Metal–Metal Interactions Involving Metalloporphyrins. II. The Inner-Sphere Reduction of Tetraphenylporphineiron(III) Chloride by Chromium(II) in Benzene

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Abstract: [^{36}Cl] Tetraphenylporphineiron(III) chloride has been reduced by bis(2,4-pentanedionato)chromium(II) in 1% pyridine in benzene with transfer of 96% of the radioactivity to the chromium(III) products. In the presence of excess tetrabutylammonium chloride, the reduction proceeds with 87% transfer of activity from the heme to the chromic products and 9% of the chloride is mixed between the complexed and uncomplexed chlorides in solution. The results are interpreted in terms of an inner-sphere electron-transfer process. The work represents a method by which the study of electron-transfer processes between metals can be extended to nonaqueous systems.

Hemoproteins are extremely important to biological electron transport process, but mechanistic studies of electron-transfer reactions involving simple hemes and hemins have, except for electrochemical studies, received relatively little attention. We have recently found that bridging groups such as oxide or azide ions can allow electronic interactions between hemins to be observed magnetically.[1,2] That brought up the possibility that an ion axially coordinated to an iron in a porphyrin could serve as a bridge for the reduction of the metal by an inner-sphere process.

Castro and Davis[3] have examined the product of the cyclic reduction and oxidation of octaethylhemin with iron powder and air in deuterated acetic acid. They found some deuteration at the methine positions of the product and presented a mechanism involving attack at the periphery of the porphyrin ring.

However, the most useful criterion for the determination of whether an oxidation–reduction reaction proceeds by an inner- or outer-sphere mechanism is direct evidence for the occurrence or absence of ligand transfer.[4] This is often most readily obtained by using an inert reductant and labile oxidant to produce a inert oxidation product. Chromium(II) is well suited for this and has been used extensively. For example,[5] in aqueous media the reaction between Cr(II) and $Fe^{III}Cl$ has been examined by Dulz and Sutin and Carlyle and Espenson and found to proceed by an inner sphere process. Hambright and Fleischer, in addition, examined the rates of reduction of tetrapyridylporphineiron(III) by Cr(II) in water and found evidence for catalysis by dissolved halide. They could not deduce a mechanism for the reaction because of the lability of the iron porphine in water.

Tetraphenylporphineiron(III) chloride is only soluble in nonaqueous solvents. In benzene–pyridine (1%) and in the absence of aqueous base, it does not readily lose the coordinated chloride. Bis(2,4-pentandionato)chromium(II) is also soluble in benzene and therefore allows for the extension of the study of bridged electron-transfer reactions to nonaqueous media.

Experimental Section

Bis(2,4-pentanedionato)chromium(II) ($Cr(acac)_2$)[6] was prepared by the method of Ocone and Block.[7] It was kept under vacuum prior to use and transferred in a nitrogen filled glove bag.

[^{36}Cl] Tetraphenylporphineiron(III) Chloride (TTPFe^{36}Cl).[6] Pure μ-oxo-bis(tetraphenylporphineaquoiron(III)) (300 mg) was dissolved in benzene and shaken vigorously with [^{36}Cl] hydrochloric acid (*ca.* 90 ml, 1 *M*, 0.05 μCi/ml) for 15 min and allowed to stand overnight. The benzene solution was washed with water until the wash water no longer produced a precipitate upon treatment with a $AgNO_3$ solution. The benzene layer was dried by filtration through anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The resulting solid was dried *in vacuo* over P_2O_5 (yield 98%) and was spectrally (ir and visible) identical with an authentic sample of nonradioactive TPPFeCl. The specific activity was determined.

[^{36}Cl] Tetrabutylammonium Chloride. Polarographic grade Bu_4NBr was converted to the hydroxide on an ion-exchange column (Amberlite IRA-400) and then treated with $H^{36}Cl$ (0.05 μCi/ml). The water was removed *in vacuo* at 60° and the resulting solid was recrystallized from benzene. The product was dried *in vacuo* over P_2O_5 and had an ir spectrum almost identical with that of Bu_4NBr. Qualitative tests for Br^- were negative and the specific activity was determined directly.

