

Lattice parameters were determined from a least-squares fit of angular data from 44 reflections, centered by using automated top/bottom-left/right slit assemblies.

The structure was solved by direct methods and Fourier techniques and refined by full-matrix least-squares techniques. A summary of crystal data and intensity information is given in Table VIII.

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Registry No. B₁₀H₁₄, 17702-41-9; B₉H₁₂NH⁻, 66272-83-1; B₉H₁₄⁻, 12430-28-3; B₁₀H₁₅⁻, 39448-33-4; Ph₃P=N=PPh₃[B₉H₁₂NH], 103885-37-6; B₉H₁₁NH, 58985-53-8; B₉H₁₁NH·CN(*r*-C₄H₉), 103904-38-7; B₉H₁₁NH·CN(C₆H₁₁), 103904-39-8; B₉H₁₁NH·py, 103904-40-1; B₉H₉NH, 103904-41-2; N(CH₃)₄[B₉H₉N], 103904-43-4; B₉H₉NCH₃, 103933-00-2; K[B₉H₉N], 103904-44-5; NaNO₂, 7632-00-0.

Supplementary Material Available: Tables of atomic coordinates and isotropic temperature factors (Table Is), anisotropic temperature factors (Table IIs), and selected bond angles (Table IIIs) (6 pages). Ordering information is given on any current masthead page.

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Spectrophotometric and X-ray Absorption Edge Study of Complexation of Carbon Monoxide with Ferric Tetrasulfophthalocyanine in Alkaline Solution

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The square-planar macrocyclic chelate ferric tetrasulfophthalocyanine (C₃₂H₁₂N₈(SO₃)₄Na₄Fe) was found to reversibly complex carbon monoxide in anaerobic, alkaline solution. The complex gave an electronic spectrum substantially different from that normally observed in solution for phthalocyanines, suggesting a redox process involving the organic ring. Reexposure to O₂ generated an intermediate species that exhibited a normal electronic spectrum. By comparison of the X-ray absorption edge spectra of the complexed iron in the various stages of reaction to its oxide powders, the changes between ferric and ferrous oxidation states could be monitored. Results suggest that the combined effect of CO and hydroxide on the Fe center is to lower the unfilled d_{xy} orbital below the filled a_{1u} orbital of the phthalocyanine ligand, enabling reduction of ferric ion to the ferrous state by the macrocyclic ring.

Introduction

In a study of C₁ electrochemistry in aqueous solutions of various metal phthalocyanine tetrasulfonates, it was observed that in alkaline solution the ferric phthalocyanine underwent a substantial color change in the presence of carbon monoxide.¹ The normally bright blue aqueous complex became dull purple or brown at millimolar concentrations. Subsequent exposure to air (i.e., oxygen) caused another color change to a greenish hue. The apparent redox chemistry involves some combination of ring- and/or metal-centered charge transfers. The potential catalytic significance of a specific CO/FePc/OH⁻ interaction warranted further study.

Iron phthalocyanine is a relatively large, aromatic, macrocyclic square-planar N₄ chelate, consisting of four azo-bridged pyrrole units, each with a benzene ring fused to its base. By sulfonation of the benzene moieties, the compound can be made water soluble. The two lowest energy π → π* electronic transitions, which result in the Q band in the red region of the visible spectrum and the Soret band in the near-ultraviolet spectrum, are quite intense (ε = 10⁴-10⁵ l/(mol cm)), and so electronic structural changes are easily observable. Its catalytic ability is well-known, especially in the electroreduction of oxygen.²⁻⁵

X-ray absorption spectroscopy, including extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES), has been receiving increased attention among chemists for its use as an analytical tool.⁶ The X-ray absorption edge of an element can be analyzed to give the number and type of nearest-neighbor atoms, as well as their bond distances. The edge and pre-edge structure of the absorption band contains bound-state transitions that yield information about coordination geometry, type of ligand, and valence state. In this report we will discuss how observation of the Fe absorption edge enabled us to monitor the charge state of the metal center exclusive of any changes occurring on the macrocyclic ring.

