indicated two components. Extraction of the orange product with hot 1:1 toluene:CH_2Cl_2 left behind a small amount (approximately 0.05 g) of orange powder that may be a 4:1 PPh_3 adduct that precipitated before cleavage could occur. Anal. Calcd for $Rh_2C_{80}H_{60}P_4F_{12}O_8$: C, 56.29; H, 3.54. Found: C, 56.12; H, 3.87. From the toluene:CH_2Cl_2 extract an orange powder was obtained (0.15 g). This complex is most likely $Rh(O_2CCF_3)(PPh_3)_3$. Anal. Calcd for $RhC_{56}H_{45}P_3F_3O_2$: C, 67.07; H, 4.52; P, 9.27. Found: C, 67.86; H, 4.71; P, 9.58. IR (Nujol mull): single $\nu_{asy}(CO_2)$ 1678 cm^{-1} (lit.[25] 1670 cm^{-1}). Addition of hexane (5 mL) to the filtrate from the original reaction mixture and cooling led to formation of a yellow precipitate. Filtration and washing with hexane afforded 0.12 g. This compound is most likely $Rh(O_2CCF_3)_3(PPh_3)_2$. Anal. Calcd for $RhC_{42}H_{30}P_2F_9O_6$: C, 52.19; H, 3.13; P, 6.41. Found: C, 51.95; H, 3.10; P, 6.12. IR (Nujol mull): $\nu_{asy}(CO_2)$ 1710 cm^{-1}. When the above procedure is repeated without rigorous exclusion of air, the reaction proceeds in qualitatively the same manner, but $OPPh_3$ is isolated (checked by IR and elemental analysis) and the products give less satisfactory analyses due presumably to $OPPh_3$ coordination or possible side reactions.

Trimethyl Phosphite Complex. $Rh_2(O_2CCF_3)_4$ (0.169 g, 0.256 mmol) was dissolved in toluene (3 mL). To this green solution was added dropwise $P(OMe)_3$ (0.30 mL, 2.54 mmol). This reaction is fairly exothermic. A red-brown solution initially resulted, probably due to axial adduct formation. After 1 h the solution was yellow with pure yellow precipitate. Addition of hexane (2 mL) and cooling followed by filtration and washing with hexane afforded a pale yellow solid (0.30 g). Anal. Calcd for $RhC_{13}H_{27}P_3F_6O_{13}$: C, 22.27; H, 3.88; P, 13.25; mol wt 701. Found: C, 22.50; H, 3.98; P, 13.40; mol wt 698 (in CH_2Cl_2).

Experimental Methods. Elemental analyses were performed by the Microanalytical Laboratory of the University of Illinois. Fourier transform NMR spectra were recorded on a Nicolet NT-360 spectrometer operating at 338.6 MHz for fluorine and 360.1 MHz for proton. All ^{19}F chemical shifts are with respect to internal $CFCl_3$, and all ^1H chemical shifts are with respect to internal Me_4Si. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Associates XL-100 FT spectrometer operating at 40.5 MHz. The ^{31}P chemical shifts are with respect to an external standard of 85% phosphoric acid. Infrared spectra were recorded on a Nicolet 7000 FT IR for $CHCl_3$ solutions and on a Perkin-Elmer 599B instrument for Nujol mull spectra.

Acknowledgment. Support for this research by the National Science Foundation is gratefully acknowledged.

Registry No. $Rh_2(O_2CCF_3)_4$, 31126-95-1; $Rh_2(O_2CCF_3)_4(THF)_2$, 90968-04-0; $Rh_2(O_2CCF_3)_4(Me_2SO)_2$, 72665-42-0; $Rh_2(O_2CCF_3)_4(DMF)_2$, 90968-05-1; $Rh_2(O_2CCF_3)_4(Et_3N)_2$, 90968-06-2; $Rh_2(O_2CCF_3)_4(py)_4$, 90968-07-3; $Rh_2(O_2CCF_3)_4(t\text{-}BuNC)_4$, 90990-41-3; $Rh_2(O_2CCF_3)_4(PPh_3)_2$, 77966-16-6; $Rh_2(O_2CCF_3)_4(P(OPh)_3)_2$, 77966-17-7; $Rh_2(O_2CCH_2CH_2CH_3)_4(PPh_3)_2$, 90968-08-4; $Rh_2(O_2CCF_3)_4(CH_3CN)_2$, 90990-42-4; $Rh(O_2CCF_3)_2(P(OMe)_3)_3$, 90968-09-5; $Rh(O_2CCF_3)(PPh_3)_3$, 34731-08-3; $Rh(O_2CCF_3)_3(PPh_3)_2$, 90968-10-8.

