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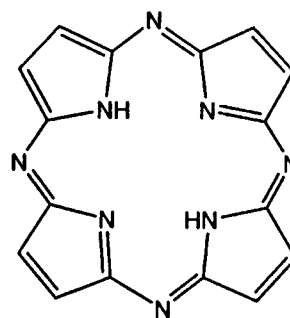
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Introduction.

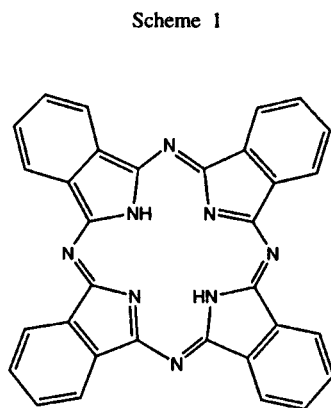
The two cornerstones in tetrapyrrolic macrocyclic ring systems are porphyrins and tetraazaporphyrins, which include phthalocyanines and porphyrazines [1,2]. Although porphyrins and phthalocyanines have been well studied, porphyrazines have received considerably less attention since their first synthesis almost fifty years ago. With the recent introduction of efficient syntheses of soluble derivatives, however, porphyrazines promise to gain in prominence over their structural relatives. Porphyrins, phthalocyanines, and porphyrazines coordinate an extensive range of metal ions within their central cavities. In contrast to porphyrins, *meso*-substitution of nitrogen in tetraazaporphyrins modulates the electronic character of the macrocycle. Combining the electronic character and extended π -system of phthalocyanines and porphyrazines with peripheral metal coordination permits the preparation of a wide variety of multimetallic complexes with novel structural, spectroscopic, magnetic, and electronic properties.

Scheme 2

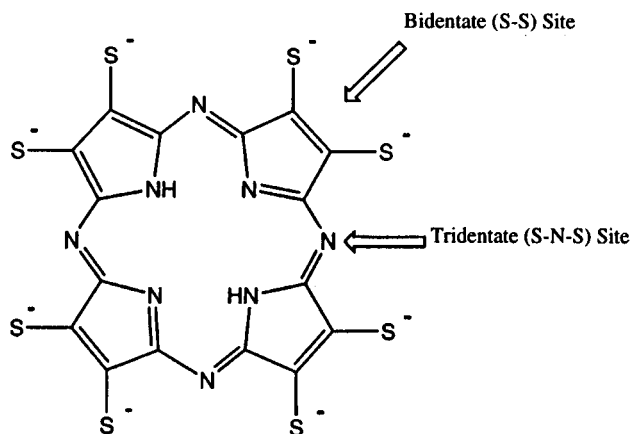


PORPHYRAZINE

Scheme 3

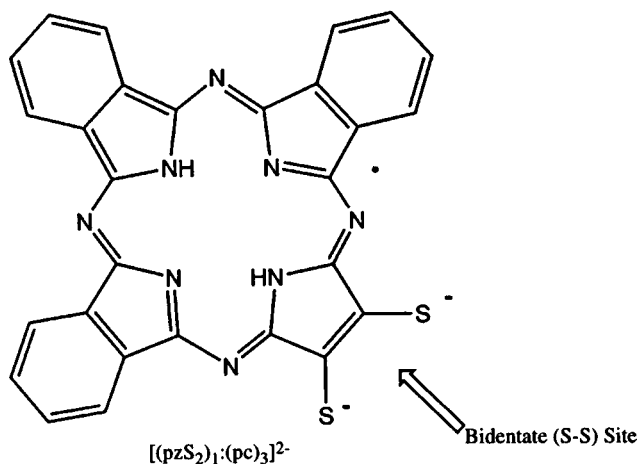


PHTHALOCYANINE



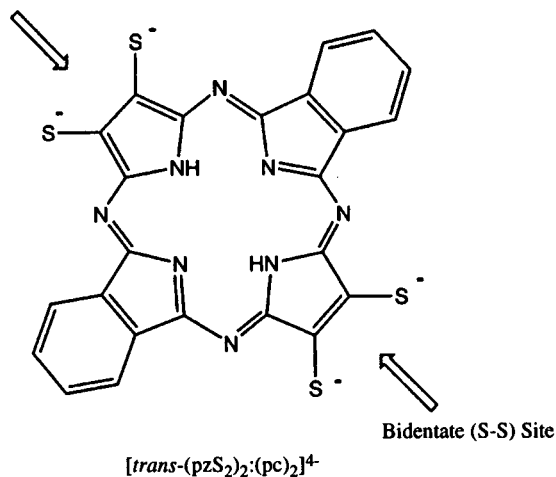
$[pzS_2]_4^{8-}$

Scheme 4

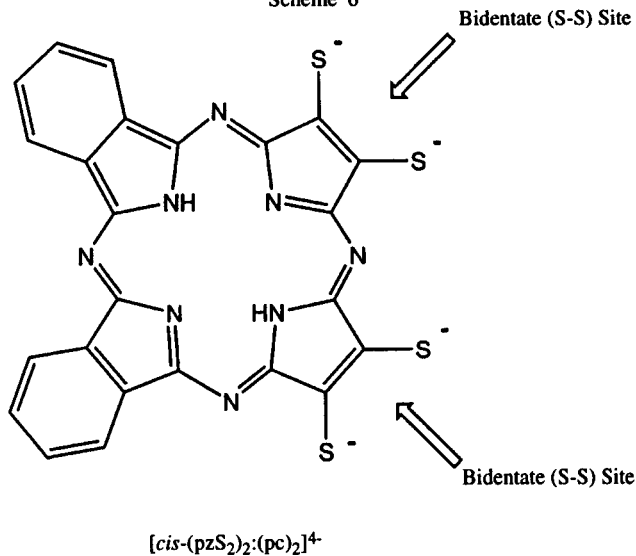


Scheme 5

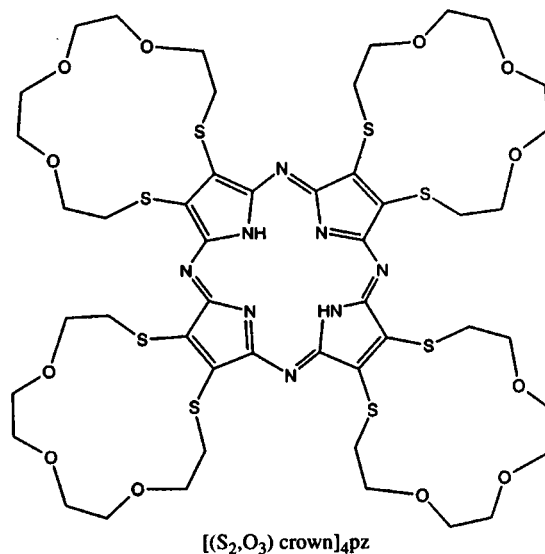
Bidentate (S-S) Site



Scheme 6



Scheme 7



The Hoffman and Barrett groups have carried out studies on the synthesis and characterization of diverse porphyrazine derivatives that are graced with heteroatom groups directly bonded to the macrocyclic core of the porphyrazine [3-31]. Such species are exemplified by the porphyrazineoctathiolate $[(pzS_2)_4]^{8-}$, the dithiolate $[(pzS_2):(pc)_3]^{2-}$, and the two tetrathiols *trans*- $[(pzS_2)_2:(pc)_2]^{4-}$ and *cis*- $[(pzS_2)_2:(pc)_2]^{4-}$. These porphyrazines exhibit unusual coordination chemistry through binding of metal ions both within the macrocyclic cavity and by the peripheral ligating groups. There is clearly the possibility of metal ion binding either *via* the bidentate S-CH=CH-S units or within the *meso*-pocket *via* bonding to the S-N-S entities. In addition, such electron rich porphyrazines show unusual UV-vis spectra, electrochemistry, magnetic properties, *etc.*

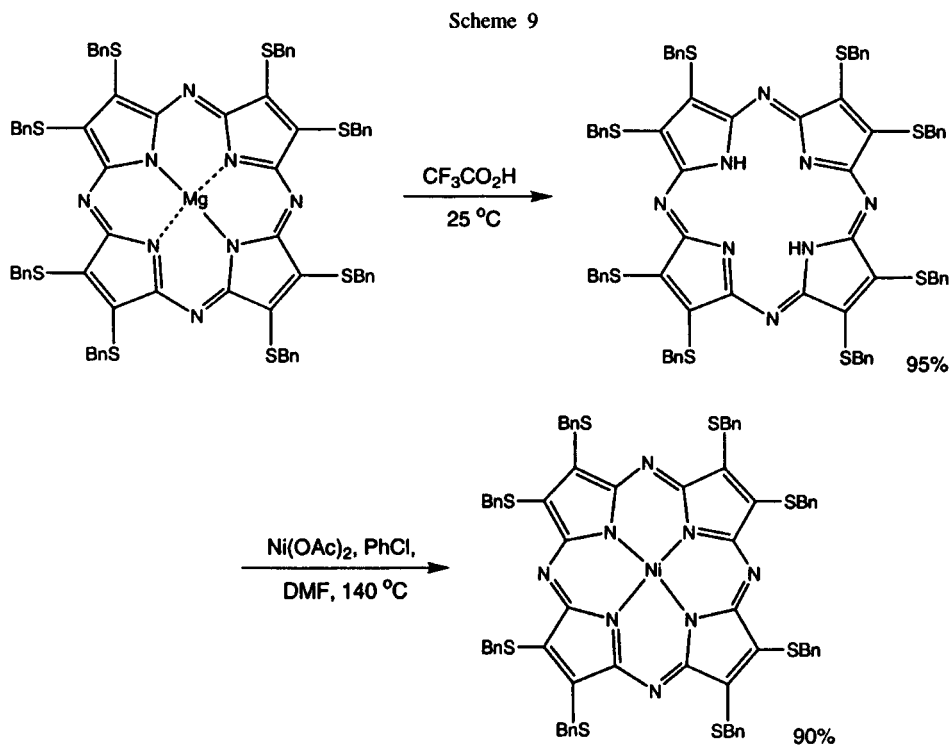
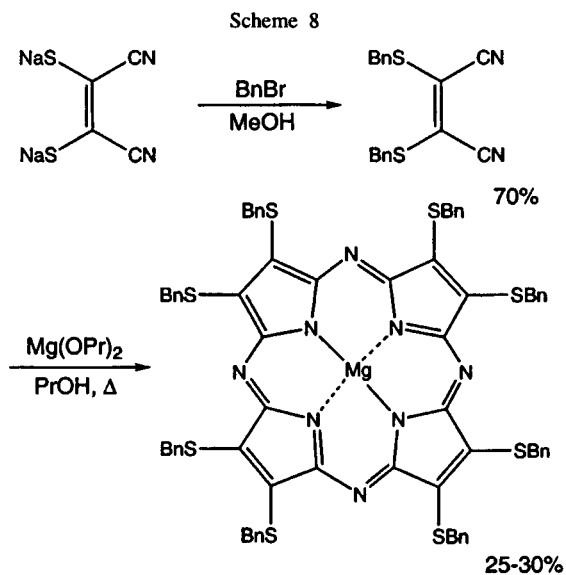
Fused phthalocyanine-crown ether arrays are well established compounds [32]. Nonetheless, prior to work in the area at Northwestern University and Imperial College, there were no studies reported on the structurally related fused porphyrazine-crown ether systems. Such compounds, which are exemplified by $[(S_2O_3) crown]_4pz$, should show rich and varied coordination chemistry. In contrast to fused phthalocyanine-crown ether systems, metal ion coordination by the crown ether units in $[(S_2O_3) crown]_4pz$ have profound effects on UV-vis spectra and other properties, since the key crown sulfur residues are in direct electronic contact with the macrocyclic central chromophore.

Synthesis of Porphyrazine Ligands.

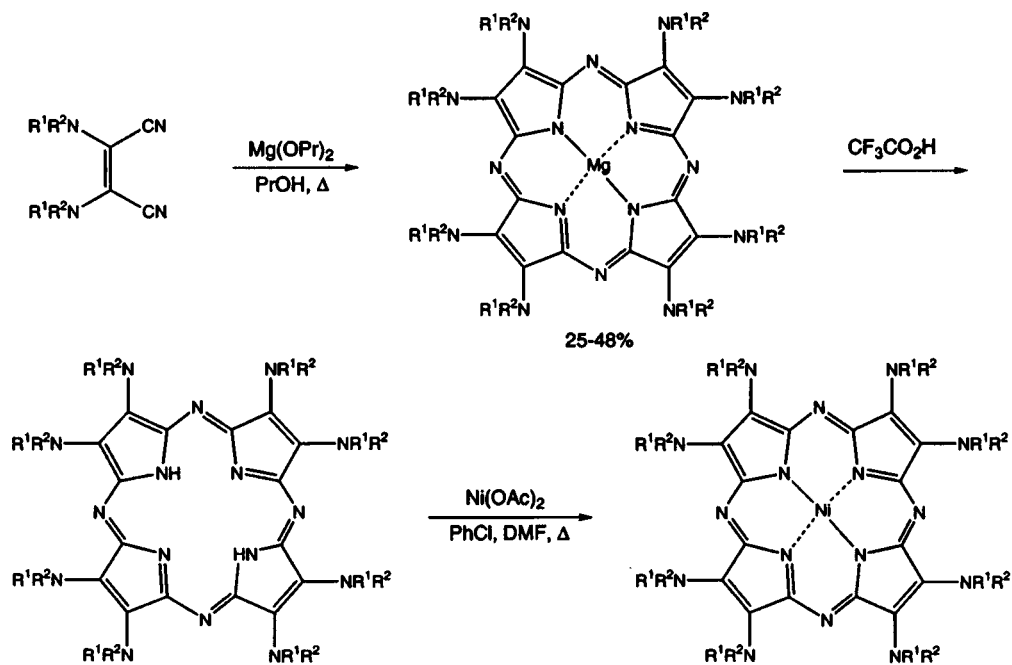
All porphyrazines were prepared from the corresponding heteroatom functionalized maleonitriles using a Linstead

magnesium alkoxide templated macrocyclization reaction in an alcohol solvent at reflux. These reactions are exemplified by the conversions of derivatives of 2,3-dimercapto-, 2,3-diamino-, and 2,3-dihydroxy-maleonitrile to provide the corresponding porphyrazine-octathiols, -octamines, and -octaols. In each case, the magnesium ion template was removed under acidic conditions and replaced with representative diamagnetic ions, Ni(II) or Zn(II), or representative paramagnetic ions, Cu(II) or Mn(III). In the case of the octathiol system, the mercapto

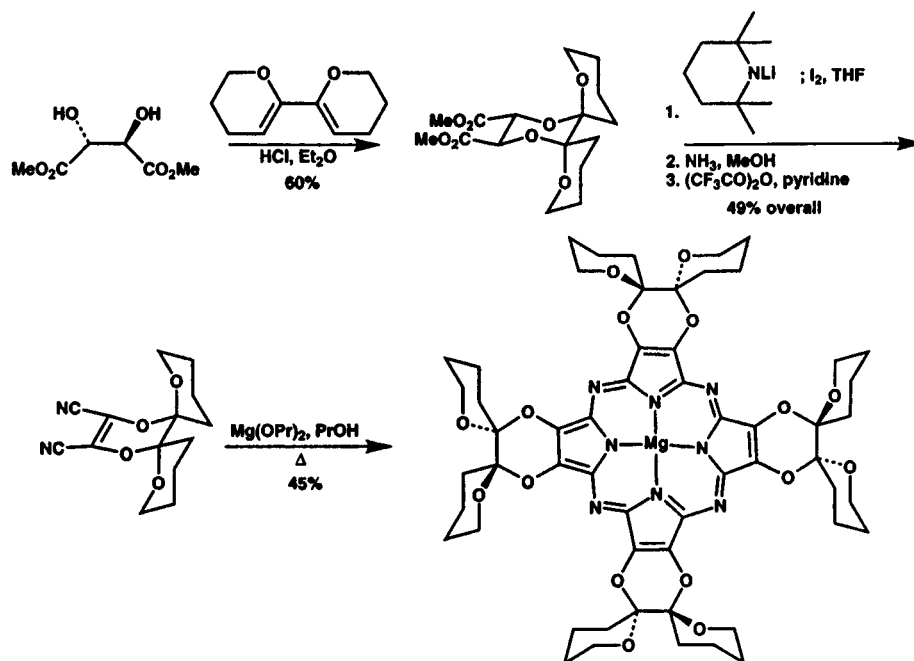
residues were conveniently protected as benzyl or substituted benzyl derivatives. The preparation of the corresponding amines was carried out with a range of different groups R^1R^2N ($R^1R^2N = NMe_2, NMeBn, NMeCH_2$ -pyridyl, *etc.*) whereas derivatives of porphyrazinooctal were prepared efficiently using Ley dispoke protection [33-37]. It should be mentioned that this synthesis represents a most concise method to elaborate homochiral coordination complexes of the porphyrin/phthalocyanine/porphyrazine class. The X-ray crystal structure of the parent tetra-dispoke porphyrazinooctal following removal of the Mg(II), which is shown below, clearly illustrates the chiral nature of these intriguing heterocycles.



