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prophyrin IX systems containing axial ligands such as F^-, N_3^-, and O_2^-.

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Registry No. Fe(TPP)(HIm)Cl, 54453-30-4; Fe(TPP)Cl, 16456-81-8; TFE, 75-89-8; HIm, 288-32-4.

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Synthesis and Properties of Substituted (Phthalocyaninato)iron and -cobalt Compounds and Their Pyridine Adducts

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A direct route to peripherally substituted (phthalocyaninato)metal derivatives R_mPcM (R = *t*-Bu, *m* = 4, M = Fe, Co; R = CH_3O, *m* = 8, M = Fe, Co; R = NO_2, *m* = 4, M = Co; R = CH_3, *m* = 8, M = Fe; R = Cl, *m* = 16, M = Fe) is described. Their thermal stabilities, UV/vis and mass spectra, and solubilities are reported. The coordination behavior of these metallomacrocycles to base molecules has been investigated in a model reaction with pyridine. The synthesis of the pyridine adducts $R_mPcM(py)_2$ is presented. The new complexes have been characterized by thermal analyses (TG, DTA). The thermal properties of the pyridine adducts, and in the case of the cobalt complexes the coordination number of the central metal atom, are correlated with peripheral substituent effects.

Introduction

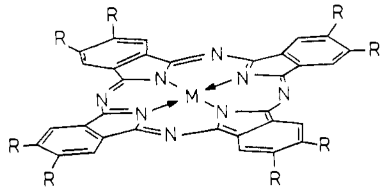
Our interest in the coordination chemistry of peripherally substituted metallophthalocyanines is based on a concept for the design of one-dimensional organic conductors.[1] The basic structural feature of these conducting materials is a linear arrangement of transition-metal atoms (e.g., Fe, Ru, Co), bridged by linear bidentate π-electron-containing ligands (e.g., pyrazine, 1,4-diisocyanobenzene, cyanide). This one-dimensional structure is stabilized by planar, tetradentate macrocyclic systems (e.g., phthalocyaninate, Pc^{2-}, tetraaza[18]annulenate, taa^{2-}) complexing each central metal atom in its equatorial plane.[2]

Detailed investigations of related macrocyclic systems show a correlation of the coordination behavior of the metal complex with its peripheral substituents.[3]

In our work the knowledge of a similar relationship would help in assessing the factors governing the stabilization of the required linear-chain compounds.

A wide variety of peripherally substituted phthalocyanines is described with the emphasis lying in the synthesis of these compounds.[4–8] In contrast, very little is known concerning the chemical behavior and physical properties of these complexes.[9–13] In order to study this effect, we worked out several routes to peripherally substituted phthalocyaninato systems.

Recently we reported the syntheses of 2,3,9,10,16,17,23,24-octasubstituted phthalocyanines **1** with R = CF_3 and $-(CH_2)_nOR'$.[14,15]



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In this paper we present some of our new results on the synthesis and properties of substituted (phthalocyaninato)iron and -cobalt and the pyridine adducts of these metallophthalocyanines. The thermal stabilities, UV/vis spectra, and solubilities of the metal complexes are also discussed.

Results and Discussion

Synthesis of R_mPcM. Both the "nitrile" and "anhydride" methods[4,16,17] were used for the preparation of the substituted (phthalocyaninato)iron and -cobalt derivatives **4–11** (Table I).

In the anhydride method substituted phthalic anhydrides **2** were employed as starting materials; these are converted to metal-containing phthalocyanines in the presence of urea and metal halides when ammonium molybdate is used as a catalyst (method A, Table I). The nitrile method can be used in two ways: (1) by starting with substituted phthalonitriles **3**, which react with metal halides (method B), or (2) by using metal carbonyls (method C)[18] to produce the metallophthalocyanines. All of the conversions were carried out in high-boiling solvents. Substituted phthalonitriles **3** often must be prepared through the sequence dicarboxylic acid → anhydride → imide → amide

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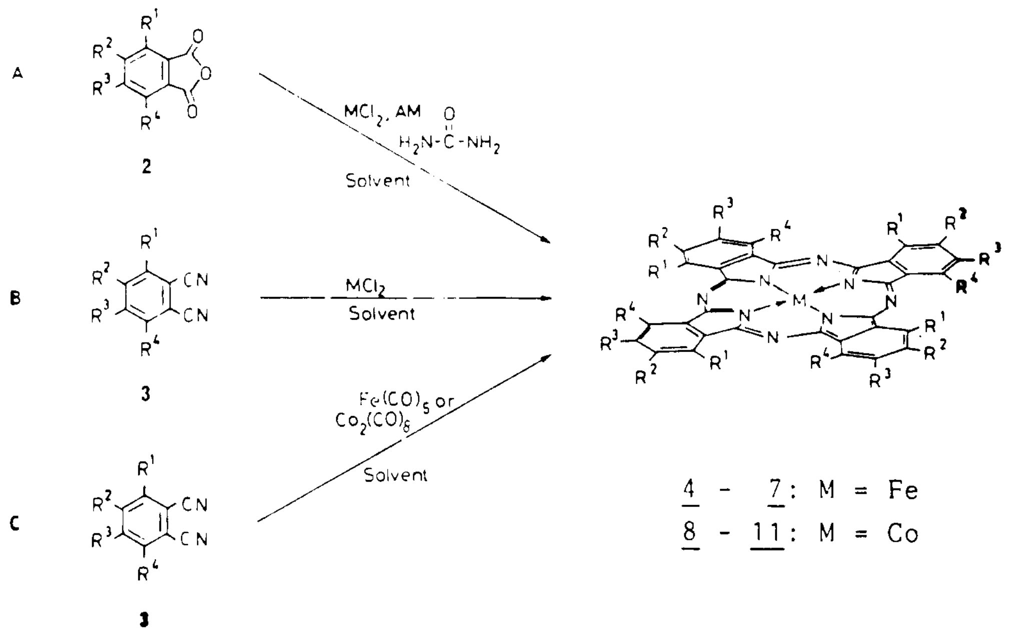
Table I. Summary of Syntheses of Substituted (Phthalocyaninato)iron and -cobalt Compounds



