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Synthesis and Study of Electronic Spectra of Planar Polymeric Phthalocyanines

Franco Cataldo

Progega s.n.c., Via M. Mencatelli 14, 00128, Rome, Italy

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ABSTRACT

The electronic spectra of planar polymeric phthalocyanines complexed with copper and iron have been studied in concentrated sulphuric acid in comparison with the spectra of the 'monomeric counterparts used as model compounds both in concentrated sulphuric acid and in the vapour phase. Interpretation of the transitions associated with the B-band (Soret band) and the Q-band have been made. Using oleum as solvent, it was possible to observe in fresh solutions the radical cation transitions of both monomeric and polymeric phthalocyanines occurring in the near-IR region between 850 and 1100 nm. The polymeric phthalocyanines were also characterized by Fourier transform IR spectroscopy. © 1997 Elsevier Science Ltd

Keywords: Phthalocyanine, monomeric, polymeric, eletronic spectra interpretation, sulphuric acid, oleum, radical cations.

INTRODUCTION

Octaaza[18]annulene metal complexes are well known, with the trivial name of phthalocyanines. Phthalocyanines are a class of synthetic pigments and dyes which are broadly used due to their unique fastness properties in blue to green hues.[1]

Many data have been published concerning their synthesis, structure elucidation, polymorphism and their application as colouring matters.[1–4]

In recent years phthalocyanines and related annulenes have been used as redox catalysts, as photocatalysts, as semiconductors, in gas sensor devices, as photoconductors, in medical applications, and in solar energy conversion, dye transfer photography and non-linear optical systems, etc., demonstrating the versatility of this class of molecule.[1–4]

A related class of polymeric phthalocyanines can be obtained by reacting 1,2,4,5-benzenetetracarboxylic dianhydride (in place of phthalic anhydride) with metal salts and urea.[5–8] However, these materials never reached any industrial application[1,4] and limited data are available on their optical properties because of their insolubility in common solvents due to the relatively high molecular weight.

The purpose of this paper is to study the electronic spectra of polymeric phthalocyanine in sulphuric acid and oleum in comparison with the spectra of their 'monomeric' analogues.

The reason for this interest in polymeric planar phthalocyanines (PPc) lies not only in their potential application as pigments of different colour and hue in comparison with their monomeric counterparts, but also in their potential application in catalysis and photocatalysis, with the advantage of a virtual complete insolubility in almost all common solvents and excellent thermostability.[9] A study of the electronic spectra of these PPc in strongly oxidizing media such as oleum, could be a starting point to obtain further knowledge of the mechanisms involved in their catalytic activity.

EXPERIMENTAL

Oleum (with 30% free SO_3) and 1,2,4,5-benzenetetracarboxylic dianhydride were obtained from Merck, Darmstadt, Germany. All other reagents and solvents were from Fluka, Buchs, Switzerland. Electronic spectra in the UV–visible–near-IR (NIR) range were studied on a Shimadzu 160A spectrophotometer. Fourier transform IR (FT-IR) spectra were recorded on a Perkin–Elmer 1710 spectrometer.

Synthesis of iron phthalocyanine

A mixture of 5.0 g phthalic anhydride, 17.0 g urea and 1.5 g iron trichloride was heated for 4 h at 200°C in the presence of 60 ml *o*-dichlorobenzene. The cooled reaction mixture was then steam distilled and the residue filtered, dissolved in concentrated sulphuric acid (green solution) and precipitated by pouring into an excess of water to yield 0.94 g of a blue powder.

FT-IR spectrum (cm^{-1}, KBr): 540 vs, 655 w, 725 mw, 760 mw, 780 ms, 1060 m, 1318 m, 1400 s, 1475 m, 1600 w.

Synthesis of iron polymeric phthalocyanine

The same procedure described above was adopted by using 7.26 g 1,2,4,5-benzenetetracarboxylic dianhydride, 25.0 g urea, 2.98 g iron trichloride and 70 ml *o*-dichlorobenzene. At the end of the steam distillation, the polymeric product was dark green, while after precipitation from sulphuric acid solution it was a dark blue amorphous material (yield 9.2 g).

