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Metal Complexes of Octabutyl- and Octaoctylporphyrins Preparation and Properties

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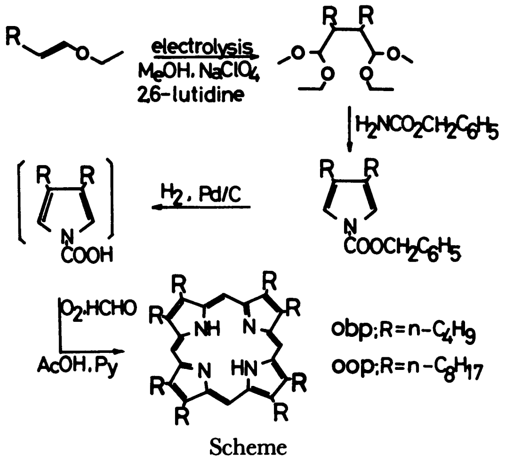
Synopsis. Octabutyl- and octaoctylporphyrin complexes of Fe^{II}, Co^{II}, Ni^{II}, and Cu^{II} ions were prepared as a family of highly lipophilic metalloporphyrins.

In one phase of our investigations on metalloporphyrins, those which are highly soluble in non-polar organic solvents were required. Potential candidates were metal complexes of porphyrins having long alkyl chains.[1] Thus, 2,3,7,8,12,13,17,18-octabutyl- and octaoctylporphyrin complexes of several metal ions such as Fe^{II}, Co^{II}, Ni^{II}, and Cu^{II} were prepared. Since, no report, to our best knowledge, on these metal complexes has been made so far, we wish to report here briefly the preparation and some chemical properties of these complexes.

Results and Discussion

Preparations. The ligands, octabutyl- (H_2obp) and octaoctylporphyrin (H_2oop), were prepared by a slight modification of Callot's method[2,3] as shown in the Scheme.



Scheme

Following essentially the literature methods[4—7] metal complexes of these porphyrins could be prepared. Thus, the reaction of acetates of Co(II), Ni(II), and Cu(II) with H_2obp or H_2oop gave the corresponding neutral metal complexes in a good to fair yield with a relative rate of formation, Co(II)<Ni(II)<Cu(II) complex. [FeCl(obp)] and [FeCl(oop)] were also prepared according to the literature procedures.[4]

As expected, they exhibited enhanced solubility in many organic solvents. Remarkably even hexane dissolves these complexes. On the other hand, they are practically insoluble in methanol, acetonitrile and dimethyl sulfoxide. The solubility trends are rather similar for the metal ions described above. The solubility differences between the two porphyrins obp and oop are also very small. However, their solubility in dioxane shows a salient feature. Namely, three neutral Co(II) complexes, [Co(oep)], [Co(obp)], and [Co(oop)] are moderately soluble in dioxane, whereas in the series of Cu(II) and Ni(II) porphyrins, only [Cu(oep)] and [Ni(oep)] are soluble in dioxane, all the other porphyrin complexes being sparingly soluble.

The UV-visible spectra of [M(oep)], [M(obp)], and [M(oop)] (M=Co, Ni, and Cu) were measured in $CHCl_3$ without adding axial ligands. As shown in Table 1 their α,β and Soret bands are very similar and in agreement with the spectra of oep complexes reported by Ogoshi.[8]

Table 1. UV-Visible Spectra of [M(obp)] and [M(oop)] (M=Co, Ni, and Cu) in $CHCl_3$

M(porp)		α		β		Soret	
		nm	log ε	nm	log ε	nm	log ε
oep[8]	Co	554	4.44	521	4.14	393	5.43
	Ni	554	4.52	519	4.07	394	5.32
	Cu	562	4.39	526	4.09	399	5.42
obp	Co	554	4.50	521	4.19	394	5.47
	Ni	554	4.53	519	4.08	395	5.30
	Cu	564	4.48	527	4.20	401	5.59
oop	Co	555	4.33	522	4.04	395	5.30
	Ni	555	4.51	519	4.11	396	5.32
	Cu	564	4.51	527	4.23	401	5.61