product	route	starting material	reacn conditions	yields, % of theory
(t-Bu)$_4$PcFe (4)	A	2a: $R^1 = R^3 = R^4 = H; R^2 = C(CH_3)_3$	nitrobenzene, 190 °C, 8 h	<2
	C	3a: $R^1 = R^3 = R^4 = H; R^2 = C(CH_3)_3$	ethylene glycol, 190-210 °C, 1.5 h	38
	C	3a: $R^1 = R^3 = R^4 = H; R^2 = C(CH_3)_3$	1,2,4-trichlorobenzene, reflux, 2 h	33
Me$_8$PcFe (5)	C	3c: $R^1 = R^4 = H; R^2 = R^3 = CH_3$	1-chloronaphthalene, reflux, 1.5 h	41
(MeO)$_8$PcFe (6)	C	3d: $R^1 = R^4 = H; R^2 = R^3 = OCH_3$	1-chloronaphthalene, reflux, 1.5 h	37
Cl$_{16}$PcFe (7)	A	2e: R^1-R^4 = Cl	nitrobenzene, 190 °C, 5 h	61
(t-Bu)$_4$PcCo (8)	A	2a: $R^1 = R^3 = R^4 = H; R^2 = C(CH_3)_3$	1,2,4-trichlorobenzene, 190 °C, 4 h	61
	B	3a: $R^1 = R^3 = R^4 = H; R^2 = C(CH_3)_3$	ethylene glycol, 190 °C, 5 h	73
(O$_2$N)$_4$PcCo (9)	A	2b: $R^1 = R^3 = R^4 = H; R^2 = NO_2$	nitrobenzene, 190 °C, 5 h	78
	B	3b: $R^1 = R^3 = R^4 = H; R^2 = NO_2$	ethylene glycol, 190 °C, 5 h	27
(H$_3$CO)$_8$PcCo (10)	B	3d: $R^1 = R^4 = H; R^2 = R^3 = OCH_3$	ethylene glycol, 200 °C, 5 h	41
ClPcCo (11)		prepared by thermolysis of PcCoCl$_2$		

→ nitrile; consequently it is sometimes easier to prepare the derivatives **4**–**11** by starting with substituted phthalic anhydrides **2**. In certain cases, in fact, the only way to prepare pure peripherally substituted (phthalocyaninato)cobalt compounds (e.g. **10**) is through the anhydride method. The usual anhydride method depends on the use of high-boiling solvents such as 1-chloronaphthalene, nitrobenzene, and 1,2-dichlorobenzene, so it is not well adapted for the synthesis of soluble (phthalocyaninato)metal derivatives, whose isolation depends upon removal of the solvent by distillation. For these compounds a *special variant of the nitrile method* with *ethylene glycol*[19] as the solvent is particularly useful. The reaction mixture can easily be worked up by the addition of water, which mixes with the solvent and causes the product to precipitate.

(Tetra-*tert*-butylphthalocyaninato)cobalt (**8**) was prepared by both methods, from which the advantage of using ethylene glycol as a solvent for soluble phthalocyanines is apparent: for the synthesis of **8** one merely heats 4-*tert*-butyl-1,2-dicyanobenzene (**3a**) up to 200 °C in ethylene glycol with $CoCl_2$.

One obtains **8** in a higher yield (with respect to the starting material *o*-xylene for **2a** or **3a**) through synthesis A. The anhydride **2a** can be prepared from *o*-xylene in three steps; **3a**, however, requires six steps. In order to isolate **8**, the solvent must be removed by distillation. Methods A and C are also adaptable for the synthesis of "(t-Bu)$_4$PcFe", but the product obtained is not that shown in structure **4**. It has been reported[9,20] that the synthesis of **4** always leads to dimeric, oxygen-containing products. Two formulas have been proposed for these dimeric substances: $H_2[((t\text{-Bu})_4PcFe)_2O]$ (**4a**) and $[(t\text{-Bu})_4PcFe]_2O$ (**4b**). In formula **4a** iron is portrayed in oxidation state +2, whereas in **4b** it has a formal charge of 3+. Formula **4b** has counterparts in $(PcFe)_2O$[21] and $((TPP)Fe)_2O$[22] (TPP = dianion of tetraphenylporphine).

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[19] This method is known for the synthesis of unsoluble metallophthalocyanines: (a) Dabrowski, R.; Waclawek, W.; Witkiewicz, Z. *Biul. Wojsk. Akad. Tech.* **1976**, *25*, 81; *Chem. Abstr.* 1976, *85*, 115942f. (b) Assour, J. M.; Goldmacher, J.; Harrison, S. E. *J. Chem. Phys.* **1965**, *43*, 159.

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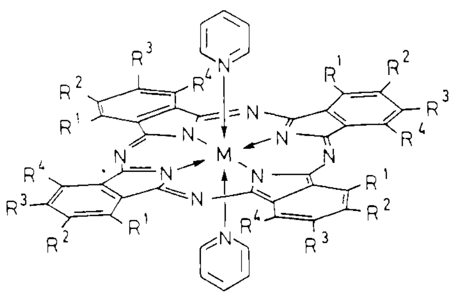
The method of Meloni et al.[18] has been applied successfully to the synthesis of substituted (phthalocyaninato)iron compounds **5** and **6**. 4,5-Dimethyl-1,2-dicyanobenzene (**3c**) and 4,5-dimethoxydicyanobenzene (**3d**, 1,2-dicyanoveratrole), respectively, were heated under reflux in 1-chloronaphthalene in the presence of iron pentacarbonyl, producing **5** and **6** in about 40% yields (see Table I). Compound **7** was prepared by the anhydride method (synthesis A) in yields of 61% as described in a patent.[23] In contrast to the previously described methods for peripherally substituted phthalocyanines, ClPcCo (**11**) is available by thermolysis of $PcCoCl_2$ under vacuum at 380 °C. (Octamethoxyphthalocyaninato)cobalt (**10**) was prepared from **3d** by using the "nitrile" method, whereas (tetranitrophthalocyaninato)cobalt (**9**) could be obtained without further transformations only through the "anhydride" method using 4-nitrophthalic anhydride (**2b**) as the starting material. Attempts to prepare **9** using 4-nitro-1,2-dicyanobenzene as the precursor were successful only if **9** was first isolated *via* its bis(pyridine) adduct (vide infra), which can be decomposed subsequently to form **9**.

Synthesis of $R_mPcML_{1,2}$. Bis(axial pyridine) adducts R_mPcML_2 (M = Fe, Co; L = pyridine) **12–20** can be prepared and isolated from all substituted (phthalocyaninato)iron and -cobalt compounds described above.



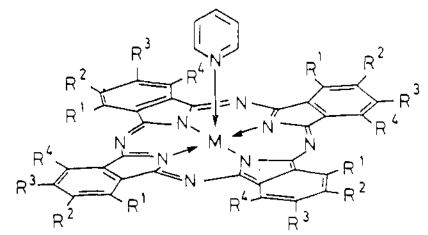
M = Fe
12: R^1-R^4 = H; $PcFe(py)_2$
13: $R^1 = R^4$ = H, R^2, R^3 = H, *t*-Bu; $(t\text{-Bu})_4PcFe(py)_2$
14: $R^1 = R^4$ = H, $R^2 = R^3 = CH_3$; $(H_3C)_8PcFe(py)_2$
15: $R^1 = R^4$ = H, $R^2 = R^3 = OCH_3$; $(H_3CO)_8PcFe(py)_2$
16: R^1-R^4 = Cl; $Cl_{16}PcFe(py)_2$
M = Co
17: $R^1 = R^4$ = H, R^2, R^3 = H, *t*-Bu; "$(t\text{-Bu})_4PcCo(py)_2$"
18: R^1-R^4 = H; $PcCo(py)_2$
19: $R^1 = R^3 = R^4$ = H, R^2 = H, H, H, Cl; $ClPcCo(py)_2$
(one possible structural isomer)
20: $R^1 = R^4$ = H, R^2, R^3 = H_2NO_2; $(O_2N)_4PcCo(py)_2$

Syntheses of bis(pyridine) adducts (**12**, **14–16**, **18–20**) of the slightly soluble (phthalocyaninato)metal derivatives can be effected by direct treatment of **5–7**, **9–11** with excess pyridine between 25 and 115 °C. The cobalt complexes **18** and **19**, however, can only be obtained at room temperature. Higher temperatures lead to mixtures of R_mPcCoL and R_mPcCoL_2 or to the pure monoadduct R_mPcCoL.

