may be easily understood through the drop in energy of the metal d orbitals from Mo_2^{4+} to Rh_2^{4+}, which leads again to a better energy matching between the δ^* orbital of the metal dimer and the ligand pπ lone pair. In the $Pd_2(HNCHNH)_4$ molecule[12] the d orbitals in Pd_2^{4+} may have become even lower than the ligand orbital so that the interaction causes the lower lying $1b_{1u}$ orbital to be mostly δ^* in character.

Finally it may be noticed that the π^* orbital (e_g type in D_{4h} symmetry) of the metal dimers might also be matched well in energy with the ligand pπ lone pair of e_g symmetry, so that interaction between them could be expected in some molecules. However, the calculations for all compounds concerned in this work show that such an interaction is nearly or completely negligible. The reason for this is simple. The relative orientation of the π^* orbital and the e_g pπ lone pair is unfavorable for any significant overlapping between them. Therefore, no interesting interaction should be expected.

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Contribution from the Institute of Chemistry, University of Wrocław, 50 383 Wrocław, Poland, and Department of Chemistry, University of California, Davis, California 95616

Five-Coordinate Complexes of 21-Thiaporphyrin. Preparations, Spectra, and Structures of Iron(II), Nickel(II), and Copper(II) Complexes

Lechosław Latos-Grażyński,*[,†] Jerzy Lisowski,[†] Marilyn M. Olmstead,[‡] and Alan L. Balch*[,‡]

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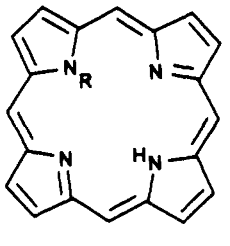
Insertion of Fe(II), Ni(II), and Cu(II) as their chloride salts into tetraphenyl-21-thiaporphyrin, STPPH, yields $Fe^{II}(STPP)Cl$ ($S = 2$, $\mu_{eff} = 5.2\ \mu_B$), $Ni^{II}(STPP)Cl$ ($S = 1$, $\mu_{eff} = 3.3\ \mu_B$), and $Cu^{II}(STPP)Cl$ ($S = {}^1/_2$). Electronic spectra of these complexes show porphyrin-like behavior with a strong Soret peak at 400 nm. The Mössbauer spectrum for $Fe^{II}(STPP)Cl$ (QS = 3.93 mm/s, IS = 0.88 mm/s at 295 K) is characterized by a large quadrupolar splitting found for related high-spin iron(II) complexes. The structures of these three isomorphous compounds (triclinic, $P\bar{1}$) have been determined by X-ray diffraction: $Fe^{II}(STPP)Cl(CH_3CN)$, $a = 10.059$ Å, $b = 13.661$ (4) Å, $c = 15.033$ (5) Å, $\alpha = 102.53$ (2)°, $\beta = 104.16$ (2)°, $\gamma = 106.37$ (2)°, $Z = 2$ at 130 K, least-squares refinement of 240 parameters using 3034 reflections, $R = 0.077$; $Ni^{II}(STPP)Cl$, $a = 10.154$ (3) Å, $b = 13.687$ (4) Å, $c = 15.064$ (4) Å, $\alpha = 101.97$ (2)°, $\beta = 103.62$ (2)°, $\gamma = 105.90$ (2)°, $Z = 2$ at 293 K, least-squares refinement of 489 parameters with 4860 reflections, $R = 0.053$; $Cu^{II}(STPP)Cl(CH_3CN)$, $a = 10.061$ (6) Å, $b = 13.646$ (7) Å, $c = 14.930$ (8) Å, $\alpha = 102.12$ (4)°, $\beta = 104.02$ (4)°, $\gamma = 108.20$ (4)°, $Z = 2$ at 130 K, least-squares refinement of 228 parameters with 3951 reflections, $R = 0.084$. The complexes share a basic five-coordinate structure with approximately square-pyramidal geometry and an apical chloride. The thiophene ring is bent from the plane of the remainder of the $STPP^-$ ligand core and is η^1-bound to the metal through a pyramidal sulfur.

Introduction

The porphyrin core is well recognized as providing a stable yet somewhat flexible environment for the coordination of a great variety of metal ions. In recent years the modification of that core has attracted attention for a variety of reasons.

Addition of substituents to one of the nitrogens to give an *N*-alkylporphyrin (**1**) has become significant in a biological context, and this represents a significant pathway for physiological porphyrin destruction.[1] Insertion of an oxygen atom into a porphyrin N–metal bond to give a complex of a porphyrin *N*-oxide (**2**) may be a significant reaction in oxygen atom transfer and oxidation processes.[2] Insertions of carbenes or nitrenes into N–M bonds, which have been observed in model systems, may be related by other biological examples of porphyrin destruction.[3]

