

Stable Free Radicals of Phthalocyanine

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The oxidation of the dilithium salt of phthalocyanine $\text{Li}_2(\text{pc}^{2-})$ with iodine gave the free radical of phthalocyanine, $\text{H}(\text{pc}^-)$, while the electrochemical oxidation of the same starting material gave the lithium salt, $\text{Li}(\text{pc}^-)$; these stable free radicals were characterized by spectroscopic and magnetic measurements.

Since the dilithium salt of the phthalocyanine dianion, $\text{Li}_2(\text{pc}^{2-})$,^{1,2} is usually soluble in aprotic polar solvents such as acetone or tetrahydrofuran (THF), it is often utilized as a starting material in the preparation of metallophthalocyanines. Through our investigations of the phthalocyanine complexes of the rare-earth elements⁴ derived from the dilithium salt, we discovered that rare-earth complexes of the free radical of phthalocyanine were formed by a one-electron oxidation in addition to the more usual complexes of the phthalocyanine dianion.⁵ Although the phthalocyanine radical has been generated *in situ* by electrolysis⁶ and observed in co-ordination compounds of the first row transition metals,⁷ there appears to be no report of the isolation of such a radical in a pure state. Consequently, an attempt was made to isolate the free radical in an unco-ordinated state or at least as an alkaline salt, by a proper choice of the oxidation process.

Such an oxidation of $\text{Li}_2(\text{pc}^{2-})$ in acetone by iodine gave black precipitates. The crude material could be purified by sublimation to give lustrous needle crystals of $\text{H}(\text{pc}^-)$ (1).†

The use of iodine as the oxidant in this system was recently reported by Marks *et al.* in their studies on a wide variety of

conducting molecular-macromolecular assemblies.⁸ In these species iodine acted as a dopant and was an essential component of the product. In our work iodine acts merely as an oxidant and is not in the product, which also does not contain appreciable amounts of lithium. The product, then, does not contain LiHpc which was reported² to be formed when $\text{Li}_2(\text{pc}^{2-})$ reacted with small amounts of water.

Cyclic voltammetry of $\text{Li}_2(\text{pc}^{2-})$ in acetone indicated that the first oxidation occurred at +0.24 V (*vs.* the saturated calomel electrode) and the corresponding reduction at +0.11



V, values that are much more negative compared with the corresponding redox potentials of metallophthalocyanines of the transition elements.⁹ The electrochemical oxidation of the dilithium salt at +0.5 V in acetone or THF gave lustrous needles of $\text{Li}(\text{pc}^-)$ (2) in almost quantitative yield.† The compounds (1) and (2) are stable in air and almost insoluble in most organic solvents.

The magnetic moment of both (1) and (2) was $1.3 \mu_B$ at 13 °C, a value smaller than the theoretical value for the free radical ($1.73 \mu_B$).

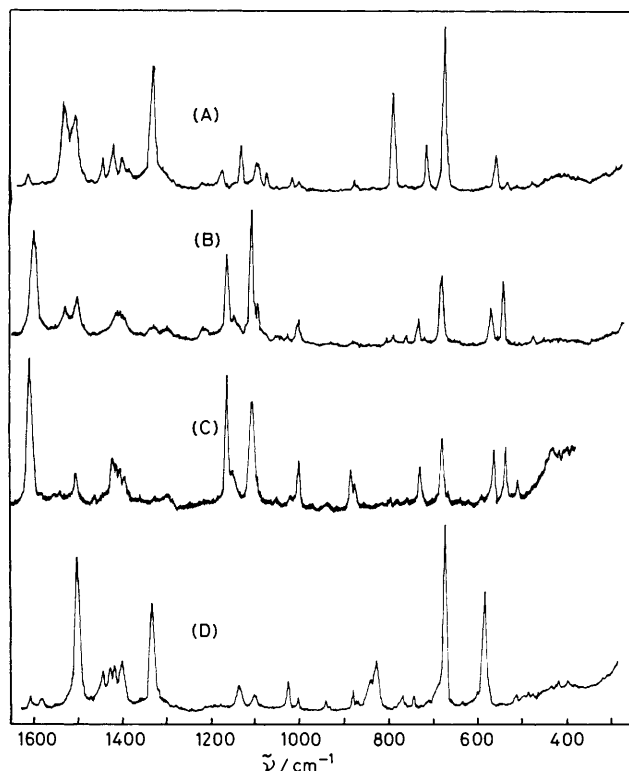


Figure 1. Raman spectra of (A) $[\text{H}_2(\text{pc}^{2-})]$, (B) $[\text{H}(\text{pc}^-)]$, (C) $[\text{Li}(\text{pc}^-)]$, and (D) $[\text{Zn}(\text{pc}^{2-})]$.