FT-IR spectrum (cm^{-1}, KBr): 435 w, 541 s, 610 w, 650 vw, 720 vw, 760 sh, 780 sh, 840 w, 900 vw, 960 vw, 1063 m, 1150 m, 1210 w, 1325 m, 1405 s, 1465 ms, 1520 w, 1580 sh, 1613 sh, 1650 s, 1710 s, 1730 vs, 1760 sh, 1780 m, 3165 s.

Synthesis of copper phthalocyanine

The same procedure as above was used, heating at 200°C 5.0 g phthalic anhydride, 23.0 g urea and 1.6 g copper dichloride in 65 ml *o*-dichlorobenzene. The crude product was greenish–blue, and after precipitation from sulphuric acid solution 1.2 g of a deep blue product was recovered.

FT-IR (cm^{-1}, KBr): 545 w, 660 w, 720 ms, 750 ms, 770 m, 810 w, 870 w, 905 m, 960 w, 1010 w, 1065 s, 1090 s, 1120 s, 1180 m, 1295 s, 1345 m, 1385 m, 1420 m, 1485 m, 1520 mw, 1608 m, 3175 m. These spectrum data are reasonably comparable to a previously published spectrum.[8]

Phthalocyanineoctacarboxytetraimide, having imide substituents attached to the benzene rings, was prepared according to ref. 8. In agreement with the literature[8] we observed the bands at 1680 and 1760 cm^{-1} due to imide groups.

Synthesis of copper polymeric phthalocyanine

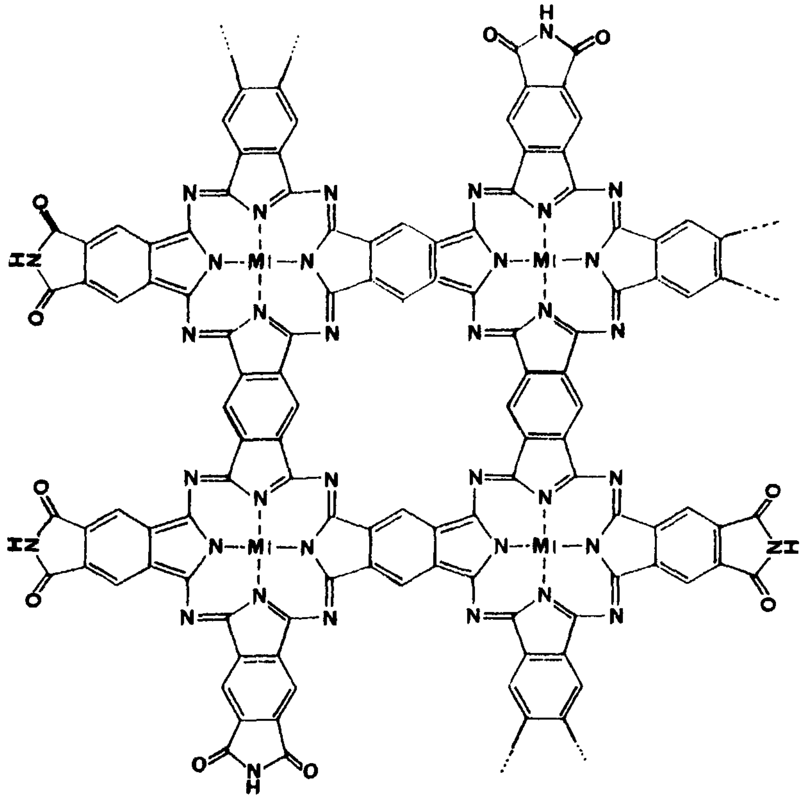
A mixture of 5.0 g 1,2,4,5-benzenetetracarboxylic dianhydride, 25.0 g urea and 1.7 g copper dichloride was heated with 65 ml *o*-dichlorobenzene as described above. The crude product was dark green, and after precipitation in water of its sulphuric acid solution, a green material was recovered (yield 1.8 g).

FT-IR spectrum (cm^{-1}, KBr): 535 w, 635 mw, 720 m, 740 sh, 775 m, 855 w, 905 w, 960 w, 1010 vw, 1065 s, 1160 m, 1190 vw, 1230 mw, 1310 s, 1385 s, 1440 sh, 1480 m, 1560 mw, 1600 vs, 1620 sh, 1775 ms, 3180 s.