Modification of porphyrins by introduction of other atoms (O, S, Se) for one or more of the pyrrole nitrogens produces new macrocycles that are of interest for use as new complexing agents and for theoretical reasons. In the latter regard, the tetraoxaporphyrin dication **3** has recently been synthesized and discussed in the context of the aromatic character of annulenes.[4] Limited reports on the oxaporphyrin **4**,[5] dithiaporphyrin **5**,[6] and diselenaporphyrin **6**[6] have appeared. We recently reported a reasonable synthesis of tetra-*p*-tolyl-21-thiaporphyrin (**7**, STTPH) and determined its structure and that of its copper(II) bicarbonate complex.[7] The thiaporphyrin incorporates one thiophene ring in its core. Thiophene–transition-metal bonding can occur in several fashions: S bound, C bound, or η^5 bound.[8] Moreover, the thiophene–transition-metal bond appears to be relatively weak but very important to the process of hydrodesulfurization.[9] Therefore, it is of interest to examine the effect of the thiophene ring on the coordination of metal ions by **7**. Here we report on the structures and spectroscopic properties of complexes of **7** with iron(II), nickel(II), and copper(II) and comment on the structural



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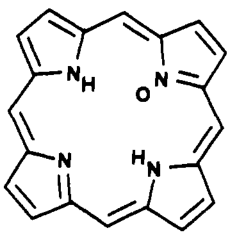

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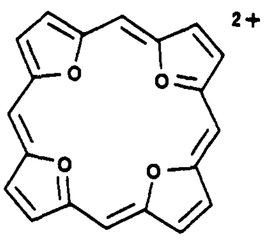

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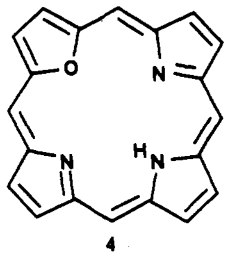

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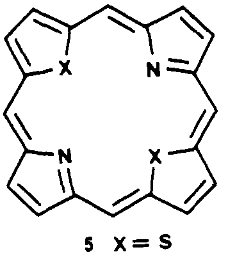
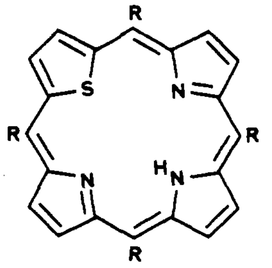


5 X = S
6 X = Se



7

[†] University of Wrocław.
[‡] University of California.

Table I. Characteristic Metal–Ligand Distances (Å) and Angles (deg)

	[Fe(STPP)Cl]	[Ni(STPP)Cl]	[Cu(STPP)Cl]	[Fe(N-CH_3TPP)Cl]^a
		Distances		
M–Cl	2.215 (9)	2.275 (1)	2.373 (3)	2.244 (3)
M–N(1)	2.127 (6)	2.094 (3)	2.055 (6)	2.155 (6)
M–N(2)	2.064 (8)	1.963 (4)	1.962 (8)	2.118 (3)
M–N(3)	2.138 (8)	2.084 (3)	2.057 (7)	2.156 (4)
M–S	2.388 (3)	2.296 (1)	2.335 (2)	2.329 (2)^b
M–N_3^{c}	0.538	0.295	0.274	0.62
		Angles		
N(1)–M–Cl	109.4 (5)	96.7 (1)	97.9 (2)	105.36 (7)
N(2)–M–Cl	117.6 (5)	111.5 (1)	118.3 (2)	114.38 (7)
N(3)–M–Cl	98.2 (5)	97.3 (1)	94.5 (2)	108.03 (7)
S–M–Cl	109.9 (5)	98.5 (1)	97.3 (1)	103.48 (6)^b
S–M–N(2)	132.3 (2)	146.0 (1)	144.4 (2)	142.13 (8)^b
N(1)–M–N(3)	150.5 (3)	162.8 (1)	163.7 (2)	145.60 (9)
C(9)–S–M	105.0 (3)	107.6 (1)	106.3 (3)	133.50 (2)^b
C(10)–S–M	103.3 (3)	108.6 (1)	107.3 (3)	112.70 (2)^b
C(9)–S–C(10)	91.2 (5)	92.4 (5)	91.3 (5)	105.80 (2)^b

^{a}Data taken from ref 10. ^{b}Geometry around N-methylated nitrogen. ^{c}Distance from the metal to the plane of the three nitrogen atoms.

relation of these to complexes of normal and modified porphyrins.

Results

Formation and Characterization of Iron(II), Nickel(II), and Copper(II) Complexes. Iron(II), nickel(II), and copper(II) are readily inserted into tetraphenyl-21-thiaporphyrin to give five-coordinate complexes, M(STPP)Cl. The resulting complexes have good solubility in dichloromethane and chloroform and moderate solubility in tetrahydrofuran and toluene. In the solid state, all of these complexes are stable to the atmosphere. In solution the nickel(II) and copper(II) complexes are stable and can be chromatographed. Solutions of the iron(II) complex are stable toward atmospheric oxidation for several hours, but they do undergo gradual demetalation to give free STPPH. Generally, iron(II) porphyrins are exceedingly sensitive toward oxidation by air, but in this regard Fe^{II}(STPP)Cl resembles Fe^{II}(*N*-CH_3TPP)Cl (*N*-CH_3TPP is the monoanion of *N*-methyltetraphenylporphyrin), which is also resistant to oxidation by dioxygen.[10] Because of the ease of demetalation, crystallization of Fe^{II}(STPP)Cl was always performed in the presence of an excess of iron(II).