Experimental Section

The tetrasodium salt of tetrasulfophthalocyanine ferric chloride, [Fe^{III}TsPc]Cl, was prepared by the condensation of 4-sulfophthalic acid (Kodak) around an iron salt in a melt of urea, as described by Weber and Busch.⁷ While it is possible to prepare either ferric or ferrous phthalocyanine in this manner, unless protected from air the ferrous derivative will be mostly oxidized by the time workup is complete.⁸ Thus, either ferrous ammonium sulfate (Fe(NH₄)₂(SO₄)₂·6H₂O; Allied Chemical) or ferric chloride (FeCl₃·6H₂O; J. T. Baker) could be used interchangeably to produce the same result. To ensure complete oxidation, however, solutions were heated to 80 °C under a purge of O₂ before use. Conversion to the ferric state was substantiated by observing an absorption maximum at 636 nm, characteristic of Fe^{III}TsPc.⁸⁻¹⁰

UV-visible absorption spectra were taken with a Beckman DU-8 spectrophotometer. The macrocycle concentration was initially 1.0 × 10⁻⁵ M. Successive spectra were obtained by purging the same test solution in situ with the appropriate gas.

The X-ray absorption measurements were carried out on beamline X-11A of the National Synchrotron Light Source located at Brookhaven National Laboratory. The electron storage ring had an electron energy of 2.5 GeV and a current between 150 and 30 mA. The details of the beamline design have been published.¹¹ During this run the monochromator was operated in the two-crystal mode using Si(111) crystals. The incident and transmitted X-rays are measured with gas-filled ion chambers in which the gas mixtures are adjusted depending on the absorption energy of the element of interest. Normally, the initial chamber is adjusted to absorb only 10% of the incident radiation.

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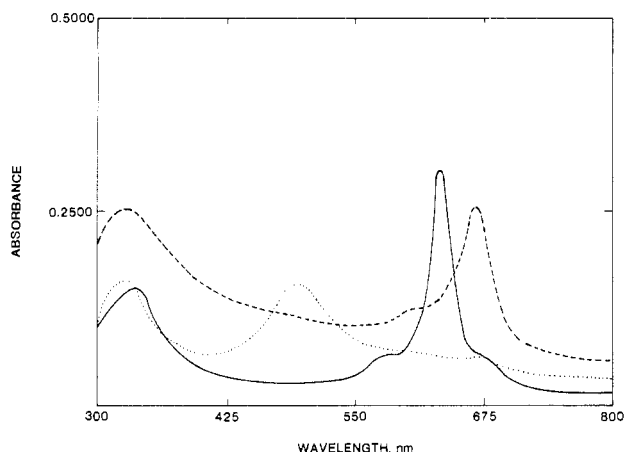


Figure 1. Absorption spectra of Fe^{III}TsPc in 1.0 M KOH: (—) initial solution in air; (···) under CO atmosphere; (---) after reexposure to air.

The liquid cell used in these measurements was designed for studying concentrated electrolytes. The Plexiglas flow-through cell was equipped with valves at either end to contain the anaerobic solutions. The cell is constructed in two parts; a body, which has one window, and the plunger, which is a Plexiglas tube sealed on one end with the second window. The plunger fits into the body and is sealed with an O ring. By adjustment of the position of the plunger the thickness of solution in the beam can be adjusted. The cell windows were 0.76 mm in thickness, and the optical path length was 2 mm. The spectra were obtained in 20-min scans. The transmission geometry used in these experiments is not the optimal configuration for carrying out the experiments. However, they demonstrate that significant insight can be obtained from this type of experiment. In order to obtain EXAFS data of sufficient quality, these experiments should be carried out in the fluorescence geometry, which would greatly enhance the signal to noise ratio.

To perform the redox chemistry, 100 mL of a 0.010 M solution of Fe^{III}TsPc are placed in a 125-mL Erlenmeyer flask that is sealed with a rubber stopper fitted with polypropylene tubes to allow gas entry and exit and also to force the test solution into the sample cell. After brief heating under an O₂ purge, the solution is made 1.0 M in OH⁻ by the addition of solid KOH pellets (J. T. Baker, 2 ppm maximum Fe content) during a thorough purge with nitrogen. A few milliliters was then transferred to the sample cell to analyze. Subsequent purging and transfer with CO and O₂ were employed to produce the other test solutions.