Activity Measurements. Liquid scintillation counting was carried out on a Packard Tri-Carb, Model 2002, using Bray's solution: naphthalene, 60 g; methanol, 100 ml; ethylene glycol, 20 ml; 2,5-diphenyloxazol (PPO), 4.0 g; 1,4-bis-2-(phenyloxazolyl)benzene (POPOP), 0.2 g; dioxane to make 1 l. of solution. Radiochloride ions, both free and complexed, were extracted and concentrated from aqueous solution with silver nitrate as follows. After several drops of 1 *M* HCl had been added, the solution was treated with excess $AgNO_3$. The solution was allowed to stand for several days and then heated for 1–2 hr. The mixture was cooled to room temperature and suction filtered. The AgCl was washed with HNO_3, air dried, and dissolved in a small quantity of NH_4OH. The $Ag(NH_3)_2Cl$ solution was eluted through a column of a cation-exchange resin (Amberlite IR-120) in the acid form. Eluent was collected until free of Cl^- ion and made just basic to phenolphthalein with 1 *M* NaOH. The water was removed *in vacuo* at 60° and the solid was redissolved in a small amount of water and quantitatively transferred to a 5- or 10-ml volumetric flask. Enough HCl was added to discharge the color of the phenolphthalein and water was added to the mark. A 1-ml aliquot was withdrawn and added to a scintillation cell containing 10 ml of the liquid phosphor. The data were corrected for background and quenching was determined by using an activity standard in the scintillation spectrometer.

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[1] Paper I in this series: I. A. Cohen, *J. Amer. Chem. Soc.*, **91**, 1980 (1969).

[2] I. A. Cohen and J. Brown, to be published.

[3] C. E. Castro and H. F. Davis, *J. Amer. Chem. Soc.*, **91**, 5405 (1969).

[4] For a recent general review, see H. Taube, "Electron Transfer Reactions of Complex Ions in Solution," Academic Press, New York, N. Y., 1970.

[5] (a) G. Dulz and N. Sutin, *J. Amer. Chem. Soc.*, **86**, 829 (1964); (b) D. Carlyle and J. H. Espenson, *ibid.*, **91**, 599 (1969), and references therein; (c) D. Hambright and E. B. Fleischer, *Inorg. Chem.*, **4**, 912 (1965).

[6] acac = the 2,4-pentanedionato anion, TPP = the tetraphenylporphine dianion, py = pyridine.

[7] L. R. Ocone and B. P. Block, *Inorg. Syn.*, **8**, 125 (1966).

Activities of water-insoluble samples were determined by dissolving the sample in benzene and treating with a few milliliters of aqueous 1 *M* $AgNO_3$. The solution was shaken for 10 min and allowed to stand in the dark for several days with intermittent agitation. When a Geiger counter indicated that negligible activity remained in the benzene phase, the entire mixture was boiled for 1–2 hr and benzene was continually added to maintain constant volume. A few drops of 1 *M* HCl were added and the boiling continued for 0.5 hr. The mixture was cooled to room temperature and filtered. The solid AgCl was treated as above.

Reactions of [^{36}Cl] Tetraphenylporphineiron(III) Chloride with Bis(2,4-pentanedionato)chromium(II). $TPPFe^{36}Cl$ (175 mg, 0.25 mmol) was dissolved in 1% pyridine[8] in benzene (300 ml), flushed with N_2, and placed in a N_2-filled glove bag. $Cr(acac)_2$ (0.6–1.0 g, *ca.* fourfold excess) was added and the solution stirred under N_2 for 5 min. The solution changed color immediately from reddish orange to bright red. The reaction mixture was transferred to a separatory funnel in air and washed twice with 80-ml portions of water. Addition of 1 *M* $AgNO_3$ to the light blue wash water did not immediately produce any precipitate, but a slight cloudiness did appear about 30 min later. The radioactivity of the wash water was determined and was about 1% of the total activity of the sample.