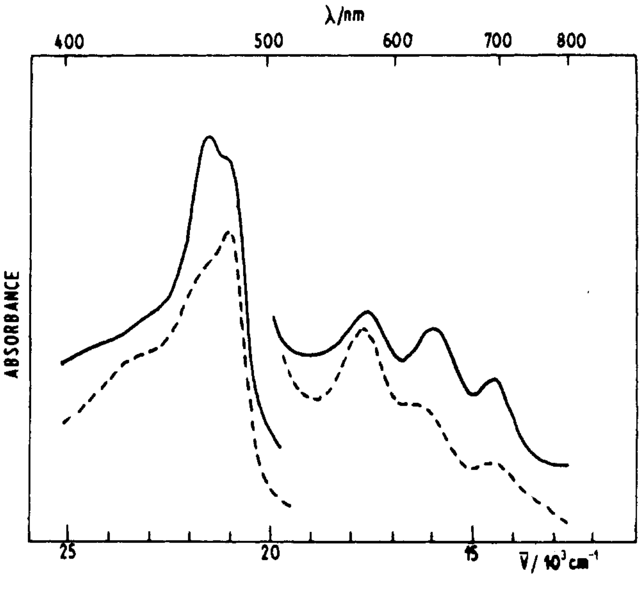


Figure 1. Electronic absorption spectra of chloroform solutions of $Fe^{II}(STPP)Cl\cdot CH_3CN$ (solid line) and $Ni^{II}(STPP)Cl\cdot CH_2Cl_2$ (dashed line).

The electronic absorption spectra of $Fe^{II}(STPP)Cl\cdot CH_3CN$ and $Ni^{II}(STPP)Cl\cdot CH_2Cl_2$ are presented in Figure 1. The corresponding spectrum for Cu^{II}(STPP)Cl has been published.[11] Both complexes have spectral characteristics that resemble those of porphyrins. Thus, the intense features at 400 nm correspond to the porphyrin Soret bands, and the weaker features in the visible region are related to the porphyrin Q-band absorptions. Due to the lower symmetry of the thiaporphyrin complexes, the low-energy portion of the spectrum is more complex than is found for the corresponding porphyrin complexes.

The three complexes are paramagnetic. The magnetic moments of Ni^{II}(STPP)Cl and Fe^{II}(STPP)Cl, as measured by the Evans technique in chloroform solution at 300 K, are 3.3 (1) and 5.2

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Table II. Delocalization Patterns in 21-Thiaporphyrin Complexes

	pyrrole			thiophene		
	N–C_α	C_α–C_β	C_β–C_β	S–C_α	C_α–C_β	C_β–C_β
Fe(II)	1.379 (12)	1.416 (11)	1.340 (13)	1.742 (9)	1.416 (11)	1.340 (13)
Ni(II)	1.383 (6)	1.457 (6)	1.380 (7)	1.744 (6)	1.412 (6)	1.370 (6)
Cu(II)	1.377 (2)	1.424 (13)	1.365 (13)	1.729 (10)	1.408 (14)	1.380 (14)
thiophene[a]				1.714 (2)	1.370 (3)	1.423 (3)

[a] Data from ref 21.

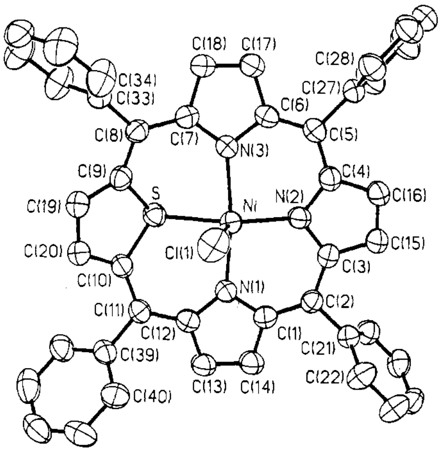

Figure 2. Perspective view of the structure of $Ni^{II}(STPP)Cl$, showing the numbering scheme used for all three $STPP^-$ complexes described here.

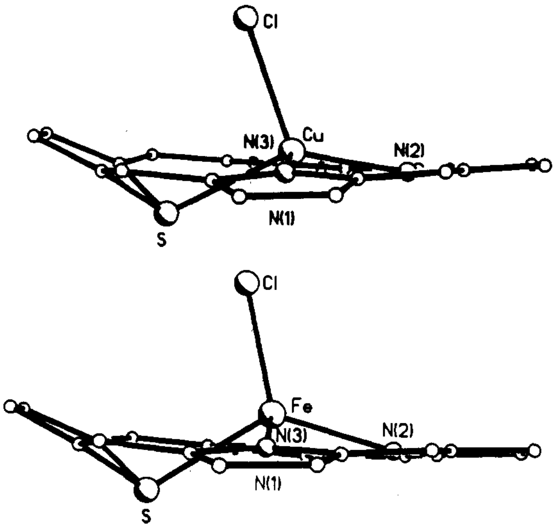

Figure 3. View of the inner cores of $Cu^{II}(STPP)Cl$ (top) and $Fe^{II}(STPP)Cl$ (bottom) from similar angles.

