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Electrochemical Reduction of New, Good Electron Acceptors: The Metallooctacyanophthalocyanines

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The electrochemical reduction of octacyanophthalocyanine, $MPc(CN)_8$ (where M = Zn, Cu, H_2), was investigated in DMF at Hg and at solid gold or platinum electrodes. Four reversible, single-electron transfer steps were observed for each complex, which corresponded to formation of a mono-, di-, tri-, and tetraanion. Each reduction process was monitored by EPR spectroscopy, which indicated that only the ligand was electroactive. The effect of the eight cyano groups is to decrease the electron density on the ligand, which leads to an easier reduction for each process with respect to the unsubstituted phthalocyanine. The shift of half-wave potentials due to the introduction of eight cyano groups on the metallophthalocyanine ligand does not produce identical potential shifts for different phthalocyanine complexes as was observed in the case of metalloporphyrins. This is perhaps a consequence of the differences in aggregation and surface-active properties between the three phthalocyanines investigated in this study. However, all three species are reduced by four single-electron transfers to yield, ultimately, the formation of a tetraanion.

Introduction

Studies of metallophthalocyanines are of interest because of their chromophoric properties involving large molar absorptivities, their exceptional chemical and thermal stability, and their many analogies with metalloporphyrins. Phthalocyanines have also been used to convert light energy to electrical energy in photovoltaic cells[4,5] or to sensitize large-gap semiconductors.[6] In this regard, direct relationships have been shown between redox potentials of a given phthalocyanine in solution and yields for conversion of light energy. These important aspects have been the subject of several recent reviews.[2,3]

Two aspects of the metallophthalocyanine structure are of importance in determining the redox properties of a given complex. The first is the 18-electron aromatic core of the phthalocyanine ring and the interaction of this core with substituents on the ring, while the second is the nature of the central metal atom. Electrochemical techniques have been used extensively in the past to evaluate the role of substituent effects on the phthalocyanine ring as well as to determine how the type of the central metal and its oxidation state and/or coordination number effect the redox properties and chemical reactivity of a given metallophthalocyanine.[7-20]

Table I. Half-Wave Potentials (V vs. SCE) of Substituted and Nonsubstituted Phthalocyanines in DMF Containing 0.1 M TEAP[a]

complex	$E_{1/2}{}^{\mathrm{I}}$	$E_{1/2}{}^{\mathrm{II}}$	$E_{1/2}{}^{\mathrm{III}}$	$E_{1/2}{}^{\mathrm{IV}}$
$H_2Pc(CN)_8$	-0.10^b	−0.45	−0.88	−1.50
H_2Pc	−0.66	−1.06	−1.93	−2.23
$ZnPc(CN)_8{}^c$	-0.15^b	−0.50	−1.10	−1.35
$ZnPc^c$	−0.86	−1.30	−1.85	−2.25
$CuPc(CN)_8$	$\simeq -0.2^d$	−0.63	−1.08	−1.25
$CuPc^e$	−0.84	−1.18	−2.01	−2.28

[a] Values are reported at a Hg electrode. The same values of half-wave potentials (±0.03 V) were obtained for the $MPc(CN)_8$ complexes at Au or Pt solid electrodes. [b] Reduction of the monomeric species (see Table II). [c] Reference 7. [d] Value good to ±0.1 V. [e] Reference 15.

In a recent electrochemical study from our own laboratory,[7] it was shown that zinc octacyanophthalocyanine, $ZnPc(CN)_8$, could be reduced in four single-electron transfer steps and that these four reactions occurred within a narrow range of easily accessible potentials. (The most positive reduction occurred at −0.15 V while the most negative reduction was found at −1.35 V.) We have now extended this study to include the free base octacyano complex, $H_2Pc(CN)_8$, as well as the copper octacyanophthalocyanine complex, $CuPc(CN)_8$. Reduction of these three $MPc(CN)_8$ complexes (where M = H_2, Zn, Cu) is reported in dimethylformamide at rotating Pt and Au electrodes as well as at a dropping mercury electrode.

