Tetrahedron Letters,Vol.25,No.31,pp 3269-3270,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

A BINUCLEATING "ACCORDIAN" TETRAPYRROLE MACROCYCLE

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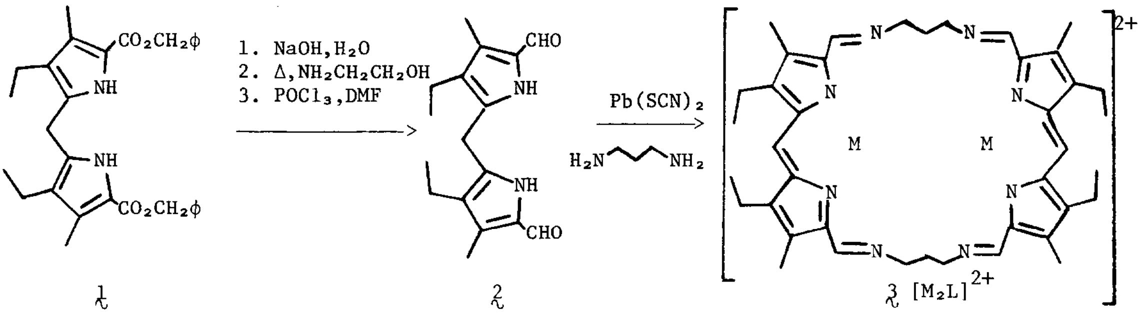
Summary: The synthesis of a side-by-side binucleating porphyrin-related ligand has been accomplished via a Schiff base template-assisted condensation of a 5,5'-diformyldipyrromethane and 1,3-propanediamine.

Cofacial dimers have been evident in porphyrin research recently.[1-3] The parallel position of the two porphyrin rings makes these species particularly suited to probe the chemistry of photosynthesis[2] and oxygen activation.[3] Potentially binucleating synthetic macrocyclic ligands have also been sought because of the unique chemical opportunities afforded by two metal ions in proximity. Hence, face-to-face macrocycles analogous to the diporphyrins, as well as ligands offering side-by-side metal ion incorporation, have been synthesized and their chemistry scrutinized.[4,5] This report announces the entrance of a newcomer to the macrocyclic circle, the first porphyrin-analog providing an opportunity for side-by-side metal ion incorporation within the same macrocyclic ring: the accordian-like tetrapyrrole macrocycle, 3.

Scheme



Dibenzyl 3,3'-diethyl-4,4'-dimethyldipyrromethane-5,5'-dicarboxylate, 1,[6-8] was saponified by aqueous NaOH, decarboxylated in boiling ethanolamine, followed by formylation using the Vilsmeier reaction. A similar procedure was employed in a recently reported synthesis of an anthracene-linked, face-to-face diporphyrin.[1] The binuclear metal ion complexes were synthesized using lead(II) ion as template.[9] Finely divided $Pb(NCS)_2$ (66.7 mg, 0.206 mmol), the dialdehyde **2**, (58.9 mg, 0.206 mmol), and 1,3-propanediamine (17.0 µl, 0.206 mmol) were refluxed and stirred in 80 mL methanol for 24 h. The resulting reddish-purple microcrystalline product, $[Pb_2L][SCN]_2$, **3** (M=Pb), precipitated, was washed with cold methanol and chloroform and was dried at 50° in vacuo. Metathesis by copper(II) was effected by dissolving the lead(II) complex of **3** (25.0 mg, 0.0213 mmol) in 50 mL methanol under reflux. $Cu(BF_4)_2 \cdot 4H_2O$ (19.8 mg, 0.0639 mmol) was added, and the mixture was refluxed for 4 h. A small quantity of $AgBF_4$ in methanol was added, and the solution was refluxed an additional hour and filtered. Upon evaporation of solvent, the dark blue crystalline product, $[Cu_2L][BF_4]_2$, precipitated and was filtered and dried in vacuo. Physical data for the compounds are given in reference 10. Other diamines are being investigated as bridges for the two dipyrromethene fragments. The potential flexibility of these linkages makes this truly an "accordian-like" molecule, by which metal ion interactions can be governed via judicious selection of the bridge.

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10. Physical data: All compounds were within experimental limits on CHN analysis (±0.4%). Compound **2**: m.p. 199-200°; m/e 286; ^1H NMR δ1.07 (6 H,t,Et), 2.28 (6 H,s,Me), 2.46 (4 H,q,Et), 3.94 (2 H,s,CH_2), 8.67 (2 H,s,CHO). Compound **3** $[Pb_2L][SCN]_2 \cdot 4H_2O$: m/e 1058 (M-2SCN); IR ν(C=N,L) 1620 cm^{-1}, ν_{asym}(SCN) 2080, 2050 cm^{-1}; NMR δ1.12 (12 H,t,Et), 2.19 (20 H,b,Et + Me), 2.70 (4 H,m,CH_2), 3.76 (8 H,t,NCH_2), 7.36 (2 H,s,CH), 8.87 (4 H,s,CH=N). Compound **3** $[Cu_2L][BF_4]_2 \cdot 3H_2O$: m/e 771 (M-$2BF_4$).

(Received in USA 28 March 1984)