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Derivation of metallophthalocyanine redox potentials via Hammett parameter analysis

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Abstract

Six redox processes of metal-free, cobalt and zinc substituted phthalocyanines are shown to be linearly dependent on the total Hammett substituent constant, $\Sigma\sigma_p$. The slopes of the linear free energy relationships are in the range 0.10–0.15 V/$\Sigma\sigma_p$.

Metal phthalocyanine species exhibit rich electrochemical behavior due to the accessibility of a range of oxidation states centred on the ligand, and, for many transition metal ions, on the metal [1–14]. Further, phthalocyanine species have been modified by the use of a wide range of substituents at the peripheral benzene rings [15]. Few attempts have been made [16–20] to analyse in any detail the variation of redox potential with substituent, via use of Hammett substituent constants [21, 22].

Orihashi *et al.* [16, 17] analysed the oxidation potentials for $R_4PcCo(II)$ and $R_8PcCo(II)$ species, showing, in separate plots, quite good correlations of the redox potential with the Hammett constant for the individual R. They noted that the slope of the correlation for the $R_8PcCo(II)$ species was roughly twice that of the slope for the $R_4PcCo(II)$ species. Luk'yanets and co-workers [18, 19] plotted the total $\Sigma\sigma_p$ parameter versus redox potentials for oxidation of zinc and cobalt species, but neither group attempted any broader analysis. Rare earth substituted diphthalocyanines have also been briefly studied [20], but they are not considered here.

We have collected a larger body of data from the literature and have chosen to analyse the data in terms of $\Sigma\sigma_p$, the sum of the Hammett parameters for all substituents. While the octasubstituted R_8PcM (with substitution in the 4,5 position of the benzene ring) species are single isomers, the tetrasubstituted R_4PcM species are almost invariably mixtures of isomers, randomly substituted in the 4 or 5 positions of each of the four benzene rings in the phthalocyanine unit. There is no evidence that the individual isomers have significantly different redox potentials. For this reason, the most straightforward assumption is that the effect of the substituent is correlated with its σ_p value (*para* substitution parameter) irrespective of its position, 4 or 5, in the ring. No data for 3-substituted phthalocyanines are included here.

Figure 1 illustrates the behaviour of a series of redox processes versus $\Sigma\sigma_p$, with the latter extracted from ref. 22. Data collected from the literature are shown in Table 1, with their statistical relationships versus the Hammett $\Sigma\sigma_p$ parameters shown in Table 2.

Within the data set there is some variation in organic solvent, as listed in the footnote to Table 1. However solvent effects on the phthalocyanine ring centred redox potentials are relatively small.

The data set for reduction of species $[(CN)_2Co(III)R_xPc(-2)]^-$ (see ref. 23 for labelling nomenclature of MPc species) near −0.9 V versus SCE, labelled VI in Table 1, was tentatively ascribed [33] to a two-electron reduction process to form $[Co(I)R_xPc(-2)]^-$. This assignment is consistent with a study [24] of the chemistry of species $[(HO)_2Co(III)Pc(-2)]^-$ where the hydroxide ion stabilises the Co(III) species to such an extent that a direct two-electron oxidation of $[Co(I)Pc(-2)]^-$ is observed in basic media. The cyanide complex ion apparently behaves in a similar fashion since the Co(II)/Co(I) process is seemingly absent [33]. In the presence of cyanide or hydroxide ion, the $L_2Co(III)Pc(-2)$/$Co(II)Pc(-2)$ redox process (L = CN, OH) is more negative than the $Co(II)Pc(-2)/Co(I)Pc(-2)$ redox process, so that direct two-electron oxidation of $[Co(I)Pc(-2)]^-$ to $[L_2Co(III)Pc(-2)]^-$ occurs [12]. Although this is an irreversible process, only the cathodic wave being seen, the potential of the cathodic peak

