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Charge-transfer band shifts in iron(III) hexacyanoferrate(II) by electro-intercalated cations *via* ground state-energy/lattice-energy link

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It is currently important to achieve and understand adjustments of optical properties: "guest cation" induced CT spectral shifts in Prussian Blue are shown to be driven (*via* its specific effect on the $Fe(CN)_6$ CT-donor entity) by the cation lattice-energy interaction, as inferred from microgravimetry of introduced alkali-metal ions, and from independent solubility correlations for other intercalated cations.

Prussian Blue[1] has a cubic structure comprising Fe^{3+}-$[Fe^{II}(CN)_6]^{4-}$ with interstitial[2,3] electroneutrality-conferring cations denoted M^{z+}. The charge-transfer("CT") band PB on ITO glass,[4] resulting from $Fe^{3+}[Fe^{II}(CN)_6]^{4-} \xrightarrow{h\nu} Fe^{2+}$-$[Fe^{III}(CN)_6]^{3-}$, has a maximum wavelength λ_{max} at about 700 nm, that can be made to shift with electro-intercalated cation M^{z+}, in $(M^{z+})_{1/z}Fe^{3+}Fe^{II}(CN)_6{}^{4-}$ [abbreviated as PB-$\{M^{z+}\}$]. Except in layer-by-layer deposition[1] or with Cs^+ present,[5] initially electrodeposited PB invariably[5] includes Fe^{3+} as the M^{z+}, which however is substantially replaced by other cations on (a single) voltammetric cycling in solutions of these cations. The values of the wavelengths λ_{max} at maximum absorption, for introduced alkali-metal ions in PB-$\{M^+\}$, fall in the sequence[4] $Na^+ > K^+ < Rb^+ < Cs^+$ (Table 1).‡ This is also the sequence of the mass changes Δm (*via* quartz-microbalance studies[6]) following one voltammetric cycle in each of the various M^+, that is attributed to M^+ gain less {water + Fe^{3+}} loss, most readily ascribed to the greatest stability[4] of PB-$\{K^+\}$ denied the smaller Na^+ by its more tenacious hydration. The strong interaction of K^+ with the intra-PB $Fe^{II}(CN)_6{}^{4-}$ through the CN^- ligand thereby provides greatest stabilisation of the CT ground state, Fe^{II} being the donor in the optical CT, this interaction hence affording the lowest λ_{max}. If K^+, Rb^+ and Cs^+ follow their ionic radii r in progressively weaker CN^- interactions hence ground-state stabilisations, the hitherto unexplained shifts of λ_{max} thereby find some physical rationalisation. (Reversibility considerations[7] are irrelevant to single-cycle observations.)

Intercalated Ag^+ and the M^{2+} provide evidence, that is more direct, for the control of λ_{max} by such lattice-energy interactions; the M^{2+} intercalations have been confirmed by XPS. Table 2 shows the shifts $\Delta\lambda_{max}$ from a "reference" value, which is the λ_{max} at 711 nm of the originally deposited PB-$\{Fe^{3+}\}$. Virtually direct measures of the strengths of the M^{z+}/$Fe^{II}(CN)_6{}^{4-}$ interactions within the PB lattice are provided by the solubility products K_S for[8] the dissolution equilibria, conventionally given for the lowest integral number n of the aquo-ions, of the sparingly soluble M^{z+} ferrocyanides, $(M^{z+})_p([Fe^{II}(CN)_6]^{4-})_q(s) \rightleftharpoons pM^{z+} + qFe^{II}(CN)_6{}^{4-}$.

Table 1 CT λ_{max} dependence on incorporated[a] closed-shell M^+

Incorporated M^+	Na^+	K^+	Rb^+	Cs^+	Ref
λ_{max}/nm	703	686	691	703	5
$(2 + \Delta m)$/μg cm^{-2}	1.21	0.31	3.72	4.64	6
r/Å	1.02	1.38	1.52	1.67	
r^{-1}/nm^{-1}	9.8	7.25	6.6	6.0	

[a] Following deposition in K^+ solution, then one cycle in M^+ solution.[5]

Here $n = p + q = (1 + 4/z)d$ where d = denominator of any fraction within the parentheses.

