Octabutoxyphthalocyanine, a New Electron Donor†

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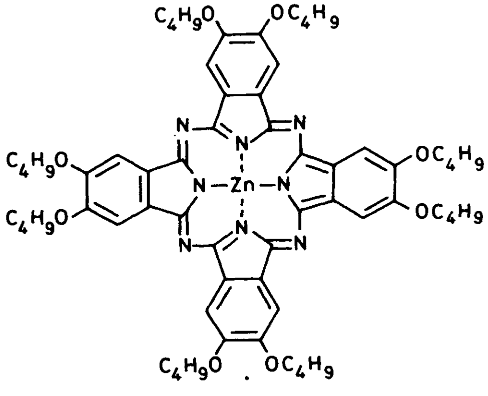
The preparation of the 2,3,9,10,16,17,23,24-octabutoxyphthalocyanine zinc complex (**1**) is described. The electron-donating groups influence the properties of the compound. The oxidation–reduction potentials studied by cyclic voltammetry in solution shift by *ca*. 20 mV in the cathodic direction showing easier oxidation and harder reduction of the ligand of (**1**) compared to unsubstituted phthalocyanines. The interaction with iodine results in the formation of iodine complexes. The electrical conductivities are mentioned.

Low molecular weight phthalocyanines exhibit a great variety of interesting properties. These are concerned with the interaction of electrons with the aromatic π-electron rich phthalocyanine system, in solution or in the solid state.[1,2] In solution the phthalocyanines show multiple reduction and oxidation steps,[3,4] and photocatalytic activity in photoredox reactions.[5,6] In the solid state great variability in the electronic conductivity exists,[2,7] and excellent electrochemical[2,8] and photovoltaic[2,7,9] activities, and photoconductivities[10] have been reported. Substituents on the phthalocyanine ligand influence the solution and solid-state properties to a large degree. Such properties have been studied using the 2,3,9,10,16,17,23,24-octacyanophthalocyanine[11] ligand containing strong electron-withdrawing groups.[4,8] In this paper we report the synthesis, and some properties, of the zinc complex of 2,3,9,10,16,17,23,24-octabutoxyphthalocyanine, (**1**), containing electron-donating groups. The zinc complex was selected because, in the phthalocyanine core, this metal ion exhibits a stable oxidation state during the electrochemical measurements. In contrast to the presence of eight methoxy substituents,[12] the eight butoxy substituents lead to good solubility in organic solvents. This is necessary in order to study the properties in the solution state.

Experimental

Measurements.—Electrochemical measurements were carried out under an argon atmosphere using a three-electrode cell (working electrode, Pt wire; reference electrode, Ag–0.1 mol dm^{-3} $AgNO_3$ in acetonitrile; counter-electrode, Pt sheet) in dry distilled solvents containing 3 × 10^{-4} mol dm^{-3} (**1**) and recrystallized 0.1 mol dm^{-3} $[NBu^n{}_4]ClO_4$ with a scan rate of 200 mV s^{-1}. Measurements on the electrical conductivity were performed using pressed powder pellets (two probe method) as previously described.[13]

1,2-*Dibromo*-4,5-*dibutoxybenzene* (**2**).—Bromine (288 g, 1.8 mol) was added dropwise, at 1—5 °C, to a solution of 1,2-dibutoxybenzene[14] (200 g, 0.9 mol) in CCl_4 (360 cm^3) with stirring. The solution was shaken with dilute aqueous solutions (5%) of $NaHSO_3$ (2 × 300 cm^3) and NaOH (2 × 300 cm^3), and then with water. After drying with $CaCl_2$ and evaporation of the solvent, the viscous oil (50 g) was dissolved in a mixture of methanol (50 cm^3) and chloroform (3 cm^3). Pure slightly yellow crystals of (**2**) precipitated at −60 °C (150 g, 48%), m.p. 29 °C (Found: C, 44.00; H, 5.35. Calc. for $C_{14}H_{20}Br_2O_2$: C, 44.25; H, 5.30%). ^1H N.m.r. ($CDCl_3$), δ 7.05 (2 H, s), 3.95 (4 H, t), and 2.0—2.8 (14 H, m).



