

Chapter 1

An introduction to the phthalocyanines

1.1 Discovery and structural determination

The compound that was later called phthalocyanine (Pc) was first observed as a highly coloured by-product in the chemical conversion of some *ortho*-(1,2)-disubstituted benzene derivatives. Braun and Tcherniac (1907), working at the South Metropolitan Gas Company (London), observed a dark insoluble material during the preparation of *ortho*-cyanobenzamide from phthalimide and acetic acid. Similarly, de Diesbach and von der Weid (1927), of Fribourg University, obtained a 23% yield of an exceptionally stable, blue material during the reaction of *ortho*-dibromobenzene with copper cyanide in refluxing pyridine. Hindsight allows us to interpret these by-products as being metal-free and copper(II) Pc, respectively.

The chain of events, which eventually lead to the full elucidation of the structure of Pc, began in 1928 at the Grangemouth plant of Scottish Dyes Ltd, during the industrial preparation of phthalimide from phthalic anhydride (Cronshaw, 1942). The glass-lined reaction vessel cracked, exposing the outer steel casing to the reaction, resulting in the formation of a blue–green material. Owing to the business interests of Scottish Dyes, the material was examined by two employees, Dandridge and Dunsworth, whose preliminary studies revealed that the iron-containing by-product had potential as an exceptionally stable and insoluble pigment. A patent covering the preparation and properties of the substance was granted in 1929 (Dandridge *et al.*, 1929). Imperial Chemical Industries (ICI) acquired Scottish Dyes in 1928. ICI were eager to understand the structure of this novel coloured substance and a sample was sent to Professor Jocelyn F. Thorpe

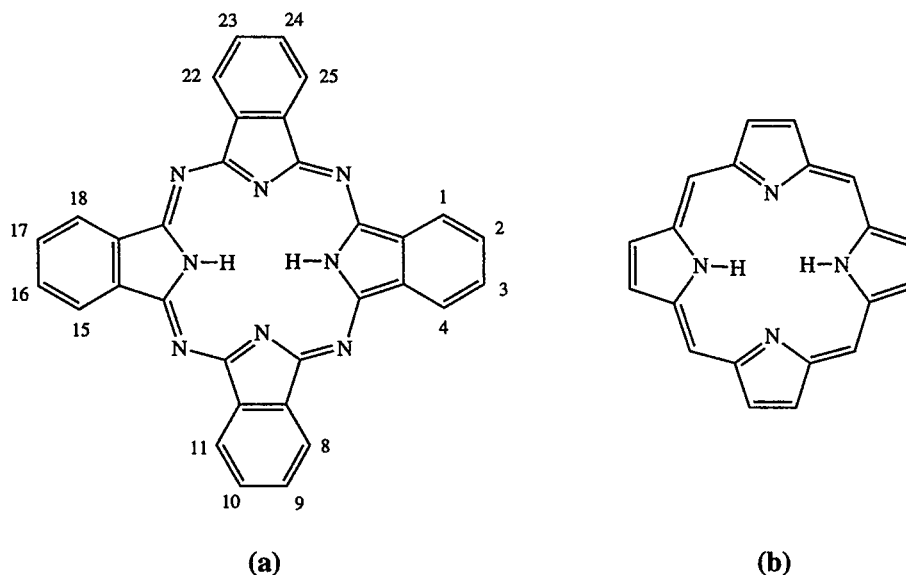


Figure 1.1. (a) The structure of phthalocyanine with each of the possible sites of substitution at the benzo-positions numbered using the accepted notation. Note that the hydrogen attached to each of the benzo-positions is not shown. (b) The structure of the simplest example of a porphyrin macrocycle; porphine.

at Imperial College, London. He, in turn, gave it for investigation to a newly appointed lecturer, the remarkable Reginald P. Linstead (1902–66), ‘as it appeared that the substance might prove to be of academic interest’ (Barton *et al.*, 1968). Thus, a collaboration between Linstead and ICI was initiated that culminated in the publication of a series of six papers in the *Journal of the Chemical Society* describing the structure of Pc and the synthesis of some of its metal derivatives (Linstead, 1934; Linstead and Lowe, 1934a, b; Byrne *et al.*, 1934; Dent and Linstead, 1934a, b).

