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Electrochemistry of Manganese Phthalocyanine in Nonaqueous Media

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The electrochemical behavior of manganese(II) phthalocyanine dissolved in pyridine, dimethyl sulfoxide, or dimethylacetamide is reported, in the presence of perchlorate, chloride, and bromide supporting electrolyte anions. Electron-transfer couples representing net oxidations of manganese, and of the phthalocyanine ring, and two net reductions of the phthalocyanine ring are characterized by a range of electrochemical techniques, with emphasis on cyclic voltammetry. Heterogeneous rate constants are reported for several of these couples in the presence of perchlorate ion. All the couples show close to ideal reversible behavior except at higher scan rates for chloride and bromide as supporting electrolyte anions, where some deviation is observed. This system does not exhibit such sensitivity to environment as was previously observed with iron phthalocyanine.

Introduction

Recent studies have clearly established the involvement of manganese in the photosynthetic production of oxygen.[1] Since the process requires several oxidizing equivalents of chlorophyll, whose radical cation ultimately effects oxidation of the manganese site, the energetics of manganese redox processes are of singular importance.[2] We have therefore extended our studies of metal phthalocyanines[3,4] and those of other[5-9] to include redox potentials, products, and electron-transfer kinetics of $PcMn^{II}$.[4]

We report here the oxidation of $PcMn^{II}$ to $PcMn^{III}$, ligand oxidation of the latter, and two successive one-electron reductions of the former. Differential pulse and pulse polarography, cyclic voltammetry, controlled-potential coulometry, electronic spectroscopy, magnetism, and ESR are presented to characterize the products.

Experimental Section

Preparation and purification of $PcMn^{II}$, solvents, and supporting electrolytes have been previously described.[3,4,10] Argon gas, deoxygenated and dried, was employed to purge the solutions. Platinum, hanging-mercury drop, and dropping-mercury electrodes were used in conjunction with Princeton Applied Research Models 173, 174A, 175, and 179, a 9002A X-Y recorder, and a Tektronix 5103W storage oscilloscope in electrochemical studies. All voltages are referred to commercial silver–silver chloride or saturated calomel electrodes fitted with Luggin capillaries. The voltages reported here are corrected to a saturated calomel electrode whose potential was monitored from time to time against the ferrocene/ferrocenium couple. Electronic spectra were recorded with a Varian Cary 14 or Perkin-Elmer Hitachi Model PE-340 UV–vis–near-IR microprocessor spectrometer. Magnetic measurements were obtained in solution by the Evans method[11-13] with the use of a Varian EM-360 NMR spectrometer. ESR spectra were observed with a Varian E-4 spectrometer, calibrated with DPPH as external calibrant, in frozen solution.

Results and Discussion

Four electron-transfer steps lying between +1.0 and −1.9 V (vs. SCE) were observed by use of continuous-scan voltammetry (Figure 1). They represent two net oxidations and two net reductions of the bulk solution. This is similar to our experience with $PcFe^{II}$,[3b] which exhibits one oxidation and two reduction waves in the same region. Earlier authors[6] who studied polarograms of electrochemically generated $(PcMn)^-$ were unable to obtain reproducible results in the region 0 to −1.4 V. We did not investigate waves reported by Clack and Hush[6] at potentials more cathodic than −1.9 V.

Table I. Voltammetric Data for (Phthalocyaninato)manganese(II) Redox Couples[a]

		$E°$, V		
solvent	supporting electrolyte	$Pc^{2-}Mn^{III}/Pc^{2-}Mn^{II}$	$Pc^{2-}Mn^{II}/Pc^{3-}Mn^{II}$	$Pc^{3-}Mn^{II}/Pc^{4-}Mn^{II}$
pyridine	TEAP	0.005	−0.785	−1.52
	(TEA)Br	−0.035	−0.710	−1.52
	(TEA)Cl	−0.105	−0.800	
	LiCl		−0.800	−1.49
Me_2SO	TEAP	−0.080	−0.755	−1.39
	(TEA)Br	−0.085	−0.700	−1.41
	(TEA)Cl	−0.125	−0.765	(−1.47)
	LiCl	−0.125	−0.815	−1.41
DMF	TEAP	−0.140	−0.690	−1.46
	(TEA)Br	−0.115	−0.780	−1.48
	(TEA)Cl			
	LiCl	−0.155	−0.800	−1.50
DMA	TEAP	−0.110	−0.740	−1.34
	(TEA)Br	−0.130	−0.800	−1.52
	(TEA)Cl			
	LiCl	−0.140	−0.800	

