Notes

Electrosynthesis and Resonance-Raman Spectrum of Phthalocyaninatoiron(II)

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The electrosynthesis of phthalocyanine complexes [M(pc)] of iron, cobalt, nickel, and copper has been carried out and the method provides a facile, one-stage, room-temperature preparation. The electronic and i.r. spectra have been studied for all four complexes and resonance-Raman data are presented also for [Fe(pc)] dissolved in aniline. Excitation profiles based on the electronic absorption band of [Fe(pc)] at 606 nm suggest that this electronic absorption is a vibronic shoulder on the side of the main electronic (0–0) transition at 668 nm.

Phthalocyanine (H_2pc) acts as a quadridentate ligand to a wide range of elements [1] and Linstead and co-workers [2–4] prepared complexes with Group 1—4 metals as well as the first-row transition elements, vanadium to zinc. The usual methods of preparation involve either the use of protonated phthalocyanine as starting material or a template reaction with a phthalic derivative.[5] With few exceptions, the methods require high temperatures, often in excess of 300 °C. The electrochemical synthesis provides a facile, one-stage, room-temperature preparation for several [M(pc)] complexes.

Raman spectra of metal phthalocyanines have not been studied extensively, largely because of the extremely low solubility of the complexes in all common solvents and also because both the metal-free ligand and its metal complexes are typified by highly fluorescent emissions. Indeed, the fluorescent characteristics of these species are of interest because they are understood to be closely connected to the mechanism of photosynthesis.

Published Raman studies for some [M(pc)] complexes [6] (usually run as solids) show 15 or more bands in the spectrum of each, but only three of the bands have frequencies which depend appreciably on M. Introducing a metal atom into the pc ligand has a much greater influence on the spectrum than the type of metal in the [M(pc)] series. This is also apparent from i.r. absorption spectra. However, the complexes exhibit extremely intense visible absorption bands ($\varepsilon = 10^4$—10^5 dm^3 mol^{-1} cm^{-1}) and it is evident that resonance Raman (r.R.) spectroscopy would be a favourable experimental technique to study these complexes in solution provided that suitable concentrations can be obtained and the accompanying fluorescent emissions can be tolerated. Huang *et al.*[7] reported the first detailed investigation of the Raman spectrum of an [M(pc)] complex in solution in 1978. They studied the r.R. spectra and excitation profiles of [Pt(pc)] dissolved in α-chloronaphthalene and in α-chloronaphthalene–n-octane mixtures at 295 K.

We report now for the first time some r.R. data for [Fe(pc)] dissolved in aniline. We have also measured excitation profiles based on the electronic absorption band at 606 nm.

Experimental

Preparation of Samples.—Phthalocyanine complexes of the first-row transition elements, iron to copper, were prepared electrochemically in methanol–1,2-dichlorobenzene (80 : 20) according to the general method of Tuck.[8] The transition metal (typically 0.1 g) was anodically dissolved (using a platinum flag) in the presence of 0.03 mol dm^{-3} H_2pc and 0.05 mol dm^{-3} NEt_4Br. The latter acted as an electrolyte during the anodic dissolution. A current density of 30—50 mA cm^{-2} was used for 3—9 h and *ca.* 1.0 g of [M(pc)] was precipitated. The products were filtered off and washed with 1,2-dichlorobenzene. They were generally highly crystalline, deep blue or green solids, sometimes with a purple lustre. All of the products were neutral species containing metal in the + 2 oxidation state, as readily shown by coulometry. The C, H, and N analyses agreed with theoretical values to within ±1%, and the i.r. data for the solid complexes are in good agreement with the work of Aleksandrov *et al.*[9] The spectra confirm that all of the complexes prepared electrochemically prefer the β conformation.

A sample of [Fe(pc)] (Ventron Chemical Co.) was used in addition to our electrochemically prepared sample for the r.R. spectra in an attempt to find a sample with the lowest possible fluorescent background.

Technical grade aniline was distilled three times prior to use and stored in the dark. Technical grade quinoline was used without further purification.

Instrumental Details.—Raman spectra were recorded at room temperature using a modified Cary model 81 instrument.[10] The spectra were excited using the lines of a Coherent Radiation model CR3 argon-ion laser which was used also to pump a Coherent Radiation model 590 dye laser filled with either Rhodamine 6G (for use in the region 578—633 nm) or sodium fluorescein (535—575 nm region). Laser power levels at the sample varied from 50 to 800 mW, depending upon the particular line chosen. However, photodecomposition of the solutions occurred at power levels >500 mW.