Linstead used a combination of elemental analysis, ebullioscopic molecular mass determination and oxidative degradation (which produces phthalimide) to arrive at the correct structure for H_2Pc (Fig. 1.1(a)). He showed that Pc is a symmetrical macrocycle composed of four iminoisoindoline units with a central cavity of sufficient size to accommodate various metal ions. This structure was confirmed later by X-ray diffraction techniques (Section 1.3). It was noted that Pc is closely related to the naturally occurring porphyrin ring system (Fig. 1.1(b)), the differences being the four benzo-subunits and the nitrogen atoms at each of the four *meso* positions. Indeed, occasionally Pc is referred to as *tetra-benzotetraazaporphyrin*. Like the porphyrin macrocycle, Pc was assumed to exhibit aromatic behaviour owing to its planar conjugated array of 18 π -electrons, as predicted by Hückel’s theory of aromaticity, published only a few years previously. In addition to the structural description, Linstead’s initial series of

papers contained the experimental details for the preparation of Pcs from phthalonitrile (*ortho*-dicyanobenzene), which is still considered the best precursor for Pc synthesis on a laboratory scale (Chapter 2). Linstead conceived the name *phthalocyanine* as a combination of the prefix *phthal*, originally from the Greek *naphtha* (rock oil), to emphasise the association with its various phthalic-acid-derived precursors, and the Greek *cyanine* (blue). The Pc research programme at Imperial College continued until it was interrupted by the Second World War and included the synthesis of naphthalocyanines (Bradbrook and Linstead, 1936), the realisation that Pc could complex with at least 24 different metal ions (Barrett and Linstead, 1936; Barrett *et al.*, 1938), the synthesis of Pc analogues from 1,2-dicyano-containing heterocycles (Linstead *et al.*, 1937) and an investigation of the relationship between the porphyrin and Pc ring systems by means of the synthesis of a number of intermediate compounds such as tetra-benzoporphyrin (Barrett *et al.*, 1940).

1.2 The use of Pcs as industrial colorants

The potential of Pcs as pigments was immediately obvious to workers at ICI, which started manufacture of copper Pc in 1935 using the trade-name Monastral Blue (Cronshaw, 1942). The story of the serendipitous discovery and the rapid development of the Pcs as colorants is told by the ICI film *The Discovery of a Pigment: The Story of Monastral Blue* (n.d. 1940?), in which Linstead has a starring role. This film truly captures the excitement of scientific discovery and its 'newsreel' soundtrack gives a highly entertaining description of this 'triumph of British chemistry'.

It was found that the brightness of copper Pc pigment was greatly improved by reprecipitation from sulfuric acid to produce small α -type particles. Halogenated Pcs were discovered to be valuable additives to stabilise these particles towards conversion to the larger and duller β -type crystals (Section 3.1). Water-soluble dyes based on sulfonated Pcs and, subsequently, reactive dyes for permanent textile coloration were quickly developed. Today, many thousands of tons of Pcs are produced world-wide, per annum, to satisfy the growing industrial demand for blue and green colorants. The diverse uses of Pcs as colorants in the photographic, printing, plastics and textile industries have been documented in detail in the two-volume series *The Phthalocyanines* by Moser and Thomas (1983a, b).