[a] Average of anodic and cathodic peak voltages quoted to nearest 5 mV. All data obtained by cyclic voltammetry.

The potentials of the three couples between 0 and −1.9 V were obtained under a variety of solvent and electrolyte combinations by three-electrode cyclic voltammetry on platinum electrodes ($E° = (E_{pa} + E_{pc})/2$) and are summarized in Table I. The values of $E°$, so reported from slow speed scans, are essentially independent of scan rate except in the presence of a halogen supporting electrolyte anion. The values of $E_{pa} - E_{pc}$ obtained at the diffusion limit (10 mV/s scan rate) were, in each case, within a few millivolts of ideality. Polarographs were obtained at this, or a lower, scan rate for some of the electron-transfer couples. Differential pulse polarograms (at 1 mV/s scan rate, modulation voltage 25 mV p–p) were also recorded, and $E_{3/4} - E_{1/4}$ was determined. Half-wave potentials from the various methods agreed within 30 mV. Values of $n = 1 \pm 10\%$ (n is the number of electrons involved in the electron-transfer step) for the first and second reduction steps were confirmed by three-electrode coulometry by employing a platinum mesh electrode. Studies at higher scan rates gave values of E_{pa}, E_{pc}, i_{pa}, and i_{pc} (anodic and cathodic peak potentials and currents, respectively) which were subsequently analyzed by the methods of Nicholson and Shain.[14]

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(1) Cheniae, G. M. *Annu. Rev. Plant Physiol.* **1970**, *21*, 467.
(2) Bodini, M. E.; Wallis, L. A.; Reichel, T. L.; Sawyer, D. T. *Inorg. Chem.* **1976**, *15*, 1538.
(3) (a) Lever, A. B. P.; Wilshire, J. P. *Can. J. Chem.* **1976**, *54*, 2514. (b) Lever, A. B. P.; Wilshire, J. P. *Inorg. Chem.* **1978**, *17*, 1145.
(4) Myers, J. F.; Canham, G. W. R.; Lever, A. B. P. *Inorg. Chem.* **1975**, *14*, 461. This paper contains an introduction to the phthalocyanine nomenclature utilized here.
(5) Rollman, L. T.; Iwamoto, R. T. *J. Am. Chem. Soc.* **1968**, *90*, 1455.
(6) Clack, D. W.; Hush, N. S.; Woolsey, I. S. *Inorg. Chim. Acta*, **1976**, *19*, 129.
(7) Wolberg, A.; Manassen, J. *J. Am. Chem. Soc.* **1970**, *92*, 2982.
(8) Li, C.; Chin, D. *Anal. Lett.* **1975**, *8*, 291.
(9) Kadish, K. M.; Bottomley, L. A.; Cheng, J. J. *J. Am. Chem. Soc.* **1978**, *100*, 2731.
(10) Lever, A. B. P. *Adv. Inorg. Chem. Radiochem.* **1965**, *7*, 27.
(11) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.
(12) Loliger, J.; Scheffold, R. *J. Chem. Educ.* **1972**, *49*, 646.
(13) Crawford, T. H.; Swanson, J. *J. Chem. Educ.* **1971**, *48*, 382.
(14) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