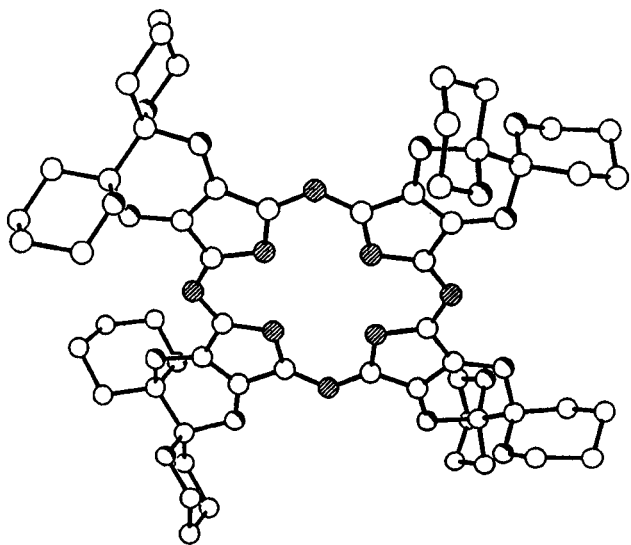
Scheme 10



Scheme 11

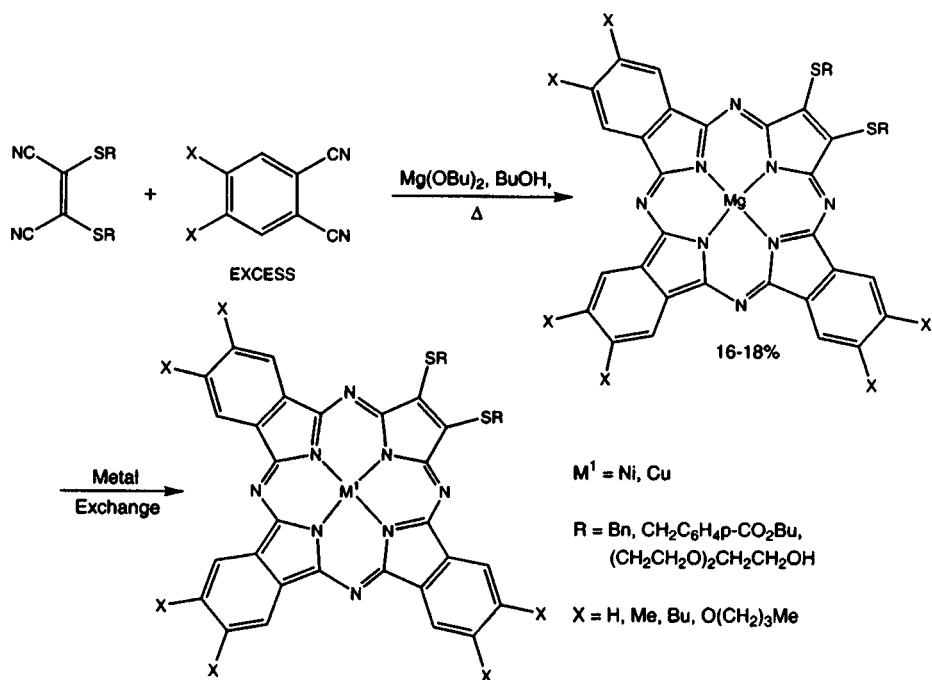


Scheme 12

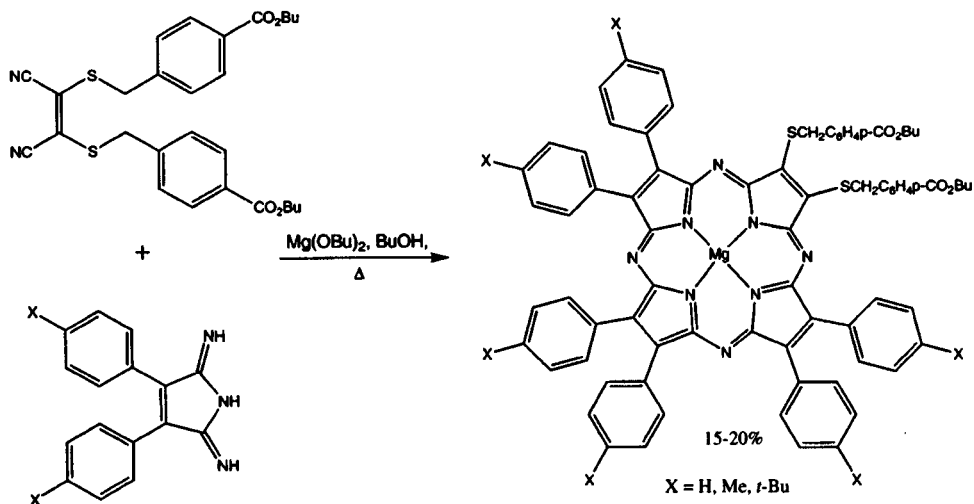


It is possible to adapt the Linstead macrocyclization for the elaboration of porphyrazines bearing 2, 4, or 6 heteroatoms instead of 8. In these cases mixtures of two nitriles were allowed to react with magnesium butoxide to provide mixtures of all possible porphyrazines. Of course, statistical crossover macrocyclization has the potential downside of tedious and suffering in purification. Yet there is salvation in careful synthetic planning. For example, derivatives of porphyrazinedithiol were easily isolated from the macrocyclization of a 2,3-dimercaptomaleonitrile derivative with excess of a substituted dicyano-benzene. In this case, purification was greatly facilitated by the poor solubility of the phthalocyanine and may be further aided by choice in X and thiol protecting group R. In the same way, it was straightforward to elaborate derivatives of porphyrazinedithiol from the Linstead macrocyclization of a diiminopyrroline with a protected dimer-captomaleonitrile.

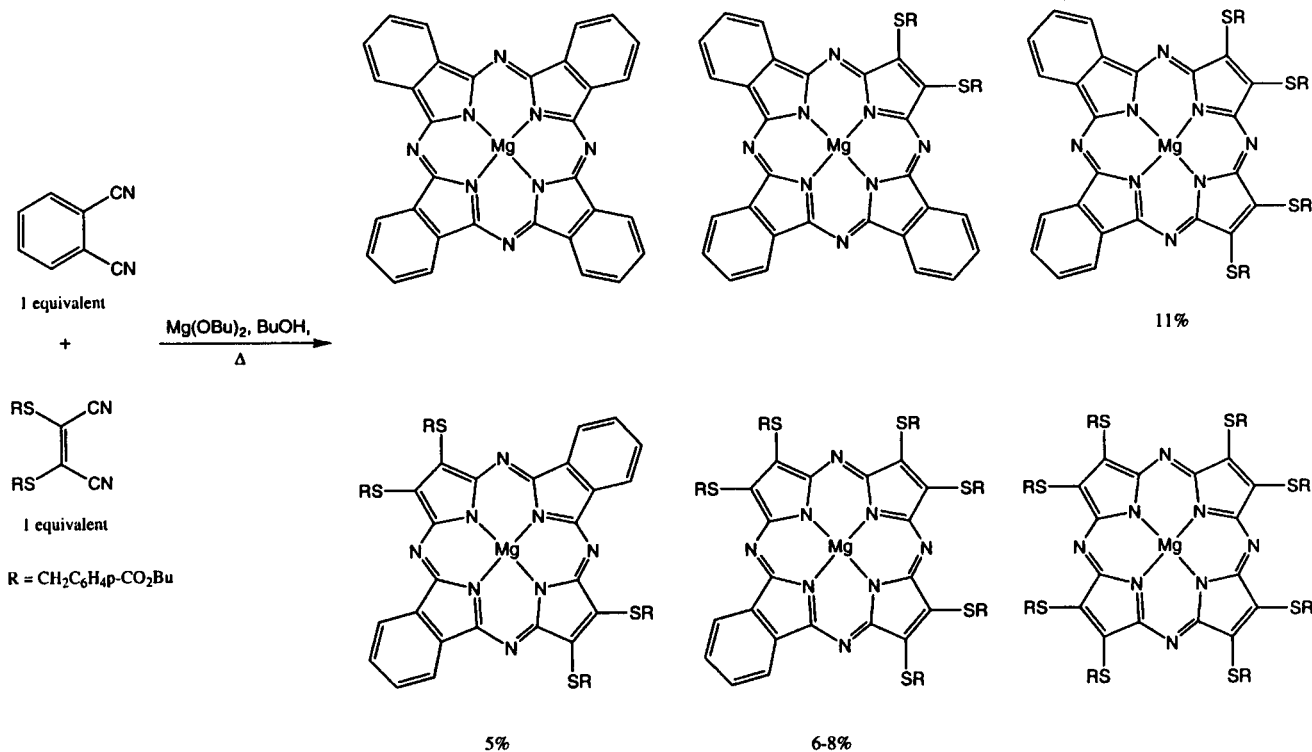
Scheme 13



Scheme 14



Scheme 15



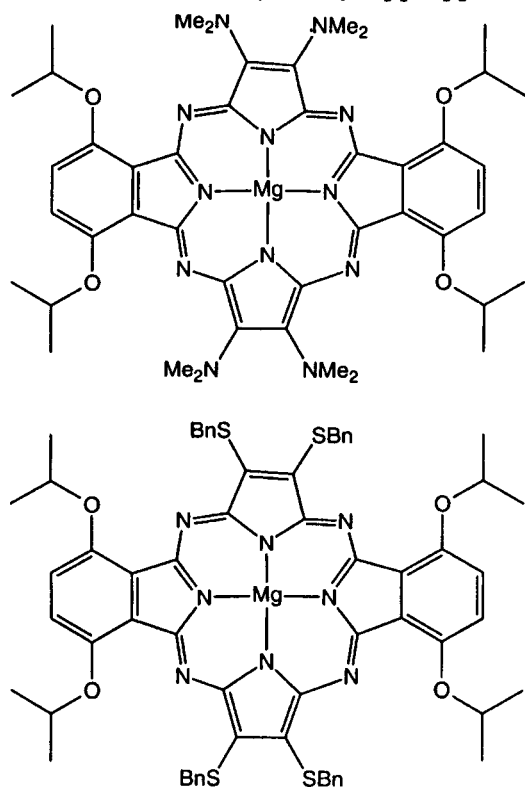
The crossover macrocyclization of equimolar quantities of a phthalonitrile with a 2,3-dimercaptomaleonitrile derivative produces a mixture of six macrocycles. The use of the *para*-[(butyloxy)carbonyl]benzyl protection was crucial in permitting chromatographic separation of the dye mixture simply because it is more polar than the corresponding benzyl derivative. In this way, it was possible to isolate and characterize the *cis*- and *trans*-por-

phyrzinetetralthiol systems and the corresponding S_6 system. All of these crossover macrocyclization procedures have been applied to the synthesis of N_2 , *cis*- N_4 , *trans*- N_4 , N_6 , O_2 , *cis*- O_4 , *trans*- O_4 , and O_6 systems. Nonetheless, there is need for improvement. The crossover macrocyclization of 4,7-di-*iso*-propoxy-1,3-diimino-isoindoline with substituted maleonitriles was especially effective for the elaboration of *trans*-porphyrzine arrays including

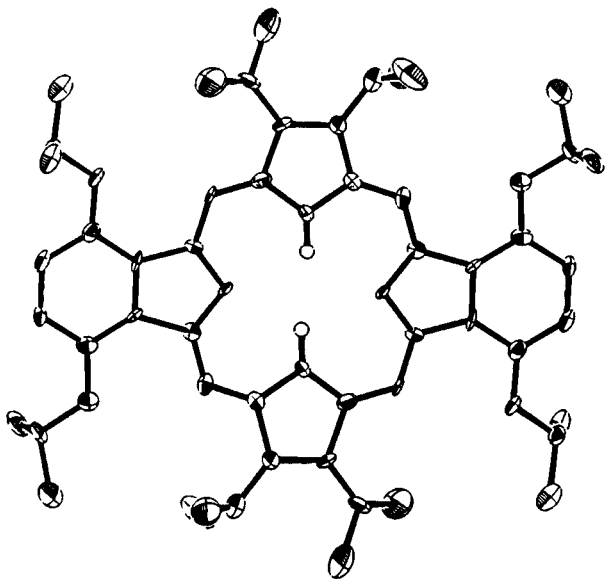
derivatives of porphrazine-tetraathiol, -tetraamine, and -tetraol. Presumably, steric hindrance provided by the *iso*-propoxy groups disfavor formation of the corresponding *cis*-isomers. The efficacy of the method is underscored by the

examples that follow including the remarkable efficiency in the preparation of the dispoke protected porphrazine-tetraol system. That these crossover macrocyclizations provide the *trans*-array is confirmed by two X-ray crystallographic studies.

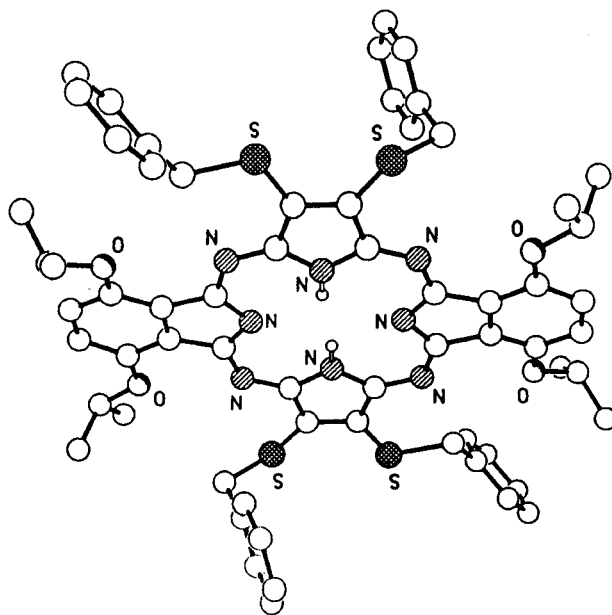
Scheme 16
trans-Macrocycles: $M[pz(X_2)_2:(Y_2)_2]$



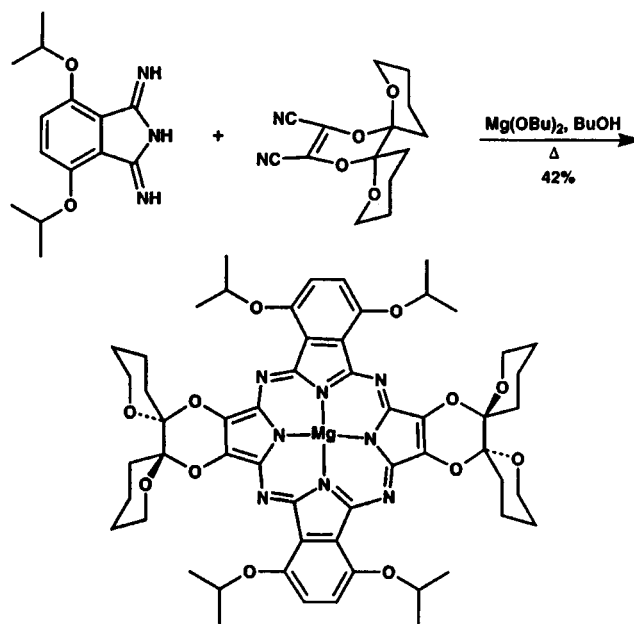
Scheme 17
Ortep of *trans* dimethylamino/isopropoxy pz/pc hybrid



Scheme 18



Scheme 19

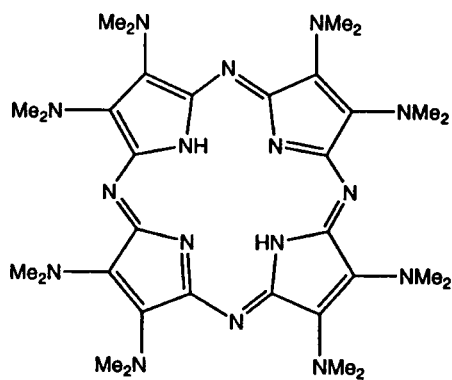


Properties of Heteroatom Substituted Porphyrazines.