The benzene layer was taken to dryness *in vacuo* at 25° and residual pyridine was removed from the solid at room temperature by high vacuum (10^{-3} mm) and collected in a $-80°$ trap overnight.

The chromium-containing products were extracted from the solid reaction product by treatment with 350 ml of methanol. The methanol was centrifuged, suction filtered through a fine pore fritted glass Büchner funnel, and taken to a dryness *in vacuo*. The resulting solid was redissolved in a small amount of methanol, refiltered, and transferred to a tared beaker. Visible spectra of this solution indicated the absence of any iron porphine. The methanol was slowly evaporated and the chromium products were assayed for radioactivity.

The residue from the methanolic extraction contained the iron porphine. This was dissolved in benzene and transferred to a tared beaker. After the benzene had evaporated, the solid was assayed for activity. The visible and ir spectra of this material were identical with those of μ-oxo-bis(tetraphenylporphineiron(III)) (hematin).

When the reaction was carried out in the presence of tetrabutylammonium chloride, the procedure was modified slightly because it was found that simply washing the benzene solution with water was not particularly effective in removing all the Bu_4NCl. Therefore, after the solid chromium-containing product was recovered from methanol as described above, the solid was washed with 20 ml of water and centrifuged briefly. The water was decanted onto a large fritted glass Büchner funnel containing a few milliliters of 1 *M* $AgNO_3$ solution. AgCl precipitated immediately; a few drops of 1 *M* HCl were added; the mixture was stirred for 1 min and suction filtered. This was repeated to the solid four more times, until no precipitate appeared upon the treatment with $AgNO_3$. The solid AgCl contained the ionic chloride in the reaction product. The aqueous filtrate from this procedure also contained coordinated chloride, as evidenced by a small amount of postclouding about 5 min later. The solid remaining after the water washes contained most of the chromium products. This solid was dissolved in benzene, combined with the aqueous filtrates, and treated as described under activity measurements.

Results

Before an atom-transfer mechanism can be considered for the electron-transfer reaction in this case, certain criteria must be met regarding the inert character of the tetraphenylporphineiron(III) chloride. Two experiments are pertinent to this point.

(1) Tetraphenylporphineiron(III) chloride was found to be inert to exchange with ionic chloride under the conditions of the experiment. A mixture of TPPFeCl and $Bu_4N^{36}Cl$ in 1% pyridine–benzene was taken to dryness *in vacuo* at room temperature after 5 min. The hemin was separated from the salt by a water wash and no activity above background was observed in the recovered TPPFeCl.

(2) Because the chromium(II) sample used was certainly contaminated with chromium(III) as a result of unavoidable air oxidation, the possibility of chloride transfer from the hemin to the chromium(III) without electron transfer had to be considered. Thus, a sample of $Cr(acac)_2$ was opened to air and allowed to oxidize prior to mixing with TPPFeCl in 1% pyridine benzene. After 4 hr the chromium products and the hemin were separated. Qualitative analysis indicated that no chloride was present in the chromic fraction, and the TPPFeCl was recovered unchanged and contained no $(TPPFe)_2O$.

Chloride transfer was then established both in the absence and presence of added Bu_4NCl.

(3) The results indicating radiochloride transfer between $TPPFe^{36}Cl$ and $Cr(acac)_2$ are presented for three experiments in Table I. On the average, 96% of the radiochloride activity was recovered with the oxidized chromium products and negligible activity remained with the iron porphine. The lack of a AgCl precipitate in the water wash upon treatment with $AgNO_3$ indicated the absence of dissociated chloride. Although some complexed chloride was present in those washes, the activity therein only accounted for about 1% of the total.