0020-1669/81/1320-2550$01.25/0

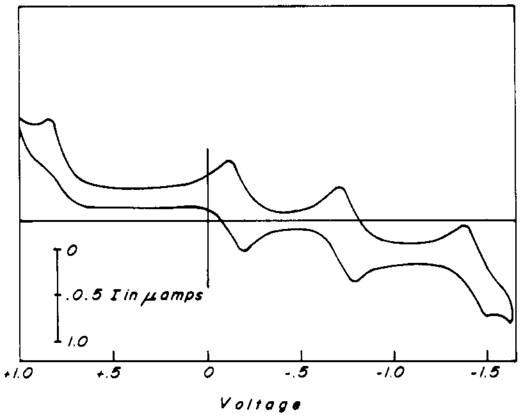

Figure 1. Cyclic voltammogram of $PcMn^{II}$ dissolved in dimethylformamide containing tetraethylammonium perchlorate as supporting electrolyte. The scan rate is 50 mV/s.

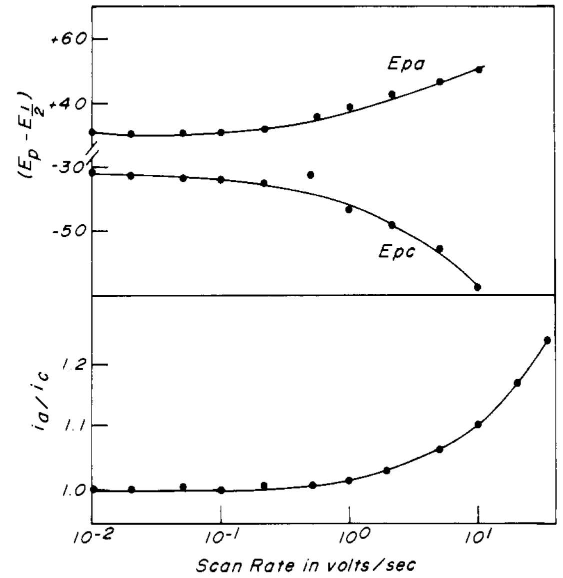

Figure 2. Nicholson–Shain analytical plots for the $(py)ClMn^{III}Pc^{2-}/(py)_2Mn^{II}Pc^{2-}$ couple in pyridine containing lithium chloride as supporting electrolyte.

This identified deviations from reversibility arising from electron-transfer kinetics or coupled chemical reactions. Internal cell resistance was compensated electronically.

First Oxidation: $[Pc^{2-}Mn^{III}S_2]^+/Pc^{2-}Mn^{II}S_2$.[4] As indicated by slow scan rate data and use of tetraethylammonium perchlorate (TEAP) as supporting electrolyte, this couple is nearly reversible at the diffusion limit in all solvents investigated, indicating little kinetic inhibition from either slow electron-transfer or coupled chemical reactions. Controlled-potential electrolysis at +0.1 V yields a species whose electronic spectrum is characteristic of typical mononuclear manganese(III) phthalocyanine species reported by Calvin and co-workers.[15] On this basis we assign the first oxidation product to a $Pc^{2-}Mn^{III}$ species.

The dependence of the half-wave potential upon solvent reflects an increased stabilization of the divalent state with the stronger coordinating solvents (pyridine > Me_2SO > DMA = DMF). A similar but more pronounced dependence is seen with iron phthalocyanines.[3] Cobalt(II) phthalocyanines, however, exhibit a reversed trend with the stronger donor solvents favoring cobalt(III). The rationale for this varied behavior has been presented.[16] The $PcMn^{III}/PcMn^{II}$ redox potential also depends upon the supporting electrolyte, with the trivalent state being favored by the more strongly coordinating anions (Cl^- > Br^- > ClO_4^-). Evidently their coordination to manganese(III) is important. This is confirmed by their electronic spectra which show a marked dependence of the visible (Q) band near 700 nm upon the counterion.[17]

Table II. Heterogeneous Rate Constants k_s (10^{-3} cm/s)

	$Pc^{2-}Mn^{III}/Pc^{2-}Mn^{II}$	$Pc^{2-}Mn^{II}/Pc^{3-}Mn^{II}$
py/TEAP	2.9	6.8
Me_2SO/TEAP	3.6	6.7
DMF/TEAP	6.8	7.1