(1) μ_B. Thus, these complexes have high-spin ground states with $S = 1$ and $S = 2$ for nickel(II) and iron(II), respectively. For the iron complex, the susceptibility of the solid has also been examined over the temperature range 4–300 K. Above 10 K, the effective magnetic moment remains constant (5.3 (1) μ_B), but between 10 and 4 K, the moment decreases continuously so that at 4 K it is 4.75 (9) μ_B. This decrease at low temperature is characteristic of an effect resulting from zero-field splitting that is frequently encountered in high-spin ($S = 2$) iron(II) complexes.[12] The copper(II) complex gives an ESR spectrum that is consistent with an $S = {}^1/_2$ ground state.[11]

The Mössbauer spectrum of $Fe^{II}(STPP)Cl$ recorded at 295 K exhibits a quadrupole doublet with an isomer shift of 0.84 mm/s (vs α-Fe) and a quadrupole splitting of 3.74 mm/s. This quadrupole splitting is unusually large for iron(II) porphyrins, which generally have quadrupole splittings of less than 2.75 mm/s. However, two situations do produce these large splittings. Several symmetrical, five-coordinate iron(II) porphyrins with large displacements of the iron out of the N_4 plane have quadrupole splittings of ca. 4.0 mm/s.[13] Likewise, the unsymmetrical environment present in $Fe^{II}(N\text{-MeTPP})Cl$ produces Mössbauer spectral parameters (quadrupolar splitting 3.93 mm/s; isomer shift 0.88 mm/s)[14] that are similar to those of $Fe^{II}(STTP)Cl$.

X-ray Structural Studies. Isomorphous crystals of $Fe^{II}(STPP)Cl\cdot CH_3CN$, $Ni^{II}(STPP)Cl\cdot CH_2Cl_2$, and $Cu^{II}(STPP)Cl\cdot CH_3CN$ were suitable for X-ray diffraction. The nickel complex consists of an ordered molecule of $Ni^{II}(STPP)Cl$ and a disordered molecule of dichloromethane. A view of the complex is shown in Figure 2. The copper complex consists of well-separated molecules of $Cu^{II}(STPP)Cl$ and a molecule of acetonitrile, which occupies the site of the dichloromethane molecule in the crystals of the nickel complex. The structure is similar to that of $Cu^{II}(STTP)HCO_3$,[7] with chloride replacing bicarbonate as the axial ligand, and the nickel complex. The iron complex is also similar, but suffers from disorder. Relative to the copper and nickel complexes, there is a 10% occupancy of a sulfur site lying below N(3) and an 8% occupancy of a sulfur site lying below N(2), and there is a corresponding 18% occupancy of a nitrogen site lying above the sulfur atom. There is also disorder in the location of the chloride ligand. The discussion only describes the most highly occupied site. Additionally, there is disorder at the acetonitrile site with 15% occupancy by a dichloromethane molecule. Bond distances and angles for the metal ion coordination core are given in Table I. Table II gives structural data relating to the geometry of the pyrrole and thiophene rings in the complexes.

The three complexes have a number of common features. All have a five-coordinate metal ion that is bonded to three nitrogen atoms, the thiophene sulfur, and an axial chloride in a roughly square-pyramidal arrangement. The thiophene ring is sharply bent out of the plane of the N_3 porphyrin core, while the three pyrrole rings are only slightly tipped away from that plane. The thiophene sulfur is coordinated to the metal in a pyramidal fashion.

Despite these common structural features, there are some significant variations in the detailed geometry about each metal. Figure 3 allows a comparison between the porphyrin cores of the iron(II) and copper(II) complexes, the compounds where the differences are greatest. Other differences can be evaluated in Table I. There is a shortening of all M–N distances as one proceeds from Fe(II) to Ni(II) and to Cu(II). This is seen in other cases where one compares the structures of similar high-spin complexes and reflects the effect of decreasing nuclear screening with increasing atomic number. The Fe–N bond lengths fall in the range 2.068–2.108 Å found for other five-coordinate, high-spin iron(II) porphyrin complexes[15] including $[Fe^{II}(TPivP)Cl]^-$ and $Fe^{II}(N\text{-}CH_3TPP)Cl$.[10] The Ni–N bond lengths are, as expected, longer than those (1.93–1.96 Å) found for diamagnetic Ni^{II}

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porphyrins[16] and similar to that (2.038 (4) Å) seen in a six-coordinate, high-spin nickel(II) porphyrin complex.[17]

In contrast to the behavior of the M–N bonds, there is a systematic lengthening of the M–Cl bonds for the same series. The largest effect, the 0.10-Å increase on going from Ni(II) to Cu(II), can readily be ascribed to the filling of the out-of-plane σ^* orbital in the Cu(II) complex. The M–S distances show an irregular trend within the series, but as with the N–M distances, the Fe–S distance is the largest. As a consequence of the relatively long Fe–N and Fe–S distances, the iron ion is further from the N_3 plane than the copper or nickel ions are.

The thiaporphyrin ring has had to distort from its intrinsic planar geometry[7] to accommodate the coordination of these metal ions. Most notably, the thiophene ring is sharply bent from the core plane, while the trans pyrrole ring is slightly bent in the opposite direction as seen in Figures 2 and 3. The angle between the SC(9)C(10) plane and the N_3 plane is 40.0° in the iron complex, 38.1° in the nickel complex, and 38.4° in the copper complex.