Results

The sequence of colors found in alkaline Fe^{III}TsPc by successive treatment with CO and air is shown by the spectra in Figure 1. In 1.0 M KOH, λ_{\max} for Fe^{III}TsPc appeared at 630 nm. Upon purging of the solution with CO, the Q band disappeared and was replaced by a new band at 494 nm, shown by the dotted trace. A thorough and vigorous purging was necessary to achieve the color transition, indicating that the last traces of O₂ had to be removed before the CO interaction could occur. At 1.0×10^{-5} M concentration, the Fe^{III}TsPc solution appeared red-violet or light purple. Prolonged purging with highly purified N₂ or Ar would eventually regenerate the original blue complex. Subsequent exposure to air, however, caused an immediate reaction to form a green complex, whose absorption spectrum is shown by the dashed trace. The Q band had reappeared, but λ_{\max} now stood at 668 nm, corresponding to what is generally thought to be ferrous phthalocyanine.⁸⁻¹⁰ This complex gradually decolorized with time, leaving only an ultraviolet band after standing overnight.

The stability of this complex, obtained by exposing a CO-purged solution of alkaline Fe^{III}TsPc to O₂, was found to be dependent on pH and partial pressure of O₂. Under the conditions employed for the XANES experiment (1.0 M KOH and 10 mM complex concentration with pure O₂ gas), considerable demetalation occurred within minutes. Even so, sufficient Fe remained complexed so that a spectrum could be obtained. Under slightly less forcing conditions, such as 0.1 M KOH and 1 mM complex concentration, with air the reaction was found to proceed quite cleanly, producing the green solution without demetalation. After the mixture was allowed to stand for 1 h, the color of the complex would return

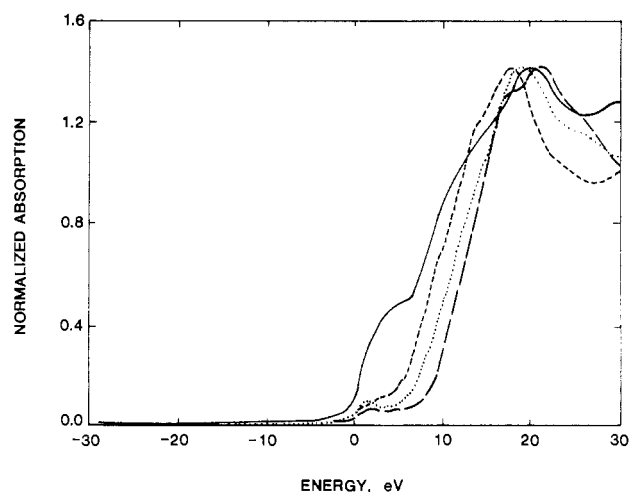


Figure 2. Absorption edge structure for various oxidation states of Fe: (—) Fe foil; (---) FeO powder; (···) Fe₃O₄ powder; (-·-·) Fe₂O₃ powder.

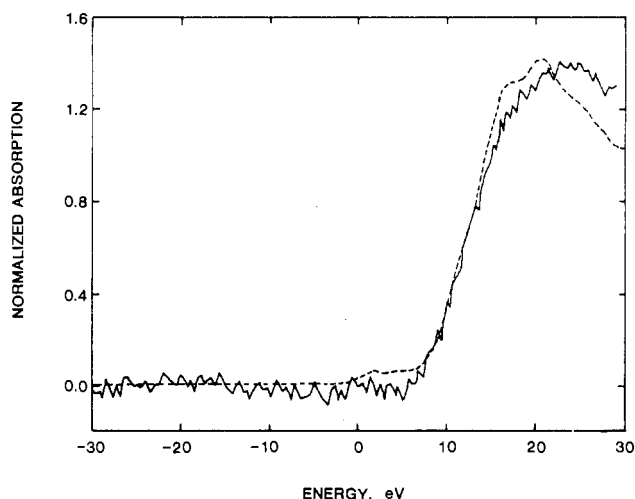


Figure 3. Absorption edge for Fe as Fe^{III}TsPc in alkaline solution ([FeTsPc] = 1.0×10^{-2} M; [OH⁻] = 1.0 M; (---) Fe₂O₃ edge).

