interstrand contacts join the $(Se_6I^+)_n$ strands into a two-dimensional sheet of $(Se_6I)_n^{n+}$ (Figure 6). The overall structure consists of these sheets separated by layers containing MF_6^- anions.

Cation-Anion Interactions. The number of cation-anion interactions in the $(Se_6I^+)_n$ cation (Table VIII) are fewer than those in the $Se_6I_2^{2+}$ cation (Table V). This is consistent with the lower charge in $(Se_6I^+)_n$. In addition, it is conceivable that some of the cation-anion interactions in the $Se_6I_2^{2+}$ cation are replaced by the Se(2)-Se(3″) intercationic contacts in $(Se_6I^+)_n$. The complete description (including figures) of the coordination around the selenium atoms in $(Se_6I)_n \cdot nMF_6$ (M = As, Sb) is given in the supplementary material.

Summary and Conclusion

Our attempts to prepare selenium-rich selenium-iodine cations, in the solid state, led to the discovery of $Se_6I_2(AsF_6)_2 \cdot 2SO_2$, $(Se_6I)_n \cdot nAsF_6$, and $(Se_6I)_n \cdot nSbF_6$. Both cations contain a hexaselenium ring in the chair configuration; i.e., they are iodine derivatives of the unstable allotrope of selenium, Se_6.[17] In the sulfur system the solid S_7IMF_6 (M = As, Sb)[6] and $(S_7I)_2I(SbF_6)_3 \cdot 2AsF_3$[7] have been prepared containing S_7I^+ and $(S_7I)_2I^{3+}$. These cations are both iodine derivatives of the S_7 ring in the chair configuration, which as a neutral species is unstable with respect to S_8.

The structure of $Se_6I_2^{2+}$ is endo and cubelike. Weak intracationic selenium-iodine contacts (2 × 3.709 (2), 2 × 3.719 (2) Å) complete the distorted cube. There is substantial selenium-selenium bond alternation within the Se_6 ring. The bonds between the dicoordinate selenium (2.227 (2) Å) correspond to a bond order of ca. 1.5,[44] which implies substantial 4pπ-4pπ bonding. The selenium-iodine bond distance (2.454 (2) Å) is also significantly shorter than that expected for bond order 1 (average 2.510 (2) Å in SeI_3^+)[11] and implies significant 4pπ-5pπ bonding. These thermodynamically stable 4pπ-4pπ and 4pπ-5pπ bonds arise as a consequence of charge delocalization within the Se_6 ring and onto the iodine atoms. The cluster-like structure adopted by $Se_6I_2^{2+}$ maximizes charge delocalization, π bonding, and intracationic selenium-iodine contacts.

The structure of the $(Se_6I^+)_n$ cation consists of Se_6I_2 units linked through common bridging iodine atoms. Each Se_6I_2 unit is similar to that of $Se_6I_2^{2+}$, except that the selenium-iodine bond length (average 2.739 (3) Å) corresponds to a bond order of 0.5; the selenium-selenium bond alternation within the Se_6 ring is much less substantial, corresponding to the lower charge per Se_6 ring. There are four (rather than two) weaker intracationic selenium-iodine contacts (average 3.870 (3) Å), two to each adjacent Se_6I_2 units. The $(Se_6I^+)_n$ cations are linked through weak selenium-selenium intercationic contacts, giving rise to sheets containing linked $(Se_6I^+)_n$ cations separated by sheets containing the MF_6^- anions.

Thus, whereas selenium-iodine neutral compounds have not been isolated, there is a rich chemistry of binary selenium-iodine cations. As well as the salts described in this paper, SeI_3MF_6 (M = As, Sb),[11] $Se_2I_4(Sb_2F_{11})_2$,[12] and $Se_2I_4(AsF_6)_2 \cdot SO_2$[13] have all been prepared and their X-ray crystal structures determined. In addition $Se_4I_4^{2+}$ and $Se_6I_2^{2+}$ [33,38] have been identified in solution by ^{77}Se NMR spectroscopy. The chemistry of these sulfur and selenium iodide cations has recently been reviewed.[5]

Acknowledgment. We thank F. Grein for assistance with the ab initio total energy calculations and the National Sciences and Engineering Research Council of Canada for financial support.