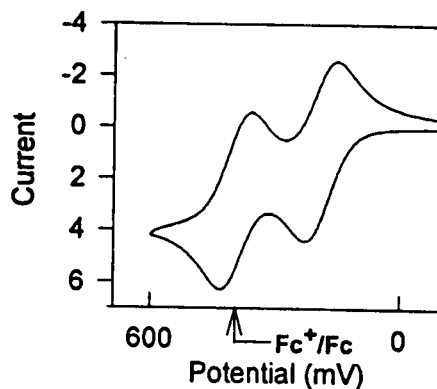
In general, phthalocyanines are robust compounds of low solubility in most solvents, concentrated sulfuric acid being a notable exception. Porphyrazines, especially when functionalized with peripheral heteroatoms, are quite soluble in diverse solvents. For example, octakis(dimethylamino)porphyrazine is very soluble in all common solvents from hexanes to methanol. The corresponding porphyrazines bearing hydroxyalkyl side chains are even soluble in water. Octakis(dimethylamino)porphyrazine is very electron rich; cyclic voltametry shows that this pigment is easier to oxidize than ferrocene to the ferrocenium

cation. As such, the compound may be oxidized either with air, under acidic conditions, or with manganese dioxide to provide the corresponding *seco*-porphyrazine. The structure of this substance was unequivocally established by an X-ray crystallographic study. Oxidation of the octakis(dimethylamino)porphyrazinatozinc(II) with manganese dioxide gave either the corresponding *seco*- or *trans-diseco* porphyrazines depending on the stoichiometry of the reaction. This oxidative ring scission of a $\text{Me}_2\text{NC}=\text{CNMe}_2$ unit has also been observed in hexa-propyl(dimethylamino)porphyrazinatozinc(II). An X-ray crystallographic study established the structure as a dimer entity with bridging axial coordination of zinc.

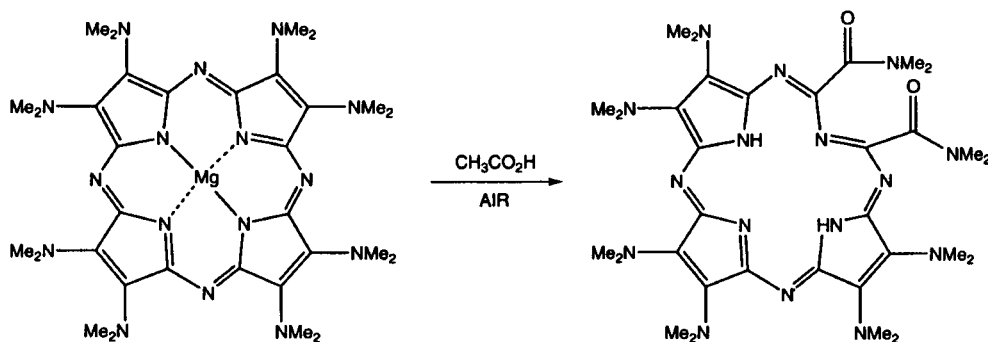
Scheme 20



SOLUBLE IN HEXANES.....METHANOL

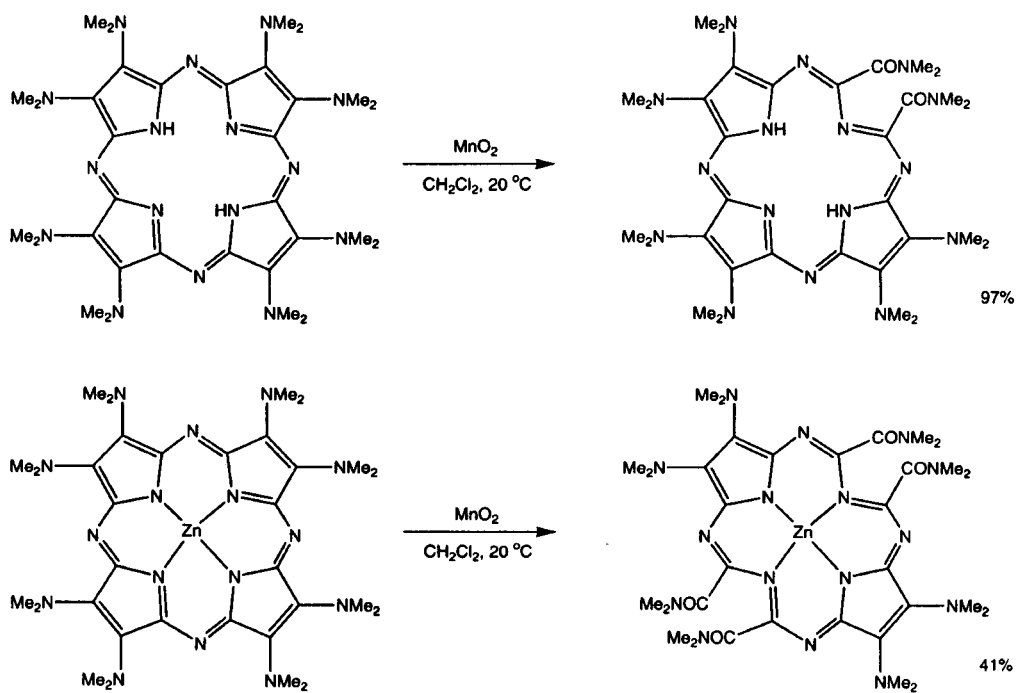


Scheme 21

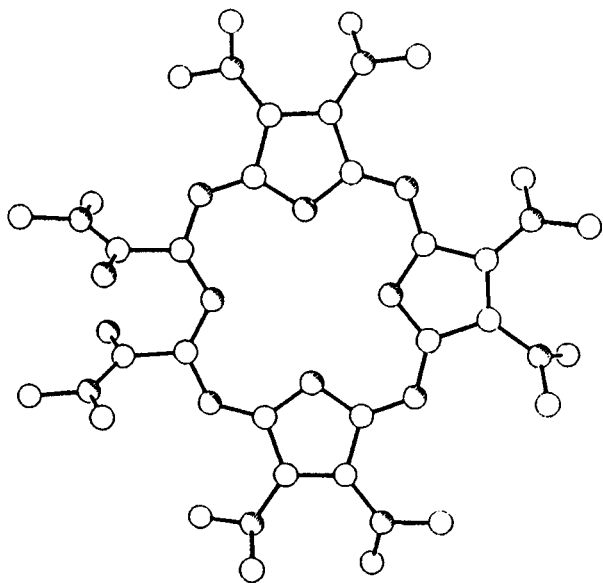


62%

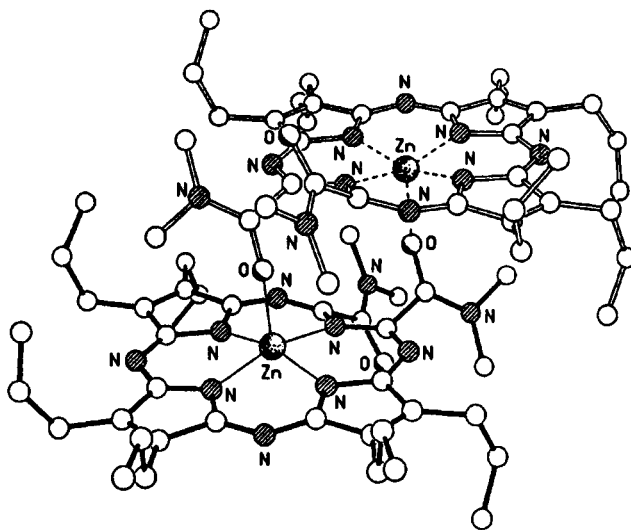
Scheme 22



Scheme 23



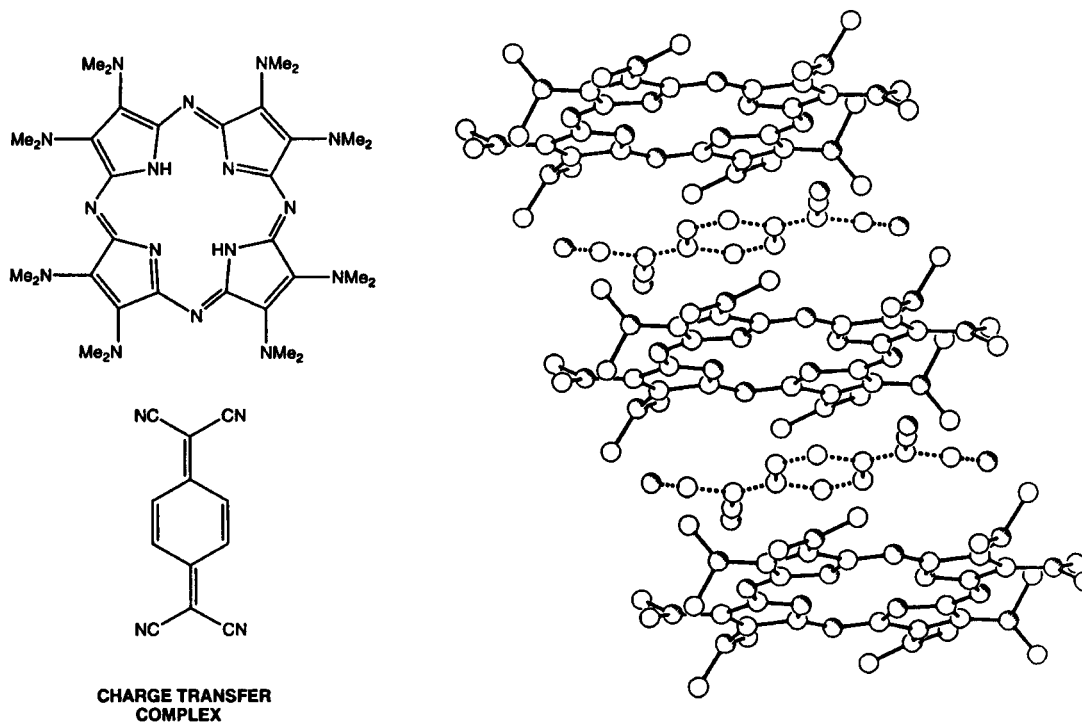
Scheme 24



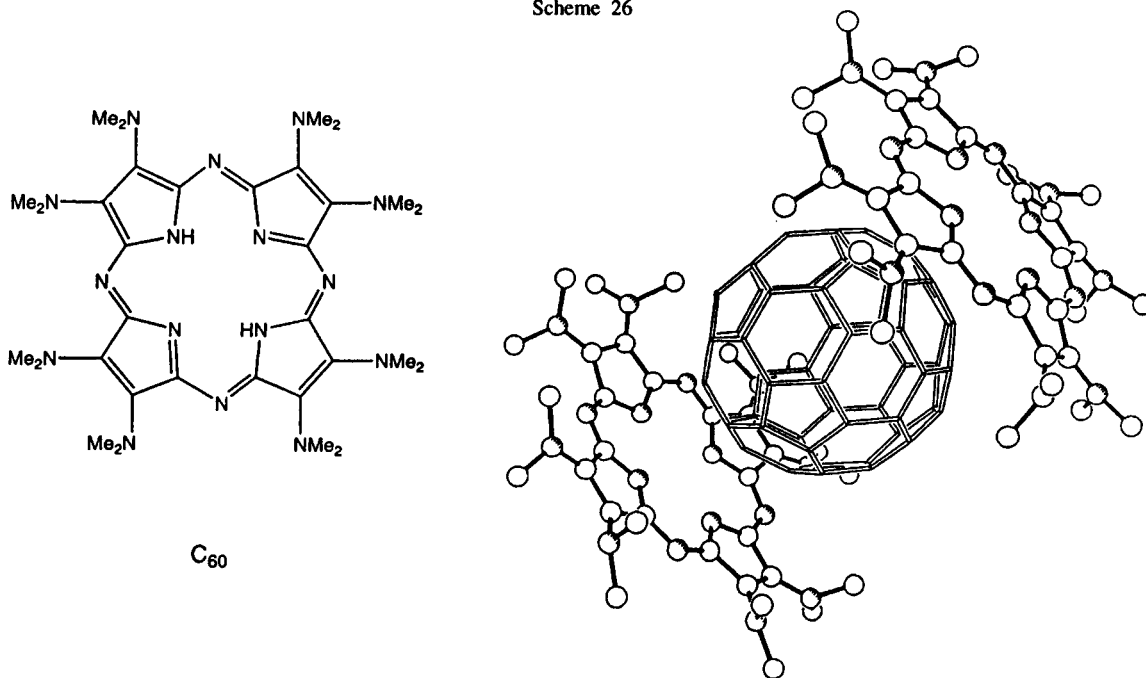
As stated earlier, octakis(dimethylamino)porphyrazine is an electron rich pigment. It forms a 1:1 charge transfer complex with TCNQ which has been characterized by X-ray crystallography and infra-red spectroscopy. Addi-

tionally the octamine forms a 2:1 complex with C_{60} as a toluene solvate. Again, this substance was fully authenticated by a X-ray crystallographic study and this has shown that the macrocyclic rings are distorted from planarity whilst enrobing the fullerene sphere.