1.3 Metal phthalocyanines (MPcs)

It is possible to place around seventy different elemental ions in the central cavity of Pc (see Table 1.1) and the choice of central metal cation can strongly

Table 1.1. *Elements that form complexes with phthalocyanine and their commonly encountered oxidation states*

| Atomic number | Element (symbol) | Observed metal | |
|-------------------|------------------|-----------------|-------------------------------------|
| | | oxidation state | Abbreviation |
| 1 ^a | Hydrogen (H) | 1+ | H ₂ Pc (metal-free) |
| 3 ^a | Lithium (Li) | 1+ | Li ₂ Pc |
| 4 ^a | Beryllium (Be) | 2+ | BePc |
| 5 ^b | Boron (B) | 3+ | B-sub-Pc (1 axial) |
| 11 ^a | Sodium (Na) | 1+ | Na ₂ Pc |
| 12 ^a | Magnesium (Mg) | 2+ | MgPc |
| 13 ^a | Aluminium (Al) | 3+ | AlPc (1 axial) |
| 14 ^a | Silicon (Si) | 4+ | SiPc (2 axial) |
| 15 ^c | Phosphorus (P) | 3+ | PPc (1 axial) |
| 19 ^a | Potassium (K) | 1+ | K ₂ Pc |
| 20 ^a | Calcium (Ca) | 2+ | CaPc |
| 21 ^a | Scandium (Sc) | 3+ | ScPc (1 axial), ScPc ₂ |
| 22 ^a | Titanium (Ti) | 3+,4+ | TiPc (=O or 2 axial) ^e |
| 23 ^a | Vanadium (V) | 3+,4+ | VPc (=O or 2 axial) ^e |
| 24 ^a | Chromium (Cr) | 2+,3+ | CrPc |
| 25 ^a | Manganese (Mn) | 2+ | MnPc |
| 26 ^a | Iron (Fe) | 2+,3+ | FePc |
| 27 ^a | Cobalt (Co) | 2+,3+ | CoPc |
| 28 ^a | Nickel (Ni) | 2+ | NiPc |
| 29 ^a | Copper (Cu) | 2+ | CuPc |
| 30 ^a | Zinc (Zn) | 2+ | ZnPc |
| 31 ^a | Gallium (Ga) | 3+ | GaPc (1 axial) |
| 32 ^a | Germanium (Ge) | 4+ | GePc (2 axial) |
| 33 ^a | Arsenic (As) | 3+ | AsPc (1 axial) |
| 39 ^{a,d} | Yttrium (Y) | 3+ | YPc (1 axial), YPc ₂ |
| 40 ^{a,d} | Zirconium (Zr) | 4+ | ZrPc (2 axial), ZrPc ₂ |
| 41 ^a | Niobium (Nb) | 4+ | NbPc (2 axial) |
| 42 ^d | Molybdenum (Mo) | 4+,5+ | MoPc (=O or two axial) ^e |
| 43 ^a | Technetium (Tc) | 4+ | TcPc (?) |
| 44 ^a | Ruthenium (Ru) | 4+ | RuPc (2 axial) |

1.3 Metal phthalocyanines

Table 1.1. (*cont.*)