Registry No. $Se_6I_2(AsF_6)_2 \cdot 2SO_2$, 100908-48-3; AsF_5, 7784-36-3; I_2, 7553-56-2; Se, 7782-49-2; $Se_8(AsF_6)_2$, 52374-78-4; SeI_3AsF_6, 59544-89-7; $(Se_6I)_n \cdot nAsF_6$, 87800-53-1; $(Se_6I)_n \cdot nSbF_6$, 121867-50-3; $I_2Sb_2F_{11}$, 53108-64-8.

Supplementary Material Available: A discussion of the complete coordination around the selenium and iodine atoms in $Se_6I_2(AsF_6)_2 \cdot 2SO_2$ and $(Se_6I)_n \cdot nMF_6$ (M = As, Sb), Figures S1-S11, showing the coordination around various atoms in these compounds, and tables of crystallographic data (Table S1) and of the thermal parameters for $Se_6I_2(AsF_6)_2 \cdot 2SO_2$ $(Se_6I)_n \cdot nAsF_6$, and $(Se_6I)_n \cdot nSbF_6$ (Tables S2, S4, and S6, respectively) (19 pages); tables of observed and calculated structure factors (Tables S3, S5, and S6) (22 pages). Ordering information is given on any current masthead page.

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

Preparation and Structural Characterization of a Six-Coordinate 21-Thiaporphyrin Complex: $Rh^{III}(STPP)Cl_2$ (STPP = Tetraphenyl-21-thiaporphyrin Anion)

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Treatment of tetraphenyl-21-thiaporphyrin (STPPH) with rhodium(III) chloride in acetonitrile in the presence of metallic zinc yields diamagnetic $Rh^{III}(STPP)Cl_2$. The electronic and ^1H NMR spectra are reported. $Rh^{III}(STPP)Cl_2$ crystallizes in the monoclinic space group $P2_1$ with a = 10.522 (2) Å, b = 13.065 (2) Å, c = 12.898 (3) Å, and β = 108.06 (2)° at 130 K with Z = 2. Refinement of 2760 reflections and 344 parameters yielded R = 0.062. The rhodium is six-coordinate with bonds to the three pyrrole nitrogens (Rh-N = 2.00 (1), 2.033 (9), 2.080 (8) Å), the thiophene sulfur (Rh-S = 2.32 (3) Å), and the two axial chloride ligands (Rh-Cl = 2.333 (3), 2.346 (3) Å). The rhodium atom lies near the plane of the three pyrrole nitrogen atoms, while the thiophene ring is sharply tilted out of that plane. The thiophene group is bound to the rhodium through the pyramidal sulfur in the η^1 fashion. The thiophene ring is bent so that the dihedral angle between the $SC_\alpha C_\alpha$ and $C_\alpha C_\alpha C_\beta C_\beta$ planes is 26.4°. The structure is compared to those of the related high-spin, five-coordinate $M^{II}(STPP)Cl$ (M = Fe, Ni, Cu).

Introduction

The novel features of rhodium porphyrins, including their versatile redox behavior,[1] the formation of reactive Rh-H,[2,3] Rh-Rh,[3] and Rh-C[4] bonds, and their relation to naturally occurring porphyrins, have attracted considerable attention. Generally, the properties of a metal ion in a porphyrin can be modified by alterations in the axial ligands or chemical changes in the porphyrin periphery. In view of the versatile behavior of rhodium porphyrins, alteration of properties through core modification offers considerable promise. For example, polypyrroles (corroles), with a shrunken central binding site, have been examined as ligands for rhodium.[5]

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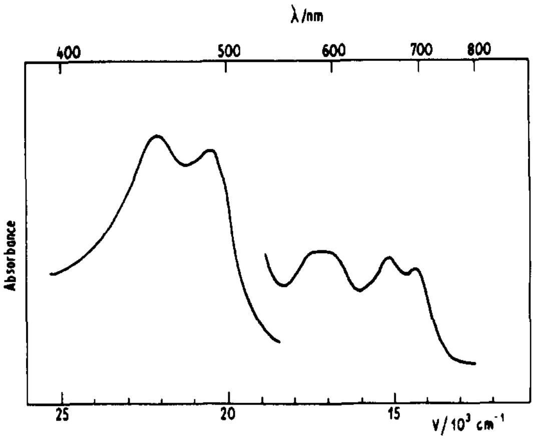
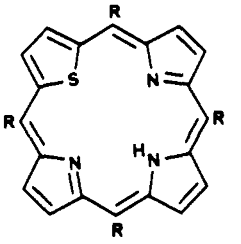


Figure 1. Electronic absorption spectrum of a chloroform solution of $Rh^{III}(STPP)Cl_2$ at 23 °C.

