

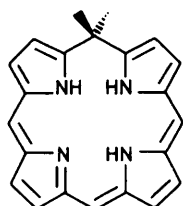
Phlorin † Complex of Gold(III)

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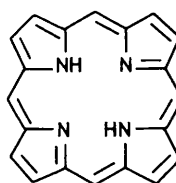
The neutral and air stable complex of gold(III) with phlorin has been prepared and characterized by u.v.-visible, i.r., and ^1H n.m.r. spectroscopy.

It is well known that phlorin (1) has played an important role in chlorophyll chemistry.¹ However, phlorins are usually unstable and easily oxidized to porphyrin (2),² except those having sterically hindered substituents

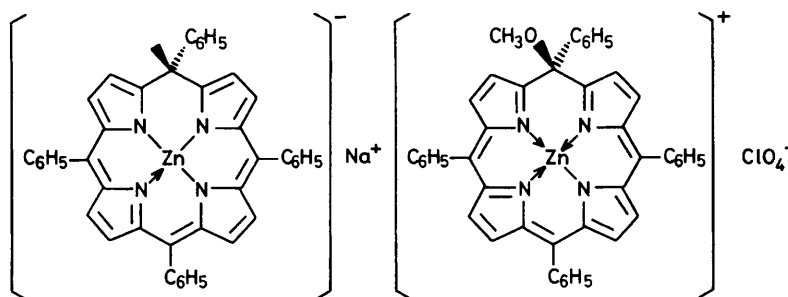
not been given, because of its low solubility and chemical lability. In order to investigate a neutral metal phlorin complex, it is necessary to choose a tervalent metal which has more negative reduction potentials than the



(1)

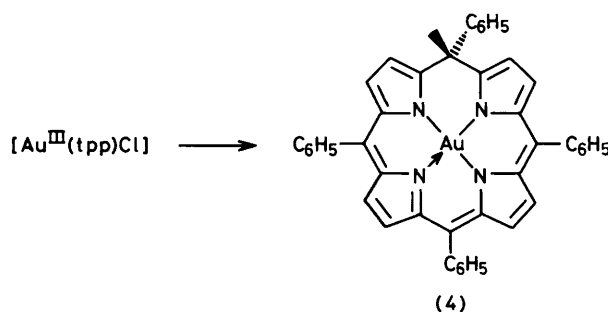


(2)



(3)

(5)



(4)

at the *meso* positions.^{3,4} As for metal complexes of phlorin, there are some reports only of zinc(II) complexes.⁵ The zinc complex of 5,10,15,20-tetraphenylphlorin (3) is ionic,⁶ and its detailed spectral data have † 5,22-Dihydroporphyrin.

porphyrin ring reduction. One such metal is gold. Electrochemistry of gold(III) porphyrins⁷ shows that the first and second reductions of the complexes occur on the porphyrin ring, and the metal oxidation state remains unchanged. It was, therefore, expected that the reduc-

tion of gold(III) porphyrins might afford neutral phlorin complexes. Here, I report the synthesis of neutral, stable gold(III) phlorin and its structure characterization by spectroscopic measurements.

RESULTS AND DISCUSSION

5,10,15,20-Tetraphenylphlorinatogold(III) (4) is soluble in usual organic solvents and considerably stable to air, although on exposure to air for a long time complex (4) changes to the parent porphyrin complex. The u.v.-visible spectrum of (4) shows characteristic features of the phlorin chromophore,^{2,5} as judged by the absorption maxima and considerably reduced absorption coefficients of both the visible and the u.v. bands. The red band of (4) appears at a considerably shorter wavelength than that of the phlorinate anion (3) (830 nm), its position being rather similar to that of phlorin free-base upon cation formation (750 nm).^{2a}