Experimental Section

The three octacyanophthalocyanines were prepared according to literature procedures.[7] Tetra-*n*-ethylammonium perchlorates (TEAP) and tetrabutylammonium perchlorate (TBAP) were used as supporting electrolytes and, along with dimethylformamide (DMF), were purified according to earlier reported methods.[21,22] Solutions were prepared by first dissolving the phthalocyanine in DMF and then adding the supporting electrolyte. Attempts to dissolve the complexes directly in DMF containing 0.1 M TBAP led to a very low solubility and, for the case of $CuPc(CN)_8$, required a period of several days to obtain even the smallest concentration. Measurements were limited to DMF due to the especially low solubility of octacyanophthalocyanines in other solvents and the tendency of the reduced products to adsorb on the electrode, thus leading to an irreversible blocking of the electrode. This latter tendency was

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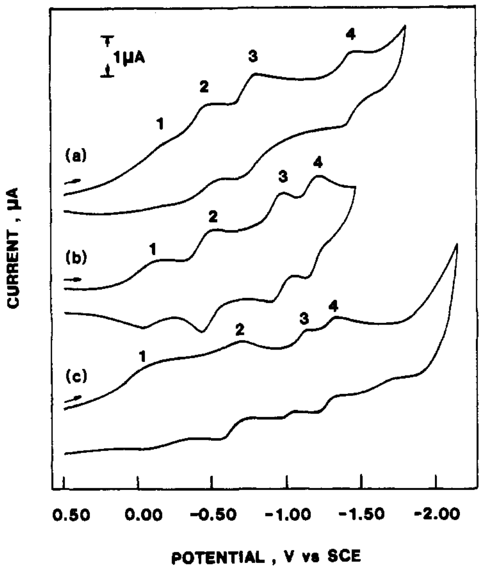


Figure 1. Cyclic voltammograms of (a) $H_2Pc(CN)_8$, (b) $ZnPc(CN)_8$, and (c) $CuPc(CN)_8$ in DMF, 0.1 M TEAP. All measurements were carried out at a Au electrode at v = 100 mV/s using saturated phthalocyanine solutions.

greatly reduced in DMF, although, as will be discussed in this paper, aggregation was always present at electrochemical concentrations of the phthalocyanines (10^{-3}–10^{-4} M).

All electrochemical measurements were carried out under argon or nitrogen with use of 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 cm^2), a Pt counter electrode, and an SCE reference electrode. ESR experiments were carried out under a nitrogen atmosphere after exhaustive electrolysis with an X-band Bruker ER 420 spectrometer provided with a TE_{104} cavity, an NMR gauss meter, a frequency meter, and a BNC 12 computer. Electronic absorption spectra were recorded under the same conditions on a Varian 2200 spectrophotometer.

Results

Reduction of $MPc(CN)_8$. The reduction of $MPc(CN)_8$, where M = H_2, Zn(II), Cu(II), was investigated by cyclic voltammetry, differential pulse polarography, rotating-disk voltammetry at Pt or Au electrodes, and classical polarography at a dropping Hg electrode. By all four techniques, single-electron transfer reactions were observed although, as will be discussed in the following sections, the resulting current–voltage curves differed substantially with the type of electrode material and the time scale of the measurement technique.

The best defined results were obtained by cyclic voltammetry at a gold electrode. This is illustrated in Figure 1 for the reduction of $H_2Pc(CN)_8$, $ZnPc(CN)_8$, and $CuPc(CN)_8$ in DMF, 0.1 M TBAP. All three phthalocyanines exist as aggregates in solution, and as such the first one-electron reduction (labeled peak 1) consists of overlapping currents due to the diffusion of monomeric and polymeric reactants. This has been described in detail for the case of $ZnPc(CN)_8$.[7]

A summary of half-wave potentials for the four reductions of each complex is given in Table I. These values were identical at Au, Pt, and Hg electrodes although, in the case of $CuPc(CN)_8$, measurements at solid electrodes became complicated due to aggregation and adsorption effects. The anion radicals of all three compounds adsorbed strongly at the electrode surface and eventually led to inhibition of the working electrode. This inhibition is reflected in the nontheoretical shapes of the second reduction peak (peak 2) and the first reoxidation peak and is especially evident for $H_2Pc(CN)_8$ and $CuPc(CN)_8$. Currents for the last two reductions (peaks 3 and 4) are better defined, and for reductions at scan rates less than 1.0 V/s, the separation between the anodic and cathodic peaks is close to the theoretical value of 60 mV.