Previous studies have shown[4,15] that the solid species $PcMn^{III}X$ (where X is halogen, hydroxide, acetate, etc.) are high spin and probably five-coordinate. In contrast, the solution susceptibility of the highly soluble (tetra-*tert*-butylphthalocyaninato)manganese(III) hydroxide, in pyridine, corresponds to two unpaired electrons within experimental error (2.6 μ_B at room temperature), implying low-spin d^4 manganese(III) which is a rare occurrence for macrocyclic ligands. Thus, in strongly coordinating solvents, manganese(III) phthalocyanines may be six-coordinate. Similarly, solutions of $PcMn^{II}$ in coordinating solvents are six-coordinate and low spin as shown unequivocally by their ESR spectra, typical of low-spin d^5, $S = {}^1/_2$ species:[18] $Pc^{2-}Mn^{II}(DMA)_2$, $g_{\parallel} = 1.86$, $g_{\perp} = 2.16$, $|A_{\parallel}| = 0.0138$, $|A_{\perp}| = 0.00484$ cm^{-1}; $Pc^{2-}Mn^{II}(py)_2$, $g_{\parallel} = 1.89$, $g_{\perp} = 2.16$, $|A_{\parallel}| = 0.0147$, $|A_{\perp}| = 0.00484$ cm^{-1}; $Pc^{2-}Mn^{II}(4\text{-}Et(py))_2$, $g_{\parallel} = 1.98$, $g_{\perp} = 2.17$, $|A_{\parallel}| = 0.0147$, $|A_{\perp}| = 0.00475$ cm^{-1}. Solutions of $PcMn^{II}$ in pyridine yielded a solution magnetic moment of 1.6 μ_B at room temperature, confirming the ESR characterization as low-spin d^5, $S = {}^1/_2$ ion.

With TEAP as supporting electrolyte, Nicholson–Shain analysis[14] is consistent with previous evidence. The oxidation of $PcMn^{II}$ in pyridine and in Me_2SO is quasi-reversible with less than 5% variation in the unit value of i_{pc}/i_{pa} over the range of scan rates observed (10 mV/s–50 V/s). The function $(ip/v^{1/2})$ is also constant. These observations are consistent with but do not prove that both manganese(II) and manganese(III) species are six-coordinate species. Similar behavior would be expected if either species were five-coordinate, but rapid solvent exchange was taking place. Considering the solution magnetic data, however, it is likely that the oxidation product is $[Pc^{2-}Mn^{III}S_2]^+ClO_4^-$ (at least for S = pyridine or Me_2SO).[18] Rather different behavior is observed when the supporting electrolyte contains bromide or chloride ion. Both anodic and cathodic peak potentials shift at higher scan speeds, consistent with a quasi-reversible electron transfer with transfer coefficient $\alpha < 0.5$.[19] There appears to be a small dependence of $E°$ upon X^-, though not as marked as was observed in the corresponding $PcFe^{III}/PcFe^{II}$ electron-transfer step.[3]

In most solvents, the more coordinating anions shift the potential cathodically relative to less coordinating ions, consistent with equilibria 1 and 2.

$$Pc^{2-}Mn^{II}S_2 \rightleftharpoons [Pc^{2-}Mn^{III}S_2]^+ + e^- \qquad (1)$$

$$X^- + [Pc^{2-}Mn^{III}S_2]^+ \rightleftharpoons Pc^{2-}Mn^{III}X(S) + S \qquad (2)$$

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(15) Engelsma, G.; Yamamoto, A.; Markham, E.; Calvin, M. *J. Phys. Chem.* **1962**, *66*, 2517.

(16) Lever, A. B. P.; Minor, P. C. *Adv. Mol. Relaxation Interact. Processes* **1980**, *18*, 115.

(17) Minor, P. C.; Licoccia, S.; Lever, A. B. P., to be submitted for publication.

(18) The ESR spectrum for a solution of $Pc^{2-}Mn^{II}$ in DMA, reported here, was that commonly obtained. However, if extreme care is taken to purify the DMA, another ESR spectrum, apparently indicative of intermediate spin Mn(II), is observed on some occasions. It is possible, therefore, that the data reported here for both ESR and electrochemical measurements may involve coordinated dimethylamine.