Table I. Experimental Measurements for the Reaction between [^{36}Cl] Tetraphenylporphineiron(III) Chloride and Bis(2,4-Pentanedionato)chromium(II)

	Experiment no.		
	1	2	3
Wt of $TPPFe^{36}Cl$, mg	174.5	182.8	194.3
Specific activity of $TPPFe^{36}Cl$, cpm/mg[a]	121.9	83.07	111.9
Total activity of $TPPFe^{36}Cl$, cpm	21,279	15,180	21,750
Approx wt of $Cr(acac)_2$, g	1	0.7	0.6
Wt of hematin recovered, mg	161.9	172.9	164.3
Wt of Cr(III) products recovered, mg	850	666	501
Total activity in recovered hematin, cpm	41.7	49.5	43.1
Total activity in recovered Cr(III) products, cpm	20,684	14,715	21,137
% activity recovered in Cr(III) products	97.2	94.7	97.1

[a] All radioactivities are corrected for background and/or quenching.

(4) The results obtained for chloride transfer in the presence of an excess amount of uncomplexed radiochloride added as $Bu_3N^{36}Cl$ are presented in Table II. Experiments 4, 5, and 6 indicate that the chromic product did contain some radiochloride, but only about 9% of that expected for total mixing of coordinated and free chloride. Because it was found that TPPFeCl does not exchange chloride with Bu_4NCl under these conditions, the 9% activity observed in the Cr(III) product infers either that the reaction takes place in part by an outer sphere process or that the Cr(III) products undergo some anion exchange with Bu_4NCl after the electron-transfer reaction. This latter exchange may be important because of the presence of

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[8] The pyridine is required to ensure reduction of all the $TPPFe^{III}Cl$ to Fe(II). Presumably the pyridine stabilizes the porphine Fe(II) by forming the well-known hemochromogin $TPPFe^{II}(py)_2$. This material is not observed as the product because during the work-up in air $TPPFe^{II}(py)_2$ is oxidized to $(TPPFe)_2O$.

Table II. Experimental Measurements for the Reaction between Tetraphenylporphineiron(III) Chloride and Bis(2,4-pentanedionato)chromium(II) in the presence of [^{36}Cl] Tetrabutylammonium Chloride

	Experiment no.			
	4	5	6	7[b]
Wt of TPPFeCl, mg	168.4	151.0	150.4	50.5
Total activity of TPPFeCl, cpm[a]	0	0	0	36,360
Approx wt of $Cr(acac)_2$, g	1.3	0.9	0.75	0.2
Wt of $Bu_4N^{36}Cl$, mg	296	508	304	117
Molar ratio Bu_4NCl/TPPFeCl	4.5	8.5	5.1	6.8
Specific activity of $Bu_4N^{36}Cl$, cpm/mg	366	106.7	106.7	0
Total activity of $Bu_4N^{36}Cl$, cpm	108,300	54,210	32,440	0
Wt of hematin recovered, mg	157.9	130.3	129.7	49.6
Total activity of recovered hematin, cpm	63	32.8	18.4	49.8
Wt of Cr(III) products recovered, g	1.1	0.85	0.65	0.189
Expected activity of Cr(III) product,[c] cpm	19,870	5,698	5,298	5,300
Total activity of recovered Cr(III) products, cpm	1,785	708	280	31,720
% of expected activity found in Cr(III) products	9	12	5.3	(87.3)[d]

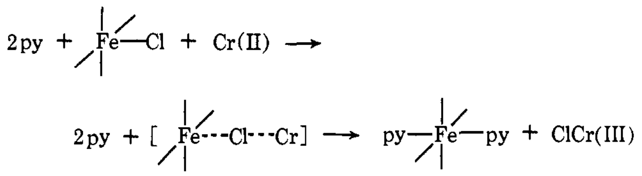
[a] All radioactivities are corrected for background and quenching. [b] In experiment 7, the Bu_4NCl was inactive and the TPPFeCl contained ^{36}Cl. [c] If ionic and complexed Cl^- were mixed. [d] This is the per cent activity of that expected for *no* mixing of the ionic and complexed chloride.