Compounds **12**, **14–16**, and **18–20** appear as blue-green to blue powders and are poorly soluble in organic solvents. Although these complexes can be isolated by filtration, the bis(pyridine) adducts **13** and **17** of the *tert*-butyl-substituted phthalocyanines **4** and **8** can be isolated only after removal of the excess pyridine by distillation.

The pentacoordinated $(t\text{-Bu})_4PcCo(py)$ (**21**) can be prepared by treatment of the bis(pyridine) adduct **17** with 1 N tartaric acid solution.

Chemical and Physical Properties of (Phthalocyaninato)iron and -cobalt Compounds. With the exception of compounds **4** and **8**, the solubility behavior of the substituted phthalocyanines **5–7** and **9–11** is the same as that of unsubstituted PcFe and PcCo. The *tert*-butyl-substituted derivatives **4** and **8** are soluble in the common organic solvents as,[9-13] for example, acetone, THF, CH_2Cl_2, $CHCl_3$, toluene, benzene, and to a small extent *n*-hexane. During the syntheses **4** and **8** are produced as isomeric mixtures, which were not separated.



M = Co
21: $R^1 = R^4$ = H, R^2, R^3 = H, *t*-Bu; $(t\text{-Bu})_4PcCo(py)$
22: R^1-R^4 = H; PcCo(py)
23: $R^1 = R^3 = R^4$ = H, R^2 = H, H, H, Cl; ClPcCo(py)
(one possible structural isomer)

Various authors have reported on "$(t\text{-Bu})_4PcFe$" and have determined that during the synthesis **4** is produced as an oxygen-containing dimer with composition **4a**[9] or **4b**.[20]

If one regards the appearance of **4a** formally as

$$\underset{\mathbf{4}}{2(t\text{-Bu})_4PcFe} + H_2O \rightarrow \underset{\mathbf{4a}}{H_2[((t\text{-Bu})_4PcFe)_2]O}$$

then the iron must be present as iron(II). Russian authors[9] report comparative PES investigations of "$(t\text{-Bu})_4PcFe$" and PcFe. They determined the bonding energy of the $2p_{3/2}$ electrons of iron in "$(t\text{-Bu})_4PcFe$" as 708.5 eV, and in PcFe as 708.8 eV, and conclude that the valence state of iron in both compounds is +2. The bonding energy of Fe^{3+} is about 711 eV. The formulation of **4a** as a dimer is based upon the molecular weight determination; the authors therefore propose the composition $H_2[(t\text{-Bu})_4PcFeOFePc(t\text{-Bu})_4]$. The hydrogens are supposed to be bound to the nitrogen atoms of the phthalocyaninato ring. The iron in **4b** is presumed to be in oxidation state +3. The oxidation of iron to iron(III) is ascribed to the presence of traces of oxygen, which cannot be excluded during the synthesis.[24]

A decision between **4a** and **4b** cannot be made on the basis of elemental analysis. Mass spectra of the dimers always yield m/e = 792 (M^+ from **4**). We did not observe a molecular peak for the dimers **4a** (m/e = 1602) or **4b** (m/e = 1600).

The IR spectrum of "$(t\text{-Bu})_4PcFe$" is also of no value in deciding between **4a** and **4b**, since the $(N\text{-}H)^+$ vibration[25] between 2900 and 3000 cm^{-1} is in the same area as the C–H vibrationof the *tert*-butyl groups.[9] The Fe–O–Fe IR absorptions at 890, 850, and 820 cm^{-1} that occur in $(PcFe)_2O$[21] are interfered with by the γ-C–H vibrations of the *tert*-butyl groups that appear in the same region. If one heats $(PcFe)_2O$ or **4a**/**4b**, respectively, at 300 °C (2 h under N_2), the IR spectrum of $(PcFe)_2O$ is unchanged; in the IR spectrum of **4a**/**4b** the intensities of the bands at 920 and 850 cm^{-1} are weaker.

UV–vis measurements were carried out on solutions in both coordinating and noncoordinating solvents. In contrast to the results of ref 9, however, we observed divergent results with respect to the electronic spectra of "**4**"—both as synthesized directly and as tempered at 250–300 °C. The electronic spectra of the dimers (**4a**/**4b**) when compared with those of $(PcFe)_2O$ exhibited similarities. In the visible spectrum (600–800 nm, chlorobenzene) the strongest band (Q band)

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for $(PcFe)_2O$ at 687 nm has shoulders at 658 and 708 nm, whereas for **4a**/**4b** the band at 692 nm has a shoulder at 708 nm.[26]

More significant than the UV–vis spectra in noncoordinating solvents are the UV–vis spectra in coordinating solvents such as, for example, pyridine.

Intermediates have been observed in the UV/vis region for both $(PcFe)_2O$ and **4a**/**4b** in pyridine; these intermediates are formed very rapidly ($(PcFe)_2O$, $\lambda_{max} = 621$ nm; **4a**/**4b**, $\lambda_{max} = 625$ nm), whereas the final products, $PcFe(py)_2$ ($\lambda_{max} = 656$ nm) or $(t\text{-}Bu)_4PcFe(py)_2$ ($\lambda_{max} = 657$ nm) are produced in a later, significantly slower step. Tentatively, we assign the band at about 620 nm to an intermediate of composition (py)PcFeOFePc(py). This assignment is supported by the spectrum of the structurally determined manganese compound (py)PcMnOMnPc(py), which also shows a strong band at about 620 nm.[29,30] That reduction of $PcFe^{III}$ compounds occurs in pyridine, yielding $PcFe(py)_2$, is also reported by other authors.[27,28,31]

After it has been tempered at 300 °C (vide supra), $(PcFe)_2O$ also exhibits this same spectral behavior. However, in the spectrum of tempered **4a**/**4b** the formation of the intermediate with a $\lambda_{max} = 625$ nm is not observed. On the contrary, the spectrum of $(t\text{-}Bu)_4PcFe(py)_2$ appears instantaneously.

Tempered **4a**/**4b** exhibits the same behavior in pyridine as does β-PcFe: the bis(pyridine) adduct is produced rapidly. Tempering of **4a**/**4b** leads to $(t\text{-}Bu)_4PcFe$ (**4**). The transition of the dimer to **4** begins between 220 and 250 °C. It is known, through combined studies with TG/DTA and EGA, that $(PcFe)_2O$ decomposes between 370 and 400 °C to yield β-PcFe and oxygen, whereupon the oxygen immediately reacts exothermally to produce CO, CO_2, and phthalimide.[32] Phthalodinitrile and nitrogen are further byproducts of this reaction. The lower thermal stability of **4a**/**4b** in comparison with that of $(PcFe)_2O$, as well as the results of photoelectron spectroscopy, makes the structure $H_2[((t\text{-}Bu)_4PcFe)_2]O$ (**4a**) a reasonable formulation for the dimer.

