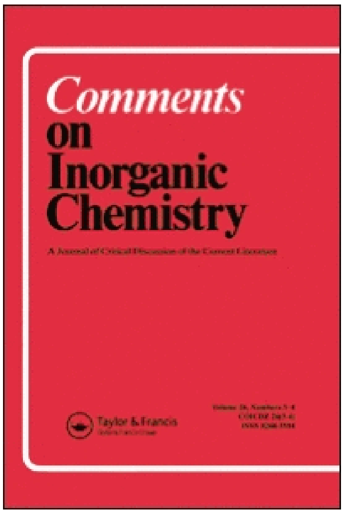

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# The Coordination Chemistry of Planar Pentadentate "Porphyrin-Like" Ligands

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# The Coordination Chemistry of Planar Pentadentate "Porphyrin-Like" Ligands

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The coordination chemistry of pentadentate porphyrin-like ligands is reviewed. The review is largely limited to planar or near-planar unsaturated pentaaza macrocycles and is concerned with pentadentate or potentially pentadentate systems derived from pyrrole, pyridine, bipyridine, phenanthroline, and terpyridine. Some discussion, however, is devoted to novel nonporphyrin macrocycles containing fewer than five nitrogen atoms. Specifically excluded from review are complex binucleating systems as well as saturated ligands of the aza crown ether or cryptand type.

**Key Words:** *macrocycle, planar pentadentate, coordination chemistry, porphyrin, pyrrole, pyridine, bipyridine, phenanthroline, terpyridine*

## INTRODUCTION

Although the porphyrins are among the most widely studied of all known macrocycles,[1] relatively little work has been devoted to the synthesis and study of larger porphyrin-like systems.[2-15] Large porphyrin-like macrocycles are, however, of considerable interest to the coordination chemist: Suitably designed systems could act as versatile ligands capable of stabilizing higher coordination geometries and/or binding larger metals than those accommodated within the normally tetradentate porphyrin core. In this Comment

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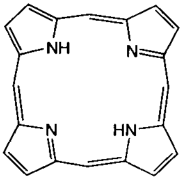
we discuss the coordination chemistry of what we consider to be the simplest higher homologues of the porphyrins, namely unsaturated planar pentadentate nitrogenous macrocyclic ligands. Our objective is not only to summarize what has been accomplished to date but also to point out directions for future research.

This paper is organized according to the primary nitrogen donor incorporated within the macrocycle. Planar pentaaza pyrrole, pyridine, bipyridine, phenanthroline, and terpyridine containing systems appearing in the literature through 1987 are discussed with the exception that complex binucleating systems derived from these donors are specifically excluded from review. Also excluded are saturated ligands of the aza crown ether type as well as three-dimensional systems of the cryptand and related families. Some discussion, however, is included of various novel nonporphyrin macrocycles containing fewer than five nitrogen atoms since we consider this work relevant to the problem of designing large pentadentate porphyrin-like ligands.

## GENERAL CONSIDERATIONS

As illustrated by porphine, **1**, the simplest member of the family, porphyrins are 18 $\pi$-electron macrocycles containing two pyrrole-type and two pyridine-type nitrogens held within a nearly circular core of ca. 2.0 Å radius.[16] Along with the closely related phthalocyanines (e.g., **2**), they are capable of forming complexes with nearly every known metal and semi-metal.[17] Although a variety of "capped," "sitting atop," and "sandwich" complexes have been recorded, both the porphyrins and phthalocyanines generally act as dianionic ligands, stabilizing idealized square planar, square



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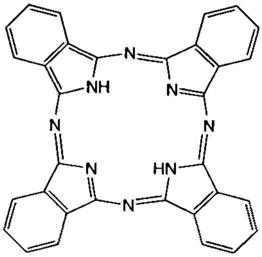


**2**

pyramidal, and octahedral geometries.[17] This is particularly true for the more common cations of the first transition series.