Quantitative comparison of different-dimensionality K_S values being disallowed, values of $1/n \log\{K_S/(\text{mol dm}^{-3})^n\}$ are listed instead in Table 2, providing average values per ion free of the units problem. Column 3 also lists the wavelengths of any additional maxima appearing in difference spectra. These comprise PB-$\{M^{z+}\}$spectra minus the reference PB-$\{Fe^{3+}\}$ spectrum, both spectra having first been "normalised" by scaling all values so that the absorbances at λ_{max} are unity.

The Table 2 values of $1/n \log K_S$ fall in the sequence of the shifts $\Delta\lambda_{max}$ from the λ_{max} at 711 nm of the originally deposited PB-$\{Fe^{3+}\}$. The $1/n \log K_S$ values are a measure of relative contributions of the intra-lattice M^{z+}–$[Fe^{II}(CN)_6]^{4-}$ interactions to the lattice energies of $(M^{z+})_{1/z}Fe^{3+}Fe^{II}(CN)_6{}^{4-}$, which in turn directly influence the corresponding CT ground-state energies. These interactions thus undoubtedly underlie the observed variations of $\Delta\lambda_{max}$. Specifically, those M^{z+} with $1/n \log K_S$ near or more negative than the PB-$\{Fe^{3+}\}$ value -5.9 show stronger interactions reflected in the corresponding $\Delta\lambda_{max}$. Thus PB-$\{Cu^{2+}\}$shows the only substantial extra CT band, which implies some additional ground-state stabilisation. (Parenthetically, CT interactions of this kind probably contribute to the lattice energies governing the insolubilities of most ferrocyanides of redox-active M^{z+}, closed-shell M^{z+} ferrocyanides being all soluble.[8])

Mn^{III} being an accessible state in a CT interaction, the anomalous (positive $\Delta\lambda_{max}$) result for Mn^{2+} is ascribed to an enhanced NIR CT absorption which when superimposed on the main CT band of PB, shifts the observed net maximum of the summed two absorptions to greater wavelengths. Any expected CT band involving the more readily realisable Fe^{3+} would then lie beyond the 1000 nm spectrophotometry limit studied, while Co^{2+} and Ni^{2+} have M^{III} states of inaccessibly high energy. Their weak ~ 520 nm difference-spectrum maxima imply only modest additional stabilisations of PB.

For PB-$\{Pb^{2+}\}$ the substantial $\Delta\lambda_{max}$ (Fig. 1) is accordingly matched by a large $1/n \log K_S$. The huge shift probably invalidates the spectrum differencing procedure showing an apparently extra CT band. The only XPS to give a clear spectrum of the intercalate is that of PB-$\{Pb^{2+}\}$(Fig. 1, inset). For all others [except Ag^+, XPS not available], apparent noise superimposed on the XPS in reality reflects the variability[3] of interstitial sites in the PB channels,[2] that also evokes a "smudginess" (*sic*) in locating these XRD-established sites[3] in comparable metallo-hexacyanometallates. Fractional occupancy of 'N-holes'[9–11] by M^{z+} would enhance the effect.

While on graphite PB can be formed[12] from $Ag_3Fe(CN)_6$, here Ag^+, having the greatest $1/n \log K_S$ value, in nitrate solution actually dissolves PB leaving a purple–red residue that shows a 540 nm maximum, matching the difference-spectrum

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Table 2 Dependence of $\Delta\lambda_{max}$ (shifts of λ_{max} of PB CT band) on inserted M^{z+}, following 1–5 CV cycles in M^{z+} solution

M^{z+}	$\Delta\lambda_{max}{}^{a}$/nm	$(\log K_S)/n$	Difference-spectrum maxima/nm	n	Notes
$Fe^{3+}{}_{uncycled}$	$0_{uncycled}$	See below			Reference spectrum
Mn^{2+}	+19	−4.0	870	3	+ Wide IR band?
Ni^{2+}	−1	−4.7	(520)	3	Weak extra band
Co^{2+}	−9	−5.3	(520)	3	Weak extra band
Fe^{2+}	−9	(Not available)	(520)	3	Weak extra band
Cu^{2+}	−11	−5.3	505	3	Extra band
[$Fe^{3+}{}_{uncycled}$	…reference…	−5.9		7	in $(\log K_S)/n$ … sequence]
Pb^{2+}	-50^{b}	-6.0^{b}	565(?)[c]	3	Solid solution?
Ag^{+}	−51	−8.8	535	5	Solid solution? (see text)
[Ag^{+} salt	(~no PB max)		500–540[d]		Residue from dissolved PB]