Bending of the thiophene ring allows this group to coordinate the metal ion in an η^1 fashion through the sulfur atom, which acquires a pyramidal (sp^3-hybridized) geometry. Thus, the metal lies out of the thiophene plane, with the angle between the SC(9)C(10) plane and the S-metal bond being 69.5° in the iron complex, 63.3° in the nickel complex, and 65.6° in the copper complex. Similar angles have been found in two ruthenium–thiophene[8e,f] complexes and in an iron–benzothiophene[8j] complex that have η^1-S bonding. The Fe–S distance (2.388 (3) Å) is practically equal to the sum of the covalent radii (2.38 Å) and is slightly longer than that found recently for the Fe–S bond (2.289 (1) Å) in diamagnetic [Fe(dibenzothiophene)(CO)$_2$(η^5-C_5H_5)][BF$_4$].[8j] However, a fairly wide range (2.27–2.56 Å) of comparable Fe–S distances exists.[18] Moreover, Fe^{II}(STPP)Cl is high-spin and should be expected to have longer metal–ligand bonds. Likewise, the Ni–S distance (2.296 (1) Å) is clearly a bonding distance. It is somewhat shorter than a previously determined Ni–S distance (2.396 (1) Å) in a thioether complex.[19] Similarly, the Cu–S distance (2.335 (2) Å) falls in the range of Cu–S distances (2.297–2.4110 Å) observed in other compounds.[20] The Cu–S distance in Cu^{II}(STPP)Cl is slightly longer than that (2.277 (3) Å) previously reported for the related bicarbonate complex, Cu^{II}(STTP)HCO$_3$.[7]

The thiophene ring in these complexes is significantly altered relative to free thiophene. In particular, it is no longer planar. Thus the dihedral angle between the SC(9)C(10) plane and the C(9)C(10)C(19)C(20) plane is 11.8° in the iron complex, 13.4° in the nickel complex, 14.7° in the copper complex, and 15.3° in Cu(STPP)HCO$_3$. This folding is a characteristic of thiaporphyrin coordination and is not found to this degree in free tetra-*p*-tolyl-21-thiaporphyrin (dihedral angle 2.4°),[7] in thiophene itself,[21] or in any of the other known, crystallographically characterized thiophene complexes.[8] Clearly, the folding results from the need to accommodate a metal ion within a macrocyclic core of limited size.

Additionally, the bond distances within the thiophene ring are altered, as can be seen in Table II. There is a slight elongation in the C_α–S distances in the complexes relative to free thiophene. the C_α–C_β distances are longer and the C_β–C_β distances are shorter in the complexes than in free thiophene. The pattern of C_α–C_β and C_β–C_β distances follows that seen in the pyrrole rings. These bond length changes indicate that π delocalization through the thiophene ring is altered in the thiaporphyrins. ^{1}H NMR studies of S$_2$TPP and STPPH have demonstrated a shift in the ring current that is in agreement with the observed bond length changes.[7,22] Theoretical calculations on S$_2$TPP yield a pattern of π-bond orders in the thiophene (S–C_α = 0.375; C_α–C_β = 0.419; C_β–C_β = 0.711 Å) that agrees qualitatively with that seen in Table II.[23]

The geometry of Fe^{II}(STPP)Cl is very similar to that of the *N*-methylporphyrin complex Fe^{II}(*N*-MeTPP)Cl.[10] These similarities are readily apparent upon comparing the first and last columns of Table I. Both complexes have five-coordinate iron binding and an out-of-plane chloride ion. The thiophene ring and the N-methylated pyrrole are both bent out of the porphyrin plane in the same direction. The Fe–N and Fe–Cl distances are similar in both complexes. These similarities are also seen in the spectroscopic and magnetic properties of the two complexes.

Discussion

Structural and spectroscopic data are now available for three high-spin five-coordinate complexes of STPP$^-$ with divalent first-row transition-metal ions. In addition, it is likely that Co^{II}(STPP)Cl ($S = {}^3/_2$)[24] and Zn^{II}(STPP)Cl ($S = 0$)[24] have similar structures. These five-coordinate complexes are all geometrically and magnetically similar to their *N*-methylporphyrin counterparts, where the series from Mn(II) through Zn(II) is known and the Mn(II),[25] Fe(II),[10] Co(II),[26] and Zn(II)[27] examples are characterized by X-ray crystal structures. The similarity of structures for the two iron(II) complexes is readily apparent from Table I, and both have high-spin ($S = 2$) ground states. Likewise, both Ni^{II}(*N*-MeTPP)Cl, which demethylates too easily to be readily crystallized, and Ni^{II}(STPP) have high-spin ($S = 1$) ground states, as shown by their magnetic susceptibilities and ^{1}H NMR spectra.[28] The fact that both STPPH and *N*-MeTPPH coordinate as monoanions facilitates the formation of five-coordinate structures for neutral complexes that incorporate an additional out-of-plane anionic ligand. Thus, the thiaporphyrin ligand differs from the porphyrin and porphyrin *N*-oxide ligands, which coordinate as dianions and form, with divalent metal ions, neutral complexes that have nearly planar, four-coordinate geometries.