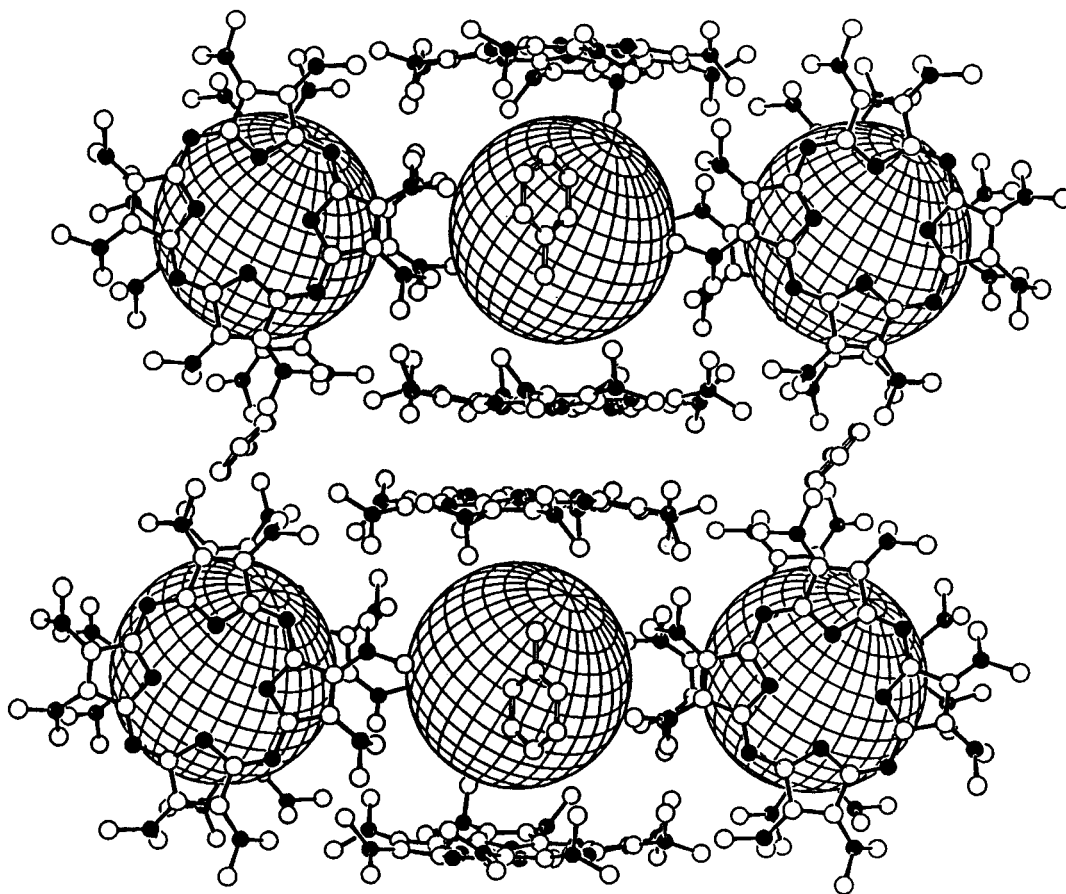
Scheme 25



Scheme 26



Scheme 27

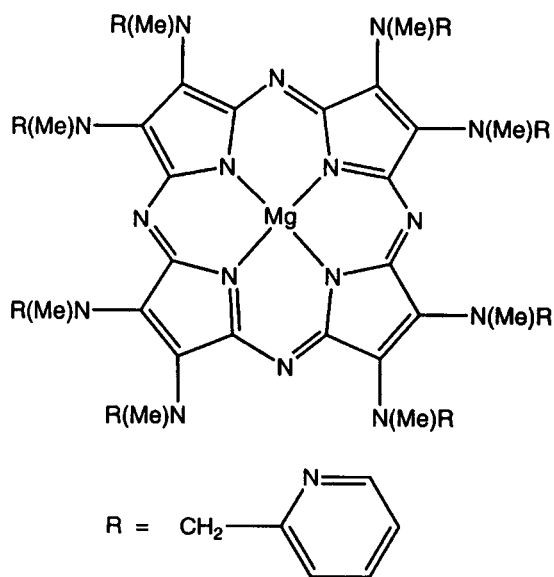
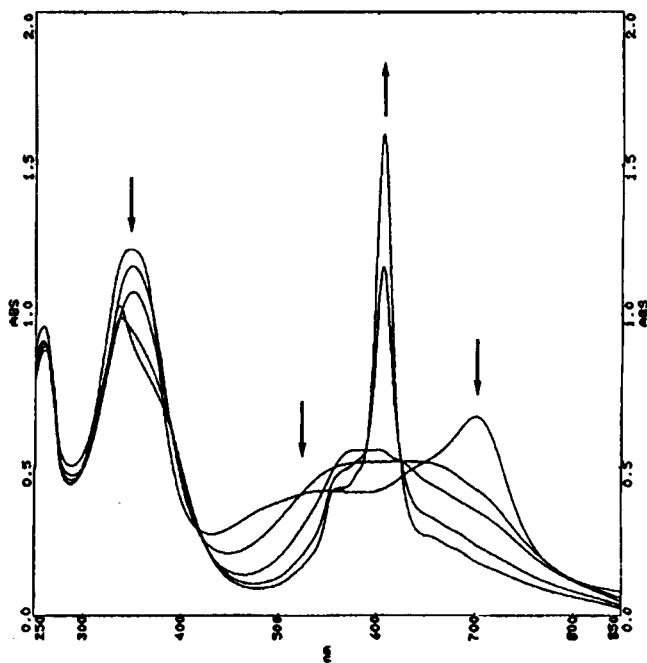


Peripheral Metal Ion Complexation by Heteroatom Substituted Porphyrazines.

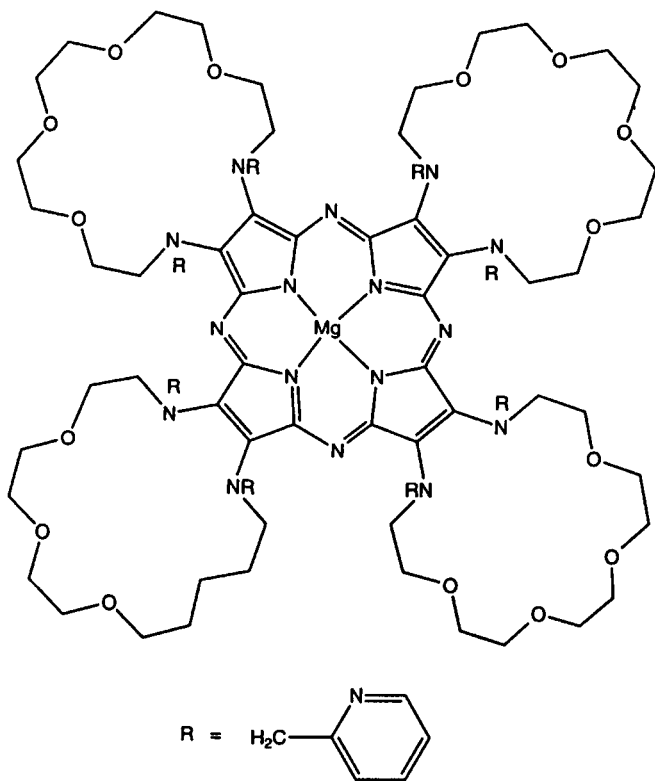
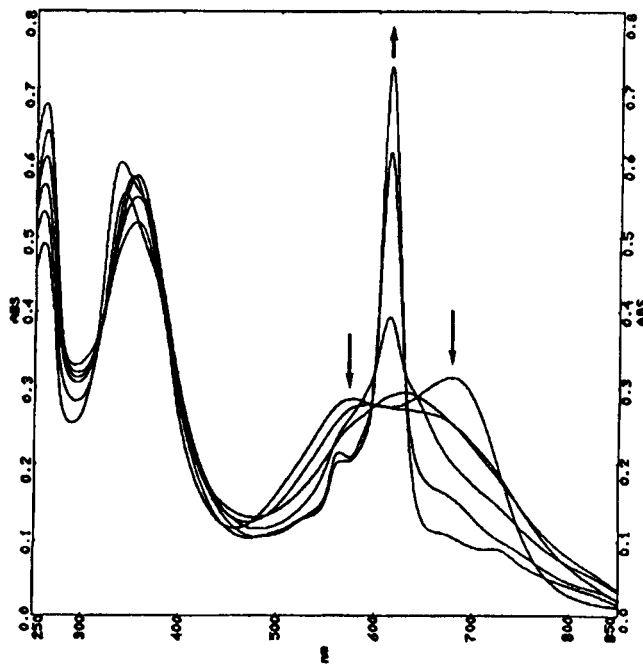
As described in the introduction, porphyrazines endowed with peripheral heteroatoms are able to bind additional metal ions over and above that encapsulated within the macrocyclic cavity. Such binding should be apparent by changes in the UV-vis spectrum, since the heteroatoms are in direct electronic contact with the aromatic π -system. For example, the porphyrazine bearing eight *N*-methyl-*N*-2-pyridylmethyl residues peripherally

coordinated Co(II), Cu(II), and Zn(II) and only a slight excess of the metal salt was required before the $n\text{-}\pi^*$ peak disappeared and the Q band sharpened. The same porphyrazine also coordinated Hg(II), Cd(II), and Ag(I) but less effectively. The corresponding crowned porphyrazine readily and efficiently complexed Hg(II), Ag(I), or Pb(II) whereas Cu(II), Co(II), Zn(II), and Cd(II) were coordinated less avidly. Representative UV-vis titrations are given below. Clearly, such profound changes in the UV-vis signature, upon peripheral metal ion coordination, are relevant to ion selective sensors.

Scheme 28

UV/Vis Titration Using CoCl_2 (0, 1, 2, 3, 4 equivalents)

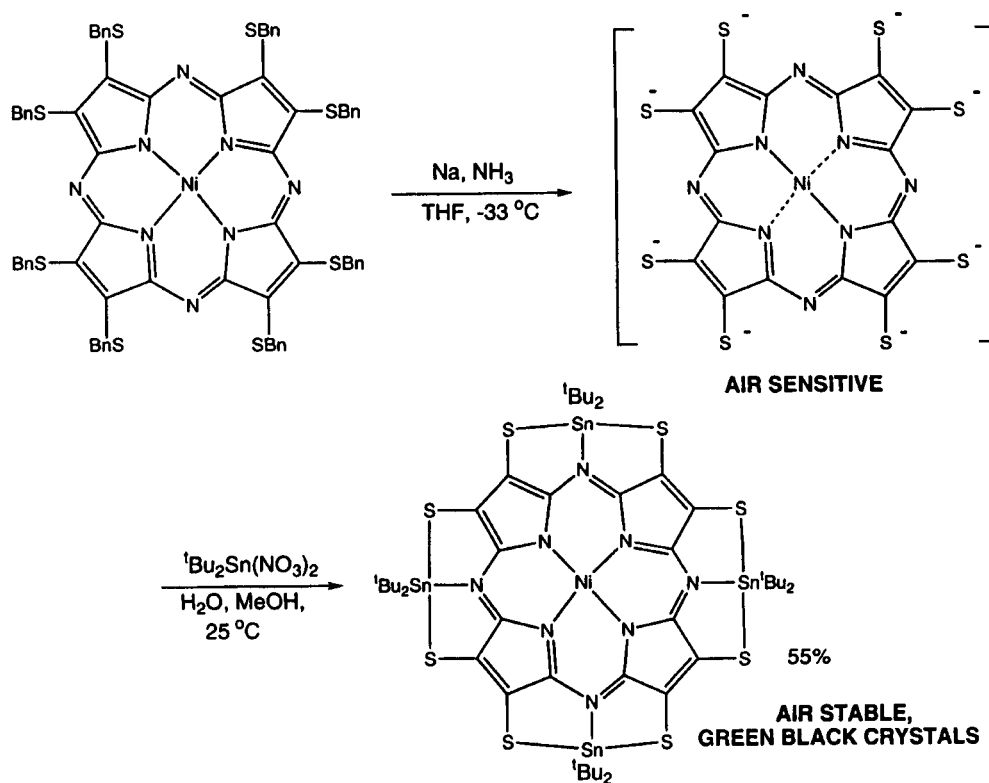
Scheme 29

UV/Vis Titration Using $\text{Hg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (0, 1, 2, 3, 4, 6 equivalents)

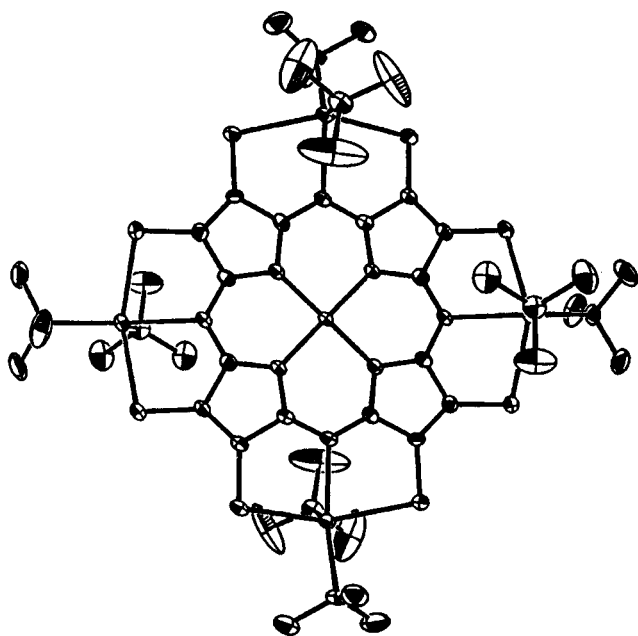
Dissolving metal reduction of octabenzylthioporphyrazinatonicel(II) gave an intense purple, air sensitive and water soluble pigment that was presumably the corresponding octathiolate. This smoothly condensed with di-*tert*-butyltin dinitrate to produce the corresponding star porphyrazine as air-stable green-black crystals. The structure of this substance was established by an X-ray crystallographic study and this showed the molecule to contain four pentacoordinate di-*tert*-butyltin residues bound within the *meso*-pocket. This coordination had a profound

effect on the UV-vis spectrum with the disappearance of the Soret band, presumably to shorter wavelength. Titration of the *star*-porphyrazine with tetrabutylammonium fluoride required eight equivalents for completion giving a new air stable purple *star*-porphyrazine that was tentatively assigned as the $[\text{Sn}^t\text{Bu}_2\text{F}_2]^{2-}_4$ species. This new complex, which was derived from a "tetra-tin walk" and the absence of *meso*-pocket binding, showed the restoration of the Soret band in the UV-vis spectrum.