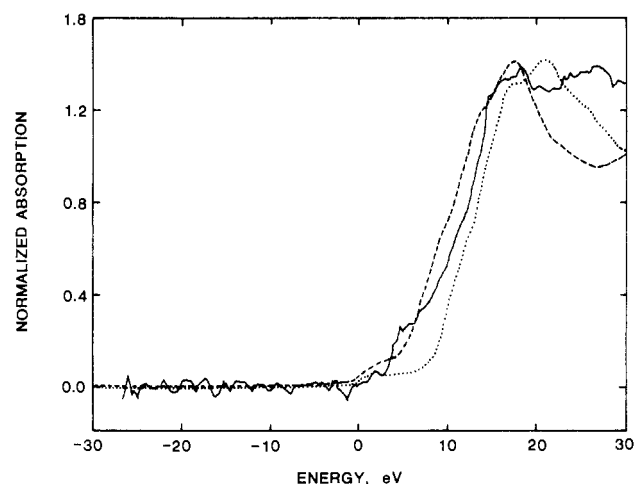


Figure 4. Absorption edge for Fe as Fe^{III}TsPc in alkaline solution: effect of CO ([FeTsPc] = 1.0×10^{-2} M; [OH⁻] = 1.0 M; CO saturating purge; (---) FeO and (···) Fe₂O₃ powder edges).

to the original blue, indicating completion of the chemical cycle.

The reaction sequence was then monitored with the X-ray beam from the synchrotron. Absorption edge spectra for the various (phthalocyanato)iron complexes and iron oxide powders are shown in Figures 2–5. In each figure, the pre-edge was normalized to a step at the edge. Energies are reported relative to the Fe binding energy (7112 eV). The same energy was subtracted for all spectra.

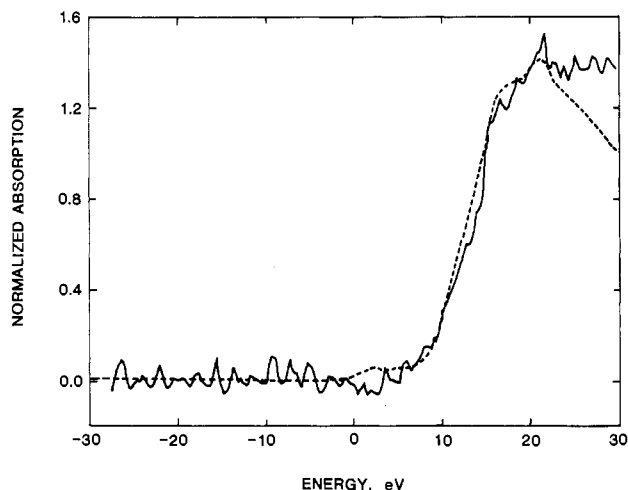


Figure 5. Absorption edge for Fe as Fe^{III}TsPc in alkaline solution: reexposure to O₂ after CO purge ([FeTsPc] = 1.0 × 10⁻² M (initially); [OH⁻] = 1.0 M; (---) Fe₂O₃ edge).

The spectrometer readings were stable, as evidenced by Fe foil edges taken before and after the run.

Absorption edge spectra of an Fe foil and various iron oxide powders are shown in Figure 2. As the oxidation state of the metal increased, the edge shifted to higher energies. In going from the ferrous to the ferric oxide, a 2.5–3.0 eV positive shift of the absorption edge was observed. This correlates well with the work of Wong et al.¹² on vanadium oxides, where they saw a 2.5-eV main-edge shift with unit change of metal valency. This formula appears to hold even for nonintegral oxides where the charge exchange between ferrous and ferric sites is sufficiently rapid. The edge for Fe₃O₄, where the implied oxidation state is 2.5, lies nearly midway between the edges for ferrous and ferric oxide.

In Figure 3, the absorption edge for Fe^{III}TsPc in alkaline solution is shown. The cross-hatched trace is that of Fe₂O₃, reproduced here on the same axes. The absorption edge of Fe in ferric phthalocyanine is almost coincident with that of ferric oxide.

