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Cobalt(II) and rhodium(I) metal complexes of thia- and oxasapphyrins[†]

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Summary — The synthesis and X-ray crystallographic characterization of the following heterosapphyrin metal complexes is presented: cobalt(II)-3,7,18,22-tetraethyl-2,8,17,23-tetramethyl-27-oxasapphyrin diacetate **2**; cobalt(II)-3,7,18,22-tetraethyl-2,8,17,23-tetramethyl-27-thiasapphyrin dichloride **3**; and bisrhodium(I)-3,7,18,22-tetraethyl-2,8,17,23-tetramethyl-27-thiasapphyrin tetracarbonyl **4**. The complexes **2** and **3** were formed by addition of a solution of the metal salt in methanol to the heterosapphyrin dissolved in chloroform. Complex **4** was synthesized by addition of $[RhCl(CO)_2]_2$ to a solution of thiasapphyrin, which contained triethylamine. In all three complexes, the relevant metal cation is coordinated to two pyrrolic nitrogen atoms, where one ligating nitrogen is localized in the bipyrrole moiety and the other one in an adjacent pyrrole. Crystals of **2** are triclinic, space group $P\bar{1}$, in a cell of dimensions a = 10.583(4), b = 11.798(3), c = 15.264(5) Å, α = 87.12(2), β = 71.00(2), γ = 86.89(2)°, V = 1798(1) Å^3, ρ = 1.33 gcm^{-3}, $F(000)$ = 762, with Z = 2. Crystals of **3** are monoclinic, space group $P2_1/c$, in a cell of dimensions a = 17.455(6), b = 15.857(6), c = 12.482(5) Å, β = 107.61(3)°, V = 3293(2) Å^3, ρ = 1.39 gcm^{-3}, $F(000)$ = 1444, with Z = 4. Crystals of **4** are also monoclinic, space group $C2/c$, in a cell of dimensions a = 21.355(3), b = 13.558(1), c = 13.557(1) Å, β = 112.279(9)°, V = 3632.2(7) Å^3, ρ = 1.60 gcm^{-3}, $F(000)$ = 1776, with Z = 4. For **2**, the Co(II) ion assumes a tetrahedral coordination geometry consisting of two monodentate acetate groups (Co-O$_{avg}$ 1.964(3) Å) and two nitrogen atoms (Co-N$_{avg}$ 1.990(3) Å) of the oxasapphyrin. The oxygen of the macrocycle is not involved in coordination to Co(II) and is 2.951(4) Å away. For **3**, the Co(II) is also in a tetrahedral coordination environment. However, the cobalt ion is disordered about two equivalent orientations of the macrocycle. The average Co-N bond length is 2.026(5) Å, while the Co-Cl bonds average 2.273(3) Å. The sulfur atom is 2.720(5) Å from the Co(II) center in **3**. In **4**, a 2:1 metal-to-macrocycle complex is observed. Each of the Rh(I) ion adopts a square-planar coordination geometry with Rh-N bond lengths averaging 2.083(1) Å and Rh-C bond lengths averaging 1.850(2) Å. The dihedral angle between the pyrrole ring planes of the bipyrrole is largest for the Rh(I) complex, **4**, and is 42.7°. The dihedral angle is smallest for **3** (22.6°), followed by 29.6° for **2**.

expanded porphyrin / heterosapphyrin / cobalt(II) / rhodium(I) / η^2-coordination

