

## Binuclear 'Clamshell' Metallophthalocyanines

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Polynuclear multi-electron transfer catalysts for photo- and electrocatalytic processes are becoming of increasing importance.

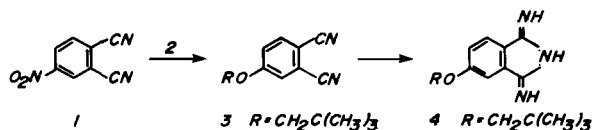
Porphyrin dimers [1–5] have been synthesized to study the electrocatalytic reduction of oxygen [3]. Usually these species permit the two-electron reduction of oxygen to hydrogen peroxide. The desired four-electron reduction to water has only been achieved with a specific di-cobalt cofacial porphyrin dimer [3]. Such systems are not very stable.

Phthalocyanines (Pc) are stable under thermal and photochemical conditions [6] and the four-electron reduction of oxygen is catalyzed by Fe(II)Pc in alkali [7].

Binuclear phthalocyanines are expected to be much more efficient but their synthesis has been hindered by the notorious insolubility of phthalocyanine monomers. Polymeric Pcs and polymer bound Pc have been prepared to simulate the geometry of binuclear phthalocyanines but these systems are ill-defined and difficult to optimise [8]. While substituted and soluble phthalocyanines have been prepared [9–12], well defined binuclear Pc systems have not previously been characterised.

We report here binuclear 'clamshell' metal free and metallated phthalocyanines which contain a stable five atom bridge, and which are freely soluble in many organic solvents.

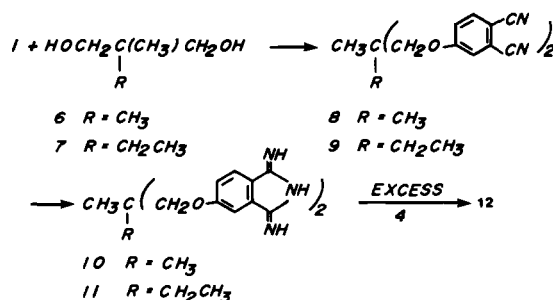
4-Nitrophthalonitrile (1) [12, 13] reacts with 2,2-dimethyl-1-propanol (neopentanol) (2) [14] to yield 4-neopentoxypthalonitrile (3). Conversion of 3 into its isoindoline 4 [15] and self-condensation of 4 in 2-N,N-dimethylaminoethanol gave, after flash



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chromatography [16] using toluene as eluant, 2,9,16,23-tetraneopentoxypthalocyanine (5a, 45% yield) as a mixture of isomers [17]. Phthalocyanine 5a is soluble in organic solvents, indeed to the extent of 800 g/L in methylene chloride. Conversion [6] of 5a into its copper(II) 5b, cobalt(II) 5c and zinc 5d [10, 18] derivatives was readily achieved.

Soluble binuclear phthalocyanines were prepared by the generation of bisalkoxyphthalonitriles from symmetrical diols. Treatment [14] of 1 with 2,2-dimethyl-1,3-propanediol (6), and with 2-ethyl-2-methyl-1,3-propanediol (7) gave the bis-phthalonitriles 1,3-bis(3,4-dicyanophenoxy)-2,2-dimethylpropane (8) and 1,3-bis(3,4-dicyanophenoxy)-2-ethyl-2-methylpropane (9).



Compounds 8 and 9 were converted to their isoindolines (10 and 11 respectively) and condensed with an excess of 4 (25 equivalents) to give 1,3-bis(9,16,23-trineopentoxypthalocyaninoxy)-2,2-dimethylpropane (12a, 17% yield) and 1,3-bis(9,16,23-trineopentoxypthalocyaninoxy)-2-ethyl-2-methylpropane (13, 10% yield) respectively, as a mixture of isomers [17], along with large amounts of monomer 5a. These binuclear complexes are also extremely soluble in organic solvents and can be readily separated from the monomer using flash chromatography and toluene/2-methoxyethanol mixtures previously described [12]. Metal free 12a was readily converted to the di-copper(II) 12b, and di-cobalt(II) 12c derivatives.

Compounds 3, 8 and 9 all gave parent ions in their mass spectra in the ET mode and phthalocyanines 5a–d, 12a–c and 13 exhibited parent ions using the FAB technique [19, 20].