In Figure 4, the absorption edge of alkaline Fe^{III}TsPc after exposure to CO is shown. The absorption edge for FeO is included, as is that for Fe₂O₃. The X-ray edge of the complex now lies closer to the Fe²⁺ edge. Coordination of CO caused a partial transfer of negative charge onto the metal center; as a result, the absorption edge is shifted 1–2 eV to lower energy.

In Figure 5, the absorption edge of the complex after reexposure to air is shown. The Fe absorption edge of the complex had returned to a position corresponding to the ferric state, even though the visible spectrum indicated the ferrous state.

Discussion

The oxygen sensitivity of the CO-purged solution led us initially to consider the observed chemistry as reduction and reoxidation. The literature has a substantial number of references on the reduction of metal phthalocyanines in solution, both chemical and electrochemical.^{13–36} A number of MPc anions have been ana-

Table I. Absorption Maxima of Reduced FePc²⁻ in Comparison to Those of the Fe^{III}TsPc(OH)(CO) Complex^a

FePc ⁻ (pink)	FePc ²⁻ (purple)	FePc ³⁻ (violet)	Fe ^{III} TsPc(OH)(CO)
800 (0.017)	740 (0.044)	530 (0.885)	675 (0.40)
665 (0.026)	625 (neg)	373 (neg)	494 (0.97)
596 (neg)	506 (0.633)	338 (0.932)	326 (1.00)
515 (0.245)	395 (neg)		
325 (0.748)	340 (0.746)		

^a neg = negligible.

lyzed by their optical absorption, electron spin resonance, and magnetic susceptibility.^{13–29} MPc's with closed valence shell configurations, such as Mg-, AlCl-, or ZnPc, give straightforward results: all electrons go into the ring e_g(π*) orbitals, resulting in a color sequence blue → blue → purple → blue → blue-green as successive electrons are input.²⁷ Even for transition metals whose valence shell is nearly filled, such as Ni- or CuPc, spectral results are quite similar upon reduction.^{6,19,26,27}

For the more d-electron-deficient transition metals, the color sequence for successive MPc reduction and resultant spectra are different from the filled-shell case and are generally unique to each metal. In a 4-electron reduction of FePc in THF with lithium benzophenone, Taube observed a color sequence green → red → blue-violet → violet → green-blue.²⁰ Clack and Yandle employed sodium metal to reduce FePc in THF, obtained a color sequence green → pink → purple → violet → green-blue.²⁷ On the basis of color above, it would appear that at least a 2-electron reduction of the Fe^{III}TsPc(OH) macrocycle has occurred with CO complexation. Clack and Yandle tabulated the absorption maxima and relative oscillator strength obtained for the 1–4-electron reduction products. The relevant data, converted from cm⁻¹ to nm, are shown in Table I. Absorption data for the CO complex is included for comparison. Neither the 2- nor the 3-electron reduction data quite match the aqueous alkaline spectrum.

Charman¹⁹ reduced FePc in an alkaline methanol solution with NaBH₄. The spectrum depended on the concentration of borohydride. At a BH₄⁻ concentration of 0.02%, wavelength maxima (with relative intensities in parentheses) were 830 (0.30), 690 (0.35), 610 (0.32), and 515 nm (1.00). At 0.2% BH₄⁻, the spectrum changed to 780 (0.12), 618 (0.49), and 492 nm (1). One can infer from the previous citations that the lower NaBH₄ concentration, which gave a red solution, can be assigned to a 1-electron reduction. The higher concentration produced a spectrum that certainly represents further reduction but is a rather poor fit to our spectra and the THF data.

There are some examples where FePc was reduced electrochemically. Li and Chin³⁰ reduced FeTsPc in Me₂SO to obtain a green 1-electron-reduction product. Further reduction decomposed the complex. The redox process was most likely the simple reduction of ferric to ferrous ion, since, as is described in the Experimental Section, preparation and work up of FeTsPc's in

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an aqueous aerobic environment produces the ferric salt. Lever and Wilshire, however, electroreduced the ferrous unsulfonated form of FePC in Me₂SO and obtained a purple solution after the first charge equivalent was transferred.³² Thus, solvent and ligand field effects have a great influence on the overall ground-state electronic configuration.