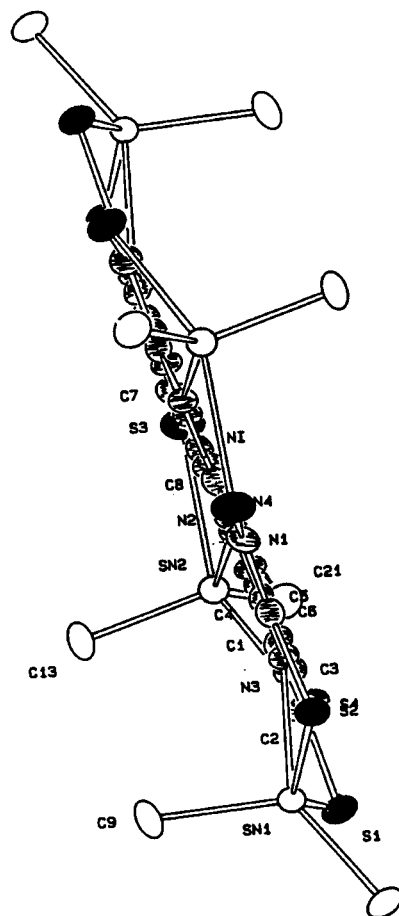
Scheme 30



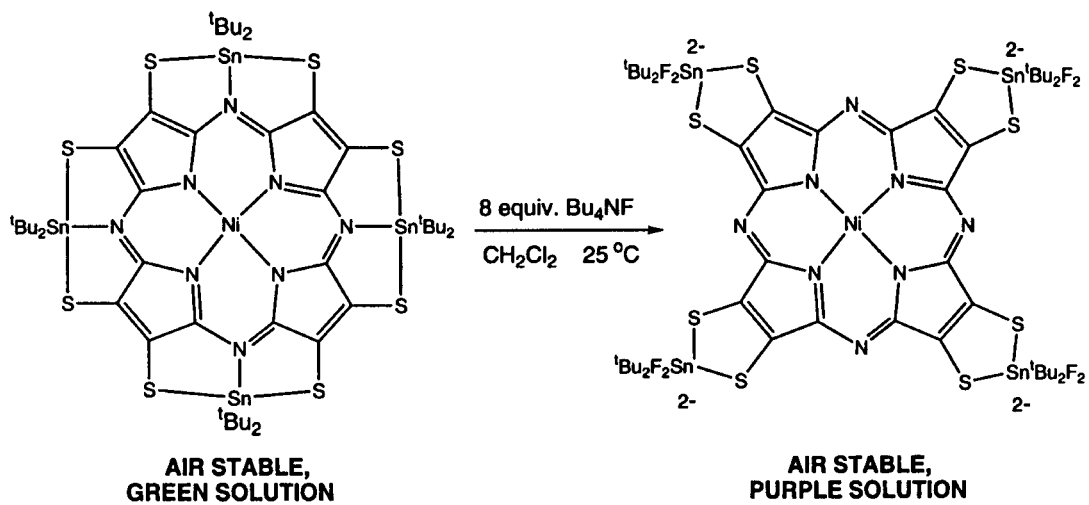
Scheme 31



Scheme 32

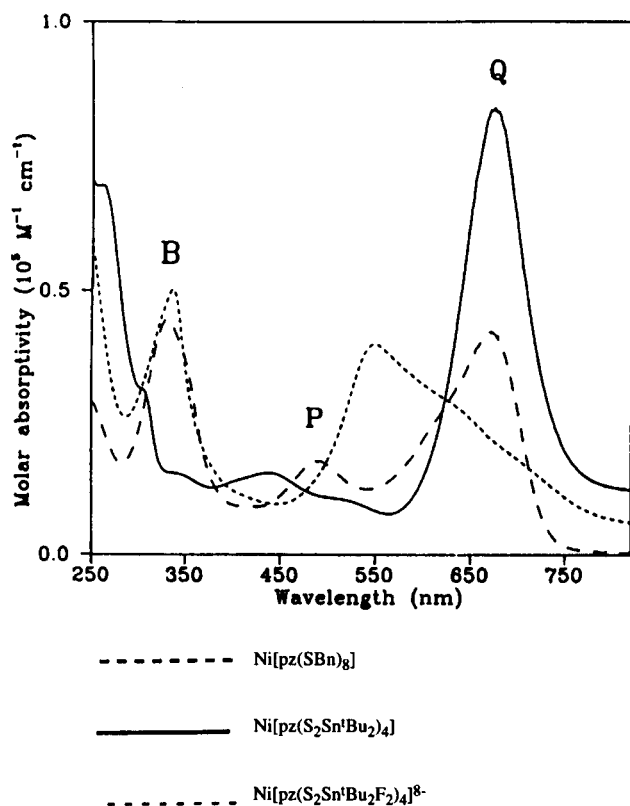


Scheme 33



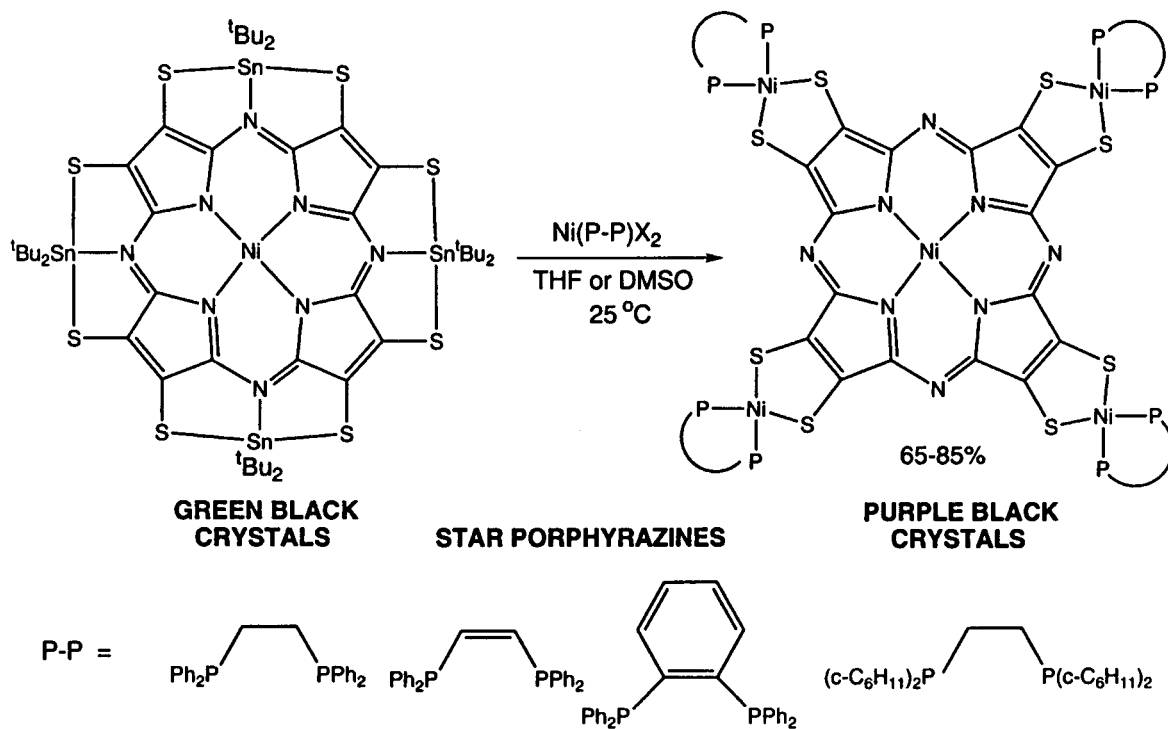
STAR PORPHYRAZINES

Scheme 34

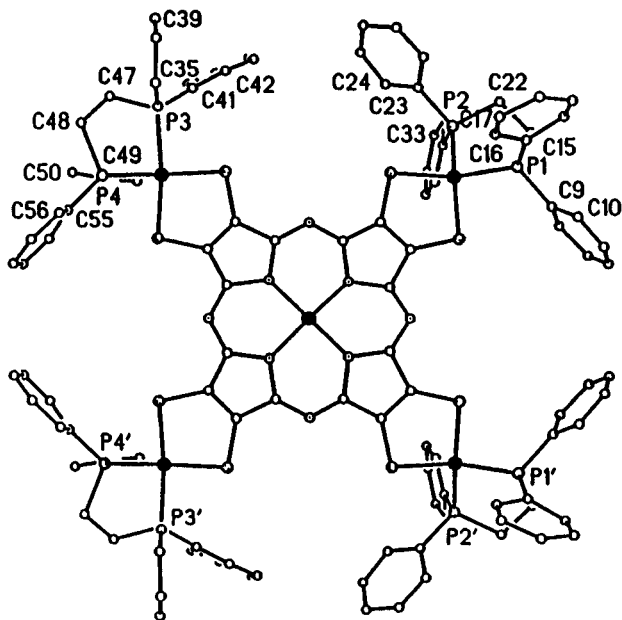


The tetra-tin star porphyrazine is a convenient starting material for the preparation of other multimetallic arrays. Thus, reaction of this green macrocycle with (diphos)NiCl₂ and related salts gave the corresponding tetra-nickel star porphyrazines. The structures of these complexes were unmistakable in the light of both X-ray crystallographic data and, in all cases, the presence of the Soret band in the UV-vis spectra. This metathetic exchange of metals is especially important given the ease of handling of the tetra-tin star compared with its precursor, the air fearing porphyrazine octathiolate.

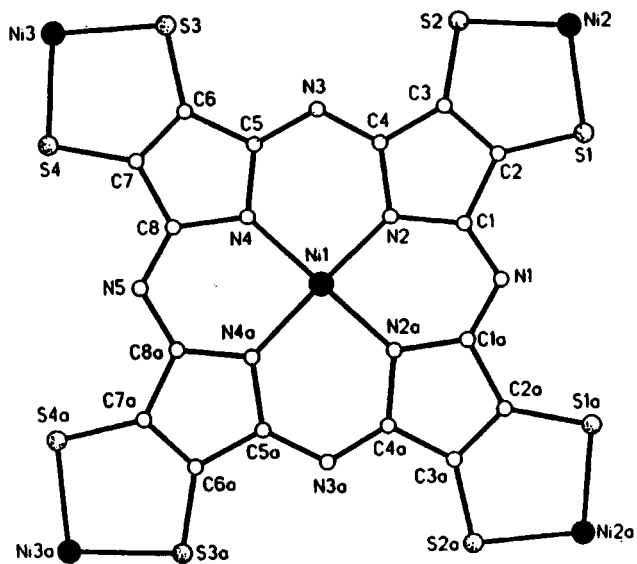
Scheme 35



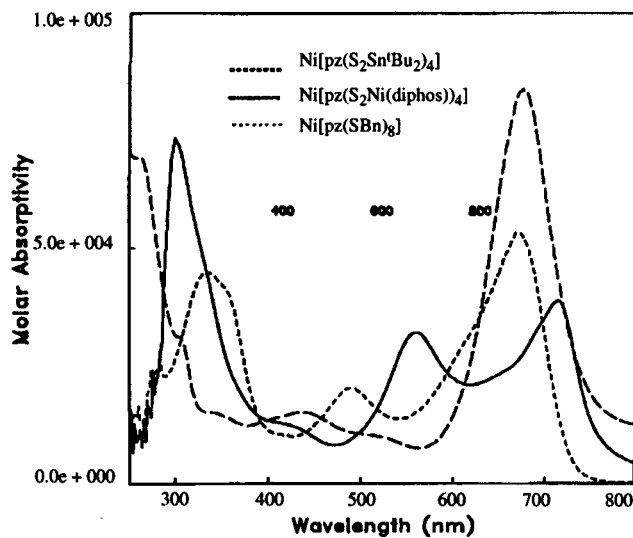
Scheme 36



Scheme 37

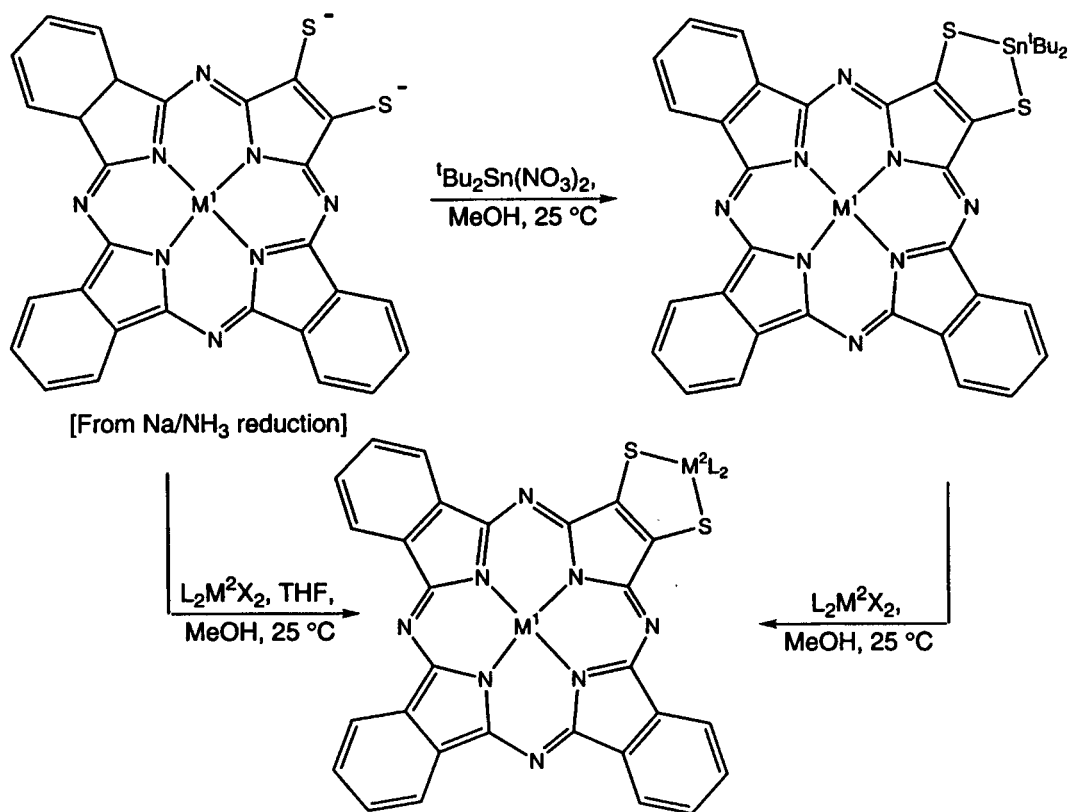


Scheme 38

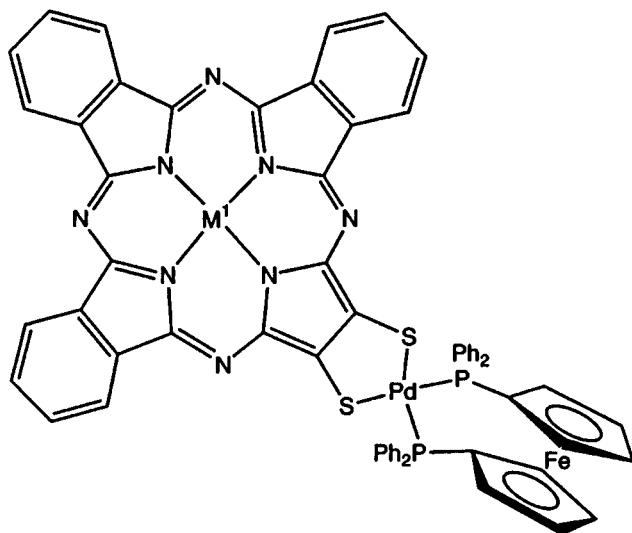


Dissolving metal reduction of benzyl and *para*-[(butyloxy)carbonyl]benzyl protected porphyrazine-dithiols and -tetrathiols gave the corresponding air sensitive thiolates, which again could be converted into peripherally metalated derivatives. Representative examples are given by the preparation of the solitary phthalocyanines with a single palladium, platinum, or molybdenum entity directly fused to the macrocycle. Again, these unusual coordination complexes were fully authenticated in several cases by X-ray crystallography. The molybdenum(IV) solitary exhibited rich electrochemistry with 5 reversible redox waves by cyclic voltametry.

Scheme 39

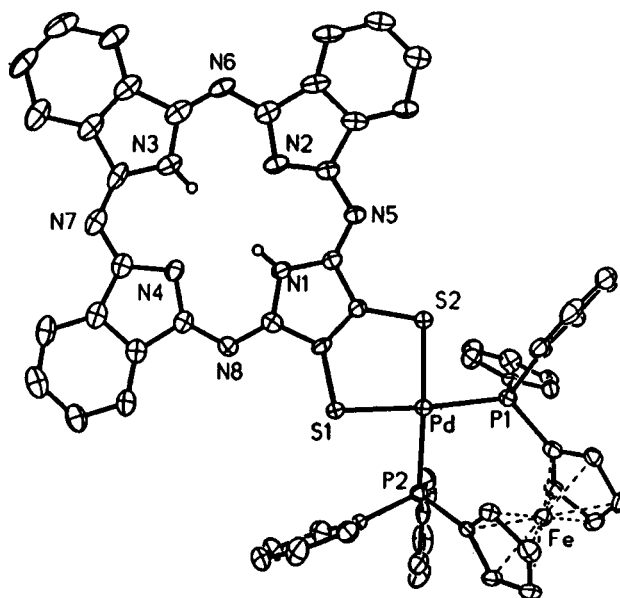


Scheme 40

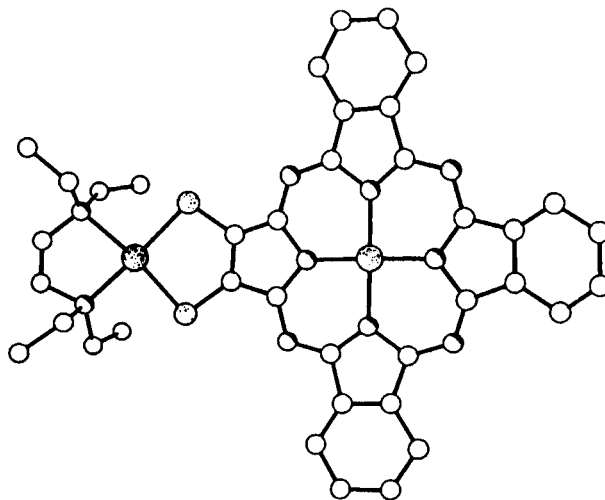
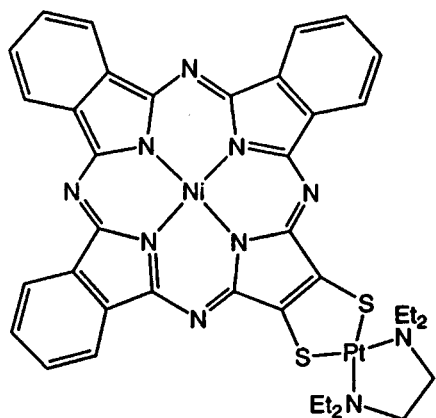