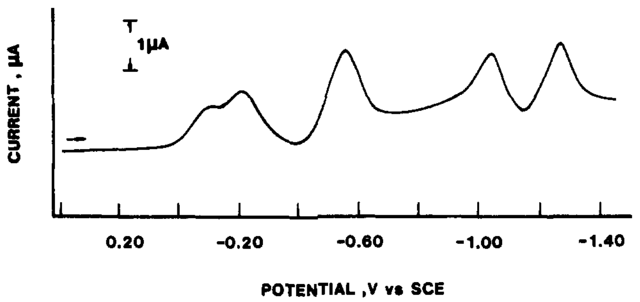


Figure 2. Differential pulse voltammogram of $ZnPc(CN)_8$ at a Pt electrode in DMF, 0.1 M TEAP.

Reduction of $CuPc(CN)_8$ at a rotating-disk or dropping mercury electrode gave current–voltage curves that were difficult or impossible to analyze. This was not true for $H_2Pc(CN)_8$ and $ZnPc(CN)_8$, which gave better defined waves in DMF. The last three reduction waves of $H_2Pc(CN)_8$ and $ZnPc(CN)_8$ at a rotating-disk electrode gave diffusion-controlled currents of equal magnitude. A study of the limiting current as a function of rotation rate showed that i_L was proportional to $\omega^{1/2}$ for each process, thus indicating reductions that were controlled only by the rate of diffusion. This was true for freshly prepared solutions at low concentrations (~1.3 × 10^{-4} M). However, increased aggregation occurred at higher concentrations. In addition, after supporting electrolyte was added, the solution color changed as a function of time and led to the appearance of a flocculate in suspension.

Similar problems were observed for investigations at a DME, but at this electrode, the first reductions of $H_2Pc(CN)_8$ and $ZnPc(CN)_8$ were better defined and gave a wave whose limiting current was of the same magnitude as that measured for reduction waves 2, 3, and 4. Inspection of the Hg drops in the bottom of the cell, however, revealed that they did not form a compact layer but rather remained thinly divided at the bottom of the cell. This property of the Hg is consistent with the partial inhibition of the working electrode and the relatively poor quality of the obtained signals.

Differential pulse polarography was then used in an attempt to increase resolution. An example of such a voltammogram is shown in Figure 2 for the reduction of $ZnPc(CN)_8$. As expected, the first reduction peak is broader than the last three reduction peaks, indicating the presence of two overlapping processes. A somewhat broad but well-defined first peak was also observed for the first reduction of $H_2Pc(CN)_8$. On the other hand, $CuPc(CN)_8$ was characterized by several very broad overlapping reduction peaks ranging from 0.0 to −0.7 V. This reflects the presence of several adsorbed and aggregated species in solution.

Exhaustive Reduction and Spectral Characterization. Exhaustive coulometric reduction was carried out for each compound in order to determine the overall number of electrons in the first reduction process and to electrogenerate the anions for determination of their electronic absorption spectra as well as for EPR characterization of the generated paramagnetic species. This coulometric reduction was carried out at a large mercury pool electrode in DMF containing 0.1 M TEAP. The applied potential was −0.30 V for coulometric reduction of $H_2Pc(CN)_8$ and $ZnPc(CN)_8$ and −0.50 V for coulometric reduction of $CuPc(CN)_8$. In each case a value of n = 1.0 ± 0.1 was obtained. Similar values of n = 1 were calculated for the last three reductions by comparing the wave heights for each reduction by stationary-electrode voltammetry or comparing the peak heights by cyclic voltammetry.

Electronic absorption spectra of the neutral $MPc(CN)_8$ and the electrochemically generated anion radicals and dianions are shown in Figures 3 and 4. Upon addition of the first electron the solutions changed from green to blue-green. These solutions then changed to purple upon formation of the dianion. In the

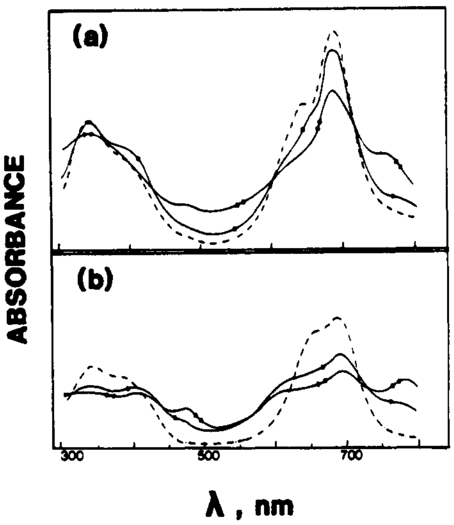


Figure 3. Electronic absorption spectra of (a) $H_2Pc(CN)_8$ (---) and (b) $ZnPc(CN)_8$ (---) and their corresponding mono- (-◆-) and dianions (-◆-◆-) in DMF, 0.1 M TEAP.