While the similarity between reduced FePc spectra and that obtained for the Fe^{III}TsPc(OH)(CO) complex has been pointed out, it is unlikely that the macrocyclic ligand in the CO complex has been reduced. Hydroxide ion has no reducing power, leading to the suggestion that reduction must be performed by CO.

However, this can be discounted on several grounds. First is the nature of the CO coordinate bond itself. As a π -acid acceptor ligand, CO donates electrons to a metal through its σ bond but accepts electrons from off-axis orbitals on the metal into its own empty π^* orbitals. The result is a strong bond with little net charge exchange. For example, calculations by Case, Huynh, and Karplus on carboxyhemoglobin show a 0.45-electron σ donation onto the iron center but a 0.25 electron withdrawal through the π bond for a net 0.2-electron charge density decrease for CO.³⁷ While calculations on the bonding of CO to iron porphyrin have been performed for a number of heme-containing compounds,³⁷⁻³⁹ no calculations for FePc(CO) are available.

Second is the limited reducing power of CO. On the scale of standard reduction potentials, the CO₂/CO couple lies at -0.10 V vs. NHE.⁴⁰ For those instances where electroreduction of the macrocycle was performed, potentials far negative of the E° for CO/CO₂ were required.

Third, no evidence of any chemical reaction, save for the initial coordination, was observed. It was speculated that CO could be oxidized to CO₂ or CO₃²⁻ in alkaline solution. Hieber demonstrated that iron pentacarbonyl will react in aqueous alkali to produce CO₂ and HFe(CO)₄⁻, a carbonylate anion.³² Pentacyanoferrate(III), [Fe(CN)₅(H₂O)]²⁻, a complex more analogous to phthalocyanine, will complex NO (nitroprusside) and react with OH⁻ to form [Fe(CN)₅(NO₂)]⁴⁻,^{42,43} but no such reaction for the corresponding carbonyl complex has been reported.

Any production of CO₂ from reduction of the macrocycle would immediately manifest itself as a drop in pH. Accordingly, a 1.0 $\times 10^{-4}$ M solution of Fe^{III}TsPc was made alkaline with NaOH so that the pH = 10.53, corresponding to a free OH⁻ concentration of 3.4 $\times 10^{-4}$ M. The blue solution was heated to 63 °C and thoroughly purged with N₂; upon switching of the purge to CO, the purple color was achieved in a few seconds. The initial pH change was only -0.05 + 0.02, however. Since FePc does not strongly bind CO₂ and any free CO₂ under these conditions would immediately react with hydroxide ion, it can be concluded that the spectral shift is due to CO coordination itself and not any subsequent redox chemistry. It should be noted, however, that the pH of freshly prepared Fe^{III}TsPc alkaline solutions, with or without CO, is not stable but shows a negative drift, which indicates a source of acid equivalents, possibly metal hydrolysis, which has been observed by others⁴⁴ but not fully elucidated.

Finally, there is the XANES data to consider. The X-ray absorption edge shift for the CO complex (Figure 4) indicates from 0.5 to 0.75 of a unit of negative charge transferred onto the iron center that could plausibly be accounted for by the combined effects of OH⁻ and CO.

Since the oxidation state of the iron center is reduced by nearly a unit charge, and the redox process is apparently intramolecular, and CO is an unlikely reducing agent in this instance; one must consider oxidation of the organic ring. While the amount of

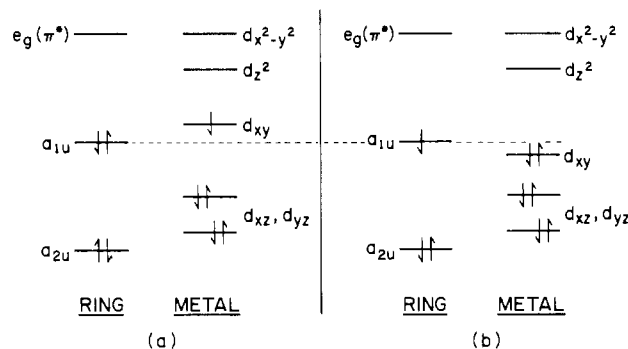


Figure 6. Molecular orbital diagram for Fe^{III}TsPc: (a) before CO exposure; (b) after CO exposure.