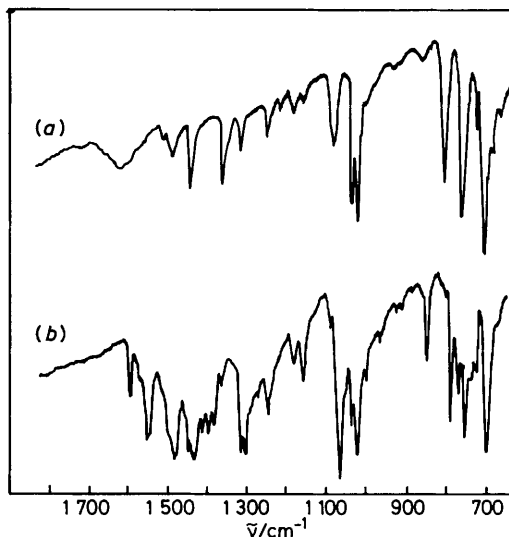


FIGURE Infrared spectra of (a) chloro(5,10,15,20-tetraphenylporphyrinato)gold(III) and (b) 5,10,15,20-tetraphenylphlorinatogold(III)

Assignment of the phlorin structure (4) is supported by the ¹H n.m.r. spectrum. In the parent complex, [Au^{III}(tpp)Cl] (tpp = 5,10,15,20-tetraphenylporphyrinate), four phenyl protons fall into two groups: the signal for the *ortho* proton appears as a multiplet at 7.88 p.p.m., those for the *meta* and *para* protons as an overlapping multiplet at 7.52 p.p.m. The difference in chemical shifts between these protons and those of benzene and the deshielding of the *ortho* proton compared with *meta* and *para* protons results from the porphyrin ring current. In [Au^{III}(tpp)Cl], the ring current also deshields eight equivalent β-protons, which appear at 8.84 p.p.m. Disruption of the aromatic system and consequent loss of ring current cause the phenyl protons of (4) to appear as a multiplet (three phenyls) centred at 7.51 p.p.m., and as two multiplets at 7.82 and 6.52

p.p.m. (one phenyl). Similarly, the β-protons of (4) are no longer equivalent and appear as two overlapping AB quartets at higher magnetic field (7.3–7.1 p.p.m.). Two AB quartets are consistent with the C₂ symmetry of (4). Similar upfield shifts of the protons of 5,10,15,20-tetraphenylphlorinatozincate(1–) (3) and 5-methoxy-21-dehydro-5,10,15,20-tetraphenylporphyrinatozinc(II) (5)⁸ have been observed. The methine proton adjacent to one phenyl group appears as a singlet at 6.28 p.p.m.^{1,9}

The parent complex [Au^{III}(tpp)Cl] exhibits only weak i.r. absorption in the range 1470–1700 cm^{–1} (Figure), while the phlorinate complex (4) has very strong bands in this region. These bands arise from the activation of a porphyrin vibration which is forbidden or weak in the i.r. under D_{4h} symmetry.¹⁰

Finally, reduction of 2,3,7,8,12,13,17,18-octaethylporphyrinatogold(III) gave a green powder of phlorin, which was very sensitive to air and an analytically pure sample could not be obtained. This suggests that the steric hindrance of the *meso* phenyl groups stabilizes the phlorin structure.

EXPERIMENTAL

Preparation of 5,10,15,20-Tetraphenylphlorinatogold(III) (4).—To a methanol-dioxane (1 : 1 v/v, 100 cm³) solution of chloro(5,10,15,20-tetraphenylporphyrinato)gold(III)¹¹ (100 mg) was added an excess amount of methanolic solution of sodium tetrahydroborate until the colour of the solution turned from orange to green. After removal of solvent under reduced pressure, residual solid was recrystallized from dichloromethane-methanol (1 : 1 v/v) to give purple-green crystals of (4) (94% yield) (Found: C, 65.3; H, 3.65; N, 6.9. Calc. for C₄₄H₂₈AuN₄: C, 65.25; H, 3.5; N, 6.9%). U.v.-visible (CH₃CN): λ_{max}(ε/dm³ mol^{–1} cm^{–1}) 442 (5.5 × 10⁴) and 758 nm (1.6 × 10⁴).

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