SOLITAIRE PHTHALOCYANINES

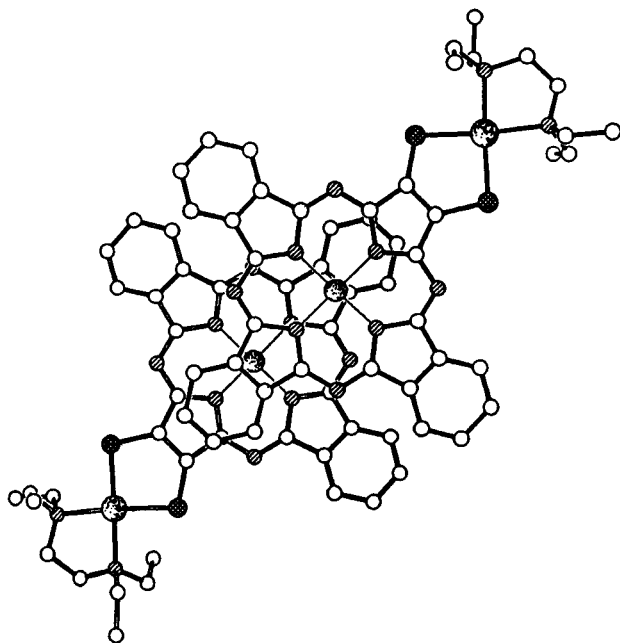
Scheme 41



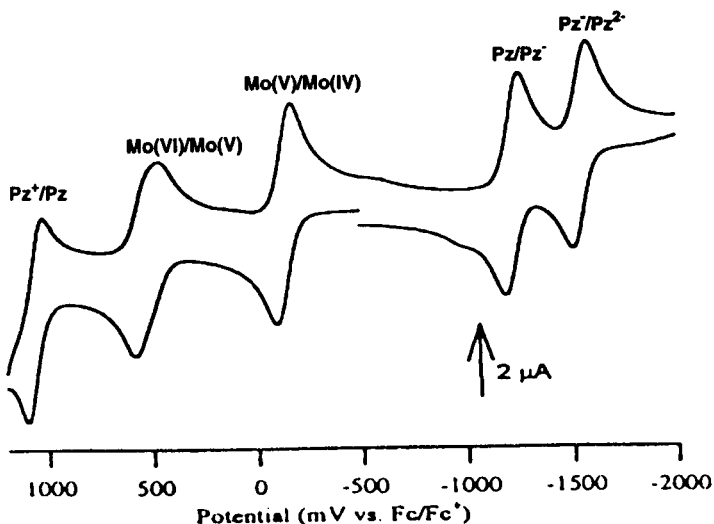
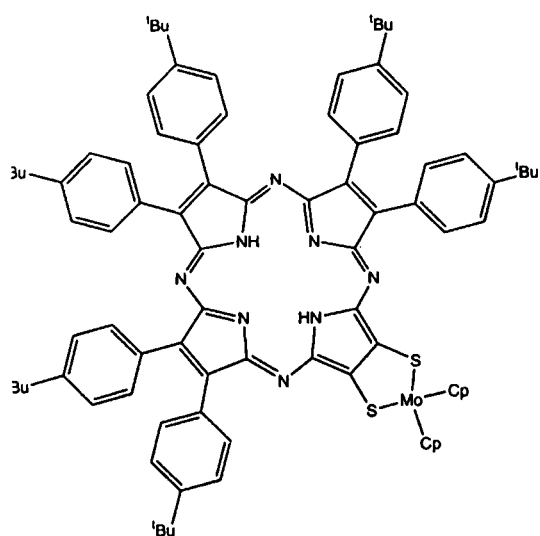
Scheme 42



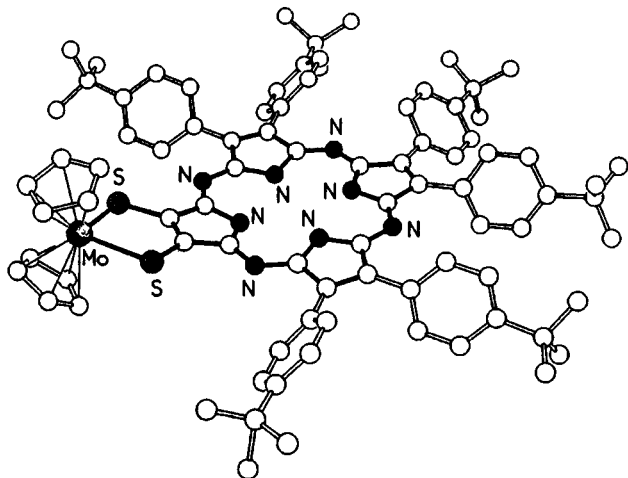
Scheme 43



Scheme 44



Scheme 45

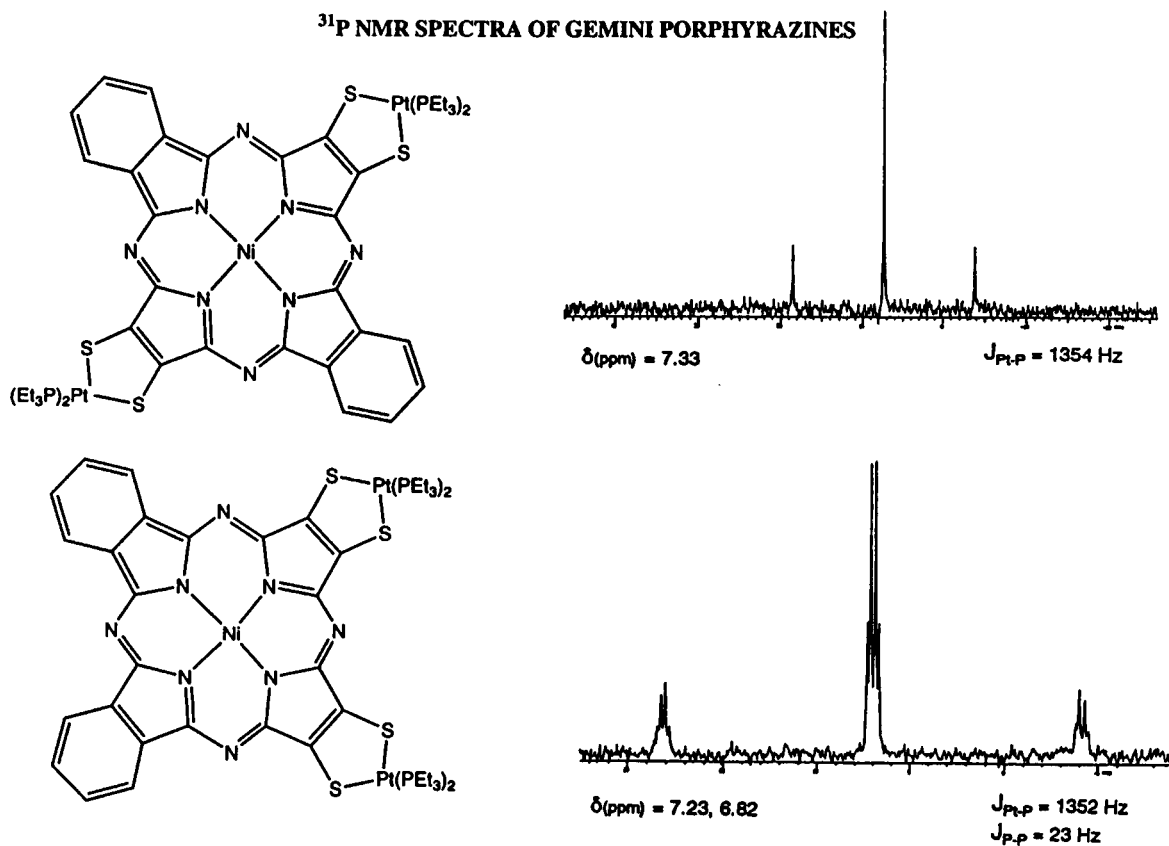


In the same way, porphyrazine tetrathiolates, prepared from the corresponding protected tetrathiol by dissolving metal reduction, were condensed with metal salts to reveal porphyrazines with two peripherally coordinated metal entities, the *Gemini*-porphyrazines. In each case, there are two possible geometric isomers, respectively with the *cis*- and *trans*- stereochemistry. For example, there are two possible isomers with two peripherally bound $(Et_3P)_2Pt$ residues, and with Ni(II) within the central macrocycle cavity. Both are clearly diamagnetic and may be readily distinguished by NMR spectroscopy. In the ^{31}P NMR spectrum, the *trans*-isomer shows only a single peak with two satellites ($J_{Pt-P} = 1353$ Hz). In contrast, the *cis*-isomer shows an AB quartet again with satellite AB quartets ($J_{Pt-P} = 1352$ Hz, $J_{P-P} = 23$ Hz). Clearly, these resonances are consistent with the assigned geome-

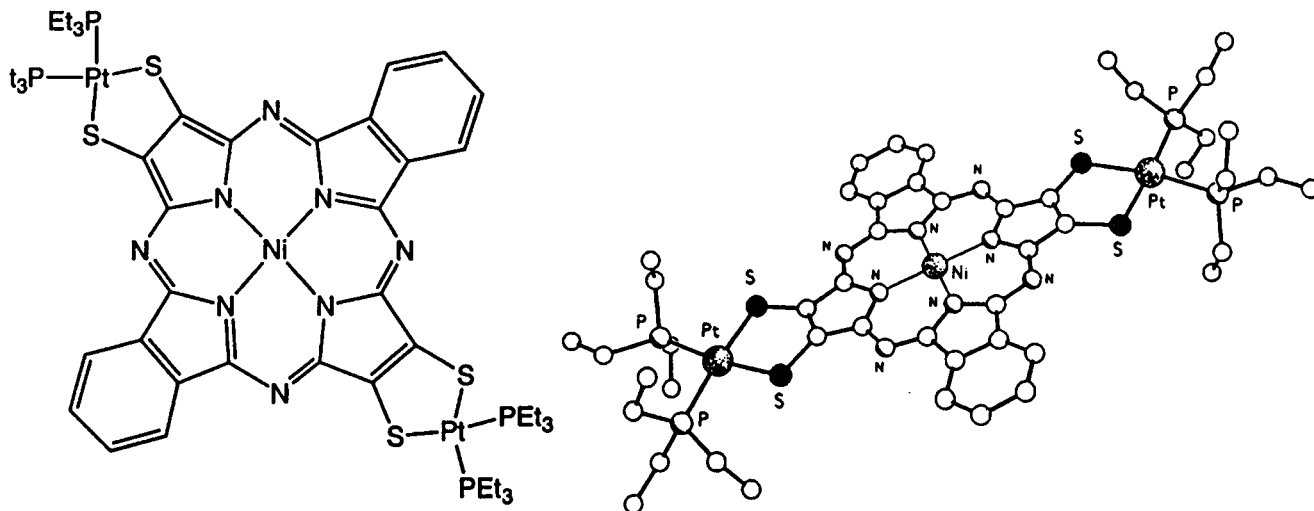
tries and with square planar platinum. This stereochemical assignment was confirmed by an X-ray crystallographic study of the *trans*-isomer. It is possible to use both *solitaire*- and *Gemini*-porphyrazines to probe long range metal-metal interactions. The synthetic methods already outlined were applied in the preparation of two porphyrazines, one with a single pendant dicyclopentadienylvanadium(IV) residue and one with two such metal species. Both are paramagnetic compounds amenable to examination by EPR. Again structural assignment was rigorously established by X-ray crystallography. In the EPR spectrum the *solitaire* showed the expected 8-line pattern for an $S = 1/2$ system with hyperfine coupling to a single ^{51}V ($I = 7/2$) nucleus. In contrast, the *Gemini* showed a 15-line pattern whose ^{51}V isotopic hyperfine coupling constant is exactly one-half of the value for the

solitaire. This clearly indicated that an $S = 1$ state has been created by an exchange between the two $[\text{Cp}_2\text{V}^{\text{IV}} (S = 1/2)]$ spins that is mediated by the porphyrazine ring over 13.5 Å.