Solution measurements were made at room temperature on *ca.* 5×10^{-5} mol dm^{-3} solutions using the spinning-cell technique.

The spectra were calibrated by reference to the positions of well documented solvent bands and the total uncertainty is ±2 cm^{-1}. The enhancements of all of the r.R. bands were normalised to the band of aniline at 1 602 cm^{-1} and then corrected for the ν^4 dependence. The intensity of this aniline band is independent of the excitation lines used.

Infrared spectra of [M(pc)] complexes were examined as KBr discs on a PE model 598 spectrometer. Electronic spectra (350—750 nm) of [Fe(pc)] and H_2pc itself dissolved in aniline were recorded on a PE model 402 spectrometer.

Table. Resonance-Raman spectrum of [Fe(pc)] in aniline at 295 ± 2 K. Exciting line 633.7 nm

$\tilde{\nu}$/cm^{-1}	Intensity	Depolarisation ratio, ρ	$\tilde{\nu}$/cm^{-1}	Intensity	Depolarisation ratio, ρ
1 885	w	*	1 358	w	*
1 792	w	*	1 345	m	0.45
1 700	w	*	1 338	w	*
			1 307	w	*
1 611	w	*	1 197	m	0.47
1 588	w	*	1 132	s	0.69
1 511	w	*	1 112	w	0.56
1 496	vs	0.35	931	w	*
1 451	s	0.38	746	s	0.65
1 423	w	*	686	vs	0.17
1 379	w	*	593	w	0.21

* Intensity too small to estimate ρ.

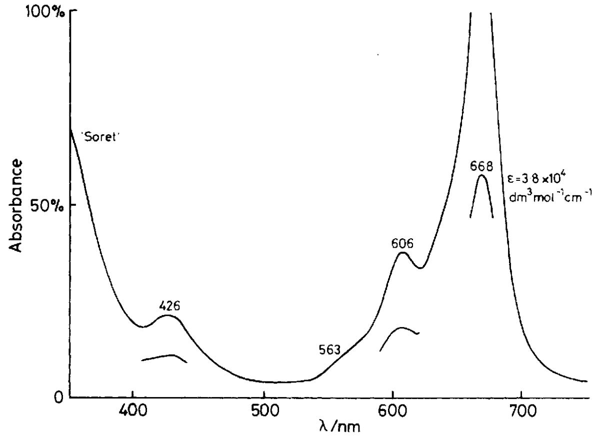

Figure 1. Electronic spectrum of iron phthalocyanine in aniline

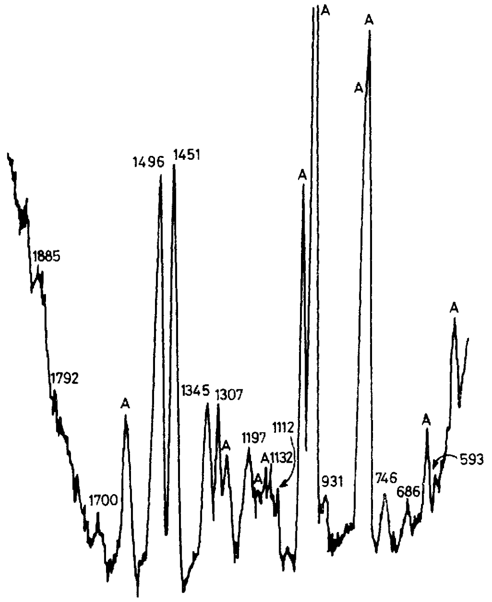

Figure 2. Resonance-Raman spectrum of [Fe(pc)] in aniline. Excitation wavelength 604.2 nm; A = solvent band

Results and Discussion

The electronic spectrum of [Fe(pc)] dissolved in aniline is shown in Figure 1. Pure aniline exhibits no absorptions above 350 nm but the deep green solution of [Fe(pc)] shows five main features at 426 (ε = 4.6 × 10^3), 563(sh) (ε = 3.2 × 10^3), 606 (ε = *ca.* 10^4), 668 nm (ε = 3.8 × 10^4 dm^3 mol^{-1} cm^{-1}), and an intense absorption in the u.v. region at *ca.* 350 nm.