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Redox Properties and Demetalation of Reduced Lead Phthalocyanine in Dimethylformamide

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The electrochemical oxidation and reduction of lead phthalocyanine, PbPc, was investigated by cyclic voltammetry, rotating-disk voltammetry, and dc polarography in DMF containing 0.1 M TEAP. At a solid electrode, PbPc is electrochemically oxidized in two steps. The first oxidation is diffusion controlled and reversibly generates the monocation radical. The second oxidation also appears to be diffusion controlled by rotating-disk voltammetry but is irreversible by cyclic voltammetry under the same experimental conditions. The reduction of PbPc occurs in three reversible one-electron steps. In addition, a fourth irreversible reduction step is observed at a mercury electrode. Analysis of the current-voltage curves and characterization of the controlled-potential electrolysis products indicates that a slow demetalation occurs after the first reduction step. However, at the more rapid measurement times of cyclic voltammetry, anion radicals and dianions may be quantitatively produced. An overall oxidation-reduction mechanism is postulated, and comparisons are made between the investigated complex and the general electrochemical behavior of main-group and transition-metal phthalocyanines.

Introduction

In recent years numerous electrochemical investigations of phthalocyanines have appeared in the literature.[2-16] This recent and quite rapid development has been due, in part, to the similarity between phthalocyanines and the biologically relevant porphyrins,[17] as well as to the involvement of phthalocyanines in solar conversion systems and in electrocatalysis.

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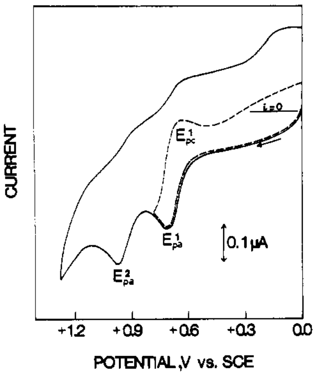

Figure 1. Cyclic voltammogram for the oxidation of 3.0×10^{-4} M PbPc at a Au electrode in DMF (0.1 M TEAP). Scan rate = 0.1 V/s.

Phthalocyanines, like porphyrins, are aromatic systems containing 18 π electrons.[2,3] The phthalocyanine ligand, PcH_2, is itself electroactive and may be electrooxidized in two steps, or electroreduced in four steps.[6-8] In addition, phthalocyanines that contain an electroactive metal center may also undergo other oxidations or reductions that invariably occur at potentials between the first oxidation and the first reduction of the ligand.[10-12]

This work is devoted to a detailed analysis of the overall oxidation–reduction mechanism of lead phthalocyanine, PbPc, in dimethylformamide. Previous studies of PbPc have revealed that this complex is only moderately stable[13] due to the rather large size of the central Pb^{2+} ion (when compared to the central coordination core of the Pc^{2-} ligand) and that the site of the first oxidation and the first reduction is at the phthalocyanine ligand.[14,15] No evidence exists for formation of $Pb^{IV}Pc$ as has been postulated for lead porphyrins.[18] In addition, neither the oxidation nor the reduction potentials fit a correlation with charge/radius as has been shown for seven other main-group phthalocyanines.[15]