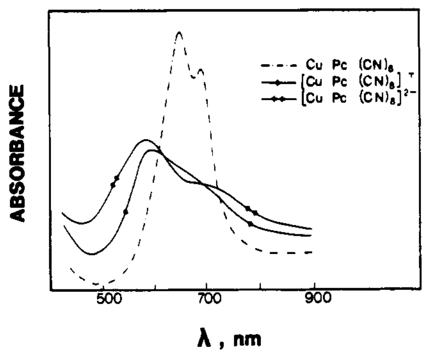


Figure 4. Electronic absorption spectra of $CuPc(CN)_8$ and the corresponding mono- and dianions in DMF, 0.1 M TBAP.

Table II. Characteristic EPR Signals of the Various Paramagnetic Signals Observed at 100 K in DMF Containing 0.1 M TEAP

species	state	ΔH, G	g	potential of electrolysis, V vs. SCE
$[H_2Pc(CN)_8]^{-\cdot}$	aggregated	3	2.0032	−0.20
	monomeric	2.7	2.0033	−0.40
$[ZnPc(CN)_8]^{-\cdot}$	aggregated	10^a	2.0020	−0.10
	monomeric	5.3^a	2.0022	−0.30
$[ZnPc(CN)_8]^{3-\cdot}$	monomeric	<4	2.0050	−1.20
$CuPc(CN)_8$	aggregated	100	2.0503	
	solid	110	2.0595	
$[CuPc(CN)_8]^{2-}$	monomeric		2.045 ($g_\perp$) 2.165 ($g_\parallel$)	−1.00

[a] See ref 26.

absence of oxygen these species were stable for several hours.

EPR measurements were carried out at 100 K after the stepwise exhaustive reduction of each phthalocyanine complex and are summarized in Table II. Aggregated and nonaggregated radical anions were indicated for $[H_2Pc(CN)_8]^{-\cdot}$ and $[ZnPc(CN)_8]^{-\cdot}$. All other EPR-active species were generated in solution as nonaggregated monomers except for $CuPc(CN)_8$, which also was run as a solid. Analysis of the EPR signals for $[H_2Pc(CN)_8]^{-\cdot}$ show that the spectra generated at the beginning of the reduction wave (−0.20 V for $H_2Pc(CN)_8$ and −0.10 V for $ZnPc(CN)_8$) exhibit a larger band width (ΔH = 3 and 10 G, respectively) than that generated by polarization at the plateau of the wave (where ΔH = 2.7 and 5.3 G, respectively). This is shown in Figure 5.

The signals at g = 2.0033 for $[H_2Pc(CN)_8]^{-\cdot}$ and g = 2.0022 for $[ZnPc(CN)_8]^{-\cdot}$ vanished upon polarization at the second step, which yielded $[H_2Pc(CN)_8]^{2-}$ and $[ZnPc(CN)_8]^{2-}$. Electrolysis of $ZnPc(CN)_8$ at a potential corresponding to the third reduction gave rise to a paramagnetic species (g = 2.0050, ΔH < 4 G), which is assigned as the trianion, $[ZnPc(CN)_8]^{3-\cdot}$. This signal disappeared upon further reduction at −1.50 V, where the diamagnetic $[ZnPc(CN)_3]^{4-}$ species is generated. When $H_2Pc(CN)_8$ is reduced at the third step by bulk coulometry, a very weak radical signal was obtained, which most likely corresponded to $[H_2Pc(CN)_8]^{3-\cdot}$. The decrease in EPR intensity for this species reflects a poor stability of this trianion on the longer time scale of bulk coulometry.