| Atomic number | Observed metal | |
|-----------------|-------------------|---|
| | Element (symbol) | oxidation state Abbreviation |
| 45 ^a | Rhodium (Rh) | 3+ RhPc (1 axial) |
| 46 ^a | Palladium (Pa) | 3+ PaPc (1 axial) |
| 47 ^a | Silver (Ag) | 2+ AgPc |
| 48 ^a | Cadmium (Cd) | 2+ CdPc |
| 49 ^a | Indium (In) | 3+ InPc (1 axial) |
| 50 ^a | Tin (Sn) | 4+ SnPc (2 axial), SnPc ₂ and Super Pc |
| 51 ^a | Antimony (Sb) | 4+,5+ SbPc (1 or 2 axial) |
| 56 ^a | Barium (Ba) | 2+ BaPc |
| 57 ^a | Lanthanum (La) | 3+ LaPc (1 axial), LaPc ₂ |
| 58 ^f | Cerium (Ce) | 4+ CePc ₂ |
| 59 ^d | Praseodymium (Pr) | 3+ PrPc (1 axial), PrPc ₂ |
| 60 ^d | Neodymium (Nd) | 3+ NdPc (1 axial), NdPc ₂ |
| 62 ^d | Samarium (Sm) | 3+ SmPc (1 axial), SmPc ₂ |
| 63 ^d | Europium (Eu) | 3+ EuPc (1 axial), EuPc ₂ |
| 64 ^d | Gadolinium (Gd) | 3+ GdPc (1 axial), GdPc ₂ |
| 65 ^d | Terbium (Tb) | 3+ TbPc (1 axial), TbPc ₂ |
| 66 ^d | Dysprosium (Dy) | 3+ DyPc (1 axial), DyPc ₂ |
| 67 ^d | Holmium (Ho) | 3+ HoPc (1 axial), HoPc ₂ |
| 68 ^d | Erbium (Er) | 3+ ErPc (1 axial), ErPc ₂ |
| 69 ^d | Thulium (Tm) | 3+ TmPc (1 axial), TmPc ₂ |
| 70 ^d | Ytterbium (Yb) | 3+ YbPc (1 axial), YbPc ₂ |
| 71 ^d | Lutetium (Lu) | 3+ LuPc (1 axial), LuPc ₂ |
| 72 ^a | Hafnium (Hf) | 4+ HfPc (2 axial), HfPc ₂ |
| 73 ^a | Tantalum (Ta) | 5+ TaPc (2 axial) |
| 74 ^a | Tungsten (W) | 2+,5+ ? |
| 75 ^a | Rhenium (Re) | 3+,4+ RePc (1 or 2 axial) |
| 76 ^a | Osmium (Os) | 4+ OsPc (2 axial) |
| 77 ^a | Iridium (Ir) | 4+ IrPc (2 axial) |
| 78 ^a | Platinum (Pt) | 2+ PtPc |
| 79 ^a | Gold (Au) | 2+ AuPc |

Table 1.1. (*cont.*)

| Atomic number | Element (symbol) | Observed metal | |
|---------------------|-------------------|-----------------|--|
| | | oxidation state | Abbreviation |
| 80 ^{a,g} | Mercury (Hg) | 4+ | HgPc (2 axial), oligomers ^g |
| 81 ^{a,h} | Thallium (Tl) | 3+ | TlPc (1 axial), TlPc ₂ ^h and TlPc ₂ |
| 82 ^a | Lead (Pb) | 2+ | PbPc |
| 83 ^h | Bismuth (Bi) | 3+ | BiPc (1 axial) |
| 89 ^a | Actinium (Ac) | ? | ? |
| 90 ^a | Thorium (Th) | 4+ | ThPc (2 axial), ThPc ₂ |
| 91 ^a | Protactinium (Pa) | 4+ | PaPc (2 axial), PaPc ₂ |
| 92 ^{a,d,j} | Uranium (U) | 4+, 6+ | UPc (2 axial), and Super Pc (2=O) ^e , UPc ₂ |
| 93 ^a | Neptunium (Np) | 4+ | NpPc ₂ |
| 95 ^a | Americium (Am) | 4+ | AmPc ₂ |

^aSee references given by Moser and Thomas (1983a, b).

^bKobayashi *et al.* (1900a).

^cGouterman *et al.* (1981).

^dSee references given by Nicholson (1993).

^eAn axial *oxo*-substituent (see Section 2.2.1) is represented by the symbol =O.

^fHaghighi *et al.* (1992).

^gGeorge *et al.* (1992).

^hJanczak and Kubiak (1983).

ⁱIsago and Kagaya (1994).