Experimental Section

Lead phthalocyanine, PbPc, was prepared according to literature procedures.[19] Tetra-*n*-ethylammonium perchlorate (TEAP) was used as supporting electrolyte and, along with DMF, was purified according to earlier reported methods.[20] All electrochemical measurements were carried out under argon or nitrogen by using a three-electrode cell. Experiments involving the dropping-mercury electrode (DME) were performed with a PRG 4 multipurpose electrochemistry device (Solea-Tacussel). A Bruker E 130 M system was utilized for measurements with a Pt or Au rotating disk electrode (RDE). The reference electrode was a saturated calomel electrode (SCE), which was electrically connected with the studied solution by a junction bridge filled with the corresponding solvent–supporting electrolyte solution. Coulometric measurements were performed with a large-mercury-pool working electrode (area 6 cm²), a Pt counterelectrode, and an SCE reference electrode. ESR experiments were carried out under a nitrogen atmosphere after exhaustive electrolysis on an X-band Bruker spectrometer.

Results

Oxidations of PbPc. In DMF (0.1 M TEAP) PbPc shows two well-defined oxidation waves at a Pt or Au rotating disk electrode. These waves are of equal height at a rotating Pt disk electrode, but at a rotating Au disk electrode the limiting height of the first wave is higher than that of the second. Analysis of the limiting currents gave values of $E_{1/2} = +0.65$ and +0.95 V at both electrodes and reveal that both processes are diffusion controlled. Diagnostic plots of E vs. log $(i/(i_l - i))$ give a slope of 60 mV for each wave and values of i_l were proportional to the rotational speed $\omega^{1/2}$, consistent with diffusion-controlled one-electron transfers.[21]

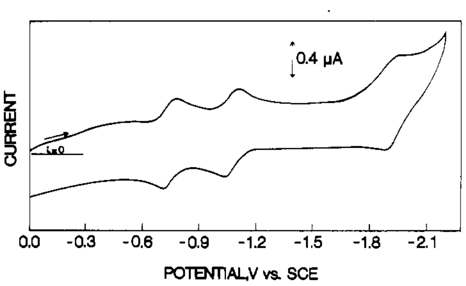

Figure 2. Cyclic voltammogram for the reduction of 3×10^{-4} M PbPc at a Au electrode in DMF (0.1 M TEAP). Scan rate = 0.1 V/s.

Two single-electron oxidations of PbPc were observed by cyclic voltammetry, but in this case, reversal of the potential sweep indicated that a chemical reaction followed the second oxidation. A typical cyclic voltammogram obtained for oxidation of PbPc at a Au electrode in DMF (0.1 M TEAP) is shown in Figure 1. Two anodic peaks, (labeled $E_{pa}{}^1$ and $E_{pa}{}^2$) are observed on the forward sweep, but well-defined rereduction peaks are not present when reversing the potential scan at +1.3 V. In contrast, when the potential sweep was reversed at +0.8 V, a well-defined rereduction peak (labeled $E_{pc}{}^1$) was obtained. Nernstian diffusion-controlled separations of 60 ± 10 mV were obtained between $E_{pa}{}^1$ and $E_{pc}{}^1$ at all scan rates up to 1.0 V/s and confirm that one electron is abstracted in the initial oxidation.

Reduction of PbPc. Stationary rotating-disk voltammograms of PbPc at a Au electrode are characterized by three waves of equal height, with values of $E_{1/2} = -0.75$, -1.04, and -1.92 V vs. SCE. Identical values of $E_{1/2}$ for the first two reductions are observed at a Pt electrode. The third wave is beyond the potential range of DMF at a platinum electrode and thus cannot be observed at this electrode. Analysis of the current–voltage curves for the three reduction as a function of rotation rate and plots of E vs. log $(i/(i_l - i))$ suggest that all three electrode reactions involve diffusion-controlled reductions.

Similar conclusions are also obtained by cyclic voltammetry at Au or Hg electrodes. At all scan rates up to 1.0 V/s, the peak potential separation ($E_{pa} - E_{pc}$) remained constant at 0.059 ± 0.005 V, consistent with diffusion-controlled one-electron transfers. This is shown in Figure 2, which illustrates a typical cyclic voltammogram for the reductions of PbPc at a Au electrode. Similar cyclic voltammograms were obtained at a Hg electrode. However, at this electrode an additional, irreversible, step was observed at −2.36 V. Analysis of this wave was difficult, due to the negative potential, which was close to the solvent limit but suggested *n* values between 3 and 4.