Résumé — Complexes métalliques de cobalt(II) et rhodium(I) thia- et oxasapphyrines. *Les synthèses et les caractérisations par diffraction RX des complexes métalliques d'hétérosapphyrine sont présentées: cobalt(II)-3,7,18,22-tétraéthyl-2,8,17,23-tétraméthyl-27-oxasapphyrin diacétate* **2**; *cobalt(II)-3,7,18,22-tétraéthyl-2,8,17,23-tétraméthyl-27-thiasapphyrin dichlorure* **3**; *bisrhodium(I)-3,7,18,22-tétraéthyl-2,8,17,23-tétraméthyl-27-thiasapphyrin tétracarbonyl* **4**. *Les complexes* **2** *et* **3** *ont été préparés par addition d'une solution du sel métallique dans le méthanol à l'hétérosapphyrin en solution dans le chloroforme. Le complexe* **4** *a été synthétisé par addition de* $[RhCl(CO)_2]_2$ *à une solution de thiasapphyrin contenant de la triéthylamine. Dans les trois complexes le cation métallique est coordiné à deux azotes pyrroliques dont l'un est localisé dans la partie bipyrrole et l'autre sur un pyrrole adjacent. Le complexe* **2** *cristallise dans le groupe d'espace,* $P\bar{1}$, *dans une maille triclinique de dimensions* a = *10.583(4),* b = *11.798(3),* c = *15.264(5) Å,* α = *87.12(2),* β = *71.00(2),* γ = *86.89(2)°,* V = *1798(1) Å*^{3}, ρ = *1.33 g-cm*$^{-3}$, F*(000)* = *762 avec* Z = *2. Le complexe* **3** *cristallise dans le groupe d'espace,* $P2_{1/c}$, *dans une maille monoclinique de dimensions* a = *17.455(6),* b = *15.857(6),* c = *12.482(5) Å,* β = *107.61(3)°,* V = *3293(2) Å*^{3}, ρ = *1.39 g-cm*$^{-3}$, F*(000)* = *1444 avec* Z = *4. Le complexe* **4** *cristallise dans le groupe d'espace,* C2/c, *dans une maille monoclinique de dimensions* a = *21.355(3),* b = *13.558(1),* c = *13.557(5) Å,* β = *112.279(9)°,* V = *3632.2(7) Å*^{3}, ρ = *1.60 g-cm*$^{-3}$, F*(000)* = *1776 avec* Z = *4. Dans* **2**, *l'ion Co(I) adopte une coordination tétraédrique comprenant deux groupes acétyl monodendés (Co-O*$_{avg}$ *1.964(3) Å) et deux atomes d'azote (Co-N*$_{avg}$ *1.990(3) Å) de l'oxasapphyrin. L'oxygène du macrocycle n'est pas impliqué dans la coordination avec le Co(II), et en est éloigné de 2.951(4) Å. Dans* **3**, *le Co(II) est aussi en coordinence tétraédrique. Cependant, l'ion cobalt est désordonné par rapport à deux orientations équivalentes du macrocycle. La longueur de liaison Co-N est de 2.026(5) Å tandis que les liaisons Co-Cl sont de 2.273 Å. L'atome de soufre est situé à 2.720(5) du centre Co(II) dans* **3**. *Dans* **4**, *un complexe 2:1 métal-macrocycle est observé. Chacun des ions Rh(I) adopte une géométrie de coordination plan-carré avec une longueur de liaison Rh-N de 2.083(1) Å et des longueurs de liaison Rh-C de 1.850(2). L'angle dièdre entre les cycles pyrrole plans du bipyrrole est plus grand pour le complexe Rh(I)* **4**, *il est de 42.7°. L'angle dièdre est plus petit dans* **3** *(22.6°) et vaut 29.6° dans* **2**.

porphyrine étendue / hétérosapphyrine / cobalt(II) / rhodium(I) / coordination η^2

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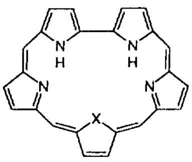
Introduction

Sapphyrins, oxasapphyrins, and thiasapphyrins (eg, **1**) were first reported more than 20 years ago [1–5]. The sapphyrin system contains five pyrroles and possesses an overall aromatic 22 π-electron annulene framework. The mono-oxa and mono-thia analogues contain four pyrroles and one furan or thiophene unit, respectively. In the case of the parent system, the two pyridine-like pyrroles are relatively easy protonated, something that is not true in the case of the smaller porphyrins. As a consequence of this facile protonation and an appropriately sized $\sim$ 5.5 Å central binding core, sapphyrins have proven to be effective anion receptors both in solution and in the solid state [1c, 2]. Indeed, it has been this discovery, more than any other, that has triggered the recent renaissance in the area of sapphyrin chemistry.