By analogy to the porphyrins, planar pentadentate ligands should be ideally suited for stabilizing complexes with planar pentagonal, pentagonal pyramidal, and pentagonal bipyramidal geometries. Schematic representations of these relatively rare 5, 6, and 7 coordinate geometries are shown in Fig. 1. Included in this figure are qualitative energy level diagrams for a set of d orbitals, derived from the specific crystal field calculations of Wasson and Lorenz.[18] These splittings indicate that idealized complexes derived from symmetric pentadentate ligands will show only two "d ← d" tran-

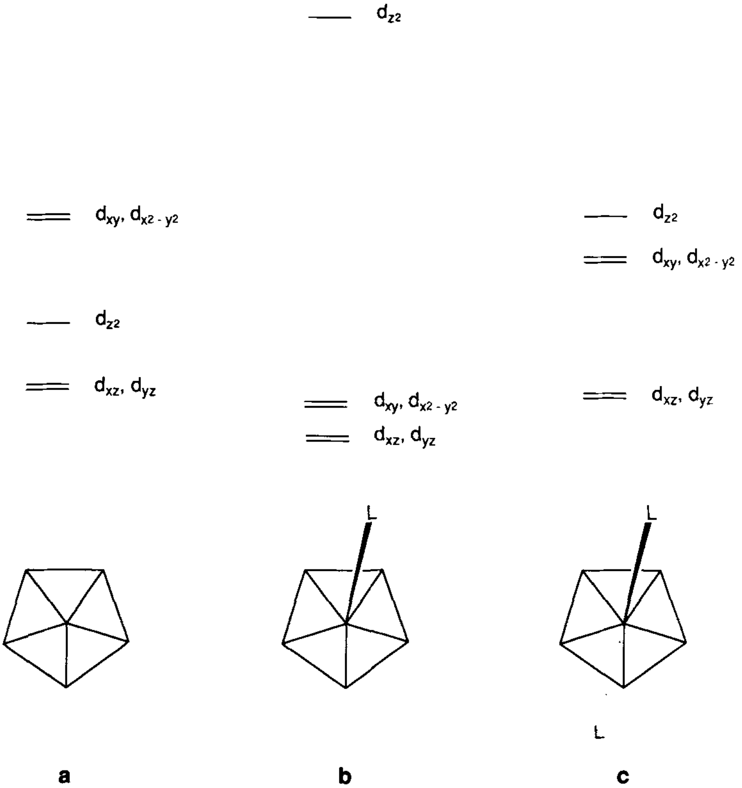
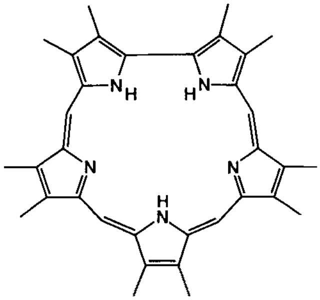


FIGURE 1 Idealized binding geometries and qualitative d orbital splitting patterns for complexes formed from planar pentadentate ligands: (a) planar pentagonal, (b) pentagonal pyramidal, (c) pentagonal bipyramidal.

sitions. They also suggest, however, that in many cases complexes derived from planar pentadentate ligands will be subject to Jahn–Teller distortions.

## PYRROLE-CONTAINING SYSTEMS

Early synthetic work on large pyrrole-containing macrocycles was largely inspired by theoretical predictions which placed the upper limit of aromaticity of $[4n + 2]$ annulenes at 22 $\pi$-electrons,[2] and led early on to the synthesis of "sapphyrins" (e.g., **3**) and "smaragdyrins" **4**.[3,4] More recently, it has prompted the synthesis of "pentaphyrin" **5**,[5,6] as well as several novel large conjugated tetrapyrrolic systems such as the "platyrins"[7,8] (e.g., **6**) and methylated "[26]porphyrin" **7**.[9]



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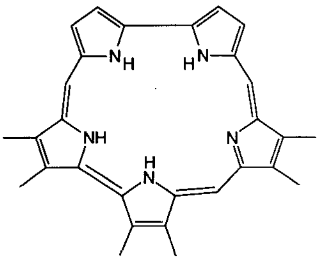