^jDay *et al.* (1975).

influence its physical properties (Lever, 1965). The macrocycle usually exists as a dianion (Pc²⁻), although it can be oxidised or reduced to different oxidation states (Section 6.3). Many ions (e.g. Cu²⁺, Co²⁺, Fe²⁺) are held so tightly that they cannot be removed without the destruction of the macrocycle. Indeed, some synthetic routes take advantage of the thermodynamic stability of certain MPcs and use the appropriate metal ion as a *template* during macrocycle formation (Section 2.1). Most metal ions do not cause a significant distortion of the macrocycle, although certain ions are too large to be accommodated completely in the cavity (e.g. Pb²⁺) and therefore lie above the plane of the Pc ring. For metal cations that are normally in an oxidation state of +1, the central nitrogen atoms ligate two ions. However, both cations

cannot be accommodated in the central cavity and so the ions protrude from the plane of the Pc ring and disrupt the intermolecular forces responsible for the well-documented insolubility of most unsubstituted Pcs (Ziolo *et al.*, 1981). Thus, alkali metal derivatives such as Li_2Pc or Na_2Pc possess enhanced solubility in polar organic solvents (Ziolo and Extine, 1981). Metal ions in an oxidation state greater than +2 usually have axial ligands that can also improve solubility (see Section 2.2).

Some large lanthanide (rare-earth) metal cations preferentially complex to two Pc rings. These *sandwich* complexes (see Fig. 2.4 later) are of great interest for their physical properties, especially electrochromism (Section 6.3). Sandwich oligomers formed by HgPc contain up to ten Pc subunits (George *et al.*, 1992). A *super-phthalocyanine*, containing five iminoisoindoline units instead of the usual four, can form by a template reaction around large cations such as uranium oxide (Day *et al.*, 1975) and Sn^{4+} (Kraut and Ferraudi, 1988). Conversely, a *sub-phthalocyanine*, with only three iminoisoindoline subunits, can be prepared by a template reaction around the small borane cation. Sub-Pcs are used to prepare asymmetrically substituted Pcs (Section 2.5) by a ring expansion reaction with an additional diiminoisoindoline derivative (Kobayashi *et al.*, 1990a; Weitemeyer *et al.*, 1995).

1.4 A gift to molecular physics

The remarkable stability of Pcs has resulted in their use in many landmark experiments in molecular physics. For many new experimental techniques they have bridged the gap between crystalline inorganic materials (e.g. metals and ionic crystals) originally used to develop the technique and their application to molecular materials.

Linstead showed that H_2Pc and most MPcs could be purified by sublimation *in vacuo* to form large single crystals. Suitable crystals (exclusively β -type, with the exception of PtPc – Section 3.1) were donated to J. Monteath Robertson (1900–89), a pioneer of organic crystallography, who was then working at The Royal Institution, London. Robertson had developed techniques, extrapolated from those of his mentor Bragg, for determining the crystalline arrangement of organic molecules with known molecular structures (Robertson, 1953). Fortunately, Pcs were highly suited to Robertson's techniques, which had been derived from the study of single crystals of the simple planar aromatic hydrocarbons naphthalene and anthracene (Arnott, 1994). Hence, H_2Pc became the 'first organic structure to yield to an absolutely direct X-ray analysis' (Robertson, 1935). The derived structures confirmed those proposed by Linstead and illustrated the electronic delocalisation of the Pc π -electron system consistent with its aromatic character (Fig. 1.2(a)).