research on oxidation of phthalocyanines is not as great as for reduction, there are a number of contributions to this area.⁴⁵⁻⁵¹ Interestingly, it appears that the color changes observed upon oxidation are similar to those initially observed upon reduction. In 85% H₃PO₄, Cahill and Taube were able to slow the oxidation of a number of MTsPc's by ceric ion, so that a magenta-red intermediate with $\lambda_{\text{max}} = 530$ nm was observable.⁴⁵ The final two-electron-oxidation products were essentially colorless. Linstead and Weiss⁴⁴ could reversibly produce a purple intermediate by treating a suspension of H₂Pc in dilute H₂SO₄ with Ce⁴⁺. Finally, Ferraudi et al. have performed a number of flash photolytic experiments on phthalocyanine oxidations.⁴⁸⁻⁵¹ In general, the effect of oxidation was to eliminate the Q band and produce a new band at 500-520 nm. In a study of Co(III) and Fe(II) TsPc's, he assigned the λ_{max} at 520 nm in the oxidized CoTsPc transient and the λ_{max} at 460 nm in the FeTsPc transient to their respective ligand radicals.

Therefore, we believe the Fe^{III}TsPc complex with CO and OH⁻ represents a relatively stable ligand radical, in which the ligand field on the iron has lowered one of its empty d orbitals, enabling charge exchange with the ring to occur. This is diagrammed in Figure 6, where a molecular orbital scheme for the organic macrocycle and the iron center are shown, before and after CO complexation.

The metal-to-ligand π -bonding CO not only serves to increase the ligand field splitting but also distorts the square-planar field to one more like a tetragonally distorted octahedron. The result may be that the d_{z^2} orbital is raised well out of range and the d_{xy} orbital is lowered below the highest occupied a_{1u} orbital of the organic ring. Intramolecular charge transfer may then occur, producing an organic ligand radical and a reduced metal center. This also explains how a ferric complex can coordinate CO, in that the act of complexation produces the ferrous state, which can then interact with the CO molecule as usual.

The rapid interaction of the CO complex with O₂ then represents not so much a reoxidation but the relative stability of the respective compounds. The subsequent reaction with O₂ may be complicated, since the electronic spectra would indicate retention of the ferrous state ($\lambda_{\text{max}} = 668$ nm). Bernauer and Fallab⁹ observed that ferric phthalocyaninetetrasulfonate exhibits an absorption maximum at 634 nm with a blue color, while the ferrous tetrasulfonate appears green with λ_{max} at 670 nm. Debate as to the interconvertibility between ferrous and ferric states continued,^{8,9} but the assignments remained unchanged. The XANES data, however, show a complete reoxidation to the ferric state (Figure 5). Besides, one should expect eventual air oxidation of

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a ferrous complex in aqueous solution. Thus, the peak shift between 670 and 634 nm for FeTsPc complexes is not always a valid indication of the valence state of the metal. It may instead be more directly an indication of the substituents that occupy the axial binding sites of the iron.

The XANES data in this report tend to verify Kunzl's law, which states that the energy shift of the absorption edge will vary linearly with the valence of the absorbing species. Figure 2 shows the positive shift of absorption edge structure with oxidation state for the 0, +2, +2.5, and +3 states of Fe.

The coincidence of absorption edges for ferric ion in either Fe₂O₃ or FeTsPc showed that edge position is a strong function of oxidation state and is not perturbed by other factors. Both Kunzl's law and the valence/edge position correlation are demonstrated by Wong et al.¹² in a detailed study of vanadium compounds. All the features of the absorption edge and pre-edge (threshold, 1s→3d pre-edge peak, absorption edge, and 1s→4p peak) are found to vary linearly with oxidation state, although the rate of change varies between these components. Also in that study, spectra of vanadyl phthalocyanine and vanadyl tetraphenylporphyrin were taken for comparison to many other inorganic vanadium complexes. The main edges of VOPc and VOTPP, where V is nominally in the +4 state, lie between those of V₄O₇ and V₂O₄.