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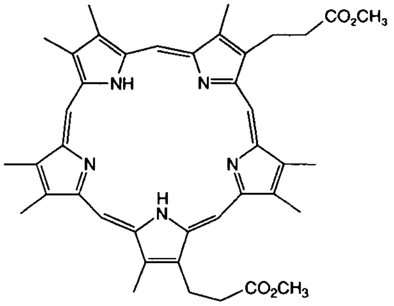

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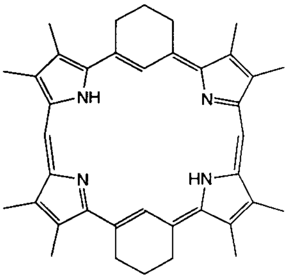
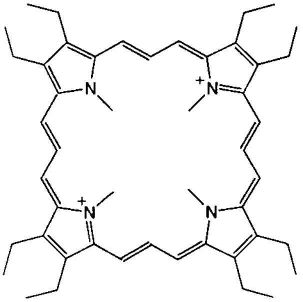


**6**

The large cavity size of the macrocyclic core prompted Bauer *et al.*[3] to suggest that the "sapphyrins" would make good pentadentate ligands, forming complexes with cations, such as $UO_2^{2+}$, which favor pentagonal bipyramidal coordination geometries.[19] Unfortunately, all efforts to bind $UO_2{}^{2+}$ in decamethylsapphyrin **3** failed.[3] Spectral evidence was obtained, however, which suggested that complexes could be formed from $Ni^{2+}$, $Fe^{2+}$, $Cd^{2+}$, $Mn^{2+}$, $Co^{2+}$ and $Zn^{2+}$. Only the $Co^{2+}$ and $Zn^{2+}$ complexes were isolated as solids. Analysis of the mass spectra sggested that the metals are coordinated to only four of the five nitrogens, with the fifth remaining in its normal proton-bearing pyrrole form.[3] At present no metal binding information is available for the closely related "smaragdyrin" and "pentaphyrin" systems. Moreover, as yet, no well-defined complexes have been prepared from the "platyrins" although spectroscopic results suggest that $Ni^{2+}$ may in fact bind to **6**.[7]



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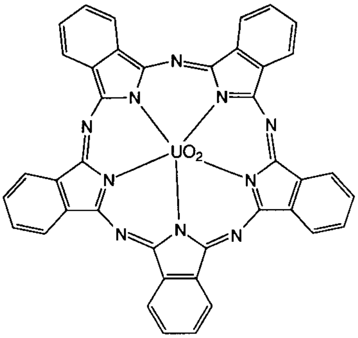
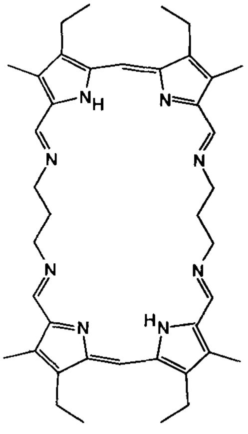


**8**

Interestingly, Marks and Day[10–12] were able to prepare and characterize, using a direct template-mediated synthesis, uranyl "superphthalocyanine" **8**, a benzpyrrole analogue of "pentaphyrin" **5**. An X-diffraction study of this 22 $\pi$-electron aromatic system revealed a nearly circular central $N_5$ binding core with an average center-to-nitrogen bond length of ca. 2.52 Å. It also indicated, as is true for many metalloporphyrin complexes, that the macrocyclic skeleton is considerably distorted from planarity.[10] Unfortunately, the uranyl "superphthalocyanine" complex stands as a "special case": All efforts to obtain the corresponding free-base form, or synthesize "superphthalocyanine" structures with other metals, led only to the isolation of the smaller phthalocyanines.[11,12] Thus at present neither the pentapyrrolic nor pentabenzpyrrolic macrocycles (compounds **3–5** and **8**) can be considered as general porphyrin-like pentadentate ligands.