RESULTS AND DISCUSSION

Copper and iron phthalocyanine (CuPc and FePc) are planar molecules and can be classified as aromatic according to the Hückel $4n+2$ rule.[1–4,10] These molecules are soluble in acidic solvents having a high dielectric constant, or in high boiling solvents such as chloronaphthalene, dimethylformamide (DMF), quinoline, etc., and sublime when heated at 400–500°C. On the basis of these properties, previous investigators were able to record and study the electronic spectra of these molecules in the vapour phase and in several solvents.[11]

On the other hand, the planar polymeric phthalocyanine (PPc) used in this work can be regarded as planar sheets of monomeric units connected to each other by benzene rings with imide end groups (Scheme 1). Elsewhere[8,9] other investigators have discussed how the monomeric units can be connected in PPc (in linear, squared fashion, as shown in Scheme 1, or in a mixed way) and have found a relatively high degree of polymerization ranging, for example, for CuPPc from 10 to 15 monomeric units. In this work, we could assume that a similar degree of polymerization has been achieved for CuPPc and FePPc with the general chemical structure based on that reported in Scheme 1. The FT-IR spectra of CuPPc and FePPc agree reasonably well with those reported for PPc[8] and clearly show the presence of imide end



Scheme 1

groups (Scheme 1) as indicated by the imide C=O stretching at 1775–1780 cm^{-1}, and the imide N–H stretching at 3160–3180 cm^{-1},[8] while the anhydride groups are absent, as shown by the lack of their typical absorption band at 1820 cm^{-1}.[8]

With this structure, PPc appear as amorphous powders and often, even after an acid conditioning operation,[1,4] show a dull colour in contrast with the bright colour of 'monomeric' phthalocyanines; this is one of the reasons which has prevented their commercial diffusion.

The high molecular weight of PPc has prevented early investigators from studying their electronic spectra in common solvents or in the vapour phase since PPc do not sublime.

The electronic spectra of simple phthalocyanines exhibit several bands which are due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The most important bands are the C-band located in the UV at about 220 nm, followed by the L-band at 240 nm and the N-band at 270 nm. In the near-UV there is the B-band or Soret band at about 320 nm, and finally there is the Q-band at 650–700 nm.[11] According to extended PPP (Pariser–Parr–Pople) calculations[12,13] and *ab initio* calculations,[14] the $n \rightarrow \pi^*$ transition appears in the region of the Soret band. In Table 1, by observing that the absorption of the B-band of CuPc and FePc in the vapour phase undergoes a hypsochromic shift in highly polar sulphuric acid, we can confirm this assignment experimentally. In fact it has been stated[15] that the R-band associated with the $n \rightarrow \pi^*$ transitions undergoes a hypsochromic shift on increasing the polarity (i.e. the dielectric constant and hence the refractive index) of the environment around the molecule under study.

On the other hand the Q-bands of CuPc and FePc undergo a bathochromic shift by passing from the vapour phase to sulphuric acid, and this transition could be assigned mostly to a $\pi \rightarrow \pi^*$ transition.[15]

TABLE 1
Electronic Spectra of Pc and PPc

Compound	*Solvent*	*UV bands* C	L	N	*Soret band* B				*Visible band* Q		
CuPc	Vapour	220	240	267	*325*			603	*657*		
CuPc	S. acid	224	254		*305*	439		703	*792*		
CuPsub[a]	S. acid	204	230	295	*330*	390		702	*753*		
CuPPc	S. acid				*321*	397		710	*744*	764	863
FePc	Vapour	217	240	305	*340*	400	440	622	*676*	760	
FePc	S. acid				*300*		430	699	*780*		825
FePPc	S. acid	230			*380*			635	*733*		

Note: The spectra in the vapour phase were taken from ref. 11.
All values are in nanometres. S. acid = sulphuric acid.
[a]Monomeric copper phthalocyanine with imide substituents.