Compound **4** is less stable than unsubstituted PcFe and the other (phthalocyaninato)iron derivatives **5**–**7**. After the compound stood 1 year in a spring-top tube, we observed new bands of middle intensity at 1720 cm^{-1}. We ascribe these bands to *tert*-butylphthalamide or -imide, which is produced by the oxidative decomposition of **4**.

We were unable to achieve the yields of 50% that had been reported for the preparation of **4**.[9,10] There were great losses of materials when we attempted column chromatography of **4**, since it decomposes on the column with a corresponding loss of color. Compound **4** is also extremely unstable in triethylamine. The initially blue color of the solution of phthalocyanine **4** in TEA changes in just a few minutes in the presence of air to olive-green and then brown. In addition to the Q band at 650 nm, whose intensity decreases, there are also bands at 627 and 703 nm that appear during the decomposition process.

Table II. UV-vis Spectra of Peripherally Substituted (Phthalocyaninato)iron and -cobalt Complexes in Pyridine

	λ_{max}, nm (rel optical dens)
PcFe	655 (1.8), 595 (0.4), 415 (0.3), 333 (1.0)
$(t\text{-}Bu)_4PcFe$ (4)	657 (1.2), 630 sh (0.4), 597 (0.3), 416 (0.3), 331 (1.0)
$(H_3C)_8PcFe$ (5)	662 (1.3), 635 sh (0.4), 600 (0.3), 418 (0.2), 337 (1.0)
$(H_3CO)_8PcFe$ (6)	657 (1.0), 632 sh (0.3), 596 (0.3), 437 sh (0.2), 406 (0.2), 342 (1.0)
$Cl_{16}PcFe$ (7)	679 (1.3), 650 sh (0.5), 618 (0.4), 437 (0.4), 357 (1)
PcCo	658 (1.8), 597 (0.3), 332 (1.0)
$(t\text{-}Bu)_4PcCo$ (8)	662 (1.6), 600 (0.3), 330 (1.0)
$(O_2N)_4PcCo$ (9)	677 (2.2), 614 (0.5), 457 sh (0.2), 425 sh (0.1), 375 sh (0.5), 342 (1.0)
$(H_3CO)_8PcCo$ (10)	655 (1.2), 597 (0.3), 400 sh (0.1), 345 sh (1.0), 330 (1.0)
ClPcCo (11)	656 (1.9), 595 (0.4), 334 (1.0)

Table III. Thermal Stabilities of Peripherally Substituted (Phthalocyaninato)iron and -cobalt Complexes

		mass loss[a]		
	dec temp, °C	% found	% calcd	DTA signal
"$(t\text{-}Bu)_4PcFe$" (4)	400–480	27.0	28.3 ($-4\ C_4H_8$)	endo
$(t\text{-}Bu)_4PcCo$ (8)	400–470	27.2	28.6 ($-4\ C_4H_8$)	endo
$(H_3C)_8PcFe$ (5)	490–555	8.2	8.8 ($-4\ CH_3$)	endo
$(H_3CO)_8PcFe$ (6)	340–415	15.0	15.3 ($-4\ OCH_3$)	exo
$(H_3CO)_8PcCo$ (10)	350–430	14.7	15.1	exo
$Cl_{16}PcFe$ (7)	410[b]			
$(O_2N)_4PcCo$ (9)	230–400	18.9	20.2	exo
ClPcCo (11)	480–535	5.2	5.8	endo

[a] The mass losses observed correspond formally to the structural fragments indicated within the parentheses. [b] Beginning.

t-Butyl-substituted phthalocyanines with germanium and tin as the central atoms have also been reported to exhibit increased sensitivies to oxidation and to light.[6] In contrast to **4**, **8** is available through synthesis as monomeric $(t\text{-}Bu)_4PcCo^{II}$. Oxygen adducts of **8** are produced only in solution, and they cannot be isolated. The complexation of oxygen that occurs in solution is reversible.

The electronic influence of the peripheral groups of the phthalocyaninato ring on the substituted (phthalocyaninato)metal compounds can be seen in the electronic spectra. In pyridine solvent, both the iron and the cobalt derivatives exist as the bis(pyridine) adducts, $R_mPcM(py)_2$. This could be demonstrated for the cobalt derivative by means of its ESR spectra.[33] By comparison of the UV/vis spectra with those of the unsubstituted PcFe or PcCo compounds, the pyridine adducts of **4**–**6**, **8**, and **10** with electron-donating substituents exhibit no great spectral changes (cf. Table II). The Q band in the chloro- and nitro-substituted derivatives **7** and **9**, however, is displaced ~20 nm toward longer wavelengths. It is also worth mentioning that the contribution to the Q-band displacement of 19 nm by the four nitro substituents of **9** is almost as large as that (24 nm) in the perchlorinated derivative **7**.

The absorption at 415 nm in the PcFe spectrum is ascribed to an Fe → L CT transition. This assignment, however, is controversial.[34] The position of this band is not changed very much in (phthalocyaninato)iron derivatives containing *tert*-butyl[9] or methyl substituents. The corresponding band maximum in the spectrum of the perchloro derivative **7** is displaced by 24 nm toward longer wavelengths, which is the

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(26) Very recently, Homborg[27] reported electronic spectra of $(PcFe)_2O$ both in 1-chloronaphthalene as solvent ($\lambda_{max} = 695$, 710 nm) and in KBr pellets ($\lambda_{max} = 675$, 718 nm). We note that these results and ours are in contrast with the results of Lever,[28] who found the Q band for (phthalocyaninato)iron μ-oxo dimers shifted to about 635 nm in THF as solvent.

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Table IV. Thermoanalytical Data for Mono- and Bis(pyridine) Adducts of Peripherally Substituted (Phthalocyaninato)iron and -cobalt Complexes, $R_mPcM(py)_{1,2}$[a]

starting material	monoadduct			bisadduct		
		mass loss			mass loss	
	dec temp, °C	% found	% calcd	dec temp, °C	% found	% calcd
$(t\text{-Bu})_4PcFe$				90–230[b] (**13**)	17.4	16.6
$(H_3C)_8PcFe$				155–225 (**14**)	18.2	18.9
$(H_3CO)_8PcFe$				60–195[c,d] (**15**)	26.1	28.1[c]
$Cl_{16}PcFe$				230–310 (**16**)	12.5	12.4
PcFe				175–260 (**12**)	20.6	21.8
$(t\text{-Bu})_4PcCo$	90–190 (**21**)	9.0	9.0	*e* (**17**)		
PcCo	130–190 (**22**)	12.0	12.1	85–135 (**18**)	21.0	21.6
ClPcCo	100–165 (**23**)	10.5	11.5	80–125 (**19**)	*f*	20.7
$(O_2N)_4PcCo$				110–220 (**20**)	16.7	17.3

