine and Tetra(3-*N*-methylpyridyl)porphine

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Numerous studies on the kinetics and mechanisms of porphyrin[1,2] and metalloporphyrin[3,4] reactions have been done using the monomeric and fully water-soluble tetra(4-*N*-methylpyridyl)porphine (TMpyP(4)).[5] Since an isomeric series of water-soluble porphyrins would yield valuable structure–reactivity information similar to that obtained with 2,4-disubstituted deuteroporphyrin dimethyl esters in nonaqueous media,[6] we report the synthesis and characterization of the ortho (2) and meta (3) *N*-methylated derivatives tetra(2-*N*-methylpyridyl)porphine (TMpyP(2)) and TMpyP(3). Although the Mössbauer parameters of the solid oxy-bridged iron dimers of the parent tetrapyridylporphines (TpyP) were similar,[7] the parent isomers were electrochemically reduced by different mechanisms in 1.0 M HCl.[8] We demonstrate that certain TMpyP and TpyP types behave differently with respect to both acid solvolysis of the zinc chelates and protonation.

Table I. ZnP Solvolysis Half-Lives (seconds) in 1.0 M Acid Solutions (25 °C)

	HCl	HNO_3
Zn-TMpyP(3)[a,b]	17	89
Zn-TpyP(3)	13	57
Zn-TMpyP(4)	28	165
Zn-TpyP(4)	24	131
Zn-TMpyP(2)	5.0×10^3	6.9×10^4
Zn-TpyP(2)	1.3×10^3	

[a] In 1.0 M $HClO_4$ for Zn-TMpyP(3), $t_{1/2}$ = 59 s, and for Zn-TpyP(3), $t_{1/2}$ = 45 s. [b] Data are an average of four determinations, ±10%.

Experimental Section

TpyP(2) and Tpy(3) were purchased from ManWin Coordination Chemicals, Washington, D.C. 20059. The tosylate salts were made by refluxing either chloroform or DMF solutions of the porphyrin with excess methyl *p*-toluenesulfonate. Both of the alkylated porphyrins spontaneously precipitated from hot chloroform solutions and were washed with ether and air-dried. The crystalline tosylate of TMpyP(3) could be filtered from the hot DMF solution, while the ortho derivative required the addition of ether to the cold DMF reaction mixture to precipitate the porphyrin salt. The tosylate (Ts) or iodide of TMpyP(3) (from CH_3I) also forms at room temperature by stirring the porphyrin and methylating agent overnight in chloroform.[5] Anal. Calcd for H_2–TMpyP·4Ts·3H_2O, $C_{76}H_{66}N_8S_4O_{12}\cdot 3H_2O$: C, 61.0; H, 5.11; N, 7.90. Found for TMpyP(2): C, 60.9; H, 5.4; N, 7.8. Found for TMpyP(3): C, 61.3; H, 5.2; N, 8.1.

The absorption spectra of the porphyrins in 1.0 M HCl (25 °C) are as follows (λ, nm (log ε)): for TMpyP(3), 632 (4.39), 582 (3.57), 432 (5.60); for TMpyP(2), 634 (3.13), 582 (3.86), 545 (3.57), 512 (4.2), 413 (5.5); for TpyP(2), 633 (3.93), 585 (4.08), 437 (5.33). The TpyP(2) spectra agree with literature data.[8] The tosylate-free bases at pH 7 followed Beer's law over a 260-fold dilution (4.5×10^{-4}–1.7×10^{-6} M).

Results and Discussion

TMpyP(4) precipitates immediately from 2.0 M $HClO_4$, and TMpyP(3) requires 24 h at 0 °C, while TMpyP(2) remains in solution. The solubilities in $CHCl_3$ at 25 °C for TpyP(4), -(3), and -(2) are (3, 226, and 12) $\times 10^{-3}$ mol dm^{-3}, respectively. The same relative order was found in the monofluoro (4, 3, and 2) phenyl-substituted tetraphenylporphine series.[9]

All reported porphyrins, TMpyP(3), TMpyP(4), and their parent TpyP's are in the diacid (H_4P) forms in 1.0 M HCl. TMpyP(2), however, has essentially the same free base (H_2P) spectra at pH 7 as in 1.0 M HCl, making it the least basic porphyrin toward proton addition known. This is presumably a consequence of the repulsive and inductive effects of the four positive *N*-methyl groups in close proximity to the central nitrogen atoms. TpyP(2) in 1.0 M HCl is a mixture of the diacid and the monocation (H_3P) forms. Both the steric effects of the bulky *N*-alkyl groups and the permanent positive charges in the ortho positions could make TpyP(2) more basic than TMpyP(2). This positive charge effect on basicity decreases with the distance of the *N*-alkyl groups from the porphyrin center, as evidenced by the similar apparent basicities of the substituted and unsubstituted meta and para derivatives.