1a. X = NH
1b. X = O
1c. X = S

Fig 1

Another interesting feature of sapphyrin is its potential ability to serve as an η^5 ligand (structure **a**, fig 3). Thus a pentadentate N_5 coordination mode is at least theoretically possible for sapphyrin and tetra- or pentadentate N_4O and N_4S coordination modes are possible for monooxasapphyrin and monothiasapphyrin, respectively. However, all attempts to prepare complexes with such coordination geometries, using a range of cations, have proved unsuccessful. Only in the case of the uranyl(VI) cation is something resembling an η^5 complex obtained. In this instance, however, metal chelation is accompanied by the nucleophilic addition of a methoxide moiety to one of the sapphyrin *meso* positions. The result is a nonaromatic sapphyrin derivative [3].

While η^5-coordination modes are not yet known, early on Bauer et al postulated that decamethylsapphyrin should form in-plane η^4-coordination complexes with first row transition metal ions, such as Zn(II) and Cu(II) [1a]. It was further suggested that in these complexes, four of the five nitrogen would be coordinated in a symmetrical fashion (structure **b**, fig 3) [1a]. While mass spectrometric evidence in favor of this proposal was put forward by Bauer et al [1a], later NMR work by our group led to the suggestion that an equilibrium exists between competing symmetrical η^4-coordination and unsymmetrically η^4-binding modes [4a].

At present, these postulated tetraligated species have yet to be characterized by X-ray crystallographic means. In fact, recent results from our group indicate that tetraligated species are not generally stable for first row transition metals [2g, 4a] and may not, in spite of the above predictions, be isolable. On the other hand, it was determined recently that exposure of sapphyrin to Ir(I) or Rh(I) carbonyl derivatives leads to the formation of out-of-plane complexes, wherein the ligated metal centers are coordinated in an approximately square planar geometry by two neighboring sapphyrin-derived nitrogen atoms and two CO molecules [4a]. Now, in an effort to generalize this chemistry, we report the result of analogous studies carried out using oxa- and thiasapphyrin. Specifically, we detail the formation and characterization of a rhodium(I) complex of thiasapphyrin that is analogous to the one formed in the case of sapphyrin itself. We also report the synthesis and structural characterization of cobalt(II) complexes formed from oxa- and thiasapphyrins, respectively, wherein the coordinated cation is bound in an η^2-fashion by the macrocycle within an overall tetrahedral coordination environment. Since in both cases the metal ion is bound almost within the plane of the macrocycle, these complexes serve to define what is a hitherto unrecognized kind of chelation for sapphyrin-type ligands. This kind of η^2 in-plane metal coordination is also unknown for porphyrins [6].

Results and discussion

Crystal structures

The structures of complexes **2** and **3** are very similar. In both cases the Co(II) ion is coordinated by two nitrogens from adjacent pyrrole rings. The coordination sphere is completed by two monodentate acetate anions in the case of **2** and two chloride anions in the case of **3**. In both complexes, the two remaining pyrrole nitrogens are protonated such that neutral complexes are formed. Likewise in both cases the Co(II) ion is found to adopt overall geometries that are of a distorted tetrahedral type. Indeed, the relevant tetrahedral-defining angles are equal to 98.3°, 107.1°, 99.2°, and 123.0° for complex **2** (table II), and 101.0°, 113.0°, 127.4° and 113.4° for complex **3** (table III). Cobalt(II)-nitrogen bond distances are equal to 1.956, 2.021 and 2.007, 2.012 Å for **2** and **3**, respectively, and are within the range typically expected for high-spin cobalt(II) complexes [7]. The conformation of both macrocycles **2** and **3** is close to planar. For instance, the mean deviation of the four nitrogens and the heteroatom (O or S) from a root mean square (RMS) plane defined by these atoms is 0.034 Å for **2** and 0.011 Å and for **3**. The metal ion lies in the plane of the macrocycle; the out-of-plane displacement from the above RMS planes is only 0.0225 and 0.011 Å for **2** and **3**, respectively. The acetate anions in **2** are additionally stabilized by hydrogen bonds between the coordinated acetate oxygens and the NH-groups of the two pyrrole rings not participating in metal ion coordination. The cobalt(II)-thiophene sulfur distance in **3** is equal to 2.725 Å. This distance is similar to the cobalt(II)-furan oxygen distance (2.950 Å) observed for **2**, leading to the suggestion that it is imposed by the macrocycle structure. Importantly, this distance, as well as the geometries around the Co(II) furan oxygen and thiophene sulfur atoms are not consistent with any substantial bonding interaction between the metals and the non-pyrrole heteroatoms in complexes **2** and **3**.