(19) Weissberger, A., Rossiter, B., Eds. "Physical Methods of Chemistry"; Wiley: New York, 1971; Part 2A, p 454.

These equilibria must reasonably occur but must be kinetically very labile since even at the highest scan rates there is no evidence for a cathodic wave corresponding to reduction of the species $Pc^{2-}Mn^{III}X(S)$, in contradistinction to the analogous iron system.[3]

Heterogeneous rate constants (k_s) for the reversible case with perchlorate ion as supporting electrolyte were obtained from eq 3[19] where $a = nF(\text{scan rate})/RT$, D_0 is the diffusion

$$\psi(\Delta E_{p,n}) = (\gamma^{\alpha} k_s/\pi a D_0)^{1/2} \qquad (3)$$

coefficient, and α is the transfer coefficient. α was polarographically determined to be 0.48 and D_0 was obtained from the Randles–Sevcik relationship. The results, reported in Table II, indicate only a slight dependence of k_s upon solvent for the $Pc^{2-}Mn^{III}/Pc^{2-}Mn^{II}$ couple (and no dependence for the reduction couples discussed below). When chloride or bromide are used as electrolyte anions, the coupled reactions (1) and (2) occur, and the expression for the peak potential must contain equilibrium constant data for eq 2. Since our data do not clearly distinguish a quasi-reversible electron transfer from an EC mechanism, we do not attempt to calculate rate constants in the presence of chloride and bromide ions.

However, since a negligible deviation of ΔE_p from the ideal 59 mV was observed at low scan rates with all solvent–electrolyte combinations, it is probable that the k_s values do not differ significantly from those reported for the perchlorate anion solutions. Thus a strong Mn–X bond is not especially rate limiting where both $PcMn^{II}$ and $PcMn^{III}$ are six-coordinate.

By comparison, when five- and six-coordination are possible, the conditions dictating different geometries for each oxidation state can provide a kinetic barrier for the redox process. In a study of the analogous complex $(TPP)Mn^{III}Cl$ (TPP = tetraphenylporphyrin), Kadish and co-workers[20] found that additional of imidazole to methylene chloride solutions yielded a six-coordinate Mn(III) species and an out-of-plane five-coordinate manganese(II) species. There was a three order of magnitude electron-transfer rate reduction for the imidazole adduct relative to the chloride. Our results are consistent with Kadish's conclusion that metal movement with respect to the equatorial ligand, rather than axial bond breakage, is rate limiting. The effect of spin-state change upon electron-transfer rates in these manganese systems remains undetermined since PcMn and (TPP)Mn are low and high spin, respectively, in both their +2 and +3 oxidation states.

Second Oxidation: $\mathbf{[Pc^{-}Mn^{III}S_2]^{2+}/[Pc^{2-}Mn^{III}S_2]^{+}}$. The second oxidation wave was observable only in DMF due to the sparing solubility of the parent species and relatively high solvent oxidation currents in all other media investigated. When the oxidation was observed in rigorously dried DMF at moderate scan rates (0.2–2.0 V/s), cathodic and anodic waves were seen at an average $E°$ of 0.870 V. Although coulometric n values were within range of unity ($n = 1.28 \pm 8\%$ over six runs), no stable species was obtained by controlled-potential oxidation. Since the species on the electrode prior to oxidation is $Pc^{2-}Mn^{III}S_2$, the probable oxidation products are $[Pc^{-}Mn^{III}]^{2+}$ or $[Pc^{2-}Mn^{IV}]^{2+}$ (neglecting solvent coordination). Although the latter cannot be entirely excluded, we prefer the former on the basis that the voltage separation between this couple and the first ligand reduction couple (see below) is 1.63 V. This is in excellent agreement with the average voltage separation (1.58 V) observed between ring oxidation and reduction in a series of main-group metallophthalocyanines[21] where no ambiguity exists.

