Molecular Complexes of Vitamin K_3 with a Porphyrin and Chlorophyll

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IT has been postulated that electron transfer in mitochondria and chloroplasts goes *via* charge transfer complexes of the types metal–porphyrin/quinone and chlorophyll/quinone respectively.[1,2] To show that such complexes exist, we studied initially the donor–acceptor complexes of cobalt(II) porphyrins with a number of aromatic nitro-compounds in chloroform.[3] Similar complexes between chlorophyll and the same acceptors have recently been reported.[4] We have now extended both series of observations and shown that these biologically important donors will form charge-transfer complexes with biologically important acceptors—the naphthaquinones. Some information about the structure of the complexes has also been obtained.

The formation of the complexes has been studied by absorption and ^{1}H n.m.r. spectroscopy. The new series of complexes are given in the Table, together with the solvents in which they were studied, and the stability constants which were found. The choice of solvent was determined by the solubility of the components. On formation of the complexes the sharp absorption bands of the donors drop in intensity and are broadened. The Table shows that by comparison with other acceptors vitamin K_3, 2-methylnaphthaquinone, forms weak complexes with the cobalt(II) porphyrin and with chlorophyll. The quinone and both the donors are very similar to molecules which are found in mitochondria and chloroplast electron-transfer chains. The fact that a depression of the donor absorption bands but no new charge-transfer bands are seen with naphthaquinones will make it difficult to study such complexes *in vivo* by absorption spectroscopy. Both donors also form complexes with fluorenone which are approximately one hundred-fold stronger than with the quinone.

TABLE

Cobalt(II) *mesoporphyrin* IX *dimethyl ester–acceptor complexes in dichloromethane*

Acceptor	*K* (moles^{-1} l.)
2,4,7-Trinitrofluorenone	875
Benztrifuroxan	750
Dinitrobenzfuroxan	150
1,3,5-Trinitrobenzene	105
3,5-Dinitrobenzonitrile	50
2,4,6-Trinitrotoluene	8
Vitamin K_3	3·5

Donor–acceptor complexes in diethyl ether

Donor	Acceptor	*K* (moles^{-1} l.)
Co^{II} mesoporphyrin IX dimethyl ester	2,4,7-trinitrofluorenone	3,000
	vitamin K_3	16
Chlorophyll a	2,4,7-trinitrofluorenone	350
	vitamin K_3	1·3

The proton magnetic resonance of 2-methylnaphaquinone (0·058 molar in $CDCl_3$) in the presence of cobalt(II) porphyrin ($7{\cdot}25 \times 10^{-3}$ molar) was measured. The different types of hydrogen show different shifts; benzene (centre of multiplets) 35 c./sec. to high field, H_3 21 c./sec., —Me 12 c./sec. Assuming that the origin of the shifts lies in the pseudo-contact term, the different shifts reflect the distances of the hydrogens from the cobalt unpaired electron. Qualitatively it is likely therefore that the benzene ring is closest to the cobalt. This mapping procedure could be of great value in studying enzyme–substrate complexes where the enzyme contains a paramagnetic centre.

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