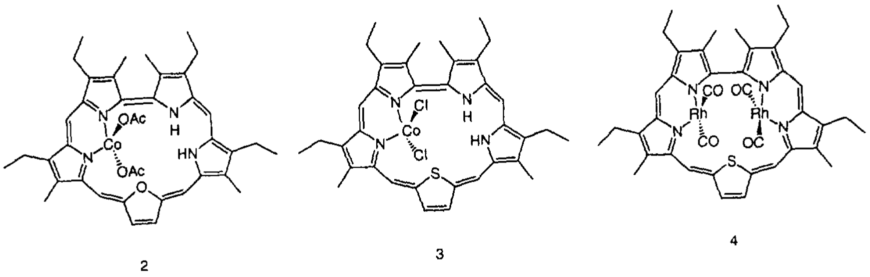


Fig 2

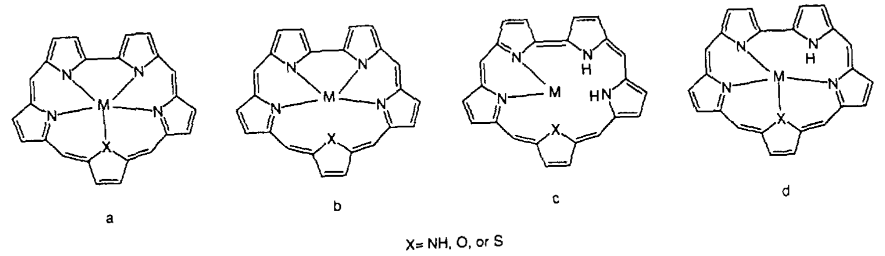


Fig 3

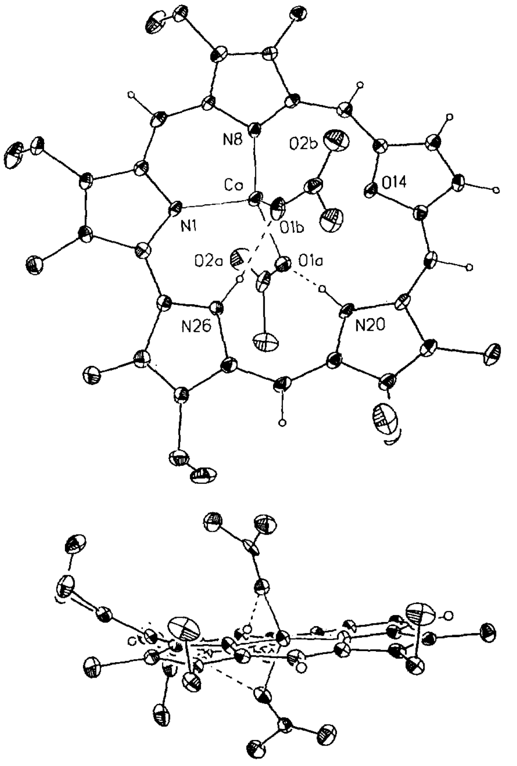


Fig 4. Front and side view of $(C_{36}H_{40}N_4O)Co(CH_3CO_2)_2$, **2**, showing the heteroatom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. H atoms are scaled to an arbitrary size.