(**1**)

1,2-*Dibutoxy*-4,5-*dicyanobenzene* (**3**).—Compound (**2**) (57 g, 0.15 mol) and CuCN (40.5 g, 0.45 mol) were heated in dry dimethylformamide (dmf) (1.2 l) for 8 h. The mixture was poured into aqueous ammonia solution (5 l) with stirring. The isolated product was dissolved in acetone (500 cm^3) with heating. The residue was washed with aqueous ammonia solution and recrystallized three times, on addition of active carbon, to give colourless needles of (**3**) (9 g, 22%), m.p. 137 °C (Found: C, 70.35; H, 7.50; N, 10.25. Calc. for $C_{16}H_{20}N_2O_2$: C, 70.55; H, 7.40; N, 10.30%). ^1H N.m.r. ($CDCl_3$), δ 7.1 (2 H, s), 4.0 (4 H, t), and 2.0—2.8 (14 H, m).

Zinc Complex, (**1**).—Compound (**3**) (2.18 g, 8 mmol) and anhydrous zinc acetate (0.37 g, 2 mmol) were mixed together in an ampoule which was flushed with argon and then sealed under vacuum. The tube was heated for 4 h at 250 °C. The dark green product was treated with 0.001 mol dm^{-3} aqueous HCl (100 cm^3) and then acetone (100 cm^3). After Soxhlet extraction with methanol the reaction product was dried over P_4O_{10} under vacuum at 150 °C. Yield 43% (Found: C, 66.45; H, 7.00; N, 9.80; O, 10.95; Zn, 5.70. Calc. for $C_{64}H_{80}N_8O_8Zn$: C, 66.55; H, 7.00; N, 9.70; O, 11.10; Zn, 5.65%). U.v.–visible spectrum in pyridine 677 (ε 1.32 × 10^{-5} dm^3 mol^{-1} cm^{-1}), 645(sh) (0.212), 610 (0.219), and 362 nm (0.567); in concentrated sulphuric acid: 827, 729, 450, 310, and 280(sh). Field desorption mass spectrum: 1 151 (M − H)$^+$.

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† *Non-S.I. units employed:* bar = 10^5 Pa, eV ≈ 1.6 × 10^{-19} J.

Table. U.v–visible absorptions and half-wave potentials of some phthalocyanines

	$\lambda_{max.}$/nm		Half-wave potentials in dmf (V *vs.* s.c.e.)[a]				
Compound	dmf	H_2SO_4	$E_{\frac{1}{2}}^{I}$(ox.)	$E_{\frac{1}{2}}^{I}$(red.)	$E_{\frac{1}{2}}^{II}$(red.)	$E_{\frac{1}{2}}^{III}$(red.)	$E_{\frac{1}{2}}^{IV}$(red.)
(**1**)	678, 622, 352	827, 729, 450, 310, 280(sh)	0.50	−1.06	−1.53[b]		
[ZnL^1][c,d]	667, 602, 335	783, 696, 434, 304, 230, 204	0.67	−0.86	−1.30	−1.85	−2.25
[ZnL^2][d,e]	694, 654, 400, 345	756(sh), 735, 697, 663, 390, 340, 227, 207		−0.15	−0.50	−1.10	−1.35

[a] s.c.e. = saturated calomel electrode. [b] In pyridine. [c] Unsubstituted phthalocyanine zinc complex. [d] Half-wave potentials from refs. 3 and 4. [e] 2,3,9,10,16,17,23,24-Octacyanophthalocyanine zinc complex.