However, a very large number of calculations has been made on the electronic spectra of phthalocyanines, and the first successful model was Gouterman's 'four orbital model', which was based on PPP calculation[16,17] where the B-band and the Q-band arise from electronic excitation from the two HOMO orbitals to the two LUMO orbitals. The resulting configurations interact pairwise, giving electronic states in which the dipoles cancel or reinforce each other. This mixing is responsible also for the vibronic subbands which are called B_X and B_Y for the Soret band and Q_X and Q_Y for the visible band. Further calculations using PPP[12,13,18] and CNDO/S[19,20] have confirmed the substantial validity of the 'four electron model'. For more recent *ab initio* investigations see refs[21–23]

In Fig. 1 we report the electronic spectra of CuPc and FePc in concentrated sulphuric acid in comparison with the spectra of CuPPc and FePPc (which are their polymeric analogues) in the same solvent (the unique known solvent for these polymers). In concentrated sulphuric acid the band structure of CuPc and FePc which is observed in the gas phase or in organic solvents is not altered, but the band positions are shifted as can be seen in Table 1. As discussed above, the B-band undergoes a hypsochromic shift in polar acidic solvents, while the Q-band undergoes a bathochromic shift. These facts have been interpreted in terms of protonation of the four bridging nitrogen atoms at the periphery of each phthalocyanine molecule, while the inner ones connected to the coordinated metal atom are not protonated.[24]

This protonation strongly polarizes the phthalocyanine molecule and the resulting dipole alters the energy of all electronic transitions associated with the macrocycle.[8] From Fig. 1 and from Table 1, it is apparent that the B-band of CuPPc absorbs almost at the same wavelength of CuPc in the vapour phase (325 nm vs 321 nm), and a similar observation pertains to FePPc, which has a broad band at about 380 nm with a shape resembling *in toto* the band of FePc in the vapour phase. We explain these experimental facts in terms of lack of protonation or of a much weaker protonation of the macrocycle of the PPc. For the lack of protonation of PPc, we cannot advocate steric hindrances since the small proton has easy access to the large cages shown in Scheme 1. Therefore a weaker protonation is attributable only to electronic factors. In fact, as shown in Table 1, imide-substituted CuPc, which is the model compound reproducing the substitution patterns present in each monomeric unit of CuPPc and its end groups, shows the B-band in sulphuric acid at approximately the same wavelength as CuPPc in the same solvent or as CuPc in the vapour phase.

From the electronic standpoint, CuPc with imide end groups is analogous to polymeric phthalocyanine CuPPc. Both molecules, due to the electron-withdrawing (ketonic and imide) substituents, reduce the basicity of the four external nitrogen atoms of the macrocycle, which can be weakly protonated.

Moreover, the monomeric units of PPc are conjugated with each other, and the heterocyclic nitrogen atoms in one unit affect electronically the basicity of the nitrogen atoms in an adjacent unit in an analogous way to the imide end group for the end units.