Recently we have prepared another core-modified porphyrin, tetraphenyl-21-thiaporphyrin (**1**, STPPH) in which one of the pyrrole rings has been replaced by a thiophene ring.[6] This ligand



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forms high-spin, five-coordinate complexes with the series of first-row transition-metal ions Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}, in which an anionic axial ligand, usually chloride, is incorporated.[7,8] Full X-ray structural characterization is available for Fe^{II}(STPP)Cl, Ni^{II}(STPP)Cl, Cu^{II}(STPP)Cl, and Cu(STTP)HCO_3, as well as for uncomplexed STTPH (STTPH is tetra-*p*-tolyl-21-thiaporphyrin).

A major component of these core-modified porphyrins is the thiophene ring. The coordination properties of this ring are of substantial interest. The presence of the larger sulfur shrinks the core size of **1** relative to those of other porphyrins. Thiophene itself is regarded a weakly bound ligand that is capable of binding metal ions in η^1-S, η^1-C, and η^5-C_4S fashions.[9] The properties of coordinated thiophene are of considerable interest to the process of fuel desulfurization, and rhodium metal is active as a desulfurization catalyst.[10] Both η^1-S and η^5-C_4S thiophene coordination have been suggested, on the basis of experimental[9] and theoretical arguments,[11,12] to be involved in this process. There are, however,

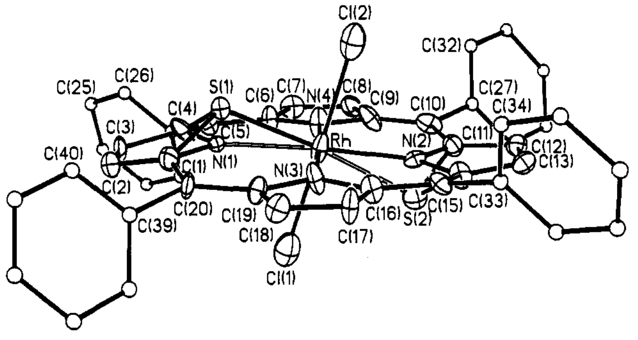

Figure 2. Perspective view of $Rh^{III}(STPP)Cl_2$, showing the numbering scheme used. The major form (70% occupancy) involves S(1) and N(2), while the minor form (30% occupancy) includes N(1) and S(2).

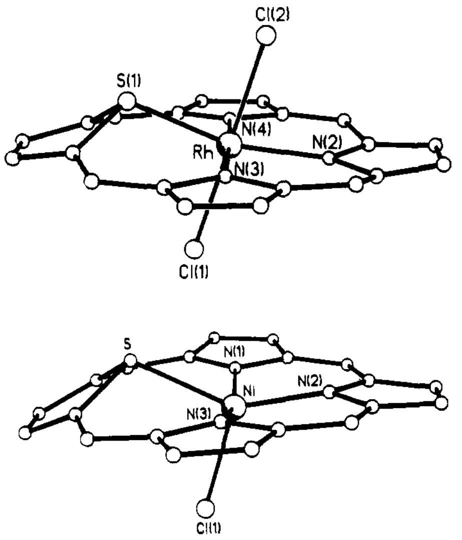

Figure 3. Comparison of the inner cores of (top) the six-coordinate Rh^{III} complex and (bottom) a typical five-coordinate complex (Ni^{II}(STPP)Cl).

only a limited number of crystallographically characterized models for thiophene–metal binding. These include both η^1-S (with iron, nickel, copper, and ruthenium) and η^5-C_4S (with chromium and rhodium) bonding modes.[9]

Here we report the incorporation of rhodium(III) into **1** and describe the first example of a thiaporphyrin incorporating a six-coordinate metal ion.