First Reduction: $\mathbf{Pc^{2-}Mn^{II}S_2/[Pc^{3-}Mn^{II}S_2]^{-}}$. Earlier work by Clack and Hush[6] mentions the intermittent appearance of two waves at −0.755 and −1.008 V. Our studies show the former wave under all conditions, but the latter is seen only in inadequately purged solutions. The former wave shows almost no electrolyte anion dependence and a rather small solvent dependence (<0.1 V, see Table I). This comparative insensitivity to environment is a strong clue to the nature of the product, which must either involve reduction of the metal to $[Pc^{2-}Mn^{I}]^{-}$ or reduction of the ligand to $[Pc^{3-}Mn^{II}]^{-}$. Our earlier studies with the $Pc^{2-}Fe^{III}/Pc^{2-}Fe^{II}$ couple[3] reflect a stabilization of low-spin d^6 $Pc^{2-}Fe^{II}S_2$ which results in a >0.7-V variation in potential for the solvents studied here. This was ascribed to back donation by the iron(II) species being enhanced by the stronger donor axial ligands. If Mn(I), expected to be low-spin d^6, is produced during this reduction, a significant solvent effect for this ion, which should be an effective π donor to Pc, is anticipated. Moreover, when the electrochemical solution is saturated with carbon monoxide, no shift in potentials is seen, from which we may conclude that this reduced species does not react with carbon monoxide. A manganese(I) species would be expected to react with carbon monoxide in parallel with the chemistry of the isoelectronic iron(II) and ruthenium(II) phthalocyanines. The absence of a strong solvent effect and of reaction with carbon monoxide argues forcefully for the first reduction product to involve reduction of the phthalocyanine ring.

Although no ESR spectrum was observed with this species, this fact lends no support to either assignment since even-electron systems are often ESR inactive. The electronic spectrum of the reduced solution, first reported by Clack and Yandle,[22] is more enlightening. Although the Q-band absorption for $Pc^{2-}Mn^{II}$ is blue shifted with respect to that of $Pc^{2-}Mn^{III}Cl$, the shift (50 nm) is small and reflects greater repulsion between metal $e_g(\pi)$ and phthalocyanine $e_g(\pi^*)$ orbitals in the former species. The monoanion, however, exhibits a Q-band blue shift of greater than 130 nm, placing it in the same spectroscopic region as other metallophthalocyanine anion radical species that have been unambiguously identified.[22] Similarly, the extinction coefficients for the visible-region transitions are smaller, by more than 1 order of magnitude, than those observed for other phthalocyanine-(2−) species.[10] Finally, the separation between the purported ligand oxidation and reduction is within the range observed with other main-group and transition metallophthalocyanines.[21] Since the metal remains bivalent and the electrochemistry is fully reversible, we assume that two solvent molecules remain coordinated.

Second Reduction: $\mathbf{[Pc^{3-}Mn^{II}S_2]^{-}/Pc^{4-}Mn^{II}S_2]^{2-}}$. In this case reduction could yield $[Pc^{3-}Mn^{I}]^{2-}$ or $[Pc^{4-}Mn^{II}]^{2-}$ as the most probable products. The potentials for this couple (Table I) indicate minimal solvent and electrolyte dependence, arguing strongly for ligand rather than metal reduction as discussed above. Although polarographic results reflected the essential reversibility of this couple, cyclic voltammetry data were often rendered unreliable by high solvent background, especially at high scan rates. A Nicholson–Shain analysis was therefore not performed.

The electrochemically produced double reduction product has an electronic spectrum similar to that of its monoanionic parent, in that the Q-band energies are of relatively high energy and low intensity. The ESR spectrum of the dianion is similar to that observed for the dianion of TsPcMn (TsPc = tetrasulfonated phthalocyanine), which has been previously assigned as d^7 $TsPc^{2-}Mn^{0}$.[23] Were this characterization

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[20] Kadish, K. M.; Sweetland, M.; Cheng, J. J. *Inorg. Chem.* **1978**, *17*, 2795.