[a] Pyridine evolution is always endothermic (DTA). The pure metallomacrocycle R_mPcM remains as the residue (IR). [b] Sluggish start of decomposition between 150 and 230 °C; 15.9% mass loss. [c] Contains additional two molecules of pyridine as solvent. The mass loss is calculated for $(H_3CO)_8PcFe(py)_2 \cdot 2py$. [d] Sluggish start of decomposition and endothermic, drifting DTA curve (loss of pyridine solvent); 15.1% mass loss between 175 and 195 °C (loss of coordinated pyridine), with a calculated mass loss of 14.0%. [e] Complexes with the stoichiometry $(t\text{-Bu})_4PcCo$:L = 1:2 (L = py, 3-Mepy, 4-Mepy) contain differently coordinated axial ligands and must be formulated as $(t\text{-Bu})_4PcCo(py)py$. [f] Contaminated with ClPcCo(py). Loss of both solvated and coordinated pyridine takes place during TG in one step.

same displacement in the same direction exhibited by the Q band itself (Table II).

Thermoanalytic Investigations. The thermal stabilities of the substituted phthalocyanines **4–11** are smaller than those of the unsubstituted PcFe or PcCo compounds (cf. Table III). Compounds **4** and **8** decompose between 400 and 480 °C. PcFe and PcCo (impure) remain behind as solid residues. On TGA the weight loss in this temperature range corresponds to the loss of four *tert*-butyl groups, which presumably split off as isobutene molecules. The weight loss from **5** corresponds to four methyl groups and from **6** to the loss of four methoxy or eight methyl groups (cf. Table III). The IR spectra of the residues from the thermogravimetric analyses of **5–7**, **9**, and **10** did show broad bands pointing to gross decomposition.

The decreasing thermal stability in the series ClPcCo (**11**) > $(H_3C)_8PcFe$ (**5**) > $(t\text{-Bu})_4PcFe$ (**4**) ~ $(t\text{-Bu})_4PcCo$ (**8**) ~ $Cl_{16}PcFe$ (**7**) > $(H_3CO)_8PcFe$ (**6**) ~ $(H_3CO)_8PcCo$ (**10**) > $(O_2N)_4PcCo$ (**9**) affects the procedure for running the mass spectra. The molecular ions in the mass spectra of **4**, **5**, **8**, and **11** can be observed by direct introduction of these substances, whereas the FD technique (pyridine as solvent) must be used for **6** and **10**. It was not possible to run the mass spectra of **7** and **9**.

Thermal treatment of the mono- and bis(pyridine) adducts **12–23** caused splitting of the axially coordinated pyridine:[1c]

$$R_mPcM(py)_{1,2} \xrightarrow[N_2]{\Delta} R_mPcM + 1,2py\uparrow$$

In all cases the pure metallomacrocycles R_mPcM (**4–11**) remained behind as residues. The thermoanalytical data for compounds **12–23** are summarized in Table IV.

The $R_mPcFe(py)_2$ complexes **12–16** lose both pyridine molecules in one endothermic step. The decomposition temperatures (Table IV) of these complexes demonstrate that electron-donating substituents in compounds **13–15** decrease the thermal stabilities of their pyridine adducts in comparison with the adducts of the unsubstituted $PcFe(py)_2$ (**12**). Compound **16**, on the other hand, which contains 16 electron-attracting chlorine atoms, exhibits a considerably higher thermal stability.

Whereas only hexacoordinated nitrogen-base adducts $PcFeL_2$ are isolated in the (phthalocyaninato)iron(II) system,[35] both pentacoordinated (PcCoL) and hexacoordinated ($PcCoL_2$) derivatives (e.g. L = py, 4-Mepy, pyz) of the cobalt(II) series can be synthesized.[36] Pentacoordinated complexes of the previously isolated PcCo base adducts were always more stable than the hexacoordinated compounds. The relative stabilities are influenced by the introduction of peripheral substituents in the phthalocyaninato macrocycles.

Thus, the tetranitro-substituted derivative **9** forms exclusively the hexacoordinated compound **20**, whose thermal stability now lies in a region that is normal for pentacoordinated PcCo derivatives. The narrowing of these differences in thermal stabilities between penta- and hexacoordinated complexes with respect to the $PcCo(py)_{1,2}$ system by means of peripheral, electron-withdrawing substituents can be seen by reference to the (chlorophthalocyaninato)cobalt pyridine adducts ClPcCo(py) and $ClPcCo(py)_2$ shown in Table IV.

The results presented here demonstrate that the peripherally substituted (phthalocyaninato)iron and -cobalt compounds **4–11** can be prepared through comparatively simple reactions from the appropriately substituted phthalic anhydrides **2** or phthalonitriles **3** by treatment with iron or cobalt halides or carbonyls. The thermal stabilities and IR and UV/vis spectra—as well as other physical properties—of these iron and cobalt phthalocyanines are strongly influenced by the peripheral substituents. A corresponding characteristic relationship of physical properties and coordination behavior with the nature of the peripheral substituent was observed with the series of bis(axial pyridine) adducts **12–20**.

Experimental Section

Veratrole and tetrachlorophthalic anhydride were commercially available. 4-*tert*-Butylphthalic anhydride, 4-*tert*-butylphthalodinitrile,[6] 4-nitrophthalimide,[37] and 4-nitrophthalic anhydride[38] were synthesized by methods described previously. Routine infrared spectra were recorded on a Pye Unicam SP 1000 as Nujol mulls or KBr pellets. ^1H NMR spectra were obtained on a Varian EM 360. Mass spectra were obtained on a Varian MAT 711 mass spectrometer by direct inlet or FD techniques. Thermogravimetric measurements and differential thermal analyses were carried out simultaneously on a Netzsch STA Model 429 under a flow of nitrogen (20 mL/min), with heating rate 2 K/min. UV/vis spectra were recorded in purified pyridine on a Beckman Acta M-VII.

(2,9,16,23-Tetra-*tert*-butylphthalocyaninato)cobalt(II) (8). 1. Nitrile Method. 4-*tert*-Butylphthalodinitrile (**3a**) (13.5 g, 0.073 mol) and 1.5 g (0.012 mol) of cobalt(II) chloride were suspended in 180 mL of ethylene glycol and heated for 5 h at 190 °C. Finally the mixture was cooled and then to it was added an equal volume of water,

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after which the solid material was collected on a filter (vacuum) and washed with methanol. The crude product was boiled 2 h, first with 500 mL of 1 N HCl and then with 500 mL of 1 N NaOH, filtered, and washed with water each time until the filtrate was neutral. The solid material was then stirred in methanol, suction-filtered, and dried in vacuo 6 h at 60 °C. The yield was 7 g, 73.4% of theory.