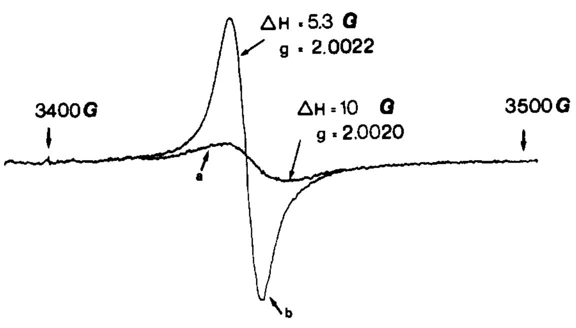


Figure 5. EPR spectra of $[ZnPc(CN)_8]^{-\cdot}$ at 100 K in DMF, 0.1 M TEAP, after electrogenation of the radical at (a) −0.10 V and (b) −0.30 V. EPR conditions: microwave field in the sample, 0.30 G; modulation amplitude, 0.5 G; microwave frequency, 9.38 GHz; sweep rate, 0.5 G/s; time constant, 0.1 s.

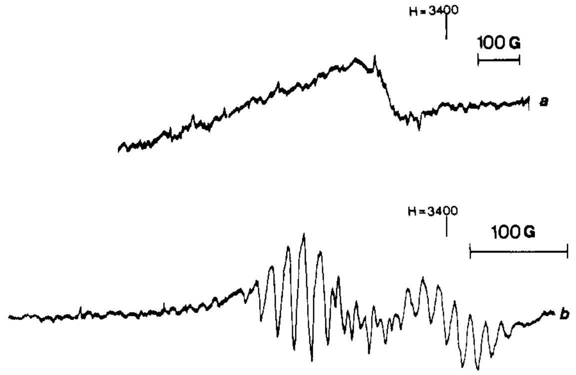


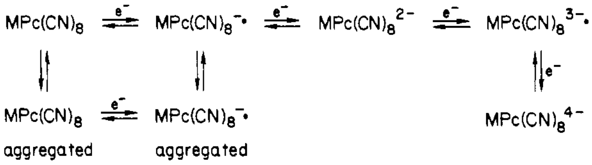
Figure 6. Solution EPR spectra of (a) $CuPc(CN)_8$ and (b) $[CuPc(CN)_8]^{2-}$ in DMF, 0.1 M TEAP, at 100 K. EPR conditions for (a): microwave field, 0.30 G; modulation amplitude, 5 G; microwave frequency, 9.40 GhZ; sweep rate, 2 G/s; time constant, 0.5 s. EPR conditions for (b): microwave field, 0.30 G; modulation amplitude, 0.5 G; microwave frequency, 9.41 GHz; sweep rate, 2 G/s; time constant, 0.1 s.

EPR spectra were recorded for the paramagnetic $CuPc(CN)_8$ species in both the solid and solution states and gave similar g values of 2.0503 and 2.0595. Both EPR spectra had peaks with large values of ΔH. Upon application of −1.00 V to a solution containing the $CuPc(CN)_8$ species, the initial signal vanished. After futher coulometric reduction at potential more negative than the second half-wave potential ($E_{1/2}$ = −1.18 V) a new signal is observed (Figure 6b), which is typical of a Cu(II) dianion. This reduction is reversible, and the original blue-green Cu(II) anion radical could be regenerated upon reoxidation at −1.00 V. However, upon reoxidation at +0.1 V precipitation of the product occurred. This precipitation may be explained by the virtual insolubility of $CuPc(CN)_8$ in DMF containing 0.1 M TBAP. (See Experimental Section.) The isolated solid was collected and, as expected, gave a solid EPR signal similar to that for the original $CuPc(CN)_8$.

Discussion

The substitution of nucleophilic groups (in this case CN substituents) or of electrophilic groups on a tetrapyrrolic macrocycle may induce significant changes in the energy required to transfer electrons. Alternatively, the addition of electron-withdrawing or electron-donating groups to the macrocycle may induce a change

Scheme I



in the site of the electron transfer (metal or ligand centered) as compared to that for the unsubstituted complex.[21]

This present work has concentrated on studying the electrochemical reduction mechanism of several octacyanophthalocyanines. In this regard the effect of the CN substituents on the reduction processes shall be discussed by comparing results in this study with previously reported results on unsubstituted porphyrins and phthalocyanines.[11,15,16,20,25] Unfortunately, solutions of the studied octacyanophthalocyanines contain both monomeric and aggregated forms, as revealed by spectrophotometric studies.[7] In the present study, the presence of aggregated phthalocyanine molecules resulted in nonideal electrochemical and spectral data. However, despite the poor quality of the electrochemical data due to the aggregation, combination of coulometric analysis and spectral characterization of the coulometrically reduced species with results from all of the electrochemical techniques leads to a self-consistent mechanism. This electrochemical reduction mechanism of $MPc(CN)_8$, where M = H_2, Zn(II), Cu(II), may be given as shown in Scheme I.