Exhaustive coulometric reduction of PbPc was carried out at −0.9 V with a Hg-pool working electrode and indicated the addition of 1.04 faradays/mol in the first reduction. Since the heights of the initial three waves were identical, it is assumed that similar values would also be obtained after reduction at potentials cathodic of −1.04 and −1.92 V.

Demetalation of PbPc. Polarization of PbPc solutions at −0.8 to −1.0 V for 10 min followed by reversal of the potential sweep from −0.8 to 0.0 V showed the presence of a large oxidation peak at −0.35 V on the first positive scan but not on the second scan. This is illustrated in Figure 3a. A similar oxidation peak is observed at the same potential for cyclic

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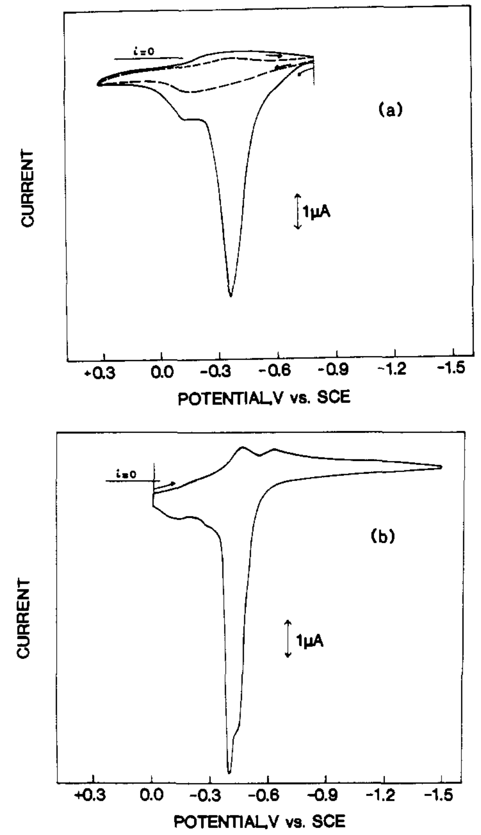


Figure 3. (a) Cyclic voltammogram of 5 × 10^{-4} M PbPc polarized at −0.8 V for 10 min at a Au electrode in DMF (0.1 M TBAP): (—) first scan; (---) second scan. (b) Cyclic voltammogram of 2 × 10^{-4} M $Pb(ClO_4)_2$ at a Au electrode under the same solution conditions. Scan rate = 0.020 V/s.

voltammograms of $Pb(ClO_4)_2$ in DMF (0.1 M TBAP). Under these experimental conditions, the reduction of Pb^{2+} to Pb^0 occurs at −0.45 V and the oxidation of Pb^0 to Pb^{2+} at −0.40 V. This is shown in Figure 3b.

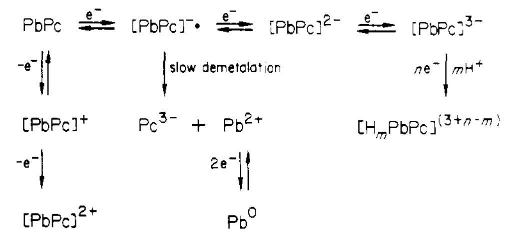
The above results suggest that the Pb^{2+} cation is expelled from the phthalocyanine ligand after the first reduction step at −0.75 V and that the liberated Pb^{2+} is immediately reduced to Pb^0. Confirmation of a Pb^0 film on the Au electrode after reduction was obtained from electron diffraction studies that showed the presence of zerovalent lead.[22] Oxidation peaks for the reaction Pb^0/Pb^{2+} were not observed on the second cycle in Figure 3a in agreement with other data suggesting that the demetalation step is slow.

Attempts were made to identify the reduced phthalocyanine ligand after demetalation. However, after exhaustive coulometric reduction at −0.8 V, the solution, which was initially clear, became turbid due to floculation. Nevertheless, ESR measurements were carried out during this reduction and showed a weak signal (at g = 2.0049, ΔH = 3.36 G) that remained after coulometric reduction at a potential corresponding to the second reduction step. This signal may reasonably be ascribed to the remaining demetalated phthalocyanine ligand.