[21] Lever, A. B. P.; Minor, P. C. *Inorg. Chem.*, in press.

[22] Clack, D. W.; Yandle, J. R. *Inorg. Chem.* **1972**, *11*, 1738.

[23] Cookson, D. J.; Smith, T. D.; Boas, J. F.; Hicks, P. R.; Pilbrow, J. R. *J. Chem. Soc., Dalton Trans.* **1977**, 211.

correct, its ESR spectrum should have $g_{\parallel}$ and $g_{\perp}$ values comparable to the electronically analogous $Pc^{2-}Co^{II}$ and $Pc^{2-}Fe^{I}$. We would also anticipate that such a species should exhibit marked solvent dependence in both its ESR spectrum and its electrochemistry because of the presence of an unpaired electron in the z^2 orbital. Indeed it is most likely to be five-coordinate (low-spin d^7, cf. $Pc^{2-}Fe^{I}S$[3b]). The ESR spectrum of the dianion is in fact very similar to that of the six-coordinate low-spin d^6 $Pc^{2-}Mn^{II}$ precursor. The reversibility observed in the electrochemistry of this species and the absence of any following reaction led us to assume that the coordination number probably remains six with two coordinated solvent molecules. The species is therefore assigned as $Pc^{4-}Mn^{II}S_2$.

Conclusion

Within the range studied, the manganese phthalocyanine system gives rise to the species $[Pc^{-}Mn^{III}S_2]^{2+}$, $[Pc^{2-}Mn^{III}S_2]^{+}$, $Pc^{2-}Mn^{II}S_2$, $[Pc^{3-}Mn^{II}S_2]^{-}$, and $[Pc^{4-}Mn^{II}S_2]^{2-}$, where in the case of the manganese(III) species, a solvent molecule may be displaced by an anion X. No evidence of manganese(I) was observed in distinction to the iron and cobalt series.[3,17] The electron-transfer rates of the $PcMn^{II}$ electron-transfer steps are similar in magnitude to those usually found in analogous porphyrin series.[24] Unlike $(TPP)Mn^{III}Cl$, however, the rate is not profoundly changed by either choice of anion or coordinating ligands. The $Pc^{2-}Mn^{III}/Pc^{2-}Mn^{II}$ couple appears at a slightly more anodic potential than in the porphyrin series. Reduction of the phthalocyanine ring, however, to form $[Pc^{3-}Mn^{II}S_2]^{-}$ appears 0.5–0.8 V anodic of the corresponding porphyrin reduction.[25] These trends are consistent with earlier views of the comparative electrochemistry of porphyrins and phthalocyanines.[3,26] This comparison illustrates the variation in coordination electronic and geometric structure accessible within the MN_4 class of compounds and its effect upon electrochemical properties.

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Registry No. $Pc^{2-}Mn^{II}(py)_2$, 77648-32-9; $Pc^{2-}Mn^{II}(Me_2SO)_2$, 77648-33-0; $Pc^{2-}Mn^{II}(DMF)_2$, 77648-34-1; $Pc^{2-}Mn^{II}(DMA)_2$, 77661-61-1; $[Pc^{2-}Mn^{III}(py)_2]^{+}$, 77648-35-2; $[Pc^{2-}Mn^{III}(Me_2SO)_2]^{+}$, 77648-36-3; $[Pc^{2-}Mn^{III}(DMF)_2]^{+}$, 77648-37-4; $[Pc^{2-}Mn^{III}(DMA)_2]^{+}$, 77648-38-5; $[Pc^{3-}Mn^{II}(py)_2]^{-}$, 77648-39-6; $[Pc^{3-}Mn^{II}(Me_2SO)_2]^{-}$, 77648-40-9; $[Pc^{3-}Mn^{II}(DMF)_2]^{-}$, 77648-41-0; $[Pc^{3-}Mn^{II}(DMA)_2]^{-}$, 77648-42-1; $[Pc^{4-}Mn^{II}(py)_2]^{2-}$, 77661-62-2; $[Pc^{4-}Mn^{II}(Me_2SO)_2]^{2-}$, 77648-43-2; $[Pc^{4-}Mn^{II}(DMF)_2]^{2-}$, 77648-44-3; $[Pc^{4-}Mn^{II}(DMA)_2]^{2-}$, 77648-45-4; $[Pc^{-}Mn^{III}(DMF)_2]^{2+}$, 77648-46-5.