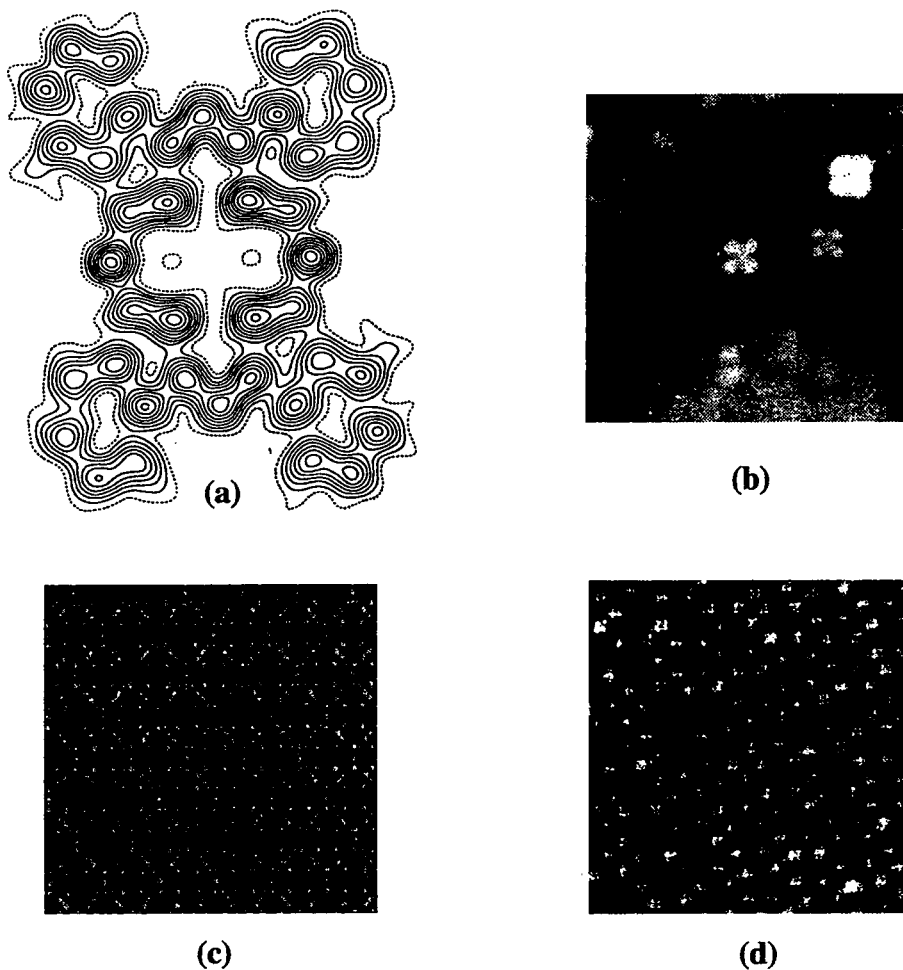


Figure 1.2. Sub-molecular-resolution images of Pc. (a) Robertson's original electron density map of H_2Pc obtained from a single β -crystal X-ray diffraction study (Robertson, 1936). Each contour line represents a density increase of one electron per \AA^2 . The molecule appears distorted because it is projected along the b -axis. (b) A field-emission microscope image of CuPc adsorbed on a fine tungsten tip (Melud and Müller, 1958). (c) A high-resolution electron micrograph of a sublimed film of chlorinated CuPc (Kobayashi and Isoda, 1993). (d) A scanning tunnelling microscopy image of a sublimed film of CuPc (Lu *et al.*, 1996). All images are reproduced with permission.

Müller (1950) reported the first *direct* image of a molecule using field-emission microscopy. CuPc molecules, sublimed onto a fine platinum electrode maintained at liquid nitrogen temperature *in vacuo*, gave a pattern on a fluorescent screen at high voltage. The classic 'four-leaf clover' shape of the molecule is clearly discernible from the image (Fig. 1.2(b)).

A more generally applicable direct imaging technique, which is suitable for detailed crystallographic structure determination, is high-resolution electron

microscopy (HREM). Uyeda *et al.* (1972) obtained the first HREM molecular images from a chlorinated Pc. The exceptional stability of this compound allowed the images to be obtained before the destruction of the material by the intense electron beam needed for such high resolutions. Subsequently, minimum-exposure techniques (Kobayashi and Isoda, 1993) provided superb images of the molecular arrangement within Pc films (Fig. 1.2(c)). The recently developed technique of scanning tunnelling microscopy (STM) has also yielded some interesting molecular images of Pcs (Fig. 1.2(d)) adsorbed on metal surfaces (Gimzewski *et al.*, 1987; Lu *et al.*, 1996) and is useful for the determination of film structure. In addition, Pcs sublimed onto metal surfaces were chosen for one of the first investigations of organic materials by low-energy electron diffraction (LEED) (Buchholz and Somorjai, 1977).

Eley (1948) first studied the electronic conduction through an organic material using Pc crystals and the Pcs still constitute the most thoroughly investigated family of molecular electronic materials (Chapter 5). The following chapters will demonstrate the continued importance of the Pcs in molecular physics.