Although pentapyrrolic systems have yet to emerge as versatile pentadentate ligands, in recent years several novel pyrrole-containing macrocycles have been prepared which support other coordination modes.[2,20–30] Many of these are simple permutations on the basic porphyrin skeleton, derived by single atom insertions,[2,20] deletions,[2] or replacements[2,21]; only a few contain rings of substantially different size.[22–30] Several of the latter have been characterized structurally, including the highly distorted five-coordinate biscopper complex[25] of Mertes' "accordion" ligand **9**,[24,25] the four-coordinated mononuclear copper complex[27] of Fenton's pyrrole-containing Schiff base system **10**,[26–28] and the $Ni^{2+}$ complex[30] of "porphycene" **11**,[29,30] a new smaller porphyrin isomer prepared by Vogel and co-workers. None of these systems, of course, enforces a pentagonal planar binding geometry around the complexed cation. Nonetheless, taken together these results do suggest that unusual pyrrole-containing macrocycles will bind metals and that it should be possible to design a large porphyrin-like macrocycle capable of acting as a versatile pentadentate ligand.



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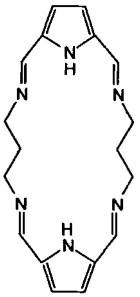

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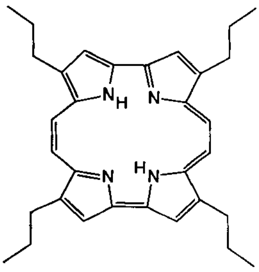
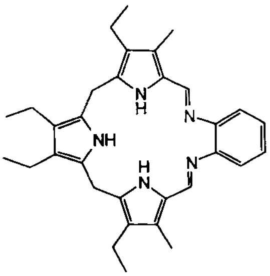


**11**

Recently, Sessler *et al.* realized the elusive goal of preparing a versatile aromatic pentadentate porphyrin-like ligand: Using an acid catalyzed Schiff base condensation procedure, these workers were able to prepare the methylene linked tripyrrane-derived pentaaza macrocycle **12**,[13] which could be oxidized to the methine bridged, 22 $\pi$-electron, aromatic free-base "expanded porphyrin" **13** by treating with N,N,N′,N′-tetramethyl-1,8,-diaminonaphthalene ("proton sponge") in the presence of air.[14] By carrying out similar oxidations in the presence of various metal salts, a variety of metal complexes, including those derived from $Cd^{2+}$, $Zn^{2+}$, $Mn^{2+}$, $Hg^{2+}$, and $Nd^{3+}$ could be prepared. At present, X-ray structural information is available for only the $Cd^{2+}$ system; it has been characterized as both the pentagonal pyramidal benzimidazole complex **14**[15] and the pentagonal bipyramidal bispyridine complex **15**.[14] In both cases the macrocycle is nearly planar with the five nitrogen donor atoms defining a nearly circular cavity with center-to-nitrogen radii of ca. 2.4 Å. In the pentagonal pyramidal benzimidazole complex **14** the $Cd^{2+}$ lies ca. 0.33 Å above the macrocycle, whereas in **15** the metal atom lies within the $N_5$ donor plane. On the basis of spectroscopic studies and analytic data, the $Mn^{2+}$, $Hg^{2+}$, and $Nd^{3+}$ complexes are also considered to be 1:1 pentaligated complexes, which, at least for the latter metals, represents a different stoichiometry than that normally obtained with porphyrins.[17] Interestingly, in the $Zn^{2+}$ complex of **13** the metal appears to be bound by only four of the five nitrogens with one pyrrole remaining in its "normal" protonated form; this is analogous to the result obtained for decametylsapphyrin **3**.[3]



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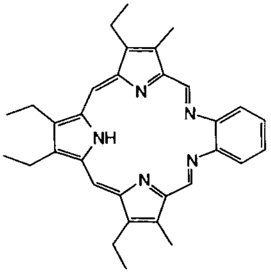
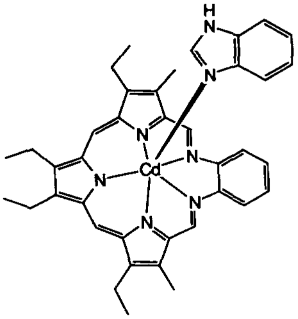
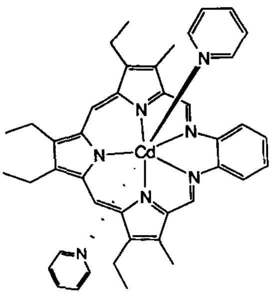