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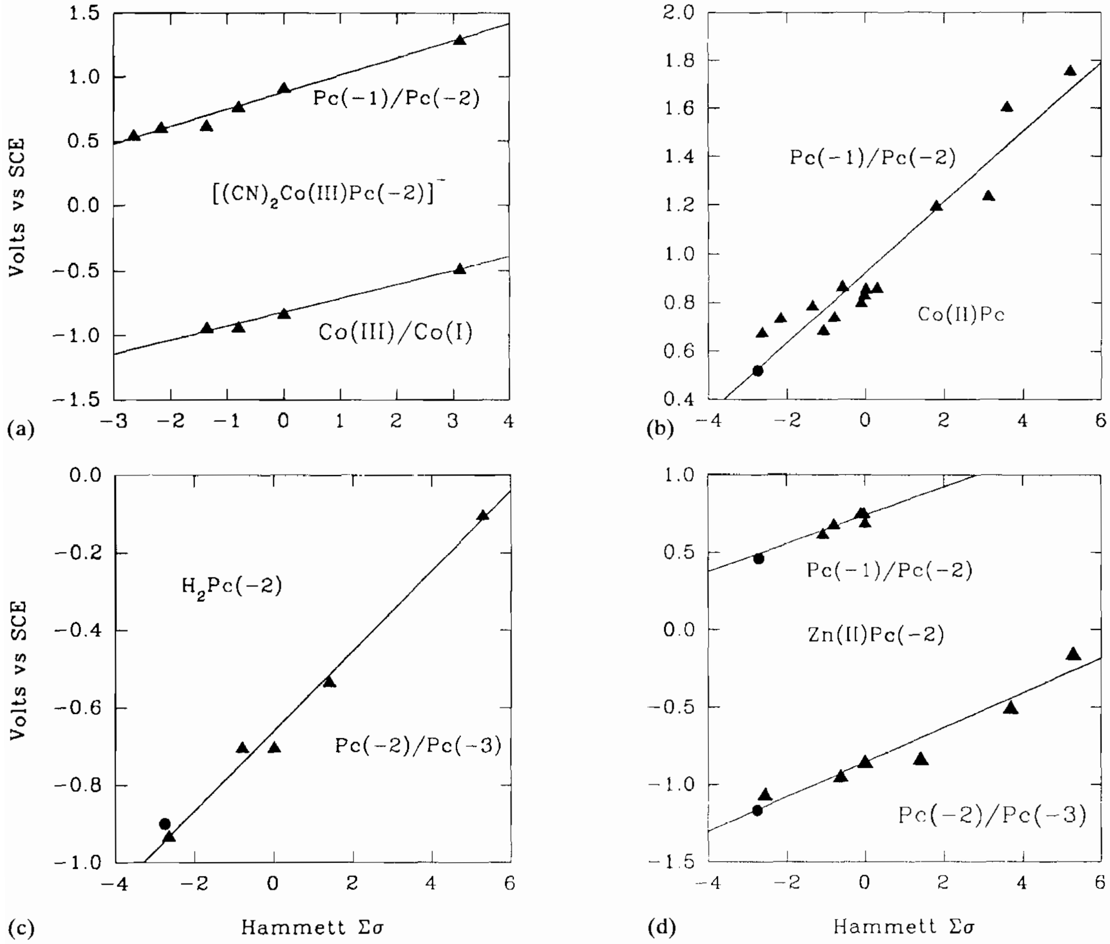

Fig. 1. Plots of a selection of phthalocyanine redox processes vs. the Hammett $\Sigma\sigma_p$ values. (a) $[(CN)_2Co(III)R_xPc(-2)]^-$ species, upper $(CN)_2Co(III)R_xPc(-1)/[(CN)_2Co(III)R_xPc(-2)]^-$; lower $[(CN)_2Co(III)R_xPc(-2)]^-/[Co(I)R_xPc(-2)]^-$. (b) $Co(II)R_xPc(-2)$ species, $[Co(II)R_xPc(-1)]^+/Co(II)R_xPc(-2)$. (c) $H_2R_xPc(-2)$ species, $H_2R_xPc(-2)/[H_2R_xPc(-3)]^-$. (d) $Zn(II)R_xPc(-2)$ species, upper $[Zn(II)R_xPc(-1)]^+/Zn(II)R_xPc(-2)$, lower $Zn(II)R_xPc(-2)/[Zn(II)R_xPc(-3)]^-$.

shows good behavior with respect to the Hammett substituent and is therefore included herein.

No Hammett data appear available for the neopentoxy group. However there is a tetraneopentoxy datum for four of the redox processes discussed here. Using the correlations shown in Table 2, and assuming the tetraneopentoxy species fits each correlation perfectly, one obtains four experimental values for σ_p(neopentoxy). The average value is found to be 0.69 ± 0.28. This data point is shown in each correlation as a filled circle; agreement of the average value is most satisfactory for all four redox processes.

There appear to be no other relatively well developed series of substituted phthalocyanines for which electrochemical data are available. All six couples have slopes close to 0.1 V/σ_p. These slopes might be compared with values of 0.46 and 0.97/V/σ_p, for oxidation (at the metal) and reduction (at the bipyridine ligand) for species $(R_2Bpy)Re(CO)_3(4\text{-}EtPy)$($R_2Bpy$ = variously disubstituted 2,2′-bipyridine) [36], and 0.35, 0.46 and 0.33 V/σ_p for oxidation, reduction and double reduction of $[(R_2BQDI)Ru(Bpy)_2]^{2+}$ [37] (R_2-BQDI = variously substituted *o*-benzoquinonediimines). The much smaller slopes for the phthalocyanine couples are surely a reflection of the large size of the phthalocyanine ring system relative to bipyridine or *o*-benzoquinonediimine, such that the effect of a single substituent is small. One might note however, that the magnitude of the slope, for a metal centered redox process, is also related to the degree of interaction between metal and ligand orbitals. Thus the data [38] for the Ru(III)/Ru(II) couple in $[(R_2Bpy)_3Ru]^{2+}$ register a slope of 0.14 V/σ_p against the Hammett value (using values listed in ref. 22).