2. Anhydride Method. 4-*tert*-Butylphthalic anhydride (**2a**) (13 g, 0.064 mol), 13.5 g (0.225 mol) of urea (water free), and 2.4 g (0.019 mol) of cobalt(II) chloride were suspended in 50 mL of trichlorobenzene, treated with 0.5 g of ammonium molybdate, and heated at 190 °C for 4 h. After the mixture was cooled, 50 mL of petroleum ether (60–90 °C) was added and the mixture was vacuum filtered. The residue that had been collected on the filter was discarded, and the filtrate was concentrated. The new material that precipitated was purified as described above with 1 N HCl and 1 N NaOH solutions: yield 4 g, 31% of theory.

Anal. Calcd for $C_{48}H_{48}N_8Co$ (M_r = 795.86): C, 72.44; H, 6.07; N, 14.08. Found: C, 73.25; H, 6.55; N, 14.65. Mass spectrum: 811 (12, $M^+ + CH_3$), 796 (79, M^+), 781 (22, $M^+ - CH_3$), 766 (16, $M^+ - 2CH_3$), 751 (12, $M^+ - 3CH_3$), 756 (8, $M^+ - 4CH_3$), 398 (4, M^{2+}).

(2,9,16,23-Tetranitrophthalocyaninato)cobalt(II) (9). 4-Nitrophthalodinitrile (3b). The conversion to 4-nitrophthalodiamide was carried out by introducing gaseous ammonia into a suspension of 4-nitrophthalimide in concentrated, aqueous ammonia. Phosphoryl chloride (68.6 g, 0.45 mol) was added dropwise to a suspension of 20.6 g (0.1 mol) of 4-nitrophthalamide in 80 mL of pyridine at 3–5 °C. The mixture was then stirred for 3 h at room temperature, poured onto ice, and filtered. The residue was washed with water until the filtrates were neutral, dried in vacuo at room temperature, and placed in a sublimation apparatus. Compound **3b** sublimes at 10^{-2} torr at a bath temperature of 150 °C: yield 8.4 g, 48.8% of theory; light yellow needles; mp 141 °C. Anal. Calcd for $C_8H_3N_3O_2$ (M_r = 173.13): C, 55.5; H, 1.74; N, 24.27. Found: C, 55.31; H, 1.5; N, 24.44. ^1H NMR ($CDCl_3$): δ 8.0–8.2 (m, 1 H), 8.5–8.7 (m, 2 H). Mass spectrum: 173 (89%, M^+), 143 (4, $M^+ - NO$), 127 (100, $M^+ - NO_2$). IR (cm^{-1}): 2240 ($C{\equiv}N$), 1350 (NO_2).

(2,9,16,23-Tetranitrophthalocyaninato)cobalt(II). 1. Nitrile Method. The synthesis and purification were carried out according to the directions given above, with use of 9.5 g (0.055 mol) of 4-nitrophthalodinitrile (**3b**) and 1.57 g (0.01 mol) of cobalt(II) chloride in 100 mL of ethylene glycol. Finally the residue obtained was placed in the thimble of a Soxhlet extractor and extracted for 24 h with methylene chloride. The extract was discarded, and the residue was dried. The extraction was then continued with pyridine as extractant until the solvent from the thimble was colorless. The extract was concentrated, after which the bis(pyridine) adduct of $(O_2N)_4PcCo$ precipitated. The complex was heated at 190 °C in vacuo, whereupon the pyridine was split from the complex: yield 2 g, 26.6% of theory.

2. Anhydride Method. 4-Nitrophthalic anhydride (**2b**) (23.5 g, 0.122 mol), 31 g (0.517 mol) of urea, 5 g (0.038 mol) of cobalt(II), chloride, and 0.2 g of ammonium molybdate were suspended in 130 mL of nitrobenzene and heated at 190 °C. After gas evolution ceased (4–5 h), the mixture was filtered hot and then washed with nitrobenzene, followed by methanol. The crude product was then finally—as described above—purified with 1 N HCl followed by 1 N NaOH: yield 18 g, 78.5% of theory.

Anal. Calcd for $C_{32}H_{12}N_{12}O_8Co$ (M_r = 751.44): C, 50.87; H, 1.35; N, 22.09. Found: C, 51.1; H, 1.6; N, 22.4.

(2,3,9,10,16,17,23,24-Octamethoxyphthalocyaninato)cobalt(II) (10) and -iron(II) (6). 1,2-Dibromo-4,5-dimethoxybenzene, Procedure a. Veratrole (138 g, 1 mol) was dissolved in 400 mL of carbon tetrachloride, and then at 0–5 °C it was treated with 2 mol of bromine dissolved in 100 mL of carbon tetrachloride. The mixture was stirred an additional 2 h at the same temperature to complete the conversion. Finally the solution was washed with 10% aqueous NaOH and then water. The solvent was removed by distillation, and the residue was dissolved in boiling chloroform. Crystallization can be induced by the addition of a little methanol: yield 266.4 g, 90% of theory; colorless plates; mp 82 °C.

Procedure b. To 138 g (1 mol) of veratrole, dissolved in 400 mL of acetic acid, was added at 0–5 °C, over a period of 1 h with stirring, 320 g (2 mol) of bromine dissolved in 250 mL of acetic acid. The bromination can be induced by the addition of a crystal of iodine. After being allowed to stand for 1 h, the suspension was diluted with water, the liquid phase was decanted, and the residue was washed with 1 L of 5% NaOH solution. The precipitate was filtered and washed with water until the washings were neutral. The dry, crude product was crystallized from $CHCl_3/EtOH$ and vacuum-dried at 60 °C: yield 254 g, 86% of theory; colorless plates.

Anal. Calcd for $C_8H_8O_2Br_2$ (M_r = 295.95): C, 32.34; H, 2.68; Br, 54.15. Found: C, 32.46; H, 2.72; Br, 54.00. Mass spectrum: 296 (100%, M^+), 281 (32, $M^+ - CH_3$). ^1H NMR ($CDCl_3$): δ 3.85 (s, 6 H, $-CH_3$), 7.05 (s, 2 H, ArH).

1,2-Dicyano-4,5-dimethoxybenzene (3d). 1,2-Dibromo-4,5-dimethoxybenzene (88.7 g, 0.3 mol) was heated under reflux (bath temperature 165 °C) for 5 h with 80.6 g (0.9 mol) of CuCN in 1.2 L of DMF. After being cooled, the reaction mixture was stirred in 3 L of concentrated ammonium hydroxide and air was led through the solution for a period of 12 h. The blue solution was suction filtered (sintered glass), and the solid residue was washed with a little dilute ammonium hydroxide and then with copious amounts of water until the filtrates were neutral. The dry, crude olive-green product was placed in the thimble of a Soxhlet extractor and extracted for 3 days with ether. The nitrile isolated from the ether was crystallized from methanol: yield 31.9 g, 57% of theory; colorless small needles; mp 179–181 °C.

Anal. Calcd for $C_{10}H_8N_2O_2$ (M_r = 188.2): C, 63.82; H, 4.29; N, 14.89. Found: C, 63.17; H, 4.33; N, 14.13. ^1H NMR ($CDCl_3$): δ 7.25 (s, 2 H, ArH); 3.97 (s, 6 H, CH_3). IR (cm^{-1}, Nujol): 2230 ($C{\equiv}N$). Mass spectrum: 188 (100%, M^+); 173 (42, $M^+ - CH_3$); 145 (22, $M^+ - COCH_3$); 127 (6, $M^+ - C_2H_7O_2$).