Results

Preparation and Spectroscopic Properties. Addition of rhodium(III) chloride trihydrate to STPPH in the presence of zinc dust results in formation of $Rh^{III}(STPP)Cl_2$ in 38% yield. Other as yet unidentified complexes, presumably differing in the nature of the axial ligation, are formed. The zinc dust is essential for metalation and presumably facilitates the reaction by producing Rh(I) species that undergo more rapid substitution. The complex is stable as a solid and in solution. It has good solubility in dichloromethane and chloroform and moderate solubility in benzene and tetrahydrofuran. The electronic absorption spectrum is shown in Figure 1. A porphyrin-like pattern is clearly present with a strong but split Soret-like band at 448 and 482 nm and weaker bands at lower energies. Relative to those of rhodium(III) complexes of normal porphyrins, the spectrum of $Rh^{III}(STPP)Cl_2$ is more complex due to its lower symmetry.

The ^1H NMR spectrum of this diamagnetic compound in chloroform-*d* at 298 K is consistent with a structure of C_s symmetry and is similar to that of the free 21-thiaporphyrin.[6] It includes resonances at 9.522 (singlet, thiophene H(2), H(3)), 8.738 (singlet, pyrrole H(12), H(13)), 8.782, and 8.872 ppm (AB quartet, J = 5.2 Hz, pyrrole H(7), H(8), H(18), H(17)) and a complex multiplet from 8 to 7 ppm due to the phenyl protons.

Crystal and Molecular Structure of $Rh^{III}(STPP)Cl_2$. Crystals of $Rh^{III}(STPP)Cl_2$ consist of discrete molecules with no unusual

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Table I. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) and Rh(STPP)Cl$_2$

	x	*y*	*z*	U^a
Rh	2604 (1)	2500	2487 (1)	26 (1)*
Cl(1)	549 (3)	2528 (4)	2822 (2)	40 (1)*
Cl(2)	4685 (3)	2471 (4)	2175 (2)	38 (1)*
S(1)	3764 (3)	3098 (2)	4129 (2)	17 (1)*
S(2)	1266 (7)	1918 (7)	876 (7)	28 (2)
N(1)	3064	3028	4151	12 (5)
N(2)	2044 (8)	2004 (8)	945 (8)	16 (3)*
N(3)	2936 (8)	1046 (7)	3070 (7)	27 (3)*
N(4)	2224 (8)	4005 (6)	1957 (6)	25 (3)*
C(1)	3427 (9)	2391 (8)	5131 (7)	28 (3)*
C(2)	3266 (8)	3053 (8)	5935 (7)	22 (3)*
C(3)	2992 (8)	4028 (7)	5556 (6)	22 (3)*
C(4)	2953 (9)	4106 (8)	4448 (8)	29 (3)*
C(5)	2441 (8)	4918 (7)	3730 (7)	20 (3)*
C(6)	2171 (10)	4849 (8)	2600 (8)	25 (3)*
C(7)	1771 (8)	5732 (7)	1868 (7)	25 (3)*
C(8)	1571 (9)	5381 (7)	817 (7)	23 (3)*
C(9)	1817 (10)	4302 (7)	871 (8)	28 (3)*
C(10)	1655 (9)	3692 (7)	−27 (8)	23 (3)*
C(11)	1688 (8)	2611 (8)	−24 (7)	23 (3)*
C(12)	1671 (8)	1970 (8)	−909 (8)	23 (3)*
C(13)	1911 (8)	991 (7)	−555 (7)	22 (3)*
C(14)	2112 (8)	949 (7)	592 (7)	22 (3)*
C(15)	2630 (8)	152 (7)	1323 (7)	19 (3)*
C(16)	2930 (10)	197 (7)	2460 (8)	20 (3)*
C(17)	3340 (9)	−674 (7)	3154 (7)	23 (3)*
C(18)	3516 (9)	−360 (7)	4171 (7)	24 (3)*
C(19)	3269 (9)	723 (7)	4142 (7)	21 (3)*
C(20)	3419 (8)	1326 (8)	5097 (7)	22 (3)*
C(21)	1984 (8)	5855 (7)	4157 (7)	18 (2)
C(22)	639 (8)	6129 (8)	3807 (8)	23 (2)
C(23)	177 (9)	6975 (9)	4232 (8)	28 (2)
C(24)	1061 (8)	7536 (10)	5034 (8)	35 (2)
C(25)	2415 (9)	7284 (8)	5404 (8)	28 (2)
C(26)	2877 (8)	6447 (7)	4971 (7)	21 (2)
C(27)	1476 (8)	4201 (7)	−1079 (7)	21 (2)
C(28)	306 (9)	4070 (8)	−1962 (7)	28 (2)
C(29)	108 (10)	4596 (9)	−2938 (9)	33 (2)
C(30)	1060 (9)	5272 (9)	−3055 (9)	31 (2)
C(31)	2241 (9)	5419 (8)	−2191 (8)	26 (2)
C(32)	2441 (8)	4879 (7)	−1207 (7)	23 (2)
C(33)	2978 (8)	−814 (8)	825 (8)	21 (2)
C(34)	4318 (9)	−1108 (9)	1139 (8)	28 (2)
C(35)	4693 (10)	−1964 (10)	689 (8)	33 (2)
C(36)	3735 (8)	−2531 (10)	−76 (7)	34 (2)
C(37)	2420 (9)	−2249 (8)	−406 (8)	33 (2)
C(38)	2038 (9)	−1394 (7)	57 (7)	27 (2)
C(39)	3545 (8)	763 (7)	6137 (7)	19 (2)
C(40)	4661 (8)	912 (7)	7048 (7)	24 (2)
C(41)	4744 (11)	395 (10)	7979 (10)	37 (3)
C(42)	3772 (10)	−301 (10)	8029 (9)	34 (2)
C(43)	2647 (9)	−443 (9)	7149 (9)	31 (2)
C(44)	2536 (9)	86 (7)	6211 (7)	24 (2)