Characteristic features of complexed thiaporphyrins include severe nonplanarity, with the thiophene ring tipped out of the plane of the thiaporphyrin, and some degree of nonplanarity of the thiophene ring itself. The thiophene sulfur is η^1-bonded to the metal ion in a pyramidal fashion. The macrocyclic ring structure should be seen as facilitating and strengthening the S–M bond, since thiophene itself is generally regarded as a poor ligand. The noncoplanarity of the M–SC$_4$ unit can be compared with the geometry of η^1-cyclopentadienyl complexes, where the relationship of the metal to C_5H_5 ring also accommodates sp^3 hybridization of the metal-bonded carbon.[29]

Experimental Section

Preparation of Compounds. Tetraphenyl-21-thiaporphyrin (7)[7] and Cu^{II}(STPP)Cl[11] were prepared as described earlier. All solvents were purified under nitrogen prior to use by standard techniques that remove traces of water.

Fe^{II}(STPP)Cl·CH$_3$CN. Tetraphenyl-21-thiaporphyrin (32 mg, 0.05 mmol) was dissolved in 15 mL of dichloromethane, and the solution was

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Table III. Crystal Data and Data Collection Parameters

	$C_{46}H_{31}N_4SClFe$	$C_{45}H_{30}N_3SCl_3Ni$	$C_{46}H_{31}N_4SClCu$
fw	763.15	809.86	770.85
color and habit	dark brown needles	dark blue plates	dark green prisms
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	10.059 (3)	10.154 (3)	10.061 (6)
b, Å	13.661 (4)	13.687 (4)	13.646 (7)
c, Å	15.033 (5)	15.064 (4)	14.930 (8)
α, deg	102.53 (2)	101.97 (2)	102.12 (4)
β, deg	104.16 (2)	103.62 (2)	104.02 (4)
γ, deg	106.37 (2)	105.90 (2)	108.20 (4)
V, Å^3	1828.8 (9)	1872.2 (8)	1796 (2)
T, K	130	293	130
Z	2	2	2
cryst dimens, mm	0.10 × 0.16 × 0.26	0.32 × 0.30 × 0.14	0.25 × 0.45 × 0.50
d_{calcd}, g cm^{-3}	1.39	1.44	1.43
radiation (λ, Å)	Mo Kα (0.71069)	Mo Kα (0.71069)	Mo Kα (0.71069)
μ(Mo Kα), cm^{-1}	5.9	8.2	7.9
range of transmission factors	0.91–0.95	0.79–0.91	0.71–0.85
R^a	0.077	0.053	0.084
$R_w{}^b$	0.074	0.062	0.087

$^a R = \sum||F_o| - |F_c||/|F_o|$. $^b R_w = \sum||F_o| - |F_c||w^{1/2}/\sum|F_o w^{1/2}|$, $w = 1/\sigma^2(F_o)$.

added to a solution of 100 mg (0.62 mmol) of anhydrous iron(III) chloride (Fluka) in 15 mL of acetonitrile. The mixture was heated under reflux in an argon atmosphere in the presence of 200 mg of iron powder for 6 h. The deep green solution was filtered while hot under argon to remove the solid material. Cooling the filtrate afforded deep green microcrystals that were collected by filtration and washed with 5-mL portions of acetonitrile, 1% aqueous hydrochloric acid, and water. After vacuum-drying, 28 mg (74%) of product was obtained. It was recrystallized from acetonitrile/dichloromethane in the presence of excess iron(II) chloride. Electronic spectrum (chloroform solution), λ_{max}, nm (log ϵ): 424 (4.66), 456 (4.88), 470 (4.36), 557 (4.03), 602 (3.84), 677 (3.60).

Ni^{II}(STPP)Cl·CH$_2$Cl$_2$. A solution of 500 mg (3.8 mmol) of anhydrous nickel(II) chloride (Alfa) in 150 mL of methanol was added to a solution of 126 mg (0.20 mmol) of tetraphenyl-21-thiaporphyrin in 100 mL of chloroform. The solution was heated under reflux for 8 h. It was cooled, and then the solvent was removed under reduced pressure. The solid residue was extracted with 50 mL of chloroform, and the chloroform was separated from the remaining solid by filtration. The chloroform solution was subjected to chromatography on a silica gel column (3 × 30 cm). Elution with chloroform gave a yellow-brown fraction containing STPPH. Further elution with chloroform/methanol (10:1 v/v) produced a green fraction that was recovered as a solid after evaporation of the solvent under vacuum. Recrystallization of this solid from dichloromethane/*n*-hexane (1:1 v/v) produced 55 mg (34%) of Ni(STPP)Cl·CH$_2$Cl$_2$. Electronic spectrum (chloroform solution), λ_{max}, nm (log ϵ): 460 (5.04), 472 (4.99), 562 (3.94), 618 (3.92), 679 (3.70).