These 'clamshell' species can be open with no interaction between Pc units or closed with Pc–Pc interaction. ESR, visible spectroscopy and electrochemistry (Tables I, II) reveal that the metal complexes 12b,c exist normally in the closed form in equilibrium with a small amount of open form. Thus the monomeric systems 5b,c show ESR and visible spectra in organic solvents typical of monomeric MPcs [6, 20] (Table II) and are models for the open form of the 'clamshell'. The electronic

TABLE I. Electrochemical Data.

Species	Solvent	Electrochemical Potentials <sup>a</sup>			
		ML <sup>+</sup> /ML	M(II)L/M(I)L	ML/ML <sup>-</sup>	ML <sup>-</sup> /ML <sup>2-</sup>
Mononuclear derivatives					
H <sub>2</sub> 5a	DCB			-1.42(65)	-1.80(105)
Cu 5b	DCE			-1.37(80)	-1.75(90)
Co 5c	DCB	+0.36	-0.94(75)	-2.06(65)	<sup>b</sup>
Zn 5d	DCB	-0.02(95)		-1.55(75)	-1.83(75)
Binuclear derivatives					
Cu <sub>2</sub> 12b	DCB	+0.33 <sup>c</sup>		-1.53(95)	-1.80(115)
Co <sub>2</sub> 12c	DCB	+0.06	-0.95(75)	-2.07(100)	<sup>b</sup>

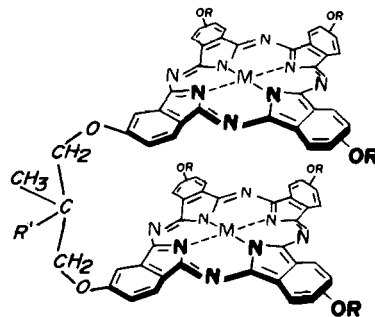
<sup>a</sup>All potentials are with respect to the ferrocenium/ferrocene couple as internal calibrant in dichloroethane (DCE) or dichlorobenzene (DCB) as indicated using cyclic voltammetry and differential pulse voltammetry [24]. The mononuclear complex concentration was ca. 5 mM, and the binuclear complex ca. 2.5 mM, both with 0.5 M tetrabutylammonium perchlorate as supporting electrolyte. Potentials may be referenced to NHE by adding 0.400 V. <sup>b</sup>No further redox couples observed before solvent 'cut-off'. <sup>c</sup>A double wave was observed indicating stronger aggregation following oxidation. The potential reported is that of the better defined couple.

TABLE II. Representative Electronic Spectra.<sup>a</sup>

Species	Soret region	Q region
Mononuclear derivatives (in dichloromethane)		
H <sub>2</sub> 5a	341(4.57) 390(4.27)	608(4.17) 642(4.36) 670(4.73) 705(4.79)
Cu 5b	338(4.82) 380(4.42)	614(4.58) 680(5.09)
Co 5c	335(4.74) 390(4.31)	620(4.52) 680(4.97)
Zn 5d	344(4.91) 384(4.57)	614(4.60) 680(5.18)
Binuclear derivatives (in dichloroethane)		
H <sub>2</sub> 12a	337(5.01) 383(4.71)	612(4.79) 636(4.91) 668(4.83) 701(4.70)
Cu <sub>2</sub> 12b	336(5.11) 396(4.72)	626(5.06) 676(4.93)
Co <sub>2</sub> 12c	320(5.00) 390(4.56)	626(4.93) 673(4.97)

<sup>a</sup>Reported in solvent indicated as  $\lambda_{\max}$  nm (log  $\epsilon$ ). In the mononuclear metallated complexes the lower wavelength of the two Q bands is a vibrational overtone. In the binuclear metallated complexes, the two Q bands arise as a consequence of the intramolecular aggregation and the presence of an open/closed equilibrium.

spectra of 12b,c show double  $\pi\text{--}\pi^*$  bands near 650 nm (Q band) shifted to the blue, typical of aggregation [21]. The aggregation is intramolecular rather than intermolecular since it is almost unaffected by dilution. Increasing the temperature of a dichlorobenzene solution of 12c from 20 °C to 70 °C causes a small increase in the 673 nm (mainly open) transition, and a small decrease in the 626 nm (mainly closed) transition. Complex 12b behaves similarly. Addition of 1 M pyridine (sufficient for five coordination [22]) does not open the di-cobalt(II) 'clamshell' 12c. However addition of stronger ligands such as cyanide ion or n-octylamine forms six coordinate open complexes (as followed by the loss of 620 nm Q band feature) which have undergone irreversible oxidation to an open di-cobalt(III) 'clamshell' 14 in air. Similarly addition of tetraethylammonium hydroxide to metal free 12 causes



