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PREPARATION OF THE PERCHLORATE SALTS OF COBALT(III)-PORPHYRINS AND THEIR REACTIONS WITH VINYL ETHER

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Cobalt(III) complexes of octaethylporphyrin(OEP) and tetraphenylporphyrin(TPP), [Co(III)(OEP)(L)$_2$]ClO$_4$;L=tetrahydrofuran(1),H$_2$O(2) pyridine(3) and [Co(III)(TPP)(L)$_2$]ClO$_4$;L=H$_2$O(4),pyridine(5) were synthesized. The reactions of (1),(2) and (4) with vinylethylether afforded organocobalt(III) complexes, whereas the reactions of (3) and (5) gave only reduced divalent complexes.

The formation of the Co(III)-Carbon bond in various cobalt complexes has been investigated in connection with the reactions of vitamin B_{12}. The reaction of a trivalent cobalt complex with an alkylvinylether has proved an alternative pathway to constitute the cobalt-carbon bond[1]. The π-olefin complex of trivalent cobalt has been recently proposed as a plausible reaction intermediate in the conversion of 1,2-diol to aldehyde catalyzed by diol dehydrase[2]. In order to further elucidate the reactivity of the cobalt(III) complexes, we have synthesized perchlorate salts of cobalt(III) porphyrins and their pyridine adducts and examined their electrophilicity toward vinylether.

Syntheses of the perchlorate complexes and their pyridine adducts.

[Co(III)(OEP)(THF)$_2$]ClO$_4$(1) (where OEP=octaethylporphyrin, THF=tetrahydrofuran) was prepared by treatment of Co(II)(OEP) in tetrahydrofuran containing 1-2% HClO$_4$ (70%) and purified by recrystallization from benzene-THF. Crystallization of (1) from dichloromethane saturated with water gave diaquo adduct(2). Similar crystallization from benzene-pyridine afforded purple red crystals of (3). [Co(III)(TPP)(H$_2$O)$_2$]ClO$_4$(4) (where TPP=tetraphenylporphyrin) was also obtained by a similar method using dioxane as the solvent instead of THF. Microanalyses of thus obtained complexes were satisfied[3]. The IR spectrum of (1) shows a strong absorption at 1090 cm^{-1} and a weak band at 945 cm^{-1} due to the ionic perchlorate ion which posesses Td symmetry. Weakly coordinated THF and H$_2$O molecules are readily replaced with stronger ligands such as pyridine. Table 1 summarizes absorption spectra of these perchlorate complexes. As for visible spectra, addition of polar solvents or pyridine to the CH$_2$Cl$_2$ solution of (2) resulted in a large bathochromic shift of the Soret band and sharpening of α and β-bands. The spectrum of (2) in CH$_2$Cl$_2$-pyridine is identical with that of (3) in CH$_2$Cl$_2$.

Table 1. Absorption maxima of perchlorate salts and organo-metallic derivatives of cobalt complexes; nm(log ε)

Compound	Solvent	Soret-band	β-band	α-band
(1)	CH_2Cl_2	373(4.82)	524(3.85)	557(3.86)
(2)	CH_2Cl_2	375(4.82)	524(3.85)	556(3.86)
	CH_2Cl_2-CH_3OH	409(4.98)	525(3.99)	559(3.99)
	CH_2Cl_2-py	418(5.09)	530(4.00)	562(3.96)
(3)	CH_2Cl_2	418(5.09)	530(4.00)	562(3.98)
(4)	CH_2Cl_2	426(4.98)	536(3.84)	620(3.59)
	CH_2Cl_2-CH_3OH	425(4.99)	539(3.88)	627(3.56)
(5)	CH_2Cl_2	434(5.01)	550(3.91)	584(3.41)
(6)	CH_2Cl_2	393(5.30)	520(4.01)	556(4.47)
(7)	CH_2Cl_2	408(5.20)	526(4.00)	
(8)	CH_2Cl_2	396(5.40)	522(4.03)	558(4.50)
(9)	CH_2Cl_2	407(5.21)	522(3.99)	

Reactions with vinylethylether.