Analysis of the EPR spectra recorded after the first reduction of $H_2Pc(CN)_8$ and $ZnPc(CN)_8$ indicate the generation of two different paramagnetic species, which may be attributed to a monomeric and an aggregated form of an anion radical. For the free base and the zinc phthalocyanine complexes the radical anion spectrum generated at the beginning of the reduction wave has a larger bandwidth than the radical anion spectrum generated at the plateau of the wave. In this case the EPR spectral bandwidth is related to the mobility of the anion in solution and, more precisely, to the speed of reorientation of the molecules. Given the fact that the EPR signal is broader when reduction occurs at the beginning of the wave (3 G for $[H_2Pc(CN)_8]^{-\cdot}$ and 10 G for $[ZnPc(CN)_8]^{-\cdot}$) than for reduction on the plateau of the wave (ΔH = 2.7 and 5.3 G), one can conclude that the aggregated species is less mobile and is therefore reduced before the monomeric species. This implies the formation of aggregated $[ZnPc(CN)_8]^{-\cdot}$ and $[H_2Pc(CN)_8]^{-\cdot}$ species in solution. Further reduction of these aggregated radical anions is not observed by any of the electrochemical techniques, thus suggesting their partial or total deaggregation. Current-voltage curves for reduction of $CuPc(CN)_8$ also show overlapping initial reduction peaks, which suggests a similar aggregation for this compound. This cannot be verified by EPR, since the electrogenerated species exhibits no signal.

EPR analysis of the species produced upon further reduction of $[H_2Pc(CN)_8]^{-\cdot}$ and $[ZnPc(CN)_8]^{-\cdot}$ show that the corresponding di-, tri-, and tetraanions are generated in solution. The high g value for $[ZnPc(CN)_8]^{3-\cdot}$ (g = 2.0050) is comparable to a similar value for the unsubstituted zinc phthalocyanine trianion, $[ZnPc]^{3-\cdot}$ (g = 2.0055)[23] and may possibly result from a mechanism suggested by McConnell for symmetrical hydrocarbon ions with vibronically degenerate ground states.[24] The orbital degeneracy is removed by electrostatic interactions with an unsymmetrical environment. The second-order spin–orbit interaction may contribute substantially (±0.004) to the average $\bar{g}$ value.

The EPR solution spectrum of the paramagnetic $CuPc(CN)_8$ species is of special interest. The starting material gives a one-banded solution spectrum at g = 2.0503 (Figure 6a). Usually copper phthalocyanine and/or copper porphyrins give a solution EPR spectrum due to a coupling of the single electron on the metal with the pyrrolic nitrogens of the ligand.[14,21] The differences between the copper octacyanophthalocyanine and other similar copper porphyrins and phthalocyanines may be explained by the high ratio of aggregated $CuPc(CN)_8$ molecules in solution, which give a signal very similar to that recorded in the solid state (g = 2.0595).

The first electrochemical reduction of $CuPc(CN)_8$ leads to the disappearance of the initial signal. The fact that no EPR signal is recorded reflects a coupling between the single unpaired electron on the central metal and the electron localized on the macrocyclic ligand of the anion radical. A similar coupling is observed for other copper porphyrin and phthalocyanine complexes.[14,21] During the second reduction of $CuPc(CN)_8$ a new EPR signal appears that is typical of a paramagnetic Cu(II) ion in a tetrapyrrolic environment. This spectrum is similar to a spectrum described for $[CuTPP(CN)_4]^{2-}$ in DMF,[21] thus giving additional evidence for the dianion formulation. Also, comparison of the dianion spectrum with the spectrum for the unreduced copper complex suggests that the dianion is not aggregated.

Comparisons with Porphyrins and Other Phthalocyanines. Metallophthalocyanines are invariably reduced more easily than metalloporphyrins (which have a similar structure), but generally the electrochemical reactivity and overall oxidation–reduction mechanisms of the two types of complexes are quite similar. Because of this similarity in reactivity, electrochemical results for the reduction of cyano-substituted phthalocyanines may be compared on one hand to results for nonsubstituted phthalocyanines and, on the other hand, to electrochemical results for reduction of the analogous unsubstituted and cyano-substituted metalloporphyrins (MTPP and $MTPP(CN)_4$,[21,22,25] where M = H_2, Zn(II), and Cu(II)). This latter comparison is of interest in terms of an electrochemical evaluation of substituent effects between ring-substituted phthalocyanines and ring-substituted porphyrins.