- 12 a  $R = \text{CH}_2\text{C}(\text{CH}_3)_3, R' = \text{CH}_3, M = \text{H}_2$   
 b  $R = \text{CH}_2\text{C}(\text{CH}_3)_3, R' = \text{CH}_3, M = \text{Cu}$   
 c  $R = \text{CH}_2\text{C}(\text{CH}_3)_3, R' = \text{CH}_3, M = \text{Co}$   
 13  $R = \text{CH}_2\text{C}(\text{CH}_3)_3, R' = \text{CH}_2\text{CH}_3, M = \text{H}_2$

formation of the di-anion **12d** which has an open conformation.

A closed conformation is expected to exhibit electrochemical redox couples at potentials negative with respect to the corresponding couples of the monomer [23]. However if the open-closed equilibrium is fast on the electrochemical time scale, the electrochemistry of the binuclear form may appear like that of the monomeric form. This is the case for the reduction potentials which require (Table I) that the binuclear metal complexes 'open' before reduction. However **12c** oxidises at a potential about 300 mV more negative than the monomer **5c**, consistent with the closed conformation.

The monomer forms **5b,c** show esr hyperfine coupling to the central metal, and super-hyperfine to equatorial nitrogen atoms [20, 22]. The closed nature of binuclear **12b,c** induces relaxation such that only broad unresolved signals are seen, centered near  $g = 2$ .

Unmetallated phthalocyanine fluoresces at 705 nm through emission from the  $\pi\text{--}\pi^*$  singlet (Q) state. An equilibrium mixture of open and closed 'clamshell' **13** shows no significant room temperature emission from the closed component due to intramolecular self-quenching. However the small proportion of open 'clamshell' **13** in equilibrium, does emit and indeed behaves exactly like a mononuclear unmetallated phthalocyanine [25]. Assuming, not unreasonably, that the molar intensity of emission of a fully open 'clamshell' **13** would be twice that of the corresponding mononuclear species **5a**, it is possible to use the intensity of emission to determine the [closed]/[open] equilibrium constant. These constants are dependent upon solvent and vary from 70 in chloroform to 9 in *o*-dichlorobenzene (at room temperature).

At liquid nitrogen temperature the equilibrium is shifted almost totally to the closed form, and emission from the open form is only weakly detectable. However, under such conditions, weak emission from the closed form of **13** can be observed at 760 nm. The energy shift of  $1000\text{ cm}^{-1}$  is a measure of the energy of interaction between the two halves of the closed 'clamshell' **13**.

Further details of the chemistry, electrocatalytic and photocatalytic properties of these unusual species will be published in due course.