(2,3,9,10,16,17,23,24-Octamethoxyphthalocyaninato)cobalt (10). 4,5-Dimethoxyphthalodinitrile (**3d**), (13.77 g, 0.073 mol) and 1.5 g (0.012 mol) of cobalt(II) chloride were heated in 180 mL of ethylene glycol at 200 °C for 5 h, after which the mixture was cooled somewhat, and an equal volume of water was added. The mixture was suction filtered while still hot, and the filtrate was washed with hot water. The purification was carried out as described above with 1 N HCl and 1 N NaOH; yield 4 g, 41.1% of theory.

Anal. Calcd for $C_{40}H_{32}N_8O_8Co$ (M_r = 811.35): C, 59.2; H, 4.0; N, 13.8. Found: C, 58.13; H, 4.09; N, 13.68. Mass spectrum (FD technique): 811 (M^+).

(2,3,9,10,16,17,23,24-Octamethoxyphthalocyaninato)iron(II) (6). A solution of 5 g (25 mmol) of $Fe(CO)_5$ dissolved in 50 mL of 1-chloronaphthalene was added dropwise to a solution of 19 g (100 mmol) of 1,2-dicyano-4,5-dimethoxybenzene (**3d**) that had been dissolved in 130 mL of 1-chloronaphthalene; the solution was kept under reflux, and the addition required 45 min. The black suspension was held at about 250 °C for a further 45 min and then cooled, after which the precipitate was suction filtered, followed by washings with $CHCl_3$, toluene, and acetone. After being boiled in dilute HCl followed by dilute NaOH (see preparation for **5**), the product was placed in the thimble of a Soxhlet extractor and washed overnight with acetone. After the product was dried in vacuo (6 h, 60 °C), 7.5 g (37% of theory) of a black-blue powder was obtained.

Anal. Calcd for $C_{40}H_{32}N_8O_8Fe$ (M_r = 808.6): C, 59.42; H, 3.99; N, 13.86. Found: C, 59.73; H, 4.09; N, 13.88. Mass spectrum (FD technique): 808 (M^+).

(2,9,16,23-Tetra-*tert*-butylphthalocyaninato)iron(II) (4). Nitrile Method in 1,2,4-Trichlorobenzene. 4-*tert*-Butylphthalodinitrile (**3a**) (18.4 g, 100 mmol) was dissolved in 15 mL of 1,2,4-trichlorobenzene and heated to 215 °C, after which 4.9 g (25 mmol) of $Fe(CO)_5$ dissolved in 80 mL of 1,2,4-trichlorobenzene was added dropwise over a period of 50–60 min; the solution was then held at 215 °C for an additional 1 h. After being cooled, the mixture was diluted with an equal volume of methanol, and the ensuing precipitate was vacuum filtered and washed with a little MeOH. After being dried at 60 °C in vacuo, dark blue **4a** was obtained: yield 6.5 g, 33% of theory.

Nitrile Method in Ethylene Glycol. 4-*tert*-Butylphthalodinitrile (**3a**) (7.4 g, 40 mmol) was stirred into 150 mL of ethylene glycol. Iron pentacarbonyl ($Fe(CO)_5$) (2 g, 10 mmol) was added to the ethylene glycol mixture, which had been heated to 190–210 °C in 0.1-mL portions over a period of 45 min. The $Fe(CO)_5$ was injected directly into the solvent with a hypodermic needle. The black-blue solution was maintained an additional 45 min at 200 °C. After being cooled and diluted with 150 mL of H_2O, the suspension was suction filtered; the solid material was washed with water until the washings were colorless and finally given three further washings with 5-mL portions of MeOH; yield 3.0 g, 38% of theory.

After being heated under a N_2 atmosphere for 2 h at 300 °C, compound **4a** obtained through the above synthesis was converted to **4**.

Anal. Calcd for $C_{48}H_{48}N_8Fe$ (M_r = 792.8): C, 72.72; H, 6.10; N, 14.13. Found: C, 72.70; H, 6.28; N, 12.93. Mass spectrum: 793 (11%, M^+); 778 (3, $M^+ - CH_3$); 763 (2, $M^+ - 2CH_3$); as well as six additional, successive methyl group losses of smaller intensities. The ion of highest mass, *m*/*e* = 793, was also present in the mass spectrum of **4a**.

(2,3,9,10,16,17,23,24-Octamethylphthalocyaninato)iron(II) (5). 1,2-Dicyano-4,5-dimethylbenzene (3c).[5,39] 1,2-Dibromo-4,5-dimethylbenzene[40] (105.6 g, 0.4 mol) and 107.4 g (1.2 mol) of CuCN were boiled under reflux for 5 h in 800 mL of DMF (bath temperature 165 °C). At the end of that time the mixture was allowed to cool, and it was then poured into 3.5 L of concentrated ammonium hydroxide. The ensuing mixture was stirred for 12 h while air was slowly bubbled through it. The precipitate was suction filtered through a sintered funnel, washed with a little dilute ammonia, and then washed copiously with warm water until the washings were neutral. According to the IR spectrum, the olive-colored crude product still contained some copper cyanide. Therefore, the organic compound **3c** was extracted with ether and crystallized from methanol: yield 27 g (43% of theory); colorless needles; mp 175–177 °C.

Anal. Calcd for $C_{10}H_8N_2$ (M_r = 156.2): C, 76.90; H, 5.16; N, 17.95. Found: C, 76.43; H, 5.45; N, 16.77. ^{1}H NMR ($CDCl_3$): δ 7.55 (s, 2 H, ArH); 2.38 (s, 6 H, CH_3). IR (cm^{-1}, Nujol): 2240 ($C\equiv N$). Mass spectrum 157 (10%, $M^+ + 1$); 156 (100, M^+); 153 (30, $M^+ - 1$); 141 (90, $M^+ - CH_3$); 128 (13, $M^+ - 2CH_3$); 114 ($M^+ - C_2H_3N$).

(2,3,9,10,16,17,23,24-Octamethylphthalocyaninato)iron(II) (5). To a solution of 19.5 g (125 mmol) of 1,2-dicyano-4,5-dimethylbenzene (**3c**) in 200 mL of 1-chloronaphthalene was added under reflux and dropwise 6.0 g (32 mmol) of $Fe(CO)_5$ that had been dissolved in 50 mL of 1-chloronaphthalene; the addition required 45 min. The reaction was allowed to reflux an additional 45 min, the mixture was cooled, and the precipitate was collected on a filter (suction) and washed with $CHCl_3$, ethanol, acetone, and finally ether. The crude product was boiled for 10 min each in 1% HCl and 1% NaOH solutions, washed with water until the washings were neutral, and then treated on the sintered glass disk with acetone and ether and filtered. After the product was dried at 80 °C in vacuo, there remained 8.8 g of violet-black powder (41% of theory).