**13**



**14**

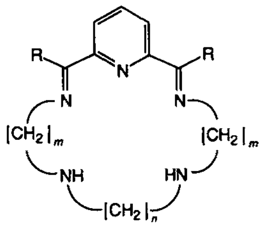


**15**

It is important to note that in both its free-base form **13**, and its complexes (e.g., **14** and **15**) the new "expanded porphyrin" of Sessler and co-workers shows properties characteristic of an aromatic porphyrin-like macrocycle. For instance in **15**, meso-like methine signals are observed for the bridging methine protons at 11.3 ppm. Moreover, both an intense Soret-like high energy absorption at $\lambda_{max}$ (log ε) 424 (4.86) nm and a very red shifted Q-like band, at 768 (4.61) nm, are seen in the electronic spectrum of **15**; the spectrum of the free-base **13** is quite similar except that the Q-like band is blue-shifted by roughly 20 nm.[14]

## PYRIDINE-CONTAINING MACROCYCLES

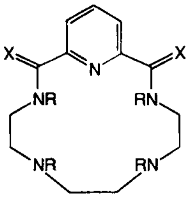
In contrast to the small amount of work dedicated to the synthesis of novel pyrrolic macrocycles, a tremendous amount of effort has been devoted to the development of pyridine-containing pentaaza macrocyclic ligands.[31–62] In fact, the very first planar pentadentate ligand, **16a**, prepared by Curry and Busch, was obtained from the $Fe^{3+}$ mediated Schiff base condensation of diacetylpyridine and triethylenetetramine.[36] Subsequent to that time, a large number of metal complexes from a variety of related pentaaza ligands (e.g., **16–18**) have been prepared and characterized.[37–52] Reduced forms of some of these macrocycles (e.g., **19a** and **19c**), obtained from the chelated imines (e.g., **16a**)[53–56] or the amides (e.g., **19b**),[57] as well as a variety of analogues, incorporating other hetero atoms (e.g., S, O, P) in the alkyl chains,[35] have also been described.



**16a** m = n = 2 R = $CH_3$
**16b** m = n = 2 R = H

**17** m = 2 n = 3 R = $CH_3$

**18** m = 3 n = 2 R = $CH_3$



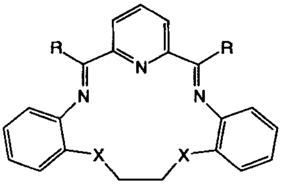
**19a** X = H, $CH_3$ R = H
**19b** X = O R = $CH_3$
**19c** X = 2H R = $CH_3$

Since much of this chemistry has already been reviewed,[31–35] only a brief discussion is given here.

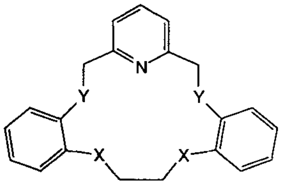
Synthetic and X-ray structural studies carried out by Nelson and Drew, and others, have served to show that in general the 15-membered and 16-membered diacetylpyridine-derived macrocycles (**16a** and **17**, respectively) support the formation of complexes in which the five nitrogen donor atoms define a pentagonal plane, but that more flexible macrocycles such as the reduced system **19a** or the 17-membered ligand **18** can support a variety of other binding geometries.[31,35,42–57] In general, therefore, ligands of type **16** and **17** have proved to be more versatile as planar pentadentate ligands. Structurally characterized seven-coordinate pentagonal bipyramidal complexes have been obtained for ligand **16a** with $Fe^{3+}$,[39,44] $Fe^{2+}$,[42,46,47] $Mg^{2+}$,[43] $Cd^{2+}$,[52] and $Zn^{2+}$[45]; for ligand **17** with $Fe^{3+}$,[44] $Fe^{2+}$,[47] $Mn^{2+}$,[51] and $Cd^{2+}$[48]; for ligand **18** with $Mn^{2+}$[50]; and for ligand **19a** with $Fe^{3+}$.[55] Six-coordinate pentagonal pyramidal structures have been characterized for $Ag^+$ with **17**,[49] and from $Cd^{2+}$ and $Hg^{2+}$ with **18**.[48] Interestingly, the only reported example of a structurally characterized "bare" five-coordinate planar pentagonal species is the complex obtained from $Ag^+$ and ligand **18**.[48]