Scheme 46

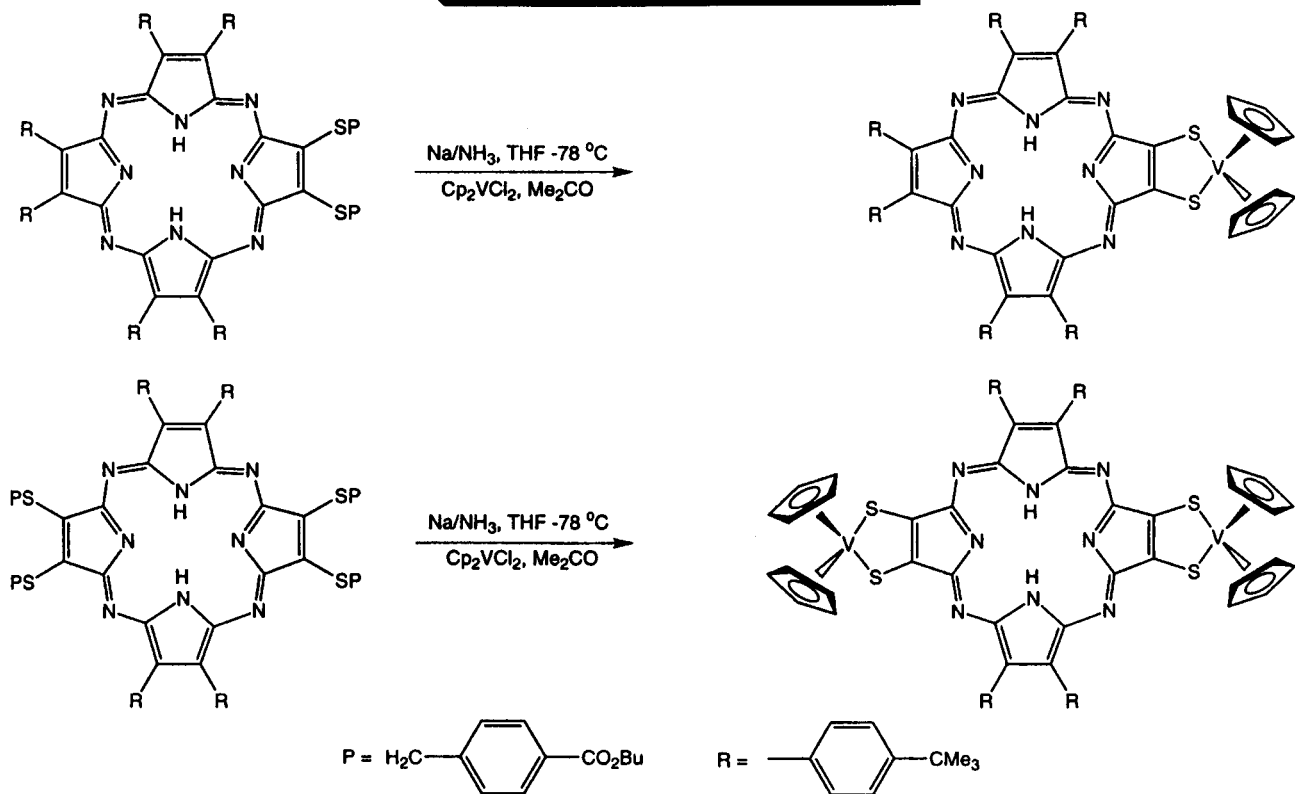


Scheme 47

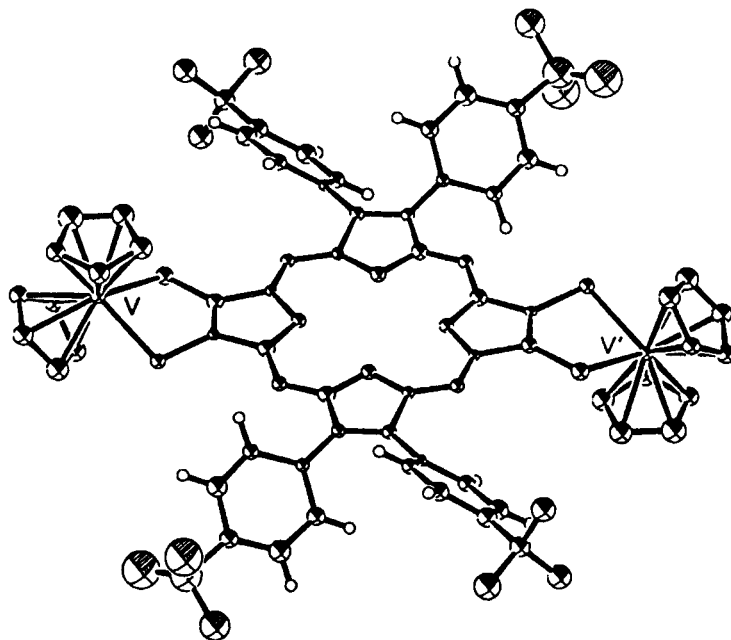


Scheme 48

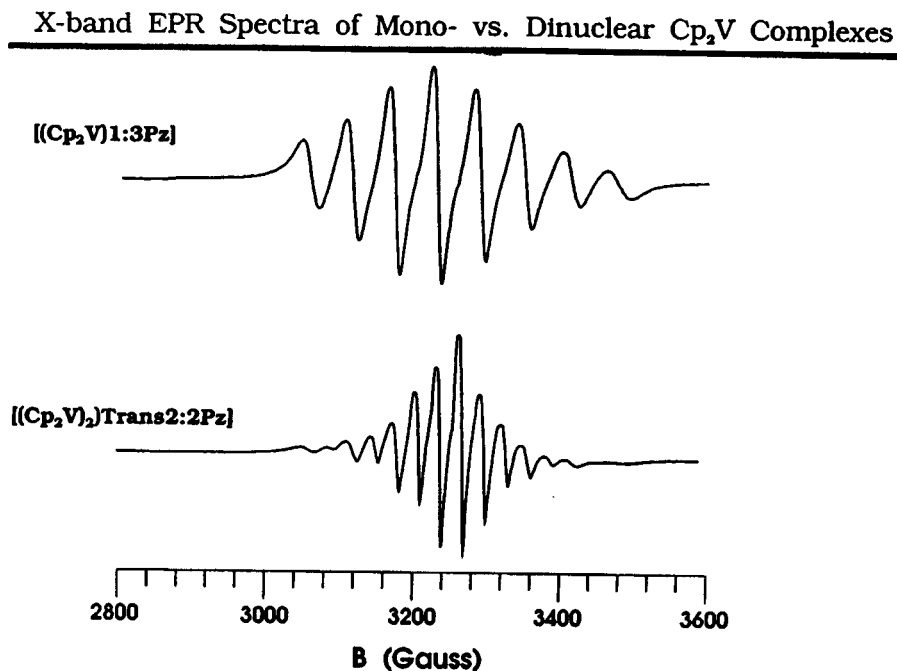
Mono- and Dinuclear (Cp₂V)Pz Complexes



Scheme 49



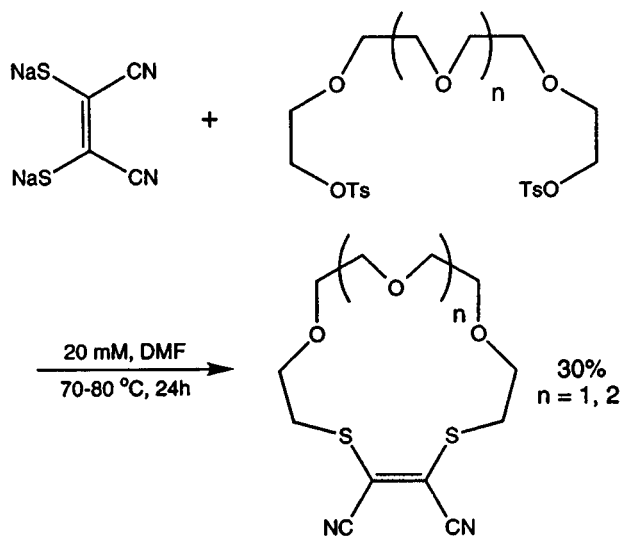
Scheme 50



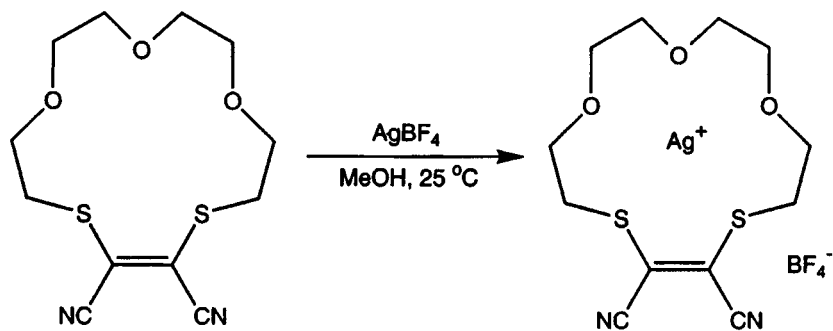
As part of our studies on the peripheral metal ion binding properties of porphyrazines, we have had occasion to examine crowned porphyrazines in which the crown residues are directly fused, and therefore in electronic communication, to the central macrocycle. As part of this study, we have additionally studied the coordination chemistry of the crowned maleonitrile derivatives themselves. 2,3-Dicyano-1,4-dithia-7,10,13-trioxa-2Z-pentadecene and 2,3-dicyano-1,4-dithia-7,10,13,16-tetraoxa-2Z-octadecene were both prepared from the corresponding poly-glycol ditosylates. Both dithia-crowns formed crystalline complexes with silver tetrafluoroborate, which were characterized by X-ray crystallography. The dithia-15-crown-5 system formed two distinct crystals. In the first species, a monomer complex, each silver ion was

coordinated by two ring sulfurs and two ring oxygens, and was in close proximity to a tetrafluoroborate fluoride. In the second crystal, a polymeric complex, each silver was coordinated by two ring sulfurs and an ether oxygen. The ribbon polymer structure contained an Ag-N backbone resulting from coordination of the silver ion by an adjacent ring nitrile. The dithia-18-crown-6 system crystallized as a single polymeric entity containing AgO_2S units linked by coordination with an adjacent ring nitrile. 2,3-Dicyano-1,4-dithia-7,10,13,16-tetraoxa-2Z-octadecene formed an unusual 1:1 complex with mercuric chloride. The X-ray crystal structure of this compound showed the presence of an essentially linear Cl-Hg-Cl unit bonded not to sulfur but to two adjacent ether oxygens of the macrocycle.

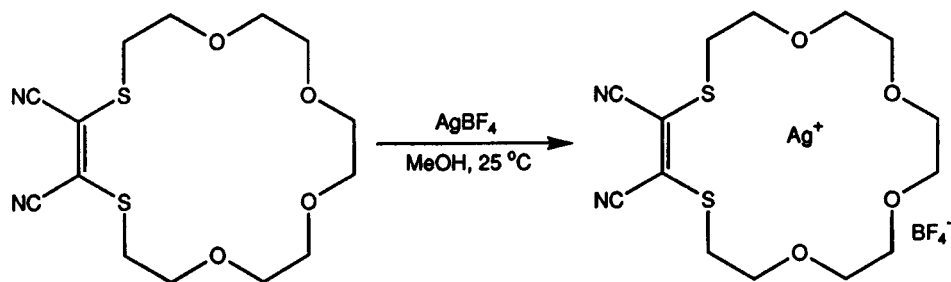
Scheme 51



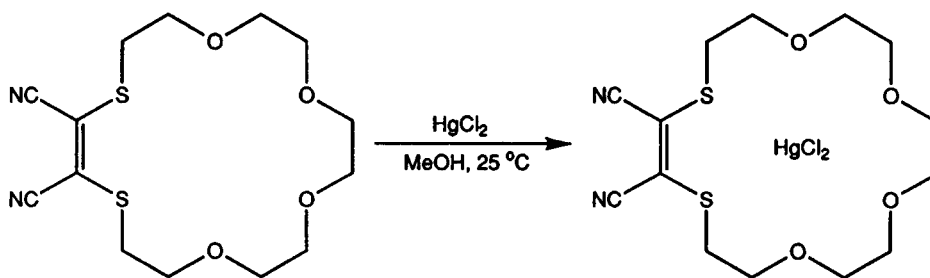
Scheme 52



Scheme 53

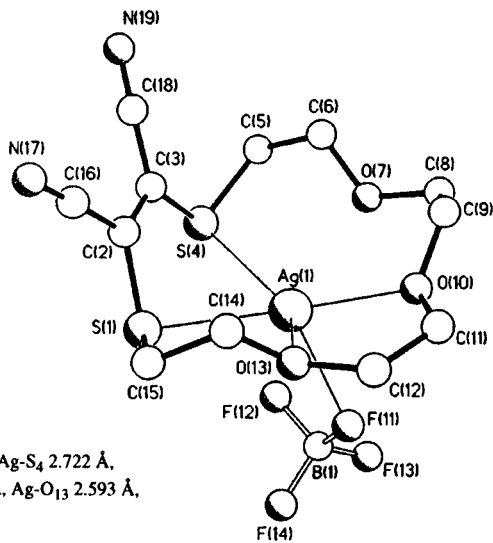


Scheme 54



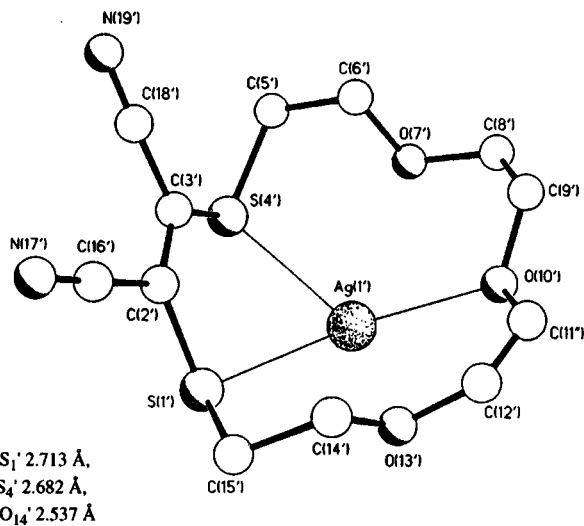
Scheme 55

Two Distinct Macrocyclic Species (1:1)

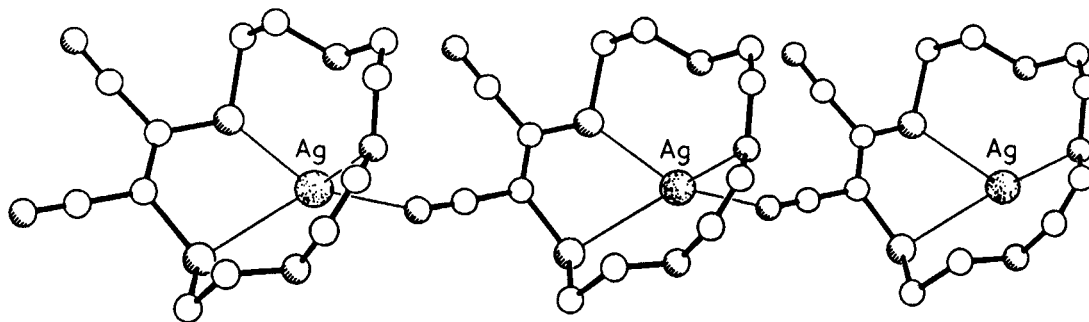


Scheme 56

Two Distinct Macrocyclic Species (1:1)

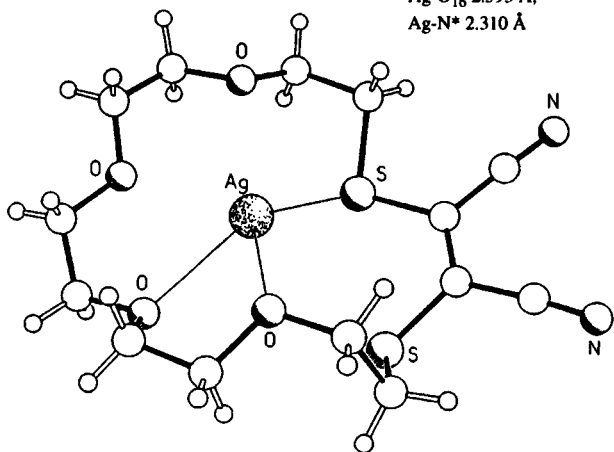


Scheme 57

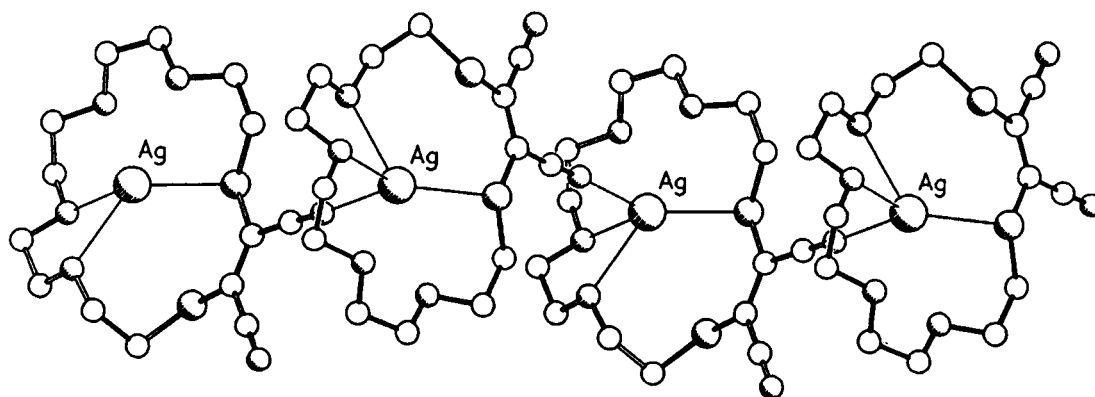


Scheme 58

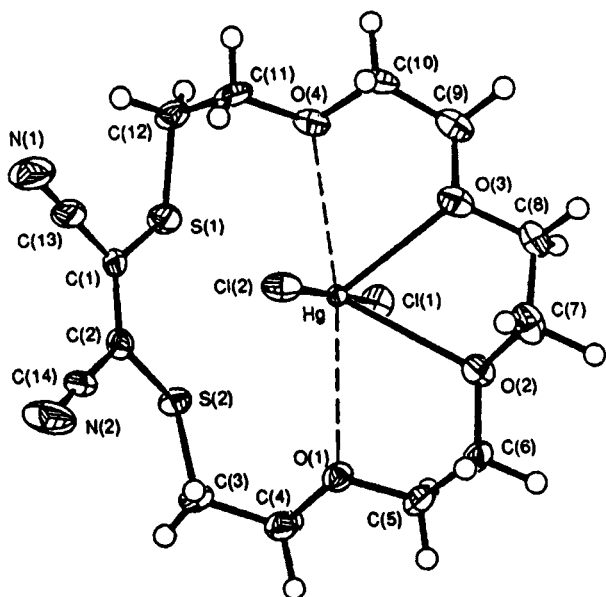
Ag-S₄ 2.533,
 Ag-O₁₃ 2.501 Å,
 Ag-O₁₆ 2.593 Å,
 Ag-N* 2.310 Å