Reactions of (1) and (2) with vinylethylether in ethanol-triethylamine afforded 2,2-diethoxyethylcobalt(III) complex [Co(III)(OEP)]$CH_2CH(OC_2H_5)_2$ (6), and the reaction of (4) gave [Co(III)(TPP)]$CH_2CH(OC_2H_5)_2$ (7), in good yields. Treatment of the dichloromethane solution of these complexes with silica gel[4] easily yielded formylmethylcobalt(III) complexes, (8) and (9), respectively. These organocobalt complexes could be fully characterized by microanalyses and spectroscopic measurements, in particular by NMR spectra. As summarized in Table 2, chemical shifts of protons for covalently bonded alkyl groups to central metal were largely shifted toward higher magnetic field which is due to the large diamagnetic ring current of the porphyrin ring[5]. The diethoxyethylcobalt(III) complexes were readily converted to formylmethylcobalt(III) complexes. Similar organorhodium complexes were obtainable from reaction of trivalent rhodium porphyrin, [Rh(III)(OEP)]Cl with vinylethylether[6]. However, no organocobalt complexes were obtained by the reactions of pyridine adducts (3) and (5) with electron rich olefins. These complexes were reduced to divalent metal complexes, probably due to an electron transfer from vinylethylether

$$\underset{L=THF(1),\ H_2O(2)}{[Co(III)(OEP)(L)_2]ClO_4} \longrightarrow \underset{(6)}{[Co(III)(OEP)]CH_2CH(OC_2H_5)_2} \longrightarrow \underset{(8)}{[Co(III)(OEP)]CH_2CHO}$$

$$\underset{(4)}{[Co(III)(TPP)(H_2O)_2]ClO_4} \longrightarrow \underset{(7)}{[Co(III)(TPP)]CH_2CH(OC_2H_5)_2} \longrightarrow \underset{(9)}{[Co(III)(TPP)]CH_2CHO}$$

$$\underset{(3)}{[Co(III)(OEP)(py)_2]ClO_4} \longrightarrow Co(II)(OEP)$$

$$\underset{(5)}{[Co(III)(TPP)(py)_2]ClO_4} \longrightarrow Co(II)(TPP)$$

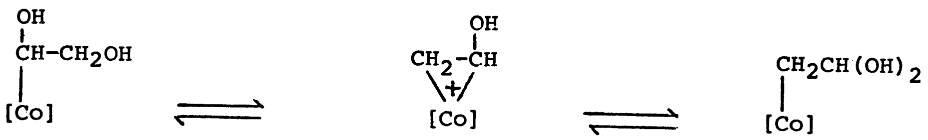
to the pyridine adducts. Therefore, electrophilicity of the trivalent cobalt porphyrin is markedly dependent on the nature of the axially coordinated ligands.

Table 2. Chemical shifts of diamagnetic complexes(δ, ppm from TMS).

	meso	α-CH_2	β-CH_3	others
($\underline{3}$)	10.06	4.04	1.80	5.66(t,2H,γ-H of py), 4.48(t,4H,β-H of py), 0.00(d,4H,α-H of py)
($\underline{6}$)	10.03	4.13	1.99	1.09(m,4H,$OC\underline{H}_2$), 0.06(t,6H,$OCH_2C\underline{H}_3$), -4.80(t,1H,$CH_2C\underline{H}$), -6.40(bd,2H,$C\underline{H}_2CH$)
($\underline{8}$)	10.34	3.83	1.88	3.20(t,1H,$C\underline{H}O$), -4.28(d,2H,$C\underline{H}_2$)
	phenyl protons			
($\underline{5}$)	9.13, 7.8			6.21(t,2H,γ-H of py), 5.06(t,4H,β-H of py), 0.90(d,4H,α-H of py)
($\underline{7}$)	9.39, 8.59, 8.16			1.44(m,4H,$OC\underline{H}_2$), 0.45(t,6H,$OCH_2C\underline{H}_3$), -2.22(t,1H,$CH_2C\underline{H}$), -4.06(d,2H,$C\underline{H}_2CH$)
($\underline{9}$)	8.82, 8.04, 7.60			3.81(t,1H,$C\underline{H}O$), -3.72(d,2H,$C\underline{H}_2$)