The simple polyaza Schiff base ligands described above (**16–19**) all suffer to a greater or lesser extent from problems associated with macrocycle flexibility. A variety of benzo-fused systems (e.g.,

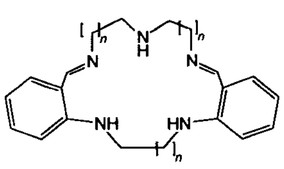
**20–23**) have therefore been prepared in an effort to develop more rigid planar pentadentate systems.[58–70] The first of these to be structurally characterized was the pentagonal bipyramidal $Mn^{2+}\cdot(ClO_4)_2$ complex of **20a** (a direct analogue of **16b**), reported by Tasker and co-workers in 1974.[58] In this and subsequent papers, these[58,60] and other workers,[59,61] have reported the synthesis and characterization of several related systems (e.g., **20b–20d**). As is true for the simple polyamine systems discussed in the paragraph above, the reduced forms of ligands **20** have also been the subject of study.[62] Recent X-ray crystal structures of the $Cu^{2+}$ and $Ni^{2+}$ complexes of **21b**,[62] however, reveal that (at least in these cases), the macrocycle does not act as planar pentadentate ligand: In a manner reminiscent of simple aza crown systems,[33] it povides both "basal" and "apical" ligation to six-coordinate metal centers.[62] Interestingly, to the best of our knowledge, the pentaazasystem **21a** has yet to be prepared.



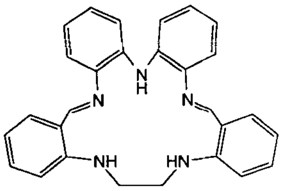
**20a** R = H X = NH
**20b** R = $CH_3$ X = NH
**20c** R = H X = O
**20d** R = H X = S



**21a** X = Y = NH
**21b** X= NH Y = O
**21c** X= O Y = NH



**22a** n = 1
**22b** n = 2

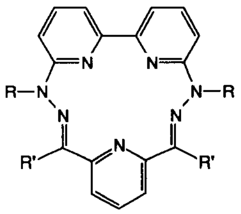


**23**

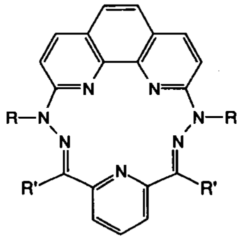
Interesting benzo-fused macrocycles of type **22**,[63] along with various reduced and heteroatom substituted analogues,[64–69] have also been prepared by Tasker and co-workers. Although capable of providing five-coordination to a variety of bound metal cations, in general, macrocycles of this class do not act as planar pentadentate ligands. Only in one $Cd^{2+}$ complex of a reduced dioxo analogue of **22a** is a coordination geometry approaching pentagonal bipyramidal observed.[64] The especially rigid tetrabenz-fused system of Black and co-workers (**23**) might prove more effective as a planar pentadentate ligand.[70] Unfortunately, as yet no structural information is available for this compound or its complexes.

## BIPYRIDINE AND PHENANTHROLINE CONTAINING SYSTEMS

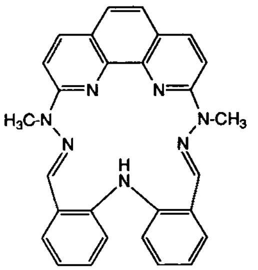
Over the last ten years, following an initial report by Tasker,[71] Lewis and co-workers have developed a series of elegant phenanthroline and bipyridine derived ligands of general structure **24** and **25**.[72–84] Presumably, here again, much of the impetus derived from a desire to prepare chelating macrocycles that are considerably more rigid than those derived from simple Schiff base condensations with polyamines. To date, a considerable body of structural and other evidence has been amassed which shows that **24** and **25** are in fact highly effective planar pentadentate *neutral* ligands. Key features of this work are summarized in the paragraphs that follow.