Scheme 59



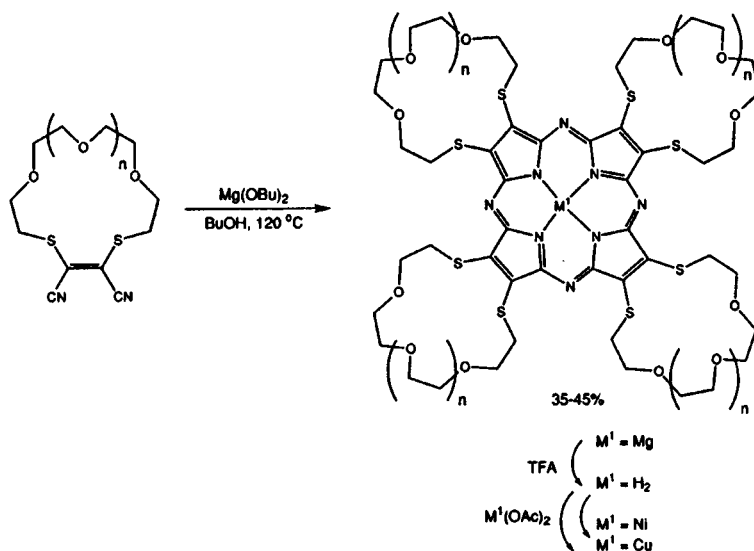
Scheme 60



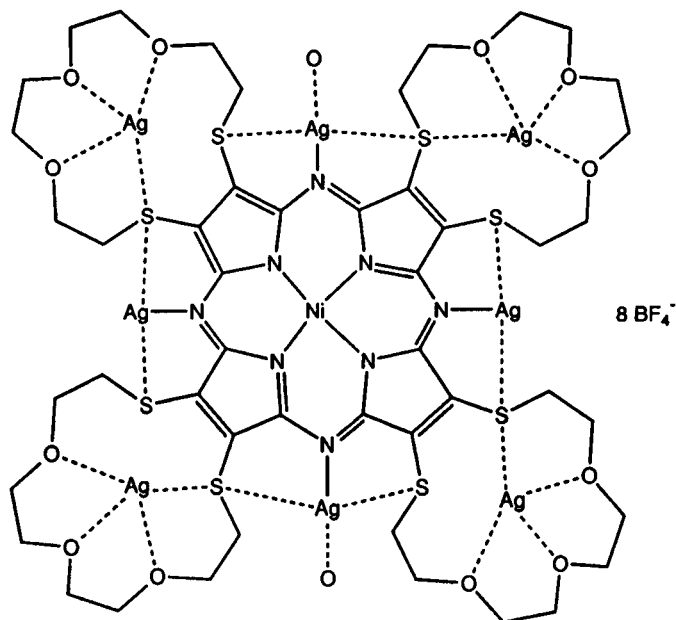
Instead macrocyclization of the two crowned maleonitriles gave the corresponding tetra-crowned porphyrazines. These polydentate ligands avidly bind metal ions and two complexes have been characterized by X-ray crystallography. Thus, reaction of the tetra-15-crown-5-porphyrazinatonickel(II) with excess silver tetrafluoroborate gave two distinct crystals. In one, four silver ions were bound in the peripheral crowns. Remarkably, an

additional four silver ions were held through S-N-S coordination in the porphyrazine *meso*-pockets. The second product of the reaction again contained 4 silver ions coordinated in the peripheral crowns. In this complex, an additional 4 silver ions were ligated not by the S-N-S atoms of the *meso*-pocket but by one sulfur atom each from two separate macrocycles forming a silver-bridged cofacial porphyrazine dimer.

Scheme 61

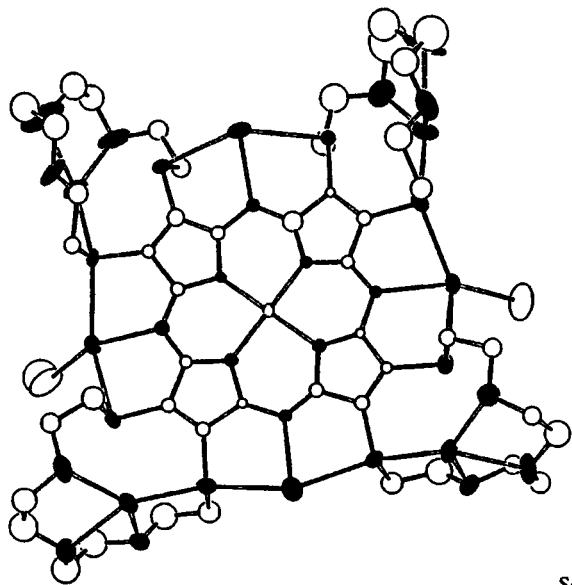


Scheme 62

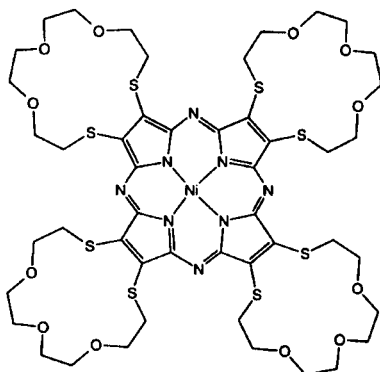
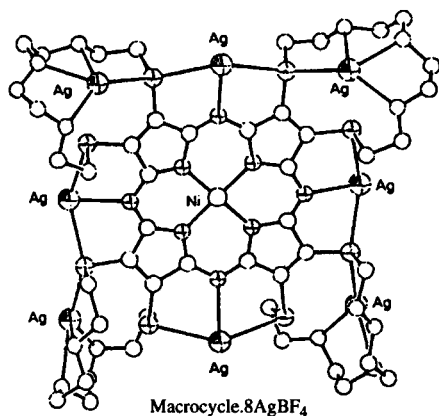
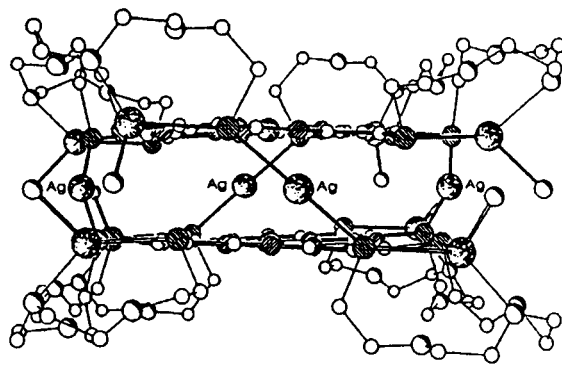


Excess AgBF_4 in MeOH and CHCl_3

Scheme 63



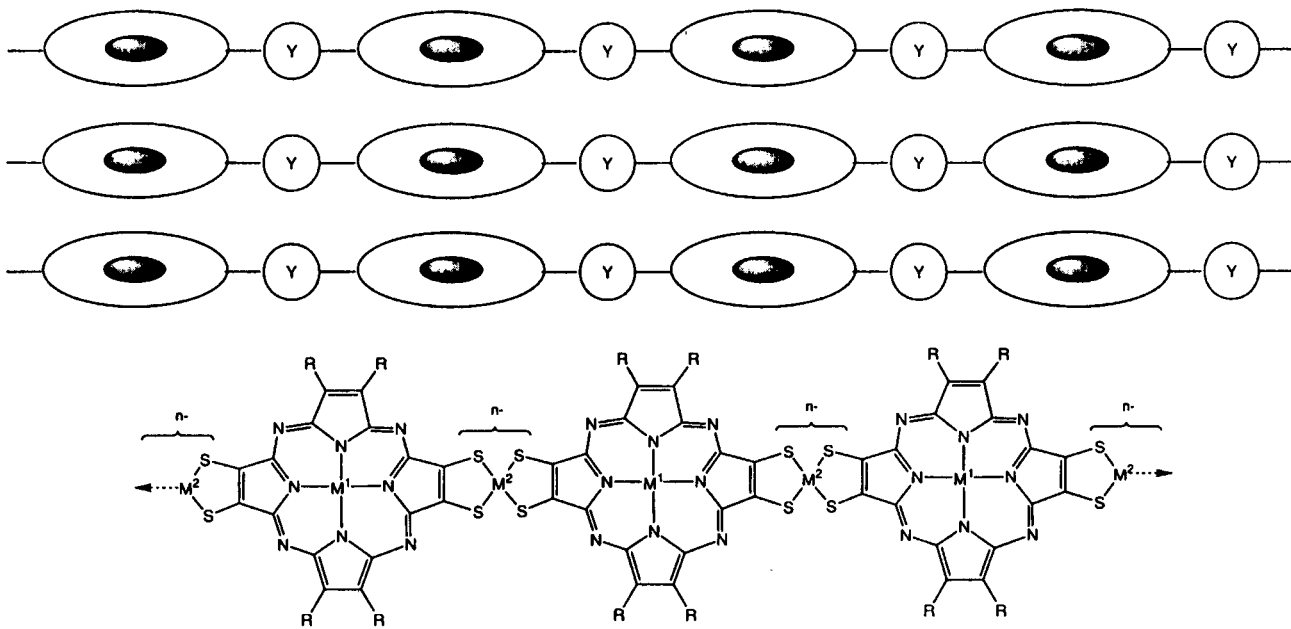
Scheme 64

Complexes with AgBF_4 Macrocycle.8AgBF₄ $(\text{Macrocycle})_2.12\text{AgBF}_4$

All of the *solitaire*-, *Gemini*- and *star*-porphyrazine units can be considered as building blocks for the elaboration of dimers, trimers and higher order oligomers by peripheral metal ion sharing by adjacent porphyrazines. Schematically, ribbon and sheet polymers are depicted below. In these structures, it should be possible to vary the cavity metal ions M^1 , the bridging metals M^2 , the periph-

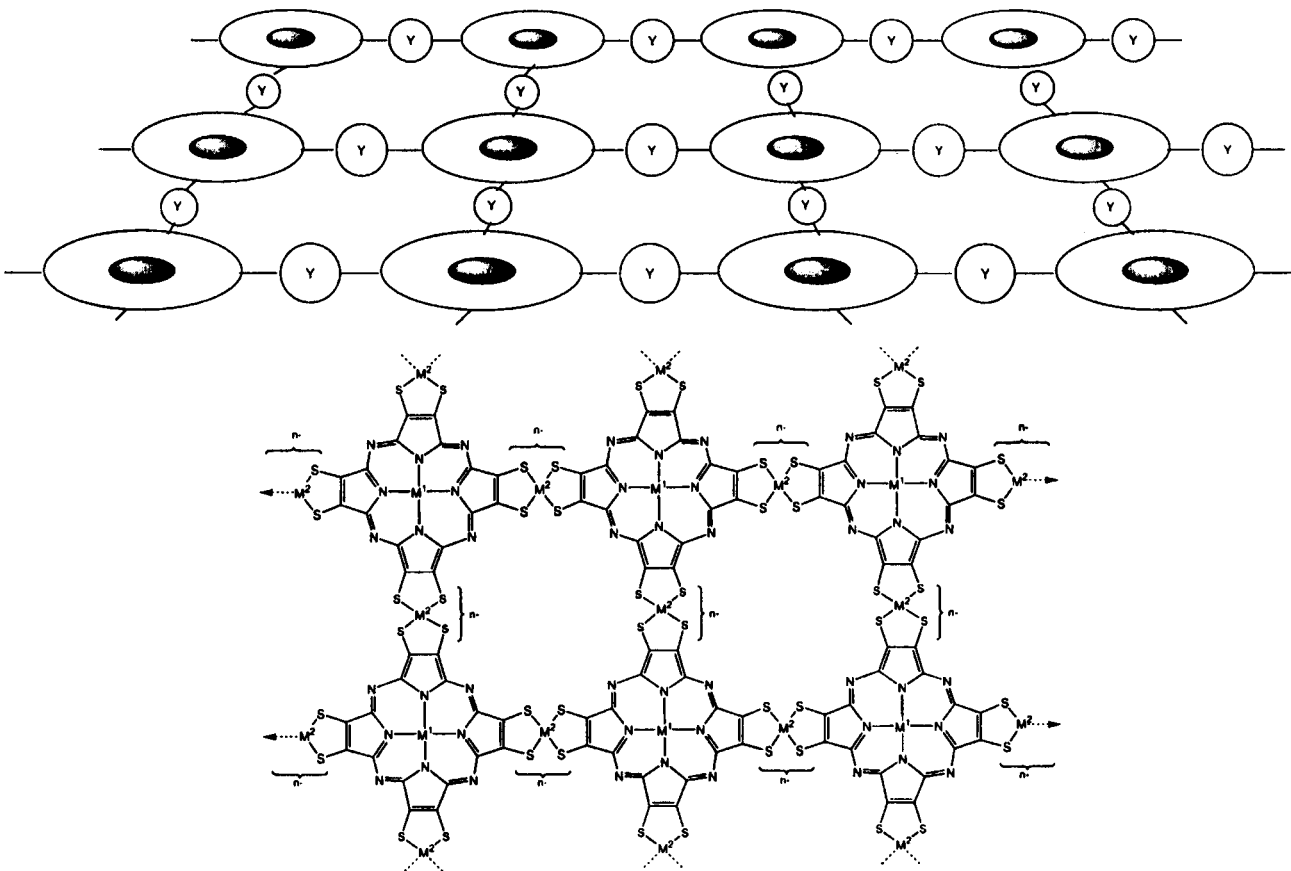
eral heteroatoms (only sulfur is illustrated) and the groups R to vary the physical and chemical properties of the oligomers. A prototype Ni(II)-Ni(III)-Ni(II)-solitaire dimer has been prepared and characterized by EPR spectroscopy. This structural class of porphyrazine oligomers has very considerable promise for future developments and applications

Scheme 65

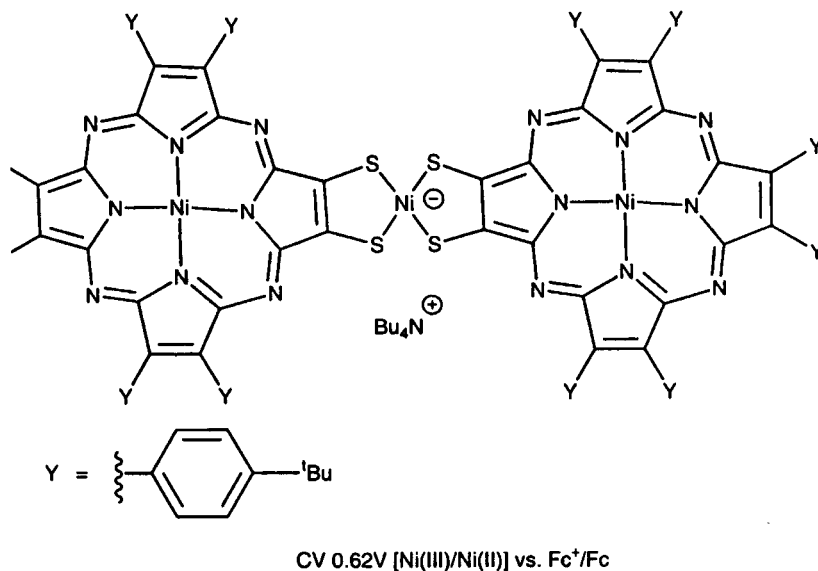
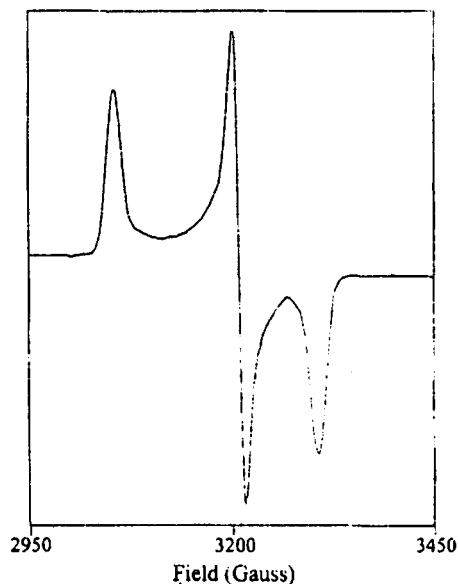


R confers solubility
Vary M^1 and M^2

Scheme 66



Scheme 67

EPR $\text{CH}_2\text{Cl}_2/\text{Toluene}$ 

Acknowledgment.

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