Experimental

Octaoctylporphyrin. A literature procedure[2] was employed with some modification. 1-Decenyl ethyl ether[9] (51.6 g) was electrolyzed in a cell with two 5 cm×15 cm graphite electrodes, to afford the acetal (15.1 g) (Scheme) in 25% yield. The acetal (14.4 g) was treated with benzyl carbamate (13.7 g) to give crude 1-benzyloxycarbonyl-3,4-dioctyl pyrrole, which was chromatographed on silica gel. A mixture of hexane and benzene (4:1) elution gave a yellow liquid (7.2 g) in 51% yield. ^{1}H NMR ($CDCl_3$) δ=0.89 [triplet, 6H, $-CH_2(CH_2)_6C\underline{H_3}$], 1.27 [singlet, 24H, $-CH_2(C\underline{H_2})_6CH_3$], 2.33 [triplet, 4H, $-C\underline{H_2}(CH_2)_6CH_3$], 5.33 [singlet, 2H, benzyl], 7.00 [singlet, 2H, pyrrole], 7.40 [singlet, 5H, benzyl]. MS $[M]^+$: 425. The *N*-benzyloxycarbonyl 3,4-dioctyl pyrrole (9.1 g) was submitted to hydrogenolysis at room temperature using Pd/C (5%, 700 mg) in a mixture of methanol and hexane (5:1) (100 ml). The resulting compounds were immediately treated with formaldehyde (35% aqueous solution, 2.2 ml), pyridine (76 ml), acetic acid (154 ml), and oxygen to afford octaoctylporphyrin (1.87 g) in 29% yield, mp 144—145 °C (lit, [10] 145.5 °C). The overall yield is 3.7% based on 1-decenyl ethyl ether. Octabutylporphyrin

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mp 265—266 °C (lit, [10] 266—267 °C) was prepared in a similar manner in 6.8% from 1-hexenyl ethyl ether.

Chloro[octabutylporphyrianato(2)-]iron(III). Chloro[octabutylporphyrinato(2)-]iron(III) was prepared by the method described by Osa5) in 89% yield, mp 202—203 °C. UV$_{max}$ ($CHCl_3$): 382 (log ε, 5.01), 509 (3.98), 538 (3.99), 639 nm (3.68). MS [M]$^+$: 847 and 849 (Calcd, 846.9 and 848.9). Chloro-[octaoctylporphyrinato(2)-]iron(III) was prepared in the same way in 65%, mp 76—78 °C. UV$_{max}$ ($CHCl_3$): 383 (log ε 5.02), 509 (3.99), 538 (4.00), 639 nm (3.68). MS [M]$^+$: 1295 and 1297 (Calcd, 1294.9 and 1296.9).

[Octaoctylporphyrinato(2)-]copper(II).5—7) A mixture of octaoctylporphyrin (100 mg) dissolved in chloroform (50 ml) and a methanol solution (10 ml) saturated with copper acetate was reacted for 1 h at room temperature. Then methanol (100 ml) was added to precipitate a red solid, which was redissolved in chloroform. Methanol was added to give [octaoctylporphyrinato(2)-]copper(II) in 86% (90 mg) yield as red crystals, mp 185—187 °C. MS [M]$^+$: 1267 (Calcd, 1267.5). [Octabutylporphyrinato(2)-]copper(II) was prepared in a similar manner in 92% yield, mp>300 °C. MS [M]$^+$: 820 (Calcd, 819.5).

[Octabutylporphyrinato(2)-]cobalt(II). A methanol solution (10 ml) saturated with cobalt acetate was added to octabutylporphyrin (100 mg) disolved in chloroform (50 ml). The mixture was heated for 1 h. Methanol was added to the filtrate yielding a red solid. The solid was dissolved in dichloromethane and filtration was followed by concentration to a small volume. Methanol was then added to give [octabutylporphyrinato(2)-]cobalt(II) in 56% (60 mg) yield, mp>300 °C. MS [M]$^+$: 816 (Calcd, 815.9). [Octaoctylporphyrinato(2)-]cobalt(II) was obtained in the similar manner in 66% yield, mp 193—195 °C. MS [M]$^+$: 1263 (Calcd, 1262.9).

[Octabutylporphyrinato(2)-]nickel(II). A methanol solution (10 ml) saturated with nickel acetate was added to octabutylporphyrin (100 mg) dissolved in chloroform (50 ml) and heated under reflux for 5 h. Evaporation of chloroform and trituration with methanol afforded a crystalline product. [Octabutylporphyrinato(2)-]nickel(II) was obtained in 84% yield, mp 273—274 °C. ^{1}H NMR ($CDCl_3$) δ=1.14 (24H, $-CH_2CH_2CH_2C\underline{H}_3$), 1.77 (16H, $-CH_2CH_2C\underline{H}_2CH_3$), 2.21 (16H, $-CH_2C\underline{H}_2CH_2CH_3$), 3.87 (16H, $-C\underline{H}_2CH_2CH_2CH_3$), 9.75 (4H, $-C\underline{H}=$). MS [M]$^+$: 815 (Calcd, 814.7). [Octaoctylporphyrinato(2)-]nickel(II) was prepared in a similar manner in 58% yield, mp 150—151 °C. ^{1}H NMR ($CDCl_3$) δ=0.86 (24H, $-CH_2CH_2(CH_2)_5C\underline{H}_3$), 1.04—2.00 (80H, $-CH_2CH_2(C\underline{H}_2)_5CH_3$), 2.24 (16H, $-CH_2C\underline{H}_2(CH_2)_5CH_3$), 3.88 (16H, $-C\underline{H}_2CH_2(CH_2)_5CH_3$), 9.76 (4H, $-C\underline{H}=$). MS [M]$^+$: 1263 (Calcd, 1262.7).

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