excess Cr(II) for several minutes after the reaction and the 1-2-hr total wet time of the work-up. Taube and King[9] have found that the exchange of Cl^- with aqueous $CrCl^{2+}$ is greatly accelerated by Cr^{2+}. It is also possible that in spite of our efforts to completely remove ionic chloride from the chromium(III) product, a small amount of the AgCl precipitate was carried through to the filtrate and was mixed with the Cr(III) products during the radiochemical assay.

Experiment 7 was the reverse of experiments 4, 5, and 6. That is, the ^{36}Cl was contained in the TPPFeCl and the Bu_4NCl was inactive. In that case, 87% chloride transfer was observed as opposed to the 96% transfer observed in the absence of Bu_4NCl (experiments 1, 2, and 3). The difference of 9% may be due to loss of some of the Cr(III) product during the extra four water water washes required to remove all the Bu_4NCl.

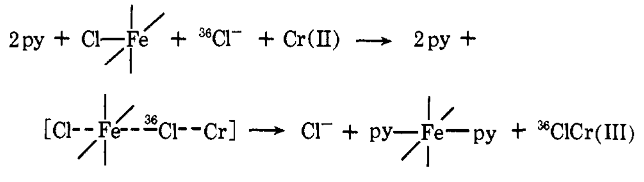
Discussion

In 1% pyridine in benzene the reduction of TPPFeCl by $Cr(acac)_2$ proceeds by an inner-sphere process, as evidenced by the extensive (96%) ligand transfer observed.



When compared to similar aqueous systems,[5] this result is not surprising. It is interesting, however, when considered with regard to the structure of the metalloporphine and the π system of the porphine ring. Iron(III) porphyrins are generally five-coordinate, with the iron above the porphyrin plane, toward the axial ligand.[10] If a ligand is bound in the sixth site, it is only weakly held. This relatively open coordination site would, therefore, appear to be an accessible route for electron transfer without ligand bridging, but is evidently not used. The porphine ring system should also be able to serve as a route for electron transfer because of the large π system and the potential for overlap with the metal d orbitals. However, this also does not appear to play any significant role in this case. This is contrary to the findings of Castro and Davis,[3] but their system was designed to observe changes at the periphery of the ring and could not lead to the observation of ligand transfer even if it occurred. In addition, it is difficult to deduce from their results whether methine deuteration occurred during the oxidation *or* reduction of the iron porphyrin and to eliminate the possibility that deuteration at the periphery of the ring occurred while the electron-transfer reaction was taking place directly at the metal. Of course tetraphenylporphine differs greatly from octaethylporphyrin, especially at the methine bridges, and it may not be appropriate to compare these two systems.

In the presence of excess uncomplexed Cl^-, the reaction is still accompanied by extensive (87%) ligand transfer, with little (9%) mixing of the complexed and ionic chloride pools and, therefore, still proceeds predominantly by the inner-sphere pathway. The apparent 9% incorporation of uncomplexed chloride in the presence of a five- to eightfold excess of ionic chloride may be due to experimental difficulties, but an outer-sphere pathway might possibly be indicated. The most interesting possibility in this regard is a route in which ionic chloride serves as a bridge between the Fe(III) and Cr(II) using the sixth coordination site of the iron and leading to chloride exchange without the occurrence of a true outer-sphere electron-transfer process.



Because of the preponderance of ligand transfer found here, inner-sphere pathways for electron-transfer process involving hemoproteins must receive continued consideration. This is especially true for multiheme systems like cytochrome oxidase, in which redox reactions may be occurring between two or more metals.

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(9) H. Taube and E. King, *J. Amer. Chem. Soc.*, **76**, 4054 (1954).
(10) E. B. Fleischer, *Accounts Chem. Res.*, **3**, 105 (1970).