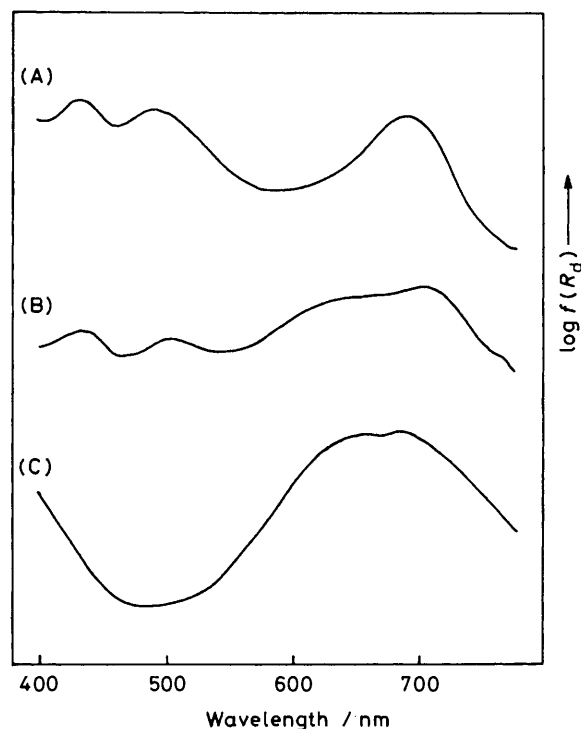


Figure 2. Reflectance spectra of (A) $[\text{Li}(\text{pc}^-)]$, (B) $[\text{H}(\text{pc}^-)]$, and (C) $[\text{Li}_2(\text{pc}^{2-})]$.

† All new compounds gave satisfactory elemental analyses.

Solid samples of (1) and (2) had similar e.s.r. signals. The lines are narrow and centred at the free spin value of $g = 2.002$.^{8,10}

The i.r. spectrum of (1) showed characteristic bands of the N-H group at 3280, 1002, and 870 cm^{-1} of lower intensity than those of phthalocyanine. Conversely, compound (2) had no such bands. Raman spectra of (1), (2), phthalocyanine, and the zinc complex of phthalocyanine, were obtained with the 514.5 nm excitation line (100 mW) of the argon ion laser. The solid samples were rotated to minimize heating. As illustrated in Figure 1, the Raman spectra of (1) and (2) are very similar, but completely different from the spectra of normal phthalocyanine species such as phthalocyanine itself or its zinc complex. These results seem to prove that formation of the phthalocyanine radical causes considerable structure deformation and/or change in the resonance enhancement of lines in the Raman spectrum.

It is well known that normal phthalocyanine derivatives have absorption bands in the visible region at ca. 650–700 nm (Q band).³ Because of these absorption bands, the colour of well ground samples of normal complexes such as $\text{Li}_2(\text{pc}^{2-})$ is clear blue. The colour of (1) and (2), though, is dark brown. As shown in Figure 2, the reflectance spectra of the radicals (1) and (2) have two bands with peaks at 440 and 490 nm. These spectral features, especially of $\text{Li}(\text{pc}^-)$ are very similar to those of the radical in $\text{Mg}(\text{pc}^-)$ obtained by electrolytic oxidation of an $\text{Mg}(\text{pc}^{2-})$ solution by Lexa *et al.*,⁶ and are considerably different from the spectra of phthalocyanine radical complexes of the transition metals.⁷ This would be expected from consideration of the much weaker co-ordination in the magnesium complex compared to that in the transition metals complexes. In $\text{Mg}(\text{pc}^-)$, then, the co-ordinated ligand should be in a state more similar to that of the free ligand.

There have been some reports of weak signals in the e.s.r. spectra of unmetallated phthalocyanine and many diamagnetic

metallophthalocyanines.^{3,10} In most of these the lines are reported to be narrow and centred at $g = 2.0023$. In view of the isolation of pure radicals in our work, these e.s.r. signals most probably originate from a free radical of phthalocyanine.

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