# Tricarbonylchromium Complexes of αβγδ-Tetraphenylporphinzinc

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*Summary* Complexes of αβγδ-tetraphenylporphinzinc in which one and two of the phenyl rings are π-substituted with tricarbonylchromium groups have been prepared and characterized.

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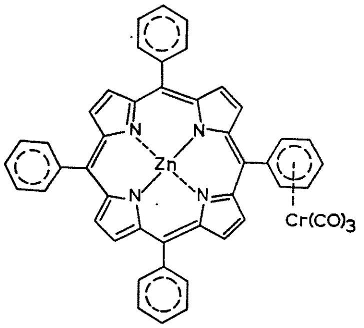
ELECTRON distribution in metallo-porphyrins is of considerable importance in many life processes, for example in photosynthesis and cell energy transfer (cytochromes in particular). We have prepared two complexes of a series the study of which should help the understanding of electron distribution and transfer in the porphyrin system. These are complexes of αβγδ-tetraphenylporphinzinc, Zn(tpp), in which a tricarbonylchromium group is attached to one and two of the phenyl rings.

The complexes were prepared by allowing $Cr(CO)_6$ and Zn(tpp) to react in refluxing di-n-butyl ether in an atmosphere of pure nitrogen. Chromatography of the resulting material on Florisil yielded three bands, a red band, Zn(tpp), a brownish-green band, (I), and a greenish-brown band, (II). Details of the spectra of these compounds are given in the Table. The n.m.r. assignments follow those of Webb and Fleischer for αβγδ-tetraphenylporphin.[1] The CO stretching vibrations and the shifts in phenyl resonances are typical of $Cr(CO)_3$ groups π-bonded to phenyl rings. For example in tricarbonylbenzenechromium the bands at 1977 and 1910 cm$^{-1}$ are assigned to CO stretching vibrations[2] and the phenyl proton resonances in the n.m.r. are shifted 1·67 p.p.m. upfield from benzene.[3]

| | U.v./visible ($CHCl_3$) | I.r. cm$^{-1}$ ($CHCl_3$) | N.m.r. (τ) ($CDCl_3$)[a] | |
|---|---|---|---|---|
| Compound | nm ($10^3\epsilon$) | CO stretching region | β-Pyrrole | Phenyl |
| Zn(tpp) | 420(600), 550(22), 595(6·0) | none | 1·17 | 1·80, 2·23 |
| (I) | 422(230), 562(13), 612(6·3) | 1978, 1910 | 1·11 | 1·81, 2·25;<br>3·33, 4·21 |
| (II) | 424(200), 570(12), 621(6·9) | 1978, 1910 | 1·09 | 1·83, 2·26<br>3·44, 4·20 |

[a] The phenyl resonances were broad and these values represent the centres of the maxima.

When solutions of the complexes in $CHCl_3$ were left for a few days the visible spectra changed to that of Zn(tpp). Heating the solid materials up to 250° gave no visible change, however the visible spectrum in $CHCl_3$ of the material that had been heated above 110° was that of Zn(tpp). This indicates decomposition and this behaviour is typical of tricarbonyl-π-arenechromiums. The n.m.r. spectra of both compounds consist of three main areas, a single band at about τ 1·1 assigned to the β-pyrrole proton resonances, two bands at about 1·8 and 2·2 assigned to proton resonances of phenyl rings without $Cr(CO)_3$ groups attached, and two bands at about 3·3 and 4·2 assigned to proton resonances of phenyl rings with $Cr(CO)_3$ groups attached. For compound (I) the ratio of intensities of proton resonances due to uncomplexed phenyls to that of complexed phenyl is 3 : 1, for compound (II) this ratio is 1 : 1. In both compounds the ratio of intensities of the β-pyrrole resonances to total phenyl is approximately 8 : 20. This led us to suggest a structure for (I) in which a $Cr(CO)_3$ group is π-bonded to one phenyl ring and for (II) in which $Cr(CO)_3$ groups are π-bonded to two of the phenyl rings. The structure for (I) is shown in the Figure. Several isomers are possible for (II).



FIGURE

Preliminary results indicate that similar complexes are formed from other M(tpp) where M is a 1st transition series metal.

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[1] L. E. Webb and E. B. Fleischer, *J. Chem. Phys.*, 1965, **43**, 3100.
[2] D. A. Brown and H. Sloan, *J. Chem. Soc.*, 1962, 3849.
[3] E. O. Fischer and H.-P. Fritz, *Angew. Chem.*, 1961, **73**, 353.