Discussion

The redox properties of PbPc fit the general behavior observed for metallophthalocyanines containing nonelectroactive divalent metals. Potentials corresponding to the first oxidation ($E_{1/2}$ = +0.65 V) and the first reduction ($E_{1/2}$ = −0.75 V) of PbPc are consistent with previous results that have demonstrated that only the phthalocyanine ligand was involved in these electron transfers.[14,15]

Scheme I



Further oxidations and reductions also involve the phthalocyanine ligand and, when combined with the demetalation reaction, lead to the overall oxidation–reduction in Scheme I.

At a solid electrode, three reversible one-electron reductions reversibly lead to mono-, di-, and trianions. On mercury, the cathodic range of the electrode is expanded to −2.8 V, and a fourth, irreversible, reduction step is observed at −2.36 V. Unfortunately, a precise determination of the number of electrons transferred was not possible. It is expected that the ion electrogenerated in this fourth step would be highly basic and would likely react with available residual protons in the solvent, thus making the overall step irreversible. Such a process is well-known for porphyrins.[23]

On oxidation, the first step is reversible and the second irreversible on the time scale of the electrochemical experiments. However, as shown in Figure 1, the first oxidation also becomes irreversible when the potential is scanned to more positive potentials than those of the second oxidation step. This irreversibility is ascribed to an electrode passivation associated with the second oxidation step and has been seen for other phthalocyanines.[24]

It has been reported that metallophthalocyanines with nonelectroactive metal centers exhibit a potential gap of approximately 1.56 V between the first oxidation and the first reduction and that this potential difference corresponds to the energy difference between the ligand-centered HOMO and LUMO in the molecule.[24] In PbPc this potential difference decreases to 1.40 V. This is a consequence of the strained structure of the molecule. Pb^{II} is out of the plane of the ligand due to its large diameter (2.42 Å) with respect to the size of the central coordination site in the phthalocyanine ligand.[25] Half-wave potentials for the first two reductions of PbPc ($E_{1/2}$ = −0.75 and −1.04 V) are more negative than those of the free base phthalocyanine, PcH_2 ($E_{1/2}$ = −0.42 and −0.82 V in DMF).[8] This is expected from the increased electron density that is induced onto the ligand when the N–H covalent bonds are replaced by nitrogen–metal interactions. However, in the specific case of PbPc, this effect remains weak owing to the poor electropositive character of Pb(II).

The first reduction step of PbPc deserves special attention, since polarization of PbPc beyond −0.8 V initiates a demetalation that results in a deposit of metallic lead onto the surface of the electrode. Exhaustive electrolyses at −0.9 V resulted not only in a demetalation but also in the formation of an insoluble species, which we ascribe to a further decomposition product of the highly unstable triply charged Pc^{3-} moiety. On the other hand, the weak ESR signal observed after exhaustive electrolysis at −0.9 V (g = 2.0049, ΔH = 3.36 G) might correspond to a small quantity of the Pc^{3-} moiety with negative charges distributed over the entire π system and the pyrrolic nitrogens.

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The demetalation step is itself rather slow and is not detected by cyclic voltammetry, even at scan rates as low as 20 mV/s. Also, the demetalation of PbPc is clearly induced by reduction of the ligand. This is at variance with mechanisms for demetalations of silver and thallium porphyrins, where the central cation is reduced and then expelled owing to the large increase of its size that the ligand cannot accommodate.[26] It is in agreement, however, with a similar mechanism that we have observed for reduced HgTPP in bonding solvents such as pyridine.[27]

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Registry No. PbPc, 15187-16-3; Pc^{3-}, 90741-23-4; Au, 7440-57-5; Pt, 7440-06-4; Hg, 7439-97-6; Pb, 7439-92-1.