1.5 A brief note on Pc nomenclature

An unambiguous system for compound nomenclature is required to distinguish the many Pc derivatives referred to throughout this book. For each Pc derivative, Chapter 2 gives the abbreviation together with a diagram of its molecular structure. In addition, a summary of the nomenclature system is given at the beginning of the book.

The cation(s) present in the central cavity is denoted simply by the standard notation listed in Table 1.1. In addition, many of the Pcs described in subsequent chapters possess substitution of the organic skeleton. Therefore, a system of abbreviations is necessary to avoid the long-winded nature of Pc nomenclature demanded by the IUPAC system. Figure 1.1 shows the accepted numbering system of the Pc ring. There are sixteen possible sites for macrocycle substitution associated with the four benzo-subunits. The 2,3,9,10,16,17,23,24 carbon atoms are termed the *peripheral* (*p*) sites and the 1,4,8,11,15,18,22,25 carbon atoms are denoted the *non-peripheral* (*np*) sites.

The abbreviation *t* signifies a peripherally tetra-substituted Pc, which is usually composed of four isomers (see Fig. 2.7 later). For example, metal-free tetra-*tertiary*-butyl Pc is abbreviated to H₂Pc-*t*-tb. Note that the substituents attached to the macrocycle are placed after Pc in the abbreviated form. There have been no reports concerning the material properties of non-peripheral tetra-substituted Pcs, although a synthetic route has been established (George and Snow, 1995). In contrast, there are important materials based on octa(*o*)-substituted Pcs both with peripheral and with non-peripheral substituents and

these are distinguished by the abbreviations *op* and *onp*, respectively. For example, the liquid-crystalline compound 1,4,8,11,15,18,22,25-octa-hexylphthalocyaninatonicel(II) abbreviates to NiPc-*onp*-C₆ where C₆ denotes that the eight non-peripheral alkyl substituents each contain six carbon atoms (i.e. hexyl, -C₆H₁₃).

Any axial ligands (*a*) attached to the central cation are presented before the ion in the abbreviated structure. For example, the Pc derivative 2,3,9,10,16,17,23,24-octadodecyloxyphthalocyaninatosilicon(IV) dihydroxide mercifully abbreviates to *a*-(HO)₂SiPc-*op*-OC₁₂.

1.6 The Pc literature

There is a vast and rapidly expanding literature related to Pcs consisting of reviews, primary publications in scientific journals and patents. The subject matter of this book is restricted to condensed phase properties and is not intended as a general survey of all areas of Pc science. Some very important areas of Pc research are not reviewed or are given merely the briefest consideration. These include the recent and encouraging reports of the use of Pcs in photodynamic cancer therapy (Rosenthal, 1991) and the many patents describing Pcs as colorants (Moser and Thomas, 1983a, b). Listed below are recommended review articles, with self-explanatory titles, that are of relevance to Pc materials:

The Phthalocyanines (Lever, 1965)

Phthalocyaninatometal and Related Complexes with Special Electronic and Optical Properties (Schultz *et al.*, 1991)

Absorption and Magnetic Circular Dichroism Spectral Properties of Phthalocyanines Part 1: Complexes of the Pc²⁻ Dianion (Stillman and Nyokong, 1989)

Organic Photoconductive Materials: Recent Trends and Developments (Law, 1993)

Third-Order Nonlinear Optical Response in Organic Materials: Theoretical and Experimental Aspects (Brédas *et al.*, 1994)

Nonlinear Optical Properties of Metallo-Phthalocyanines (Nalwa and Shirk, 1996)

Electrochromism and Display Devices (Nicholson, 1993)

Functional Supramolecular Materials. Self-assembly of Phthalocyanines and Porphyrines (van Nostrum and Nolte, 1996)

Phthalocyanine Based Liquid Crystals: Towards Submicronic Devices (Simon and Bassoul, 1993)