[a] Asterisk indicates equivalent isotropic *U* defined a one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table II. Selected Bond Lengths (Å) and Angles (deg) for Rh(STPP)Cl$_2$

Bond Distances			
Rh–Cl(1)	2.333 (3)	Rh–Cl(2)	2.346 (3)
Rh–S(1)	2.232 (3)	Rh–N(2)	2.00 (1)
Rh–N(3)	2.033 (9)	Rh–N(4)	2.080 (8)
S(1)–C(1)	1.71 (1)	S(1)–C(4)	1.69 (1)
S(2)–C(11)	1.64 (1)	S(2)–C(14)	1.65 (1)
Bond Angles			
Cl(1)–Rh–Cl(2)	179.3 (1)	Cl(1)–Rh–S(1)	94.8 (1)
Cl(2)–Rh–S(1)	84.5 (1)	Cl(2)–Rh–N(2)	80.0 (3)
Cl(1)–Rh–N(2)	100.7 (3)	Cl(1)–Rh–N(3)	90.5 (3)
S(1)–Rh–N(2)	164.4 (3)	S(1)–Rh–N(3)	89.8 (2)
Cl(2)–Rh–N(3)	89.2 (3)	Cl(1)–Rh–N(4)	87.2 (3)
N(2)–Rh–N(3)	91.7 (4)	S(1)–Rh–N(4)	88.5 (2)
Cl(2)–Rh–N(4)	93.1 (3)	N(3)–Rh–N(4)	177.0 (4)
N(2)–Rh–N(4)	90.7 (4)	Rh–S(1)–C(4)	109.6 (3)
Rh–S(1)–C(1)	100.3 (3)	C(1)–S(1)–C(4)	89.9 (5)

intermolecular contacts. Table I gives the atomic positional parameters, while Table II contains selected interatomic distances and angles. Figure 1 shows a perspective view of the complex with the atomic numbering scheme. Although the complex has no crystallographically imposed symmetry, it has approximate C_s symmetry with the plane including Rh, S, N(2), Cl(1), and Cl(2). Figure 3 compares the geometry of Rh^{III}(STPP)Cl$_2$ with that of a typical, five-coordinate STPP$^-$ complex, Ni^{II}(STPP)Cl.[7]

The structure of Rh^{III}(STPP)Cl$_2$ suffers from moderate disorder, which is included in Figure 2. There are two sulfur atom positions. The major (70% occupancy) is S(1), and the minor one is S(2). Likewise, there is a corresponding 70% occupancy of the site N(2) and a 30% occupancy of site N(1). Elongation of the core thermal ellipsoids particles for Cl(1), Rh, and Cl(2) probably reflects unresolved disorder in these positions as well. All following discussion will involve the major form.