Iodine Complex of (**1**) *prepared from Solution*.—Complex (**1**) (231 mg, 0.02 mmol) was dissolved in toluene (200 cm^3). A solution of iodine (5.1 mg, 0.02 mmol) dissolved in toluene (200 cm^3) was added with stirring. The resulting black precipitate was filtered off by suction and dried (20.3 mg, 69%) {Found: C, 51.70; H, 5.50; I, 21.45; N, 7.40; O, 8.80. Calc. for $C_{64}H_{80}I_{2.5}N_8O_8Zn$ [(**1**)·$(I_2)_{1.25}$]: C, 52.20; H, 5.50; I, 21.55; N, 7.60; O, 8.70%}.

Iodine Complex of (**1**) *prepared from Gaseous Iodine*.—(**1**) (50.0 mg, 0.043 mmol) and iodine (50 mg, 0.2 mmol) were placed in a desiccator in separate trays at 100 mbar. The maximum weight increase was 8.5 mg after *ca.* 24 h. [Composition after weight increase: (**1**)·$(I_2)_{0.77}$.]

Results and Discussion

The phthalocyanine complex (**1**) was prepared by the 'nitrile method' employing 1,2-dibutoxy-4,5-dicyanobenzene (**3**). The nitrile, (**3**), was obtained by the reaction of 1,2-dibutoxybenzene with Br_2, to give 1,2-dibromo-4,5-dibutoxybenzene (**2**), followed by the Rosenmund–von-Braun reaction with CuCN in dmf. All chemicals were inexpensive and available commercially. Therefore, large scale preparation of the compounds is possible. Unlike the analogous octamethoxy compound,[11] the octabutoxy-substituted zinc chelate exhibits solubility in organic solvents such as toluene, pyridine, dmf, and CCl_4. Solubility in alcohols, ethers, and dimethyl sulphoxide (dmso) is very poor. Complex (**1**) is a suitable material for the preparation of Langmuir-Blodgett films.

Complex (**1**) contains electron-donating groups which interact with electron acceptors. The reaction with iodine leads to charge transfer complexes (see Experimental section). Iodine is removed by heating the complexes at *ca.* 50 °C. When dissolved in organic solvents complex (**1**) decomposes after several hours or days, depending on the solvent, in the presence of the electron acceptor oxygen, and more rapidly in the presence of oxygen and irradiation with visible light. Solutions under inert gas with exclusion of light are stable over several days. Storage of solid (**1**) does not lead to decomposition.

The u.v.–visible spectrum of (**1**) resembles absorptions of unsubstituted metal-containing phthalocyanines with D_{4h} symmetry (Table).[1,2] Therefore the transitions of the chromophore have not been altered. In dmf, substituents with electron-donating and electron-accepting groups only result in small shifts of the long wavelength band (*Q* band) in comparison with unsubstituted phthalocyanines. In concentrated sulphuric acid (95—97%) the protonation of the bridging nitrogen atoms leads to a strong long-wave shift of the *Q* band.[15,16] The degree of shift depends on the extent of protonation. The shift increases with increasing basicity of the ligand depending on the substituents: octacyanophthalocyanine < phthalocyanine < (**1**).

Complex (**1**) exhibits a typical cyclic voltammogram with multiple oxidation and reduction waves as reported for other phthalocyanines in non-aqueous media.[2–4] The products of the first oxidation and the reductions (Table) are stable on the voltammetric time-scale. From the general shape, all waves appear to be reversible one-electron transfers and Nernstian, with peak splittings ($\Delta E_p = E_{pa} - E_{pc}$) of the order of 80 mV. All redox steps are ligand centred. The half-wave potentials of the oxidation and reductions exhibit a cathodic shift of *ca.* 0.20 mV compared to the unsubstituted zinc phthalocyanine. For both phthalocyanines the difference between $E_{\frac{1}{2}}^{I}$(ox.) and $E_{\frac{1}{2}}^{I}$(red.) which resembles the energy difference between highest occupied and lowest unoccupied molecular orbitals (h.o.m.o and l.u.m.o.) is around 1.6 V. In contrast, the cyano groups in octacyanophthalocyanine lower the h.o.m.o. and l.u.m.o. orbitals by *ca.* 0.7 eV compared to the unsubstituted phthalocyanine (anodic shift of the half-wave potentials). The influence of the cyano groups on the average electron density of the ligand is stronger than the opposite effect of the alkoxy substituents. Also with porphyrins, the dependence of redox behaviour on substituents has been described.[17,18]