**24a** R = H R' = $CH_3$
**24b** R = R' = $CH_3$
**24c** R = $CH_2CH_2OH$ R' = H
**24d** R = $CH_2CH_2Cl$ R' = H



**25a** R = R' = $CH_3$
**25b** R = $CH_3$ R' = H
**25c** R = $CH_2CH_2OH$ R' = $CH_3$



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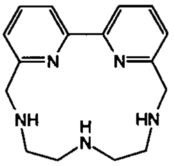


**27**

The original report by Tasker described the metal ion mediated synthesis of the $Zn^{2+}\cdot(H_2O)_2$ complex of **24a**.[71] An X-ray diffraction study revealed a seven-coordinate pentagonal bipyramidal structure with two water molecules serving as apical ligands. The Zn–N bond lengths ranged from roughly 2.0 Å to 2.3 Å, suggesting that the cavity in **24** is slightly larger than that found in the porphyrins. Consistent with this conclusion is the subsequent chemical and spectroscopic studies by Lewis and co-workers of the $Zn^{2+}$ and $Cd^{2+}$ complexes of **24b** which suggested that in the $Zn^{2+}$ complex the metal ion is held within the plane of the macrocycle in a pentagonal bipyramidal fashion but that the larger $Cd^{2+}$ cation is forced to lie above the plane in a distorted pentagonal pyramidal geometry.[72] Unfortunately, as yet no X-ray structural data is available for these two metal complexes. However, a $Cr^{3+}\cdot(H_2O)_2$ complex of **24c** was characterized structurally and revealed the presence of a seven-coordinate pentagonal bipyramidal chelated chromium atom.[73] In this case the metal–nitrogen bonds ranged in length from 2.02 Å to 2.26 Å. Interestingly, in the course of this work, Lewis found that the free-base form of **24c** could also be obtained if the initial condensation between diformyl pyridine and 6,6′-bis (α-2-hydroxyethylhydrazino)-2,2′-bipyridine was carried out under aqueous rather than the normal alcoholic conditions.[73] Quite recently, it was found that the chloroethyl analogue **24d** is capable of stabilizing an unprecedented pentagonal pyramidal $Li^+\cdot CH_3OH$ complex.[74] An X-ray diffraction study revealed the $Li^+$ cation to be displaced roughly 0.3Å above the plane of the macrocycle and chelated by the five nitrogen donor atoms with an average Li–N bond distance of 2.1 Å being observed. This exciting result demonstrates some of the potential that these planar pentadentate ligands might have in terms of extending the scope of existing knowledge in the area of coordination chemistry.

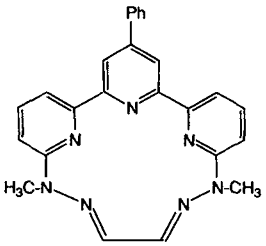
The first macrocyclic pentadentate phenanthroline-derived ligand to be prepared was **25a** which was characterized structurally as its pentagonal pyramidal $[Mn^{2+}\cdot Cl]^+$ complex.[75,76] In this structure, the $Mn^{2+}$–N bond distances were found to vary in length from 2.17 Å to 2.25 Å, and the $Mn^{2+}$ cation was observed to lie 0.53 Å above the macrocyclic plane. A structurally similar pentagonal pyramidal $[Mn^{2+}\cdot Cl]^+$ complex was subsequently obtained using ligand **25c**.[77] Nearly identical structures were also observed for two different $Co^{2+}$ complexes obtained from ligands **25a** and **25b**.[78,79] In both cases, the $Co^{2+}$ cation was found to lie within the macrocyclic plane with two solvent molecules ($H_2O$ or $CH_3OH$) serving to complete a pentagonal bipyramidal coordination sphere about the metal. Interestingly, electrochemical reduction of the complex derived from **25a**, followed by the addition of $P(OCH_3)_3$, led to the isolation and structural characterization of a highly unusual Co(I) species.[78] In this case, a pentagonal pyramidal geometry was seen to pertain about the metal with the $Co^+$ cation lying 0.36 Å above the macrocyclic plane. Structurally characterized pentagonal bipyramidal $Fe^{2+}$ and $Ni^{2+}$ complexes have also been prepared from ligand **25a**.[80–82] The latter is of interest in that it can be reduced to a stabilized, but as yet not structurally characterized, Ni(I) species.[82] This result further shows the versatility of ligands such as **24** and **25**.