The geometry of the complex reflects the balance between the constraints of the macrocycle ligand and the requirement of Rh(III) for octahedral geometry. The thiaporphyrin has had to distort to accommodate the rhodium binding. Although 21-thiatetraphenylporphyrin and 21-thiatetra-*p*-tolylporphyrin are planar,[6] the thiaporphyrin in Rh^{III}(STPP)Cl$_2$ is nonplanar with the thiophene ring severly bent out of the N$_3$ plane and lesser degrees of tipping of the pyrrole rings from that plane. Moreover, the thiophene ring itself is no longer planar. The dihedral angle between the $C_\alpha C_\beta C_\beta C_\alpha$ plane and the $C_\alpha S C_\alpha$ plane is 26.4°, larger than found in the five-coordinate complexes Cu^{II}(STPP)Cl (15.2°), Ni^{II}(STPP)Cl (13.4°), and Fe^{II}(STPP)Cl (11.8°) and much larger than seen in STTPH (2.4°).[6,7] It is clear that this distortion is caused by the six-coordinate nature of the rhodium geometry. In binding to the two chloride ligands, the rhodium is forced into the N$_3$ plane of the macrocycle, and as a consequence of accommodating an ion of this size within the macrocycle's core, the thiophene ring is bent.

This bending and tipping of the thiophene ring allows the sulfur to coordinate the rhodium in pyramidal sp^3 fashion. The geometry at the sulfur resembles that established for other η^1-thiophene complexes,[9] for coordinated thioethers[13] and ethylene sulfide (thiirare),[14] and that seen in sulfonium cation[15] and 2,5-dihydrothiophene 1-oxide.[16] This side-on type of thiophene coordination is also related to that of η^1-cyclopentadienyl complexes in which the metal-bound carbon displays sp^3 hybridization and the angle between the M–C bond and the C$_5$ plane is ca 50°.[17]

The rhodium coordination is nearly octahedral. The two Rh–Cl bonds are nearly equal (2.333 (3), 2.346 (3) Å) and are of normal length. The Rh–N distances (2.00 (1), 2.033 (9), 2.080 (8) Å) fall near the range of distances (2.02–2.04 Å) seen for other rhodium porphyrins.[18] The R–S bond length 2.232 (3) Å is slightly shorter than the range (2.298–2.353 Å) previously established for other Rh–S bonds.[19]

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Table III. Crystal Data and Data Collection Parameters for $Rh(STPP)Cl_2$

formula	$C_{44}H_{28}Cl_2N_3RhS$
fw	804.61
space group	$P2_1$
cell params	
a, Å	10.522 (2)
b, Å	13.065 (2)
c, Å	12.898 (3)
β, deg	108.06 (2)
V, Å^3	1685.8 (6)
T, deg	130 K
Z	2
d_{calcd}, g cm^{-3}	1.58
radiation (λ, Å)	Mo Kα (λ = 0.71069)
μ(Mo Kα), cm^{-1}	7.4
range of transm factors	0.76–0.86
R^a	0.062
$R_w{}^a$	0.069

$^a R = \sum||F_o| - |F_c||/|F_o|$ and $R_w = \sum||F_o| - |F_c||w^{1/2}/\sum|F_o w^{1/2}|$; $w = 1/\sigma^2(F_o) + 0.000126F_o^2$.

The Cl–Rh–Cl and N(3)–Rh–N(4) angles (179.3 (1) and 177.0 (4)°, respectively) are nearly linear, while the S–Rh–N(2) angle is somewhat bent (164.4 (3)°) as a consequence of strain induced by incorporation of a metal into a macrocycle with a limited core size. The angles between cis ligands cluster about the relatively narrow range 87.2 (3)–93.1 (3)°, near the 90° ideal except for those in the $Cl_2RhSN(2)$ plane where the distortions due to the bent S–Rh–N(2) unit lead to contracted angles for Cl(2)–Rh–S(1) (84.5 (1)°) and Cl(2)–Rh–N(2) (80.0 (3)°) and expanded angles for Cl(1)–Rh–S(1) (94.8 (1)°) and Cl(1)–Rh–N(2) (106.7 (3)°).