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#### References

- 1 D. Jeyakumar and V. Krishnan, *Nouv. J. Chim.*, **7**, 697 (1983).
- 2 F. P. Schwarz, M. Gouterman, Z. Muljani and D. H. Dolphin, *Bioinorg. Chem.*, **2**, 1 (1972).
- 3 J. P. Collman, P. Denisevich, Y. Konai, M. Marrocco, C. Koval and F. C. Anson, *J. Am. Chem. Soc.*, **102**, 6027 (1980); *ibid.*, *J. Electroanal. Chem.*, **101**, 117 (1979); J. P. Collman, F. C. Anson, C. E. Barnes, C. S. Bencosme, T. Geiger, E. R. Evitt, R. P. Kreh, K. Meier and R. B. Pettman, *J. Am. Chem. Soc.*, **105**, 2694 (1983).
- 4 (a) C. K. Chang, *J. Am. Chem. Soc.*, **99**, 2819 (1977); (b) N. E. Kagan, D. Mauzerall and R. B. Merrifield, *J. Am. Chem. Soc.*, **99**, 5484 (1977).
- 5 J. E. Baldwin, M. J. Crossley, T. Klose, E. A. O'Rear and M. K. Peters, *Tetrahedron*, **38**, 27 (1982).
- 6 A. B. P. Lever, *Adv. Inorg. Chem. Radiochem.*, **7**, 27 (1965).
- 7 J. Zagal, R. K. Sen and E. Yeager, *J. Electroanal. Chem.*, **83**, 207 (1977); J. Zagal, P. Bindra and E. Yeager, *J. Electrochem. Soc.*, **127**, 1506 (1980); E. Yeager, J. Zagal, B. Z. Nikolic and R. R. Adzic, *Proc. Electrochem. Soc.*, **80**, 436 (1979).
- 8 M. Savy, P. Andro, G. Bernard and G. Magner, *Electrochim. Acta*, **19**, 403 (1974); **22**, 1315 (1977); NBS Special Publication No. 455, 241 (1975); *Inorg. Chem.*, **18**, 2560 (1979); *J. Electroanal. Chem.*, **111**, 91 (1980).
- 9 (a) S. A. Mikhaleenko, S. V. Barkanova, O. L. Lebedev and E. A. Luk'yanets, *Zh. Obshch. Khim.*, **41**, 2735 (1971); (b) M. Hanack, J. Metz and G. Pawlowski, *Chem. Ber.*, **115**, 2836 (1982).
- 10 (a) G. Pawlowski and M. Hanack, *Synthesis*, 287 (1980); (b) C. Piechocki, J. Simon, A. Skoulios, D. Guillon and P. Weber, *J. Am. Chem. Soc.*, **102**, 5245 (1982).
- 11 C. C. Leznoff and T. W. Hall, *Tetrahedron Lett.*, **23**, 3023 (1982).
- 12 T. W. Hall, S. Greenberg, C. R. McArthur, B. Khouw and C. C. Leznoff, *Nouv. J. Chim.*, **6**, 653 (1982).
- 13 (a) H. D. K. Drew and D. E. Kelly, *J. Chem. Soc.*, 639 (1941); (b) C. R. Rasmussen, J. F. Gardecki, J. N. Plampin, B. L. Twardzik, B. E. Reynolds, A. J. Molinari, N. Schwartz, W. W. Bennetts, B. E. Price and J. J. Markowski, *J. Med. Chem.*, **21**, 1044 (1978).
- 14 T. M. Keller, T. R. Price and J. R. Griffith, *Synthesis*, 613 (1980).
- 15 P. J. Beach, S. J. Grammatica, O. A. Ossanna and L. Weinberger, *J. Heterocyc. Chem.*, **7**, 1403 (1970).
- 16 W. C. Still, K. Kahn and A. Mitra, *J. Org. Chem.*, **43**, 2923 (1978).
- 17 Compounds **5a-d**, **12a-c** and **13**, most likely exist as a mixture of positional isomers of which the given structures are but one representation.
- 18 Compound **5d** was prepared by the condensation of **3** in the presence of  $\text{ZnCl}_2$  directly by the procedure described in ref. 10a.

- 19 M. L. Gross, E. K. Chess, P. A. Lyon, F. W. Crow, S. Evans and H. Tudge, *Int. J. Spectrom. Ion. Phys.*, **42**, 243 (1982).
- 20 Complete infrared, ultraviolet,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and ESR, microanalytical and mass spectroscopic data will be presented in the full paper.
- 21 (a) H. Sigel, P. Waldmeier and B. Prijs, *Inorg. Nucl. Chem. Lett.*, **7**, 161 (1971);  
(b) K. Bernauer and S. Fallab, *Helv. Chim. Acta*, **54**, 1287 (1961);  
(c) R. D. Farina, D. J. Halko and J. H. Swinehart, *J. Phys. Chem.*, **76**, 2343 (1972).
- 22 (a) P. C. Minor, *Ph.D. Thesis*, York University (1983);  
(b) A. B. P. Lever and P. C. Minor, *Proc. IX Conference on Coordination Chemistry*, Bratislava (1983);  
(c) F. Cariati, D. Galizzioli, F. Morazzoni and C. Busetto, *J. Chem. Soc.*, 556 (1975); 496 (1976).
- 23 P. C. Minor and A. B. P. Lever, *Inorg. Chem.*, **22**, 826 (1983).
- 24 R. R. Gagne, C. A. Koval and G. C. Lisensky, *Inorg. Chem.*, **19**, 2854 (1980).
- 25 Careful control experiments exclude the possibility that the room temperature emission arises from mononuclear contaminants.