Anal. Calcd for $C_{40}H_{32}N_8Fe$ (M_r = 680.6): C, 70.59; H, 4.74; N, 16.46. Found: C, 70.86; H, 4.74; N, 16.83. Mass spectrum: 680 (41, M^+); 665 (4, $M^+ - CH_3$); 340 (5, M^{2+}).

(Hexadecachlorophthalocyaninato)iron(II) (7).[23] Urea (35 g, 0.50 mol), 48 g (0.17 mol) of tetrachlorophthalic anhydride (**2e**), 8.5 g (0.04 mol) of $FeCl_2{\cdot}4H_2O$, and 0.2 g of ammonium molybdate were finely pulverized and stirred into 150 mL of nitrobenzene. The suspension was then heated to 180–190 °C within $^1/_2$ h and then maintained at that temperature for 4 h until the evolution of ammonia stopped. The viscous olive-green suspension was cooled to 90 °C, diluted with 150 mL of ethanol, and filtered hot, and the residue was washed copiously with boiling water. The further workup of this compound proceeded as described for compound **5**. The crude product obtained in this way was extracted an additional 3 days with chlorobenzene: yield 28.8 g (61% of theory); olive-green, scaly powder.

Anal. Calcd for $C_{32}N_8Cl_{16}Fe$ (M_r = 1119.5): C, 34.33; N, 10.01; Cl, 50.67. Found: C, 34.32; N, 10.26; Cl, 50.60. Mass spectrum: M^+ not obtainable. The ion of highest mass is *m*/*e* = 268.

(2,9,16,23-Tetra-*tert*-butylphthalocyaninato)bis(pyridine)iron(II) (13). Compound **4** (0.4 g, 0.5 mmol) was extracted with 10 mL of pyridine. The green pyridine solution was concentrated under vacuum at 60 °C. From the raw product so obtained, 0.3 g of *tert*-butylphthalimide was extracted with a 20:80 pyridine–water mixture. After being dried in vacuo (3 h at 60 °C), the product was obtained as a dark green powder, yield 0.25 g (51% of theory).

Anal. Calcd for $C_{58}H_{58}N_{10}Fe$ (M_r = 951.0): C, 73.25; H, 6.15; N, 14.73. Found: C, 72.72; H, 6.55; N, 13.71.

General Directions for the Preparation of (2,3,9,10,16,17,23,24-Octamethylphthalocyaninato)bis(pyridine)iron(II) (14), (2,3,9,10,16,17,23,24-Octamethoxyphthalocyaninato)bis(pyridine)-iron(II)–2-Pyridine (15), and (Hexadecachlorophthalocyaninato)-bis(pyridine)iron(II) (16). One millimole of the substituted (phthalocyaninato)iron(II) compound **5**, **6**, or **7** was suspended in ca. 100 mmol of pyridine and boiled under reflux for 2–15 h. The solid material was suction filtered, washed with a little pyridine, and then finally washed with either methanol or ethanol and dried in vacuo at 60 °C for 4 h. All of the bis(pyridine) adducts were obtained in quantitative yields.

Anal. Calcd for **14** (dark grey powder), $C_{50}H_{42}N_{10}Fe$ (M_r = 838.8): C, 71.60; H, 5.05; N, 16.70. Found: C, 72.31; H, 5.28, N, 17.20. Calcd for **15** (green powder), $C_{50}H_{42}N_{10}O_8Fe$ (M_r = 1125.9): C, 64.06; H, 4.66; N, 14.94. Found: C, 63.99; H, 4.88; N, 14.97. Calcd for **16** (light green powder), $C_{42}H_{10}N_{10}Cl_{16}Fe$ (M_r = 1277.7): C, 39.48; H, 0.79; N, 10.96; Cl, 44.39. Found: C, 40.27; H, 0.72; N, 11.44; Cl, 43.31.

(2,9,16,23-Tetranitrophthalocyaninato)bis(pyridine)cobalt(II) (20). Compound **9**, 0.38 g (0.5 mol), was stirred in 25 mL of pyridine for 6 days at temperatures between 25 and 115 °C. The mixture was then vacuum filtered and dried in vacuo.

Anal. Calcd for $C_{42}H_{22}N_{14}O_8Co$: C, 55.46; H, 2.40; N, 21.82. Found: C, 55.40; H, 2.46; N, 21.80.

(Chlorophthalocyaninato)(pyridine)cobalt(II) (23). Compound **11**, 0.3 g (0.5 mmol), was heated in 20 mL of pyridine under reflux for 2 days; the excess pyridine was then distilled from the residue (bath temperature 140 °C).

Anal. Calcd for $C_{37}H_{20}N_9CoCl$ (M_r = 683.90): C, 65.00; H, 2.93; N, 18.43; Cl, 5.18. Found: C, 66.08; H, 3.20; N, 17.81; Cl, 5.00.

(2,9,16,23-Tetra-*tert*-butylphthalocyaninato)(pyridine)cobalt(II) (21). Compound **8**, 0.4 g (0.5 mmol), was heated 24 h in 15 mL of pyridine at 50–60 °C. The excess pyridine was then removed by distillation (bath temperature 50 °C). The residue was suspended in 50 mL of 1 N tartaric acid, and the mixture was stirred at room temperature for 24 h. The solid material was then collected on a filter (vacuum) and dried in vacuo.

Anal. Calcd for $C_{53}H_{53}N_9Co$ (M_r = 874.94): C, 72.75; H, 6.09; N, 14.40. Found: C, 73.01; H, 6.56; N, 13.85.

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Registry No. **2a**, 32703-79-0; **2b**, 5466-84-2; **2e**, 117-08-8; **3a**, 32703-80-3; **3b**, 5466-84-2; **3c**, 36360-43-7; **3d**, 88946-67-2; **4**, 78452-92-3; **5**, 31243-92-2; **6**, 88946-68-3; **7**, 50662-67-4; **8**, 70619-85-1; **9**, 27680-28-0; **10**, 88946-69-4; **11**, 88946-70-7; **12**, 132-16-1; **13**, 78251-15-7; **14**, 88946-71-8; **15**, 88946-72-9; **16**, 88980-92-1; **17**, 88946-73-0; **18**, 41677-39-8; **19**, 88946-74-1; **20**, 88946-75-2; **21**, 88946-76-3; **22**, 76857-35-7; **23**, 88946-77-4; $Fe(CO)_5$, 13463-40-6; urea, 57-13-6; 4-nitrophthalimide, 89-40-7; 4-nitrophthalodiamide, 13138-53-9; ammonium molybdate, 11098-84-3; veratrole, 91-16-7; 1,2-dibromo-4,5-dimethoxybenzene, 37895-73-1; 1,2-dibromo-4,5-dimethylbenzene, 24932-48-7.

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(39) The synthesis of this compound is also described via a Diels–Alder reaction: Mikhalenko, S. A.; Gladyr, S. A.; Luk'yanets, E. A. *J. Org. Chem. USSR (Engl. Transl.)* **1972**, *8*, 341; *Zh. Org. Khim.* **1972**, *8*, 341.

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