t; triplet, d; doublet, m; multiplet, bd; broad doublet

These facts imply that an intermediate formed in the 1,2-shifts rearrangement is thought to be base-off penta-coordinated and cationic complex.



Anomalous features of the perchlorate complexes.

As shown in Table 2, NMR spectra of the pyridine adducts and organocobalt(III) complexes showed usual diamagnetic signals. It is, however, noted that NMR spectra of ($\underline{1}$), ($\underline{2}$) and ($\underline{4}$) revealed only a broad signals in non polar solvents such as dichloromethane at room temperature due to paramagnetism derived from higher spin states of cobalt(III) ion. Similar anomalous NMR spectra have been reported for penta-coordinated cobalt(III) complex, [Co(III)(TPP)]Cl[7]. When the paramagnetic complexes are dissolved in polar solvents, as summarized in Table 3, their NMR were converted to ordinary diamagnetic ones. In particular, addition of pyridine to dichloromethane solution of ($\underline{1}$) gave a NMR spectrum of the summation of pyridine adduct and free tetrahydrofuran molecules. These facts indicate that the mixing of higher spin states is caused by weak axial coordination of ionic perchlorate in non polar solvents. On the other hand, in polar solvents, solvent molecules coordinate strongly to give hexa-coordinated low spin complexes.

Table 3. Chemical shifts of paramagnetic perchlorate complexes. (δ ppm from TMS).

solvent	meso	α-CH_2	β-CH_3	others
(1) CD_2Cl_2	very broad signal at about ~2			
CD_2Cl_2+py	10.10	4.04	1.80	3.56(m,8H,THF), 1.68(m,8H,THF) 5.66(t,2H,γ-H of py), 4.50(t,4H,β-H of py), 0.00(d,2H,α-H of py)
(2) CD_2Cl_2	very broad signal at about ~2			
Acetone-d_6	9.10	5.44	1.81	
CD_2Cl_2+MeOH-d_4	10.78	4.40	2.04	
CD_2Cl_2+DMSO-d_6	10.41	4.15	1.77	
(4) CD_2Cl_2	very broad signals at about 7			
Acetone-d_6	9.18(s,8H,β-pyrrole), 8.20(m,8H,o-H of phenyl), 7.80(m,16H,m- and p-H of phenyl)			

m; multiplet, t; triplet, d; doublet, s; singlet.

REFERENCES AND NOTES

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3) Elemental analyses of perchlorate salts.

Compound	Formula	Calcd(Found)		
		C	H	N
(1)	$C_{44}H_{60}N_4ClO_6Co$	63.26(63.28)	7.24(7.43)	6.71(6.76)
(2)	$C_{36}H_{48}N_4ClO_6Co$	59.46(59.00)	6.65(6.29)	7.70(6.99)
(3)	$C_{46}H_{54}N_6ClO_6Co$	65.05(64.56)	6.40(6.63)	9.89(9.69)
(4)	$C_{44}H_{32}N_4ClO_6Co$	65.47(65.95)	3.99(4.12)	6.94(6.92)
(5)	$C_{54}H_{38}N_6ClO_4Co$	69.79(70.14)	4.12(4.33)	9.04(8.72)

4) Silica gel may act as a weak acidic catalyst for the following reaction,

$Co\text{-}CH_2CH(OC_2H_5)_2 \longrightarrow Co\text{-}CH_2CH(OH)_2 \longrightarrow Co\text{-}CH_2CHO$

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