Physical Measurements. Electronic spectra were recorded on a Cary 14 or a Specord UV-vis spectrophotometer. Mössbauer spectra were measured with a MS 2320 POLON spectrometer with a ^{57}Co (Cr matrix) source. A Tesla 100-MHz NMR spectrometer was used for magnetic susceptibility measurements by the Evans technique with CDCl$_3$ solutions using the peak of tetramethylsilane as the reference. Magnetic susceptibilities of solids were measured by the Faraday technique with Hg[Co(SCN)$_4$]$_2$ as standard. Diamagnetic corrections (Ni(STPP)Cl·CH$_2$Cl$_2$, −736 × 10^{-6}; Fe(STPP)Cl·CH$_3$CN, −734 × 10^{-6}) were obtained by using the published values for the constitutive corrections for TPPH$_2$[30] and Pascal's constants.

X-ray Data Collection and Refinement. [Ni^{II}(STPP)Cl]·CH$_2$Cl$_2$. Crystals of [Ni(STPP)Cl]·CH$_2$Cl$_2$ were obtained from dichloromethane/*n*-hexane. Data were collected at room temperature to prevent the shattering that occurred on cooling the crystals. Crystal data are compiled in Table III. The usual corrections for Lorentz and polarization effects were applied to the data. Crystallographic programs used were those of SHELXTL, version 5, installed on a Data General Eclipse computer. Scattering factors and corrections for anomalous dispersion were from ref 31. No decay in the intensities of two standard reflections was observed during the course of data collection. Solution of the structure was accomplished by a combination of Patterson and Fourier methods. A molecule of dichloromethane in the lattice exhibits three disordered positions for the chlorine atoms with the relative occupancy 65% ("a" set), 20% ("b" set), and 15% ("c" set). These occupancies were initially determined by refinement and later fixed. The central carbon atom, C(45), is common to all three sets of chlorine atoms.

An absorption correction was applied in the final cycles of refinement.[32] All non-hydrogen atoms (except C(45), Cl(2b), Cl(3b), Cl(2c), and Cl(3c)) were assigned anisotropic thermal parameters. Hydrogen atoms were included in the structure factor calculation by use of a riding model, with C–H of 0.96 Å and $U_{iso} = U_{iso}{}^*$ for the bonded carbon. In the final difference map the largest feature was 0.74 e Å^{-3} in height, 1.1 Å from S.

[Fe^{II}(STPP)Cl]·CH$_3$CN. Crystals of [Fe^{II}(STPP)Cl]·CH$_3$CN were obtained from dichloromethane/acetonitrile recrystallization in the presence of an excess of iron(II) chloride. Data were collected at low temperature (130 K). No decay in the intensities of two standard reflections was observed during the course of data collection.

Solution of the structure was accomplished by use of the positional parameters for the isostructural Ni complex. The position of the sulfur atom is disordered among three positions in the proportions 0.82, 0.10, and 0.08 for S(a), S(b), and S(c), respectively. These occupancies were determined by requiring that all three sulfur atoms have reasonable thermal parameters. Once determined from the latter difference maps, the positions of S(b), S(c), and N(a) were fixed during refinement. The chlorine atom bonded to Fe suffers from large thermal motion or disorder, probably due to the disorder in the sulfur position. The three chlorine positions used to model the disorder had occupancies of 0.50, 0.35, and 0.15. A molecule of acetonitrile in the lattice occupies a site occupied by dichloromethane in the Ni structure. However, there is some disorder evident, and this was modeled by assuming a 15% occupancy by dichloromethane rather than acetonitrile at this site. These occupancies were initially determined by refinement and later fixed. The central carbon atom, C(46), is common to both solvent molecules. In addition, the methyl carbon spends some time as chlorine but was refined only as carbon. An absorption correction was applied.[32] In the final cycles of refinement, only Fe and the most prominent of the Cl and S atoms were assigned anisotropic thermal ellipsoids. Hydrogen atoms were included in the structure factor calculation by use of a riding model, with C–H of 0.96 Å and $U_{iso} = 1.2U_{iso}{}^*$ for the bonded carbon. In the final difference map the largest feature was 1.1 e Å^{-3} in height, 0.8 Å from the central carbon of the disordered acetonitrile/dichloromethane.

Cu^{II}(STPP)Cl·CH$_3$CN. Crystals of Cu^{II}(STTP)Cl·CH$_3$CN were dark green prisms, obtained from dichloromethane/acetonitrile recrystallization. A suitable crystal was mounted on a glass fiber with silicone grease. Some cracking was evident, but since this was the only good crystal in the sample, it was used anyway, and the data were collected by using a rather wide ω scan. No decay in the intensities of two standard reflections was observed during the course of data collection.

Solution of the structure was accomplished by taking advantage of its isostructural relationship to the corresponding Ni and Fe complexes. A molecule of acetonitrile in the lattice occupies a site occupied by dichloromethane in the Ni structure and a site occupied by a disordered

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acetonitrile/dichloromethane in the Fe structure. An absorption correction was applied.[32] In the final cycles of refinement, only Cu, Cl, and S atoms were assigned anisotropic thermal ellipsoids. Hydrogen atoms were included in the structure factor calculation by use of a riding model, with C-H of 0.96 Å and $U_{iso} = 1.2U_{iso}{}^*$ for the bonded carbon. In the final difference map the largest feature was 1.2 e Å^{-3} in height, 1.14 Å from the nitrogen of the acetonitrile.