Addition of electron-withdrawing substitutents (such as CN groups) onto a metalloporphyrin or a metallophthalocyanine leads to a thermodynamically easier reduction of the substituted complex. The direction of the potential shift is in accordance with predictions from linear free energy relationships. The eight CN groups decrease the average electron density on the total conjugated system, which results in a lowering of the energy levels for the lowest unoccupied molecular orbital (LUMO) of the pyrrolic macrocycle. This increases the electron affinity of the macrocycle from a thermodynamic point of view and thus leads to easier reductions. This increase in electron delocalization is also reflected by a decrease in the EPR bandwidth of the monomeric species upon going from nonsubstituted[23,27] to the cyano-substituted complexes.

The global effect of the CN substituents on the first and second reductions is smaller for cyano-substituted phthalocyanines (560–800 mV) than for cyano-substituted porphyrins[22] (960–1010 mV). This is true despite the fact that a greater number of groups are substituted onto the phthalocyanine ring (eight) than onto the porphyrin ring (four). This difference in the magnitude of potential shift with addition of CN groups to the two series is reasonable since the benzene rings of the phthalocyanine participate only partially in delocalization of the ligand π electrons. Therefore, the electron-withdrawing effect of the eight CN groups only indirectly affects the conjugated π system of the phthalocyanine. This is in marked contrast to the case for the β-substituted cyanoporphyrins, where the four CN groups are in direct resonance conjugation with the porphyrin π system.

In contrast to the smaller substituent effect involving the first two reductions of cyano-substituted phthalocyanines, a larger substituent effect is observed for the last two reductions. This reversal in trend between the two series of complexes leads to a difference in $E_{1/2}$ of 750–900 mV between MPc and $MPc(CN)_8$ while the difference between MTPP and $MTPP(CN)_4$ has de-

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[25] Giraudeau, A.; Louati, A.; Callot, H. J.; Gross, M. *Inorg. Chem.* **1981**, *20*, 769–722.

[26] In the case of weak signal intensity a strong modulation is often utilized. This was the case in the previous study of reduced $ZnPc(CN)_8$, where the values of ΔH reported (13.7 and 5.9 G) were upper estimates of the splittings. The values given in the table are more exact.

[27] Raynor, B. J.; Robson, M.; Torrens-Burton, S. A. M. *J. Chem. Soc. Dalton Trans.* **1977**, 2360–2364.

creased to only 350–420 mV. This reversal in substituent effects and decrease in $\Delta E_{1/2}$ for the metalloporphyrins may be due to an electron–electron repulsion in the dianions that is much stronger in the case of porphyrins than for phthalocyanines, where the conjugated system is more delocalized.

In summary, this study has shown that cyano-substituted phthalocyanines may be easily reduced by four single-electron transfers, which occur at very low potentials. The properties of these compounds are very close to those of tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ), thus suggesting the use of cyano-substituted phthalocyanines as charge-transfer complexes.

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Registry No. $ZnPc(CN)_8$, 76228-28-9; $[ZnPc(CN)_8]^{-\cdot}$, 85335-42-8; $[ZnPc(CN)_8]^{2-}$, 85335-43-9; $[ZnPc(CN)_8]^{3-\cdot}$, 85335-44-0; $[ZnPc(CN)_8]^{4-}$, 85354-79-6; $CuPc(CN)_8$, 75810-80-9; $[CuPc(CN)_8]^{-\cdot}$, 95155-95-6; $[CuPc(CN)_8]^{2-}$, 95155-96-7; $[CuPc(CN)_8]^{3-\cdot}$, 95155-97-8; $[CuPc(CN)_8]^{4-}$, 95155-98-9; $H_2Pc(CN)_8$, 76221-26-6; $[H_2Pc(CN)_8]^{-\cdot}$, 95191-81-4; $[H_2Pc(CN)_8]^{2-}$, 95191-82-5; $[H_2Pc(CN)_8]^{3-\cdot}$, 95191-83-6; $[H_2Pc(CN)_8]^{4-}$, 95191-84-7; Au, 7440-57-5; Hg, 7439-97-6; Pt, 7440-06-4.