While the data reported here represent a small database, it is evident that the Hammett $\Sigma\sigma_p$ parameter is useful in predicting the potentials of substituted phthalocyanine redox processes. If the results are construed to be fairly general, then a slope in the range 0.1–0.15 V/σ_p might be used to predict redox potentials

TABLE 1. Hammett constants and redox potentials (V vs. SCE) in organic solvent

Species	Hammett constant	Redox processes[a,b]					
		I	II	III	IV	V	VI
OCNPc	5.28	-0.1		-0.15	1.76		
$Cl_{16}Pc$	3.68			-0.5			
TNO_2Pc	3.12				1.24	1.3	-0.48
TCPc	1.8				1.2		
OCPc	3.6				1.61		
TSPc	1.4	-0.53		-0.83			
TPhSPc	0.28		0.785		0.865		
$H_{16}Pc$	0	-0.7	0.695	-0.85	0.86	0.92	-0.83
TPhPc	-0.04		0.755		0.835		
TPhOPc	-0.12		0.755		0.805		
TEtPc	-0.60				0.87		
TBuPc	-0.80	-0.7	0.685	-0.94	0.745	0.77	-0.93
TMeOPc	-1.08		0.625		0.69		
TNPc	-2.75[c]	-0.9	0.46	-1.17	0.52		
OMePc	-1.36				0.79	0.62	-0.94
OMeOPc	-2.16				0.73	0.61	
OBuOPc	-2.56		0.5	-1.06			
TAPc	-2.64	-0.65			0.68	0.55	

[a] I: $H_2R_xPc(-2)/[H_2R_xPc(-3)]^-$ collected from refs. 13, 25, 26 in DMSO; refs. 27, 28 in DMF; ref. 29 in $PhNO_2$; ref. 30 in DCB. II: $[ZnR_xPc(-1)]^+/ZnR_xPc(-2)$ collected from refs. 31, 32 in DMF; ref. 33 in DCB. III: $ZnR_xPc(-2)/[ZnR_xPc(-3)]^-$ collected from refs. 9, 10, 34, 35 in DMF. IV: $[Co(II)R_xPc(-1)]^+/Co(II)R_xPc(-2)$ collected from ref. 19 in DCB; ref. 17 in CH_3CN. V: $(CN)_2Co(III)Pc(-1)/[(CN)_2Co(III)Pc(-2)]^-$ collected from ref. 24 in acetone; ref. 17 in CH_3CN. VI: $[(CN)_2Co(III)Pc(-2)]^-/[Co(I)Pc(-2)]^-$ collected from ref. 24 in acetone (see text). [b] Abbreviations: OCNPc = octacyanophthalocyanine; $Cl_{16}Pc$ = hexadecachlorophthalocyanine; TNO_2Pc = tetranitrophthalocyanine; TCPc = tetracarboxyphthalocyanine; OCPc = octacarboxyphthalocyanine; TSPc = tetrasulfonatophthalocyanine; TPhSPc = tetrathiophenylphthalocyanine; $H_{16}Pc$ = unsubstituted phthalocyanine; TPhPc = tetraphenylphthalocyanine; TPhOPc = tetraphenoxyphthalocyanine; TEtPc = tetraeethylphthalocyanine; TBuPc = tetrabutylphthalocyanine; TMeOPc = tetramethoxyphthalocyanine; TNPc = tetraneopentoxyphthalocyanine OMePc = octamethylphthalocyanine; OMeOPc = octamethoxyphthalocyanine; OBuOPc = octabutoxyphthalocyanine. TAPc = tetraaminophthalocyanine. [c] Hammett σ_p value derived from current data, see text.

TABLE 2. Correlation of redox potential, (V vs. SCE) with Hammett $\Sigma\sigma_p$ in organic solvents

Redox process[a]	Slope	Intercept	Regression coefficient	No. of examples
I. $H_2Pc(-2)/[H_2Pc(-3)]^-$	0.10	-0.66	0.995	5
II. $[Zn(II)Pc(-1)]^+/Zn(II)Pc(-2)$	0.09	0.74	0.83	5
III. $Zn(II)Pc(-2)/[Zn(II)Pc(-3)]^-$	0.11	-0.86	0.96	6
IV. $[Co(II)Pc(-1)]^+/Co(II)Pc(-2)$	0.14	0.92	0.96	14
V. $(CN)_2Co(III)Pc(-1)^-/[(CN)_2Co(III)Pc(-2)]^-$	0.13	0.89	0.98	6
VI. $[(CN)_2Co(III)Pc(-2)]^-/[Co(I)Pc(-2)]^{-}$[c]	0.11	-0.82	0.995	4

[a] For labelling of phthalocyanine redox processes, see ref. 12. [b] No. of examples. [c] Probable two electron process, see text.

for species as yet not studied or synthesized, provided that a few specific examples are examined to derive a value for the intercept appropriate for the redox process under study.

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