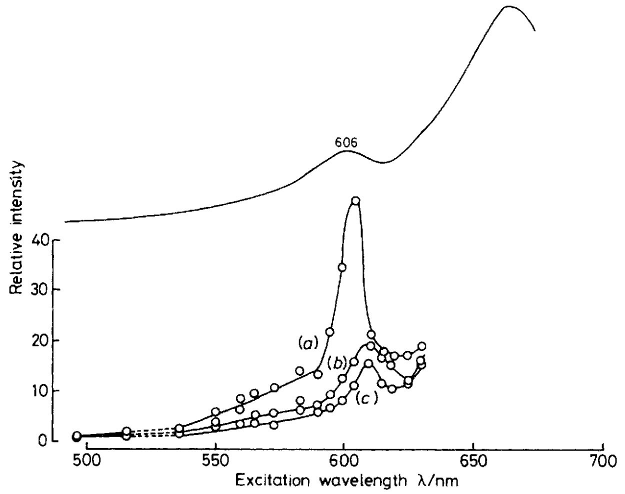

Figure 3. Excitation profiles of the Raman bands at 1 496 (*a*), 1 345 (*b*), and 1 197 cm^{-1} (*c*) of [Fe(pc)] in aniline. The electronic absorption spectrum is shown above

A representative r.R. spectrum for [Fe(pc)] dissolved in aniline is shown in Figure 2, using an exciting line of 604.2 nm. Bands due to aniline solvent are marked A and some of these mask weak features which arise from [Fe(pc)]. This becomes very evident when the spectrum is rerun using quinoline as solvent and also when an exciting line at 633.7 nm is employed. This line is much closer to the centre of the main electronic transition (668 nm) and hence even the weakest features in Figure 2 show significant resonance enhancement. The observed positions of the resonantly enhanced bands for [Fe(pc)] are shown in the Table together with their intensities and polarisation data.

Resonance enhancement is encountered for *ca.* 20 fundamental, overtone, and combination bands of [Fe(pc)] in aniline. In particular, new features are observed at 1 611, 1 588, 1 511, 1 423, 1 379, 1 358, and 1 338 cm^{-1} when an exciting line of 633.7 nm is used. These new features correspond exactly in position to some of the observed i.r. absorptions for solid [Fe(pc)] (in the α form) which have been assigned previously to non-totally symmetric vibrations.[11] This result implies that the non-totally symmetric vibrations are mixing close-lying electronic states efficiently and hence may become intense on approaching particular resonance conditions. These r.R. spectra enable the excitation profiles shown in Figure 3 to be constructed. It is notable that the Raman band at 1 496 cm^{-1} exhibits the greatest degree of enhancement and the separation between the visible absorption bands at 668 and 606 nm corresponds to a value of 1 530 cm^{-1}. This close agreement between 1496 and 1530 cm^{-1} confirms the assignment by Huang *et al.*[7] of the corresponding shoulder in [Pt(pc)] to a vibronic structure on the side of the main electronic (0–0) transition at 668 nm.

References

1 A. B. P. Lever, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 27.
2 R. P. Linstead, *J. Chem. Soc.*, 1934, 1016.
3 J. A. Elvidge and R. P. Linstead, *J. Chem. Soc.*, 1955, 3536.
4 G. T. Byrne, R. P. Linstead, and A. R. Lowe, *J. Chem. Soc.*, 1934, 1017.
5 M. de Sousa Healy and A. J. Rest, *Adv. Inorg. Chem. Radiochem.*, 1978, **21**, 1.
6 I. V. Aleksandrov, Ya. S. Bobovich, V. G. Maslov, and A. N. Sidorov, *Opt. and Spectrosc.*, 1974, **37**, 265.
7 T-H. Huang, K. E. Riechhoff, and E-M. Voigt, *Can. J. Chem.*, 1978, **56**, 976.
8 D. G. Tuck, *Pure Appl. Chem.*, 1979, **51**, 2005 and refs. therein.
9 I. V. Aleksandrov, Ya. S. Bobovich, Y. G. Maslov, and A. N. Sidorov, *Opt. and Spectrosc.*, 1973, **35**, 154.
10 N. Daneshvar, D. J. Gardiner, and B. P. Straughan, *J. Inorg. Nucl. Chem.*, 1981, **43**, 1147.
11 L. E. Lyons, J. R. Walsh, and J. W. White, *J. Chem. Soc.*, 1960, 167.

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