The fact that Wong observed that the N₄ chelates of vanadyl ion showed a slightly smaller chemical shift than V₂O₄ (13.4 vs. 14.0 eV) demonstrates the effect of coordination number and

electronegativity of the bonding ligands on total energy shift. The concept of coordination charge, where the formal valence of a metal is reduced by a factor corresponding to the degree of covalency of the bonding ligands, has been employed to explain such differences in absorption edge shifting.^{12,52} In our case, these effects were found to be small enough that we could compare the chemical shifts of iron in phthalocyanine to those of the oxide standards directly.

In summary Fe^{III}TsPc has been found to complex OH⁻ and CO and is believed to produce a reduced state of the metal and a ligand radical of the macrocycle. Further research into the chemistry of this complex and the electronic structural changes that accompany it was under way.

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Complexes of Functional Phosphines. 10.¹ Palladium Complexes with the Ligands Ph₂PCH₂COPh, (Ph₂PCHCOPh)⁻, and Ph₂PCHC(Ph)OPPh₂. Crystal and Molecular Structure of *cis*-[PdCl₂{Ph₂PCHC(Ph)OPPh₂}]

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(Diphenylphosphino)acetophenone, Ph₂PCH₂COPh (L), was synthesized by reacting Ph₂PCL with PhCOCH₂Li in THF. In the complexes [PdCl₂L₂] (1), [(η³-C₄H₇)PdCl] (2), [(*o*-C₆H₄CH₂NMe₂)PdCl] (3), [(C₁₀H₈N)PdCl] (4), and [(C₁₄H₁₃N₂)PdCl] (5), L behaves as a monodentate ligand (through phosphorus), and in [(*o*-C₆H₄CH₂NMe₂)Pd{Ph₂PCH₂C(O)Ph}][CF₃SO₃] (6), [(C₁₀H₈N)Pd{Ph₂PCH₂C(O)Ph}][CF₃SO₃] (7), and [(C₁₄H₁₃N₂)Pd{Ph₂PCH₂C(O)Ph}][CF₃SO₃] (8), L behaves as a chelating ligand (through phosphorus and the keto group). Treatment of 3-5 with NaH in THF led to the corresponding enolato-phosphine complexes 9-11, in which the P,O-chelate ligand behaves as a three-electron donor. Reaction of Li₂PdCl₄ with 2 equiv of L in the presence of NEt₃ afforded *cis*-[Pd{Ph₂PCHC(O)Ph}₂] (12). Thermolysis of 1 in toluene resulted in the quantitative formation of *cis*-[PdCl₂{Ph₂PCHC(Ph)OPPh₂}] (13). The molecular structure of 13 has been determined by X-ray diffraction: monoclinic, space group *P*2₁/*c*, with *Z* = 4, *a* = 10.602 (6) Å, *b* = 19.503 (4) Å, *c* = 14.631 (9) Å, β = 97.27(3)°, and *d*(calcd) = 1.476 g/cm³. The structure was solved by using 2780 reflections with *F*_o² ≥ 3σ(*F*_o²) and refined to conventional *R* = 0.038, *R*_w = 0.049. The coordination around Pd is square planar, with Cl(1)-Pd-Cl(2) and P(1)-Pd-P(2) angles of 91.77 (6) and 92.88 (6)°, respectively. The puckering of the six-membered ring is accompanied by a large P(1)-O(1)-C(14) angle of 131.1 (4)°. All complexes were characterized by elemental analyses and IR, ¹H NMR, and ³¹P{¹H} NMR spectroscopy.

Introduction

Since the discovery of the ethylene polymerization catalyst A by Keim et al.,³ the search for active complexes of functional phosphines has become a subject of increasing interest.⁴ During

the last few years, many functional phosphines have been shown to confer unusual physicochemical properties to their complexes, and/or allow them to partake in reactions of catalytic relevance. Thus phosphinoanisoles of type B may stabilize a polar transition state in oxidative-addition reactions,⁵ the pinacolone derivative C is a dinucleating ligand that can maintain two different metals in close proximity,⁶ and in the rhodium complex D, the hemilabile P,S-ligand generates a highly reactive, coordinatively unsaturated species in solution.⁷

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