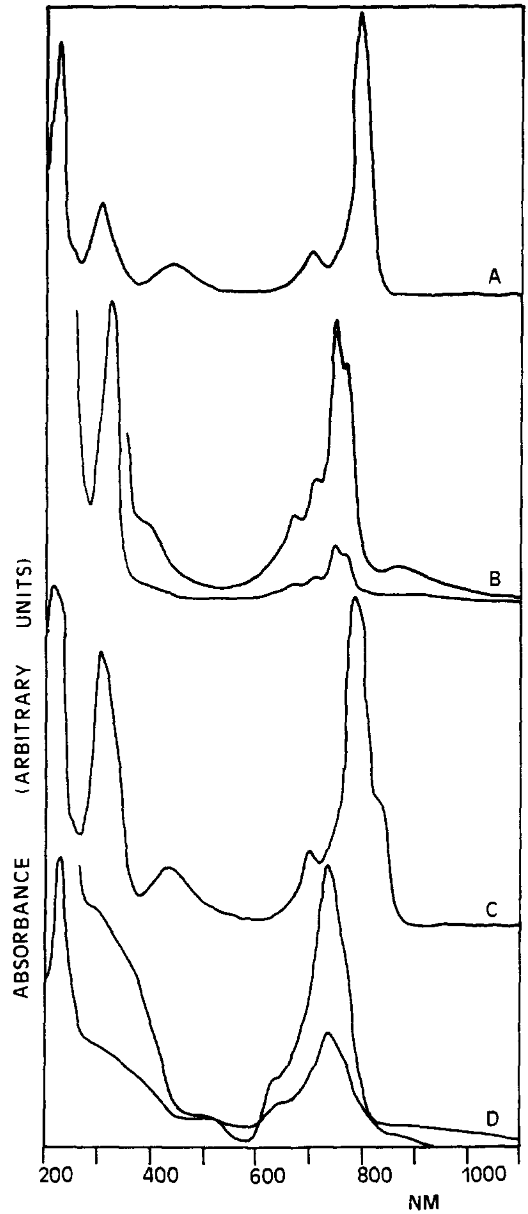


Fig. 1. Electronic spectra in concentrated sulphuric acid. A – CuPc; B – CuPPc; C – FePc; D – FePPc.

In agreement with these factors, we can also observe that the transitions of the Q-band both for CuPPc and for FePPc appear at higher energy than the transitions for CuPc and FePc in sulphuric acid, while we expected that almost the same energy was involved in the transition of monomeric and polymeric phthalocyanines in the same acidic environment in the case of protonation. The position of the Q-band is affected by the substituents attached to the four benzene rings of phthalocyanine as can be seen in Table 1 by comparing the absorption of the Q-band of CuPc in sulphuric acid with that for CuPc with imide end groups and with that for CuPPc. Again, we can observe that this transition of imide-substituted CuPc occurs at about the same wavelength as that of CuPPc.

The other solvent which we have used to study the electronic spectra of phthalocyanines is oleum containing 30% free sulphuric anhydride, a solvent which we have previously used to study the radical cation of fullerenes.[25] In general, phthalocyanines are not resistant to strong oxidizing agents like nitric acid in sulphuric acid or ceric salts in acidic media.[1–4] For polymeric phthalocyanines, it has been reported that when they are demetallated, i.e. free from the central coordination metal, they do not survive hydrolysis even in concentrated sulphuric acid, while they show good stability if the metal atom is present inside the macrocycle.[8] We have seen that CuPc, FePc and their polymeric analogues CuPPc and FePPc dissolve readily in oleum, giving unstable blue solutions which in a few hours turn to green, light green, and are then completely decolorized.

This behaviour shows that in oleum, phthalocyanines are not stable, and due to the strong oxidizing power of the medium, they are degraded to other products. In this work we have examined the spectra in oleum of these molecules immediately after their dissolution; the absorption curves are shown in Fig. 2 and the relevant bands are tabulated in Table 2. We observe that the Q-bands of CuPc and FePc in oleum absorb at the same wavelength we have recorded in concentrated sulphuric acid, while the Soret B-bands undergo a bathochromic shift and lie at the same wavelength shown originally by these two molecules in the vapour phase. We do not have any explanation of this fact, although we can advocate a charge transfer interaction between SO_3 or other chemical species present in oleum and phthalocyanine itself, with prevention of protonation. On the other hand, for CuPPc and FePPc, we did not observe any significant difference between the position of the B and Q absorption bands in concentrated sulphuric acid and in oleum.

The main feature of these spectra in oleum are the new absorption bands observed in the NIR portion of the spectrum. For example, for CuPc a new band arises at 940 nm (Fig. 2A; this band is very very weak and observable after strong expansion), while CuPPc shows a shoulder at 900 nm and a maximum at 990 nm (Fig. 2B after expansion). For FePc (Fig. 2C) the new maximum lies at a wavelength > 1100 nm while another maximum is present at 840 nm. In FePPc the new bands appear at 1030 and 893 nm (Fig. 2D after expansion).