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Electrochemical and Photochemical Reduction of Decatungstate: A Reinvestigation

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The electrochemical study of the potassium, tetrabutylammonium and tributylammonium salts of Wy strongly suggests that they contain the $(W_{10}O_{32})^{4-}$ anion, the structure of which has been described by Fuchs. The observed differences in electrochemical behavior are assigned to medium effects (i.e., solvent, acidity, counterions). The complete optical spectrum of the 1e-reduced species has been obtained for the first time. It exhibits a new band around 6500 cm^{-1}, which seems characteristic of the presence of quasi-linear W–O–W bridges, as already observed in 2/18 structures. The low-temperature ESR spectrum has been recorded for the first time, and the orthorhombic spectrum is consistent with a localization in equatorial sites. The photochemical reduction gives the same reduced species as the electrochemical reduction.

Introduction

During the course of a study on the electrochromic properties of tungstic acid gels,[2] we found that colloidal solutions obtained through acidification of a tungstate solution contained appreciable amounts of decatungstate $(W_{10}O_{32})^{4-}$. This polyanion exhibits a marked photochromism in the presence of an organic reducing agent. It was thus interesting to correlate its photochemical and electrochemical behaviors.

The first electrochemical study was performed by Boyer.[3] At this time, the polyanion called "Wy" was formulated as a dodecatungstate $(HW_{12}O_{39})^{5-}$. Later on, Termes and Pope[4] gave some evidence for the identification of Wy with the tributylammonium decatungstate, described by Fuchs and having the structure[5] depicted in Figure 1. However, some doubts remained since it was observed, in our laboratory, that the reversible reduction of the Wy polyanion in protic medium (pH 2.5) required $^1/_{12}$ faraday/mol of tungsten. Furthermore, despite of their precautions, Termes and Pope's experiments were not carried out in a strictly aprotic medium, owing to the use of $HNBu_3^+$ as counterion. Finally, it appeared that the published electronic spectra of the reduced species were not complete and that no ESR spectra were reported. This led us to reinvestigate the properties of the reduced decatungstate ions. Very recently, a similar study was reported by Yamase,[6] but still without any detailed analysis of the electronic and ESR spectra.

In the present study, we used three different salts: (i) the $HNBu_3^+$ salt, since it was used in the crystal structure determination by Fuchs et al.;[5] (ii) the NBu_4^+ salt, since it contains a proton-free counterion; (iii) the K^+ salt, since it was the first characterized compound and allows an easy electrochemical reduction in water.

Experimental Section

(i) Sample Characterizations. Thermogravimetric analysis (TG) coupled with careful spectroscopic measurements throughout the sample preparation and purification allowed us to define unambiguously the compounds. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer as KBr pellets; TG curves were carried out in air on a Cahn RG electrobalance.

(ii) Studied Samples. $\mathbf{K_4(W_{10}O_{32})\cdot 4H_2O}$ **(I).** The potassium salt was prepared according to a procedure previously described.[7] Anal. Calcd for $K_4W_{10}O_{32}\cdot 4H_2O$: WO_3, 89.9; K_2O, 7.3; H_2O, 2.79. Found: WO_3, 89.9; K_2O, 7.6; H_2O, 2.8. Calcd for $HW_{12}O_{39}K_5\cdot 4H_2O$: WO_3, 89.78; K_2O, 7.6; H_2O, 2.3. IR (cm^{-1}): 1005 (w), 985 (m), 970 (s), 960 (s), 944 (s), 910 (m), 895 (m), 805 (vs), 595 (w), 438 (m), 405 (m), 350 (w), 337 (w), 325 (w).

$\mathbf{((C_4H_9)_4N)_4W_{10}O_{32}}$ **(II).** The tetrabutylammonium salt was prepared by mixing boiling solutions of 16 g of $Na_2WO_4\cdot 2H_2O$ in 100 mL of water and 33.5 mL of 3 M HCl. After boiling for a few minutes, the clear yellow solution was precipitated by addition of an aqueous solution of tetrabutylammonium bromide (6.4 g/10 mL). The white precipitate was filtered, washed with boiling water and ethanol, dried with diethyl oxide, and then recrystallized in hot dimethylformamide to give yellowish prismatic crystals: yield 10 g;

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