μ-Superoxodicobalt Complex of a Cofacial Diporphyrin

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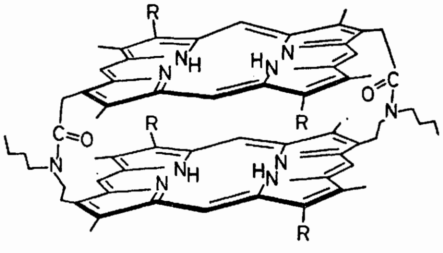
Summary A cofacial diporphyrin (**1**) with an interplanar separation of 4·2 Å has been synthesized; its dicobalt complex reacts with oxygen to give a sandwiched complex.

DIMERIC porphyrins covalently linked in a cofacial configuration have recently been reported.[1-3] It is anticipated that such binuclear metal ligands capable of constraining two metal ions at close distances should possess unusual properties. We here report the formation of a binuclear cobalt–oxygen complex of the cofacial diporphyrin (**1**).



(1)

R = n-hexyl

We have recently described an efficient synthesis for β-substituted porphyrins as well as a high-yield coupling procedure to prepare stacked macrocyclic ligands.[1,4] Employing the same method, we have prepared 2,12-dihexyl-3,8,13,18-tetramethylporphin-7,17-diacetic acid. The acetic acid side chains were then converted into n-butyl substituted amines.[1] Coupling of the diamine and the diacid chloride afforded the composite porphyrin (**1**)† in good yield (40% from monomers). This compound has been characterized by mass spectral as well as elemental analysis. Its n.m.r. spectrum ($CDCl_3$) exhibits a remarkable up-field shift for the nitrogen protons (δ — 8·5 *vs.* δ — 4 for monomer). Absorption maxima λ_{max} (CH_2Cl_2): 373 (Soret) (ϵ 201), 505 (11·7), 540 (8·88), 572 (4·7), and 625 (3·4) nm. By comparison with the monomeric porphyrin it is significant that the Soret band of (**1**) has shifted to the blue by 27 nm. Undoubtedly, the exciton coupling in the dimer must be strong owing to the rather narrow interchromophore separation.[5] This distance can be estimated from the e.s.r. spectrum of the dicopper(II) complex of (**1**); the triplet spectrum shows a zero-field splitting of 0·0415 cm^{-1}, corresponding to a separation of *ca.* 4·2 Å.[6]

When a mixture of 1-triphenylmethylimidazole (*ca.* 10^{-2} M) and the dicobalt(II) complex of (**1**) (*ca.* 10^{-3} M) in toluene-CH_2Cl_2 was exposed to air at room temperature, a μ-peroxo [$Co-O_2-Co$] complex formed immediately. This complex is diamagnetic and has no e.s.r. signals. When a trace of I_2 was added to this solution, a well defined isotropic spectrum was obtained (Figure) consisting of 15 lines (g_{iso} 2·024, $|A_{Co}|$ 10 G). Such a spectrum would be expected if the μ-peroxo dicobalt species underwent oxidation to a μ-superoxo complex in which the two equivalent ^{59}Co nuclei would give a total of $(2 \times 2 \times 7/2)+1=15$ lines.[7] If enriched $^{17}O_2$ (10%) is employed, in addition to the primary 15 lines, weak satelite peaks from molecules containing one

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† Only one of the isomeric structures is shown.

^{17}O atom in the bridge can be detected in the wings. The spacings of the outer two lines are roughly equal to $|A_{Co}|$ and the outermost ^{17}O satelites should have a separation of $14|A_{Co}| + 5|A_{O}|$; therefore, $|A_{O}| = 20{\cdot}2$ G. Observation of the rather small $|A_{Co}|$ but large $|A_{O}|$ provides direct evidence that the unpaired electron largely resides on the oxygen atoms and, thus, supports the notion that such binuclear cobalt–oxygen complexes are best described as $(Co^{III}–\dot{O}_2–Co^{III})$.[8]

The finding that oxygen forms stable sandwiched complexes with binuclear metal diporphyrins is significant in that it demonstrates the feasibility that metal diporphyrins can be developed into useful multielectron reducing materials for molecular oxygen.

We thank the Research Corporation for financial support.

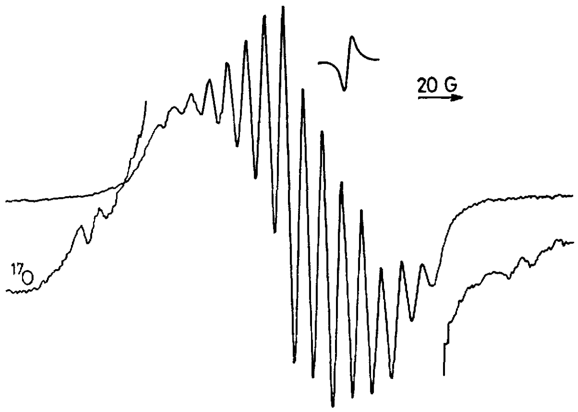

FIGURE. The e.s.r. spectrum of the μ-superoxo [Ph_3C-Im-Co-(P)-O_2-Co(P)-Im-CPh_3] complex derived from (**1**), taken at room temperature in toluene–methylene chloride (Im ≡ imidazole, P ≡ porphyrin). With a 10% ^{17}O enriched sample, the ^{17}O ($m = \pm 5/2$) satelite peaks can be detected in the two wings using higher detector sensitivity.

(*Received*, 23*rd August* 1977; *Com.* **892.**)

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