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(24) Kadish, K. M.; Davis, D. G. *Anal. N.Y. Acad. Sci.* **1973**, *206*, 495.

(25) Boucher, L. J.; Garber, K. *Inorg. Chem.* **1970**, *9*, 2644.

(26) Lever, A. B. P. "Abstracts of Papers", First Chemical Congress of the North American Continent, Mexico City, Mexico, 1975; American Chemical Society: Washington, D.C., 1975; INOR 028.

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Vibrational Spectra and Potential Constants of the Pentacarbonyl(chalcocarbonyl)metal(0) Complexes $M(CO)_5(CX)$ (M = Cr, W; X = S, Se)

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Vibrational spectra have been recorded at ambient temperatures for the five chalcocarbonyl complexes $Cr(^{12}CO)_5(^{12}CS)$, $Cr(^{12}CO)_5(^{13}CS)$, $Cr(^{13}CO)_5(^{12}CS)$, $Cr(^{12}CO)_5(^{12}CSe)$, and $Cr(^{13}CO)_5(^{12}CSe)$ as vapors and solids and in various solvents. The $\nu(CO)$ region of the normal selenocarbonyl derivative has also been investigated at 15 K. Definitive assignments are proposed for most of the fundamental vibrations of these molecules as well as for the related species $W(^{12}CO)_5(^{12}CS)$ and *trans*-$W(^{12}CO)_4(^{13}CO)(^{12}CS)$, on the basis of general quadratic valence potential fields employing both compliance and force constants. The $\nu(CO)$ and $\nu(CX)$ modes in these calculations were corrected for anharmonicity. The σ-donor/π-acceptor capacities of the chalcocarbonyl ligands are discussed in terms of the interaction displacement coordinates which were derived from the MC and CX compliance constants. The vibrational results reported provide further evidence for the transferability of compliance and force constants between species of closely related geometry and also for the similar bonding properties of the CS and CSe ligands.

Introduction

The recent discovery of the simple selenocarbonyl complex $Cr(CO)_5(CSe)$[1] presents the best opportunity to date to study the relative bonding capabilities of the three isoelectronic ligands CO, CS, and CSe in structurally related metal carbonyl complexes. The $Cr(CO)_5(CX)$ (X = O, S, Se) series is particularly suitable for a comparative vibrational study since the potential constants of $Cr(CO)_6$ are already well established.[2] Furthermore, because of the structural similarities of the complexes, most of the potential constants not involving the heteroligand should remain essentially unchanged.

In order to have sufficient vibrational data to produce reliable potential fields for the pentacarbonylchromium(0) chalcocarbonyl complexes, we prepared the all-^{13}CO- and mono-^{13}CS-labeled derivatives, and their spectra were analyzed. The anharmonicity corrections determined previously for the CO, CS, and CSe stretching modes[3] were employed to calculate harmonic frequencies, and the normal mode calculations were performed with use of compliance constants rather than the more familiar force constants for the reasons explained in detail by Jones.[4] A compliant field was also

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(1) A. M. English, K. R. Plowman, I. S. Butler, G. Jaouen, P. LeMaux, and J.-Y. Thepot, *J. Organomet. Chem.*, **132**, Cl (1977).

(2) L. H. Jones, R. S. McDowell, and M. Goldblatt, *Inorg. Chem.*, **8**, 2349 (1969).

(3) (a) A. M. English, Ph.D. Thesis, McGill University, Montreal, Canada, 1980; (b) A. M. English, J. Sedman, K. R. Plowman, and I. S. Butler, submitted for publication in *J. Mol. Spectrosc.*

(4) L. H. Jones, "Inorganic Vibrational Spectroscopy", Marcel Dekker, New York, 1971.

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