Lewis and co-workers have extended their work on planar pentadentate ligands by preparing and characterizing structurally the cobalt(II) bispyridine complex of the *monoanionic* ligand **26**.[85] Interestingly, the $Mn^{2+}$ complex of an analogous macrocycle derived from diethylenetriamine (and hence not of the benzo-fused type) had been prepared earlier but not studied to any great extent.[75] A reduced analogue of this system, **27**, has also been reported by Newkome.[86] To date, however, no well-defined metal complexes have been characterized for this potentially pentadentate ligand. Thus, at present, the coordination chemistry of macrocycles of type **26** and **27** remains relatively unexplored compared to that of **24** and **25**.

It is important to note that none of the ligands **24–27** is aromatic. Although the well-studied planar systems **24** and **25** contain five $sp^2$ hybridized donor atoms within a conjugated macrocyclic core, the nature of the connectivity, particularly the 2,6-substitution about the pyridine nucleus, precludes a delocalized aromatic π system. This absence of aromatization is reflected in the optical properties of the complexes. For instance, in the $Cr^{3+}$ complex of **24**, the lowest energy absorption band is seen at $\lambda_{max}$ (log ε) 550 (2.49) nm.[73] Not only is this at considerably higher energy transition than that seen in **13** and its complexes,[14] it also is two orders of magnitude less intense. Presumably the absence of aromaticity in **24** and **25** is reflected in the nature and reactivity of their metal complexes. Until more information is available for true aromatic porphyrin-like pentadentate ligands such as **13**, and accurate comparisons are made, it will not be possible to assess the importance of aromatic effects in large planar pentadentate ligand environments.

## TERPYRIDINE-CONTAINING SYSTEMS

Very recently, pentadentate ligands, of general structure **28**, derived from terpyridine have been prepared by Constable and coworkers.[87–91] As is true for **24** and **25**, these systems are not aromatic. Nonetheless, macrocycle **28** is proving to be a very versatile planar pentadentate ligand. To date, pentagonal bipyramidal $Ni^{2+}$ and $Sn^{4+}$ complexes have been prepared and characterized structurally.[88–90] Moreover, the free-base form of this ligand has been obtained and its structure solved by X-ray diffraction analysis.[89] At present, it appears likely that a generalized approach to pentadentate ligands based on terpyridine-derived macrocycles will prove quite useful.



**28**

## FUTURE DIRECTIONS

Although, as discussed in this Comment, a considerable amount of work has been performed using a variety of other elegant macrocyclic pentadentate ligands, at present the pyrrole containing macrocycle **13** is the only aromatic pentadentate ligand to be prepared and characterized in both its free-base and metal containing forms. The recent observation that **13** supports the formation of mononuclear pentagonal pyramidal and pentagonal bipyramidal adducts leads us to suggest that "pentaphyrin" and "sappyhyrin" should also act as effective pentadentate ligands, *even though no pentaligated complexes have as yet been documented for these systems*. In the case of decamethylsapphyrin **3**, it is tempting to suggest that mononuclear pentacoordinate species were in fact formed in solution from metals such as $Co^{2+}$ and $Mn^{2+}$ but not characterized as solids. Alternatively, it may be that the "right" metals were not investigated by Bauer *et al.* in their study of decamethylsapphyrin **3**.[3] In fact, the finding that stable $Nd^{3+}$ complexes of **13** may be prepared readily[14] suggests that cations of the lanthanide series might be attractive substrates for this potentially trianionic ligand. Finally, the observation that oxidation of **12** and metal binding to **13** are facilitated in the presence of "proton sponge" (which presumably serves to deprotonate the pyrroles) leads us to suggest that metal binding to "sapphyrins," "smaragdyrins," and "pentaphyrins" might be enhanced in the presence of strong base. In any case, we feel that these pyrrole-based macrocycles remain potentially interesting pentadentate ligands and that their coordination chemistry warrants further study.

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