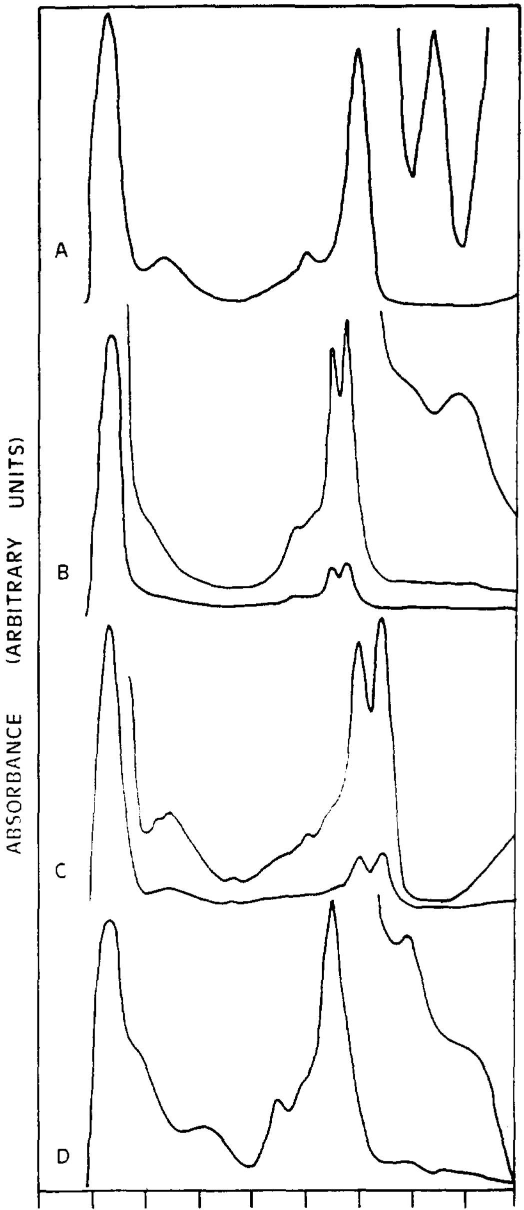


Fig. 2. Electronic spectra in oleum. A – CuPc; B – CuPPc; C – FePc; D – FePPc.

TABLE 2
Summary of Electronic Spectra of Pc and PPc in Various Medis, with Radical Cation Transition Bands

Compound	*Solvent*	*Soret band B*		*Visible band*	*Q*	*Radical cation*		
CuPc	Vapour	*325*		603	*657*			
CuPc	S. acid	*305*		703	*792*			
CuPc	Oleum	*329*	440	702	*797*			*940*
CuPPc	S. acid	*321*	397		*744*	764	863	
CuPPc	Oleum	*329*	410	672	*750*	*774*	*900*	*990*
FePc	Vapour	*340*		622	*676*	760		
FePc	S. acid	*300*	430	699	*780*	825		
FePc	Oleum	*328*	443		*796*		*840*	> *1100*
FePPc	S. acid	*380*		635	*733*			
FePPc	Oleum	*332*	391	649	*750*		*893*	*1030*

Note: The spectra in the vapour phase are taken from ref. 11.

Elsewhere other investigators have discussed the mechanism of oxidation of porphyrins and the biochemical implication of the formation of radical cations as labile intermediates during oxidation reactions.[26,27] Here we notice that the chlorophyll radical cation develops a new absorption band at 820 nm[27] and that the octaethylporphinatozinc radical cation has a tendency to dimerize to form a π–π' diamagnetic compound whose absorption band lies at 930 nm.[26] Based on these previous observations, we can say that what we observe as soon as the phthalocyanines and PPc are dissolved in oleum are the radical cation absorption bands; of course dimerization is also possible with formation of π–π' complexes. The mechanism which explains the poor stability of phthalocyanines and porphyrins toward strong oxidizing agents, and which leads to the opening of the annulene macrocycle of the molecules, involves as first step a radical cation formation.[26]

CONCLUSIONS

The experimental data obtained seem to confirm the theoretical assignments to an $n \rightarrow \pi^*$ transition for the Soret B-band and a $\pi \rightarrow \pi^*$ transition for the Q-band of phthalocyanines.

For CuPc and FePc, the hypsochromic shift of the B-band in sulphuric acid can be interpreted as due to protonation of the external nitrogen atoms of the macrocycle. This protonation occurs weakly for CuPPc and FePPc as well as for the model compound imide-substituted CuPc, because of the electron withdrawing effect of the substituents and also of the nitrogen atoms of the adjacent phthalocyanine unit (in PPc).

In oleum, both CuPc and FePc and their polymeric counterparts CuPPc and FePPc initially form radical cations, which are easily recognized from their absorption in the NIR portion of the spectrum. Some π–π' association between these cation radicals has been postulated. However, all the phthalocyanines studied do not survive the strong oxidizing power of the medium and undergo an oxidative ring opening reaction of the macro-ring.

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