[a] With respect to reference spectrum of uncycled PB, λ_{max} = 711 + 3 nm (obtained on upper section of PB deposit not immersed for cyclic voltammetry). [b] Column 2 and 3 values correspond to 12.7 and 34.4 kJ mol^{-1}, respectively. [c] Possible artefact from differencing procedure. [d] Read from direct spectrum of residue.

value for a sample cycled 129 times in low, survivable Ag^{+} concentrations $< 10^{-9}$ mol dm^{-3} (AgCl in 0.1 M KCl), while with other M^{2+}, the light doping in single CV cycles and brief exposures preclude the possible deleterious dissolutions elsewhere observed.[9–11]

An independent lattice-energy/ground-state-energy link is demonstrated in a Prussian Blue analogue. The λ_{max} of a modified PB containing the pentacyanoaquoiron(II) anion is[13] shifted 100 nm to longer wavelengths *cf.* PB proper, as would result from both the weaker average ligand field at the Fe^{II} arising from the substitution of H_2O for CN^-, as well as from the diminished lattice energy with a 3− anionic charge of the pentacyanoiron(II) ion *cf.* $Fe^{II}(CN)_6{}^{4-}$.

Straightforward substitution of ligands at the Fe^{III} chromophore allows "tuning of the optical properties of Prussian-blue analogues".[14] Equating (as we do) energy-level shifts with bulk thermodynamic energies is an allowed approximation.[15] Furthermore, spectroscopically-derived effects of ligand fields have accounted for the apparently irregular hydration- and lattice-energy excursions in transition metal complexes.[16,17] In our study an apparently reversed argument (still consistent with the bases of the earlier studies[16,17]) is presented, that lattice-energy as governed here by cation rather than ligand interactions determines the PB spectra.

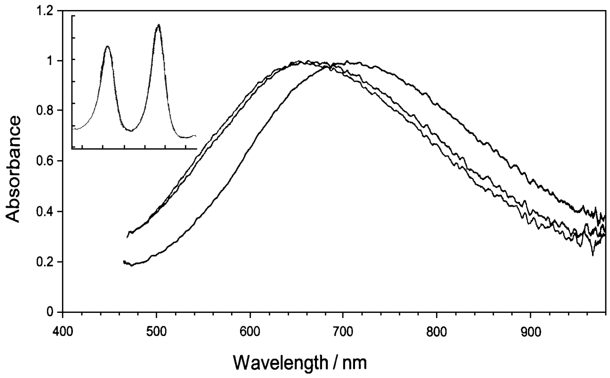

Fig. 1 Duplicate traces of PB-{Pb^{2+}} spectra, appearing at higher energy than PB-{Fe^{3+}} reference spectrum (single trace). Inset: XPS spectrum of PB-{Pb^{2+}} showing noise-free count maxima at binding energies of 138.8 eV (the higher peak, Pb $4f_{7/2}$) and 143.7 eV (Pb 2p).

Notes and references

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‡ *Experimental* (here M = mol dm^{-3}): Prussian Blue films on 4 cm^2 of 20 $\Omega\,\square^{-1}$ ITO glass were deposited from 2.55 mM $K_3Fe^{III}(CN)_6$ /2.5 mM $Fe(NO_3)_3$ in 1 mM HNO_3 at 17 μA cm^{-2} for 1000 s to give ~650 nm thick PB. The washed & vacuum-dried electrode was immersed in 0.2 M solutions of M^{z+} salts for usually 1, occasionally 5, cycle(s) of three-electrode voltammetric cycling *vs.* SCE/Pt CE (further CV often decomposing the PB). Spectra were obtained with a PC-driven Ocean-Optics USB2000 Miniature Fiber-optic spectrometer on the H_2O-washed then dried sample; and XPS on a model 220iXL VG EscaLab.

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