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Registry No. Fe^{II}(STPP)Cl·CH_3CN, 119145-08-3; Ni^{II}(STPP)Cl·CH_2Cl_2, 119145-10-7; Cu^{II}(STPP)Cl·CH_3CN, 119145-12-9.

Supplementary Material Available: Tables of atomic coordinates, all bond distances, bond angles, hydrogen atom coordinates, anisotropic thermal parameters, and crystal data and data collection parameters for Ni^{II}(STPP)Cl·CH_2Cl_2, Cu^{II}(STPP)Cl·CH_3CN, and Fe^{II}(STPP)Cl·CH_3CN (19 pages); tables of calculated and observed structure factors (71 pages). Ordering information is given on any current masthead page.

Notes

Contribution from the Departments of Chemistry
and Energetic, University of Florence,
50144 Firenze, Italy, and Department of Inorganic
Chemistry, University of Valencia, Valencia, Spain

Polynuclear Zinc(II) Complexes with Large Polyazacycloalkanes. 2.[1] Equilibrium Studies and Crystal Structure of the Binuclear Complex $[Zn_2LCl_2](Cl)ClO_4 \cdot H_2O$ (L = 1,4,7,10,13,16,19,22-Octaazacyclotetracosane)

Andrea Bencini,[2a] Antonio Bianchi,[2a] Paolo Dapporto,[2b]
Enrique Garcia-España,[2c] Mauro Micheloni,*[,2a]
and Piero Paoletti*[,2a]

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In contrast to the very large amount of work that has been done on azamacrocycles in recent years,[3-5] there have been only few investigations on "large" azamacrocycles.[1,6-10] These macrocycles are very promising compounds that have been employed in anion coordination as well as in transition-metal complex studies. In other papers we have studied a series of large polyazacycloalkanes with the general formula $[3k]aneN_k$ (with k = 7-12). One of the most interesting properties of these compounds is the ability to form polynuclear metal complexes. In the present paper, in order to complete the $[3k]aneN_k$ series, we report studies on the formation equilibria between zinc(II) and the four polyazacycloalkanes 1,4,7,10,13,16-hexaazacyclooctadecane ($[18]aneN_6$), 1,4,7,10,13,16,19-heptaazacycloheneicosane ($[21]aneN_7$), 1,4,7,10,13,16,19,22-octaazacyclotetracosane ($[24]aneN_8$), and 1,4,7,10,13,16,19,22,25,28,31,34-dodecaazacyclohexatriacontane ($[36]aneN_{12}$) (see Chart I). The crystal structure of binuclear $[Zn_2([24]aneN_8)Cl_2](Cl)ClO_4 \cdot H_2O$ is also reported.

Table I. Crystallographic Data for $[Zn_2([24]aneN_8)Cl_2](Cl)ClO_4 \cdot H_2O$

formula	$C_{16}H_{42}Cl_4N_8O_5Zn_2$
mol wt	699.13
a, Å	7.601 (7)
b, Å	14.079 (5)
c, Å	15.429 (7)
α, deg	63.17 (3)
β, deg	78.13 (8)
γ, deg	85.65 (8)
V, Å^3	1441.6
Z	2
space gp	$P\bar{1}$
D_{calcd}, g cm^{-3}	1.61
radiation	Mo Kα, graphite monochromated
λ, Å	0.7107
temp, °C	25
μ, cm^{-1}	20.8
R^a	0.071
$R_w{}^b$	0.071

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

Experimental Section

Synthesis of the Complex $[Zn_2([24]aneN_8)Cl_2](Cl)ClO_4 \cdot H_2O$. Good crystals, suitable for X-ray analysis, were obtained by slow evaporation at room temperature of a solution containing the octahydrochloride $[24]aneN_8 \cdot 8HCl$ (0.01 mol dm^{-3}), $Zn(ClO_4)_2$ (0.02 mol dm^{-3}), and $NaClO_4$ (3 mol dm^{-3}). The pH of the solution was adjusted to 12 by adding NaOH. After a few days, crystals were collected, filtered, washed with ethanol, and dried under vacuum at room temperature. Anal. Calcd for $C_{16}H_{42}N_8Zn_2Cl_4O_5$: C, 27.49; H, 6.06; N, 16.03. Found: C, 27.4; H, 6.1; N, 16.0.

Emf Measurements. All potentiometric measurements were carried out in 0.15 mol dm^{-3} $NaClO_4$ (C. Erba ACS grade). Purification and standardization of solutions used in the potentiometric titrations were performed according to the procedure described in ref 11. Hydrochloride salts of $[21]aneN_7$, $[24]aneN_8$, and $[36]aneN_{12}$ have been obtained as described in ref 8, 7, and 10, respectively.[12] $[18]aneN_6$ was purchased from Fluka. The potentiometric titrations were carried out by using equipment that has been fully described.[13] At least two titration curves for each system investigated were used. The experimental details of the emf measurements have been reported as supplementary material. The computer program SUPERQUAD[14] was used to process emf data and cal-

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