The acid solvolysis behavior of the zinc porphyrin isomers was studied in 1.0 M acid solutions at 25 °C. Under pseudo-first-order conditions, the reactions were first order in ZnP, and the observed half-lives are given in Table I. The rate differences between HCl and HNO_3 for TpyP(4)) were shown to arise from different rate laws.[5,10] In a series of zinc 2,4-disubstituted deuteroporphyrins,[6] the rates of solvolysis were faster the higher the basicity of the free base porphyrin toward protons (pK_3). The same trend is apparent here; the parent meta and para Zn–TpyP derivatives are slightly more reactive than their Zn–TMpyP adducts, while Zn–TpyP(2) reacts 4 times faster than its less basic Zn–TMpyP(2) counterpart. The lack of resonance interaction between the meso nitrogens on the pyridyl rings and the porphyrin nucleus may account for the slightly faster solvolysis rate of Zn–TMpyP(3) as compared with that of Zn–TMpyP(4).

The observed ZnP kinetic solvolysis order, TpyP(3) > TpyP(4) > TpyP(2), parallels the electrochemical reduction potentials[8] of the porphyrins in 1.0 M HCl. The meso derivative is the most difficult to reduce (most basic?), while the ortho species (most acidic) is the easiest.

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Registry No. TMpyP(2) tosylate, 59728-90-4; TMpyP(3) tosylate, 59728-92-6; TMpyP(3) iodide, 59728-93-7; Zn–TMpyP(3), 59729-16-7; Zn–TpyP(3), 59729-17-8; Zn–TMpyP(4), 40603-58-5; Zn–TpyP(4), 31183-11-6; Zn–TMpyP(2), 59729-18-9; Zn–TpyP(2), 59729-19-0.

References and Notes

(1) R. F. Pasternack, N. Sutin, and D. H. Turner, *J. Am. Chem. Soc.*, **98**, 1908 (1976).
(2) K. R. Ashley, M. Berggren, and M. Cheng, *J. Am. Chem. Soc.*, **97**, 1422 (1975).
(3) P. Hambright and P. B. Chock, *J. Am. Chem. Soc.*, **96**, 3123 (1974).
(4) P. Hambright in "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., 2d ed, Elsevier, Amsterdam, 1975, Chapter 6.
(5) P. Hambright and E. B. Fleischer, *Inorg. Chem.*, **9**, 1757 (1970).
(6) B. Shah, B. Shears, and P. Hambright, *J. Am. Chem. Soc.*, **93**, 776 (1971).
(7) M. A. Torrens, D. K. Straub, and L. M. Epstein, *J. Am. Chem. Soc.*, **94**, 4160 (1972).
(8) B. P. Neri and G. S. Wilson, *Anal. Chem.*, **45**, 442 (1973).
(9) E. B. Fleischer, R. Foust, D. Jeter, and R. Near, *Inorg. Nucl. Chem. Lett.*, **9**, 1219 (1973).
(10) B. Shah and P. Hambright, *J. Inorg. Nucl. Chem.*, **32**, 3420 (1970).

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Outer-Sphere Mechanisms in the Reductions of Polynuclear μ-Terephthalato Cobalt(III) Complexes by Chromium(II) and Vanadium(II)

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It has been suggested that the reducibility of a given uncomplexed organic ligand is a necessary prerequisite for its ability to function as an electron mediating bridge between two metal ions in an inner-sphere electron-transfer process with attack of the reductant at a remote polar group and transfer of an electron through the ligand.[1-4]

In the past it has not been possible to test this thoroughly because the reduction of mononuclear carboxylatopentaamminecobalt(III) complexes by Cr^{2+} can always proceed via an inner-sphere mechanism with attack of the reductant at the adjacent carbonyl oxygen.

It is this mechanism that has been assigned to the reduction of the terephthalatopentaamminecobalt(III) complex by Cr^{2+}.[5] Terephthalic acid represents a promising ligand in order to test the correlation concerning the reducibility of the ligand and its effectiveness in mediating electrons. Good conjugation is given as well as a suitable "lead in" functional group for precursor complex formation with Cr^{2+} and the ligand is not reducible by Cr^{2+} or V^{2+}.