As is well known, the interaction of phthalocyanines with electron acceptors enhances the electrical conductivity in the solid state.[1,7] The conductivity of (**1**) increases at 25 °C from 1.4×10^{-11} S cm^{-1} to 3.6×10^{-6} S cm^{-1} for (**1**)·$(I_2)_{1.25}$ (Table). The conductivity of (**1**) is similar to that of the octacyanophthalocyanine–zinc complex[10] ($\sigma = 2.9 \times 10^{-10}$ S cm^{-1}) but higher than that of the unsubstituted phthalocyanine–zinc complex ($\sigma = 10^{-14}$ S cm^{-1}).[19] The interaction with iodine does not enhance the conductivity by many orders of magnitude than already reported for the unsubstituted phthalocyanine–zinc complex.[2,7]

Acknowledgements

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References

1 F. H. Thomas and A. L. Thomas, 'Phthalocyanine Compounds,' Reinhold, New York, 1963; 'The Phthalocyanines,' CRC Press, Boca Raton, 1983.

2 D. Wöhrle, *Kontakte*, 1985, **3**, 38; 1986, **1**, 24.

3 A. B. P. Lever, S. Licoccia, K. Magnell, P. C. Minor, and B. S. Ramaswamy, *Adv. Chem. Ser.*, 1982, **201**, 237.

4 A. Louati, M. El. Meray, J. J. André, J. Simon, K. M. Kadish, M. Gross, and A. Girardeau, *Inorg. Chem.*, 1985, **24**, 1175.

5 J. R. Darwent, P. Douglas, A. Harrimann, G. Porter, and M-C. Richoux, *Coord. Chem. Rev.*, 1983, **44**, 83.

6 H. Ohtani, T. Kobayashi, T. Tanno, A. Yamada, D. Wöhrle, and T. Ohno, *Photochem. Photobiol.*, 1986, **44**, 125.

7 J. Simon and J-J. André, 'Molecular Semiconductors,' Springer, Berlin, 1985.

8 D. Wöhrle, B. Schumann, V. Schmidt, and N. Jaeger, *Makromol. Chem. Makromol. Symp.*, 1987, **8**, 195.
9 C. W. Tang, *Appl. Phys. Lett.*, 1986, **48**, 183.
10 H. Meier, W. Albrecht, D. Wörhle, and A. Jahn, *J. Phys. Chem.*, 1986, **90**, 6349.
11 D. Wöhrle, G. Meyer, and B. Wahl, *Makromol. Chem.*, 1980, **181**, 2127.
12 J. Metz, O. Schneider, and M. Hanack, *Inorg. Chem.*, 1984, **23**, 1065.
13 G. Manecke and D. Wöhrle, *Makromol. Chem.*, 1967, **116**, 36.
14 K. R. Irani, N. L. Phalnikar, and K. S. Nargund, *J. Univ. Bombay* (*Science*), 1950, **18**, 1.
15 D. L. Ledson and M. V. Twigg, *Inorg. Chim. Acta*, 1975, **13**, 43.
16 S. Gaspard, M. Verdaguer, and R. Viovy, *J. Chem. Res.*, 1979, 271 (*S*).
17 K. M. Kadish, X. Q. Lin, J. Q. Ding, Y. T. Wu, and C. Araullo, *Inorg. Chem.*, 1986, **25**, 3236 and refs. therein.
18 K. M. Kadish, B. Boisselier-Cocolios, B. Simonet, H. Ledon, and P. Cocolios, *Inorg. Chem.*, 1985, **24**, 2148 and refs. therein.
19 M. Mossoyan-Deneux, D. Benlian, M. Pierrot, and A. Fournel, *Inorg. Chem.*, 1985, **24**, 1878.

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