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Investigation into the Linkage Isomerism of the Sulfamidate Group: A Quantitative Assessment Using ESCA

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The ESCA spectra of several transition-metal complexes containing sulfamidate as a ligand are described. The difference in the N_{1s} and the S_{2p} binding energies, $\Delta(N_{1s}–S_{2p})$, is used to show whether or not the sulfamidate is coordinated via nitrogen. The advantages of this method over infrared analysis are discussed. It is shown that when linkage isomerism of sulfamidate occurs, the ESCA technique is capable of quantitative determination of the relative amounts of the isomers.

Introduction

Infrared and Raman spectroscopic evidence suggests that the sulfamidate ligand in $K_3[M(NH_2SO_3)Cl_5]$ (M = Rh, Ir, Os), in $K_2[Pd(NH_2SO_3)_2Cl_2]$, and in $K_2[Pt(NH_2SO_3)_2X_2]$ (X = Cl, Br) is bonded to the metal through nitrogen.[2] This is also the case for $[Ru(NH_3)_5(NH_2SO_3)]^{2+}$.[3] In aqueous alkaline solution, the visible spectra and acidity constants for $[Co(NH_3)_5(NH_2SO_3)]^{2+}$ show that the sulfamidato ligand is nitrogen bonded,[4] while in acid solution hydrolysis kinetic data and changes in the visible spectra suggest that N- and O-bonded linkage isomerism of the sulfamidato ligand occurs.[5] However, the O-bonded isomer could not be isolated. The infrared spectra for a series of first-row transition-metal sulfamidates show that both O and N coordination occurs.[6] It was suggested that monodentate coordination of the sulfamidate group occurs via oxygen while nitrogen coordination indicates the presence of a chelating or a bridging ligand, except in the case of Cr(III) or Cu(II), where simple monodentate coordination through the nitrogen occurs.[6]

In the complexes the infrared evidence is based on (i) shifts observed in the N–H bands at 3350, 3270, and 1550 cm^{-1}; (ii) shifts in the ν(N–S) band, although this tends to be sensitive to N coordination alone; and (iii) shifts in the SO_3 modes that, in practice, are limited to a broadening effect on the bands involved. Although this proves quite adequate for most of the complexes, there is difficulty in complexes containing ammine or amine ligands.[6] Thus, the mode of sulfamidate coordination in ethylenediamine complexes could not be positively identified, as the relevant bands of the sulfamidato group overlap with those of the ethylenediamine ligand in the infrared spectrum.[6] As the determination of the mode of coordination depends largely on the shifts in the N–H bands, a complication can arise from the possibility of hydrogen-bonding effects, especially in aqua complexes. Furthermore, interconversion of the N- and O-bonded isomers can occur, and the preparative route often determines the isomer or isomers formed.[6] Then, in cases where both isomers are present, a quantitative determination of their relative amounts is difficult by infrared techniques.

ESCA has been used previously to determine the mode of coordination of an ambidentate ligand in a series of metal sulfoxide complexes.[7] More recently, complexes of sulfur-substituted oxopryimidines have been examined by using ESCA, and coordination of the thio group has been confirmed and ambidentate behavior postulated.[8,9]

In this paper we show that by using ESCA it is possible to determine the mode of coordination for the sulfamidato group, from a comparison of the binding energies of the ligand core electrons, in a series of transition-metal sulfamidato complexes and some complexes containing ethylenediamine, pyridine, and ammonia ligands. The isomeric ratios are also determined by a comparison of the corresponding peak intensities, in those cases where both linkage isomers are present.

Experimental Section

Sulfamidic acid was obtained commerically from BDH Chemicals and used without further purification. Metal sulfamidates were prepared by the addition of metal carbonates or freshly prepared metal hydroxides to sulfamidic acid.[6] Sodium sulfamidate was prepared by the exact neutralization of sulfamidic acid using AnalaR grade sodium hydroxide, followed by the partial evaporation of the water.[15] Some second- and third-row transition-metal sulfamidates were prepared by similar methods using the metal hydroxides (Rh(III), Cd(II)) or the oxide (Ag(I)). Palladium sulfamidate complexes was prepared from $PdCl_2$ by the stoichiometric addition of 2 mol of sulfamidic acid. The resulting solution was heated at 60 °C for 1 h, filtered, and then evaporated to near dryness on a steam bath. Recrystallization of all samples from water or water/methanol solutions gave products shown in Tables I and II.

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