We have prepared the present series of polynuclear complexes I, II, III, and IV which contain terephthalic acid as bridging ligand because it is now well established that the oxygen atoms of a μ-carboxylato bridge where both oxygens are coordinated to two Co(III) centers do not represent favorable sites of attack for Cr^{2+}.[6,7]

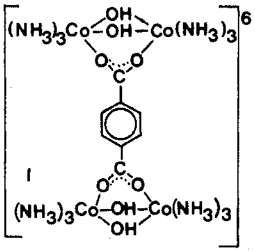
Experimental Section

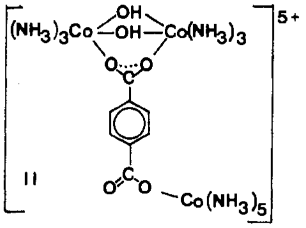
Preparation of μ_4-Terephthalato-bis{di-μ-hydroxo-bis[triamminecobalt(III)]} Perchlorate (I). To a solution of 2 g of terephthalic acid in 70 ml of dioxane and 40 ml of 0.5 M perchloric acid at 70 °C 6 g of tri-μ-hydroxo-bis[triamminecobalt(III)] perchlorate dihydrate[8] (hereafter referred to as "triol") was added in small amounts with stirring. The temperature was maintained for 15 min during which time most of the dioxane was evaporated by bubbling a stream of nitrogen through the solution. The solution was cooled to 15 °C and unreacted terephthalic acid precipitated and was filtered off. Concentrated perchloric acid (2 ml) and solid $NaClO_4$ were added to the solution which was kept at 0 °C for 2 h. Red crystals were collected and washed thoroughly with ethanol and ether and recrystallized from a minimum amount of water with 2 ml of concentrated $HClO_4$.

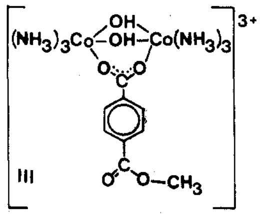
Preparation of μ_3-Terephthalato-di-μ-hydroxo-bis[triamminecobalt(III)][pentaamminecobalt(III)] Perchlorate (II). Terephthalatopentaamminecobalt(III) perchlorate was prepared as described in the literature.[9] One gram of this complex in 20 ml of 0.5 M perchloric acid was reacted at 65 °C with 2 g of triol. The temperature was maintained for 15 min. To the cooled (20 °C) and filtered solution 2 ml of concentrated $HClO_4$ and solid $NaClO_4$ were added. The solution was kept at 0 °C for a few hours. Red crystals were collected and washed with ethanol and ether.

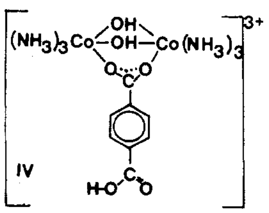
Preparation of μ-(Terephthalato monomethyl ester)-di-μ-hydroxo-bis[triamminecobalt(III)] Perchlorate (III). The complex was prepared by the same method as described for complex I. A solution of 2 g of terephthalic monomethyl ester in a mixture of 30 ml of dioxane and 15 ml of 0.5 M perchloric acid was reacted at 60 °C with 3 g of triol.

Preparation of μ-Terephthalato-di-μ-hydroxo-bis[triamminecobalt(III)] Perchlorate (IV). Complex II (1.7×10^{-3} mol; 2 g) was dissolved in 60 ml of 0.5 M perchloric acid at 40 °C. Argon was passed through the solution which was kept in a 100-ml flask fitted with a rubber serum cap until all the oxygen has been removed. Then 1.7×10^{-3} mol of $[V(H_2O)_6]^{2+}$ in perchloric acid were added using a hypodermic syringe. The mixture was allowed to react at room temperature for 1 h. A minor precipitation of uncomplexed terephthalic acid occurs. To the cooled (0 °C) and filtered solution 5 ml of concentrated $HClO_4$ was added. Red crystals of unreacted trinuclear complex II precipitated and were filtered off. The solution was then saturated with solid $NaClO_4$ and kept in the refrigerator for 2 h. Red crystals of complex II were collected and washed with ethanol and ether. Yield: 0.4 g. See Table I.









Reagents. Solutions of $[Cr(H_2O)_6]^{2+}$ and $[V(H_2O)_6]^{2+}$ ions in perchloric acid were prepared by electrolytic reduction of chromium(III) and vanadium(IV) solutions under an argon atmosphere. The organic ligands were commercially available (Merck) and were used without further purification.

Physical Measurements. Kinetic runs were followed using a Unicam SP 1700 spectrophotometer fitted with thermostated cell housing.