The differences between five- and six-coordinate complexes of 21-thiaporphyrin are best seen in Figure 3. The major difference in the six-coordinate complex is the movement of the metal toward the N_3 plane. In $Rh^{III}(STPP)Cl_2$ the Rh to N_3 plane distance is only 0.033 Å, while in the five-coordinate complexes this distance is much larger: 0.274 Å in $Cu^{II}(STPP)Cl$, 0.295 Å in $Ni^{II}(STPP)Cl$, and 0.538 Å in $Fe^{II}(STPP)Cl$.[7] The folding of the thiophene ring is a direct consequence of the location of the rhodium ion in the N_3 plane. This folding allows the carbon atoms of the thiophene ring to lie nearly coplanar with the rest of the thiaporphyrin core so that the π conjugation is not disrupted.

We have previously[6,7] pointed out the great similarity in structure of the five-coordinate, high-spin thiaporphyrin complexes $M^{II}(STPP)Cl$ (M = Fe, Co, Ni, Cu, Zn) and the *N*-alkylporphyrin complexes M^{II}(*N*-MeTPP)Cl (M = Mn, Fe, Co, Ni, Cu, Zn).[20] It remains to be seen whether the N-substituted porphyrin skeleton can accommodate a six-coordinate metal ion within its core. Steric hinderance due to the *N*-alkyl substituent is expected to severely hamper the ability of N-substituted porphyrin complexes (with simple, noncoordinating N-substitutents) to add two axial ligands.[21]

Experimental Section

Preparation of Compounds. The thiaporphyrin STPPH was prepared as described previously.[6]

$Rh(STPP)Cl_2$. A mixture of 32 mg (0.05 mmol) of STPPH, 100 mg (0.38 mmol) of rhodium(III) chloride trihydrate, and 50 mg of zinc powder was heated in dry acetonitrile for 24 h. The solution was filtered, and the filtrate was evaporated under vacuum to dryness. The solid residue was dissolved in a minimum quantity of chloroform and subjected to chromatography on a silica gel column. Elution with a mixture of chloroform and methanol (10:1 v/v) produced a yellow-brown band of STPPH and a second green band. The second band was carefully collected, and the solvent was removed under vacuum. The product was obtained in 38% yield as deep green crystals after recrystallization from dichloromethane/octane. When the zinc powder was omitted from the procedure, only STPPH was recovered; no $Rh^{III}(STPP)Cl_2$ was formed. For $Rh^{III}(STPP)Cl_2$, UV–vis spectrum in chloroform [λ_{max}, nm (log ϵ)]: 448 (4.66), 481 (4.65), 571 (3.83), 582 (3.83), 650 (3.82), 684 (3.76).

X-ray Data Collection, Solution, and Refinement. Dark green prisms of $Rh^{III}(STPP)Cl_2$ were obtained by diffusion of *n*-hexane into a green dichloromethane solution of the complex. A suitable crystal was mounted on a glass fiber with silicone grease and secured in the cold stream of the diffractometer. No decay in the intensities of two standard reflections was observed during the course of data collection. Crystal parameters are given 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 22.

The space group was determined to be either $P2_1$ or $P2_1/m$ by the observation of the conditions for present reflections of $0k0$, $k = 2n$. A successful solution of the structure could only be obtained in the space group $P2_1$. The structure was solved by Patterson methods. There is a 70:30 disorder in the position of the sulfur atom and its opposite nitrogen atom. The positional parameters of the minor nitrogen were fixed after they were located on a difference map. No absorption correction was applied. The handedness of the structure could not be determined. Refinement of either enantiomorphic form yielded the same *R* value, and other tests using SHELXTL software were inconclusive. Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms except the carbons of the phenyl rings and the minor forms of the disordered N and S atoms. Hydrogen atoms were included at calculated positions by using a riding model, with C–H = 0.96 Å and $U_H = 1.2U^*_C$. The largest feature on a final difference map was 2.4 e Å^{-3} in height (near Rh), and the largest shift in the final cycle of refinement was 0.086 for *y* of C(23).

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Supplementary Material Available: Tables of all bond distances, angles, hydrogen atom positions, data collection parameters, and anisotropic thermal parameters for $Rh^{III}(STPP)Cl_2$ (6 pages); listings of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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