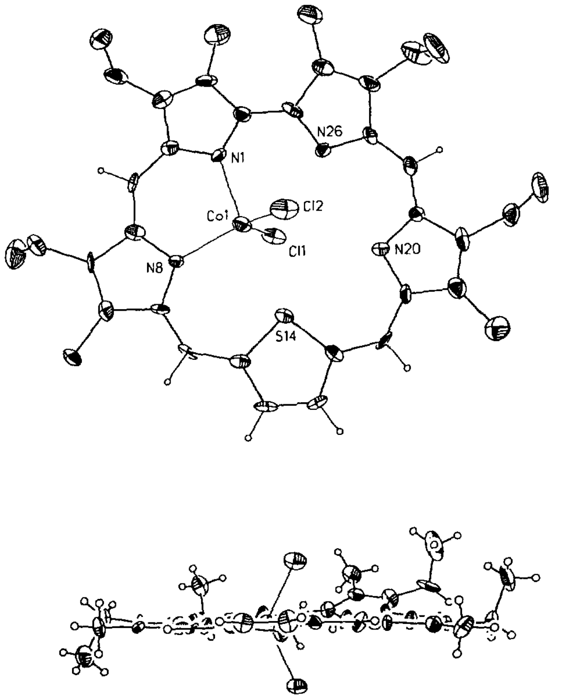


Fig 5. Front and side view of $(C_{36}H_{40}N_4S)CoCl_2$, **3**, showing the heteroatom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. H atoms are scaled to an arbitrary size.

In the rhodium(I) complex **4**, the metal ions are also bound in an η^2-fashion by the macrocyclic ligand. However, the rhodium ions are located above and below the macrocycle plane and the geometry around rhodium(I) is close to square planar. This complex differs from the previously described cobalt complexes **2** and **3** in that, as a result of a tautomeric exchange (vide infra), each metal center bridges an amine nitrogen and one imine nitrogen atom. In the case of the cobalt complexes **2** and **3**, the imine- and amine-type nitrogen atoms are localized adjacent to one another while in the rhodium(I) complex **4** imine- and amine-type nitrogen atoms alternate. The rhodium(I)-nitrogen bonds are equal to

2.083 Å while the ligand itself is slightly ruffled, with the mean deviation of the four nitrogens and the sulfur atoms from the RMS plane being equal to 1.277 Å. In complex **4**, the Rh(I) coordination sphere is filled by two carbonyl molecules coordinated to each rhodium atom. Thus, the structural pattern observed in the complex is similar to that observed for the rhodium(I) complex of sapphyrin [4a], the iridium(I) complex of selenasapphyrin [8], and for the rhodium(I) and iridium(I) derivatives of porphyrins [9].

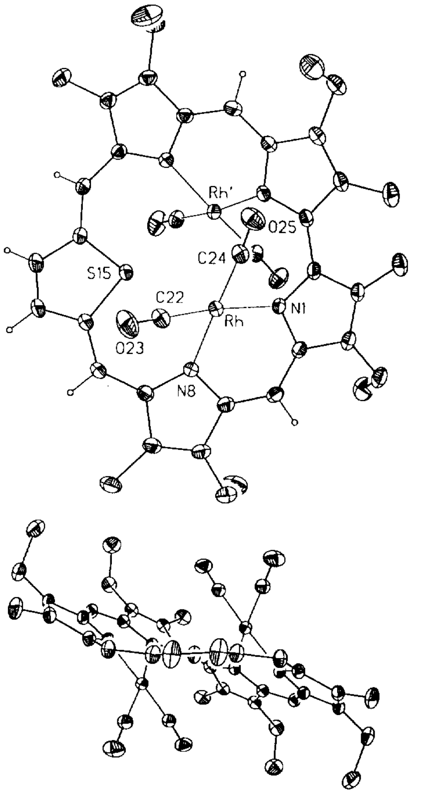


Fig 6. Front and side view of $(C_{36}H_{38}N_4S)Rh_2(CO)_4$, **4**, showing the heteroatom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. H atoms are scaled to an arbitrary size.

Solution phase structures

Compound **4**, like the analogous porphyrin complex, is diamagnetic. Well-resolved ^1H NMR and ^{13}C NMR spectra could thus be recorded. These are consistent with a non-labile structure existing in solution that is analogous to what is seen in the solid state. The UV-vis spectrum of complex **4** is typical for a heterosapphyrin metal complex. It consists of one strong Soret-type absorption band at 512 nm and three less intense absorptions of Q-band type at 617, 676, and 734 nm.

In the case of **2** and **3**, the number of resonances observed in the ^1H NMR spectra is also consistent with the corresponding solid-state X-ray crystal structures. Nonetheless the ^1H NMR spectra of these paramagnetic species are complicated. For instance, the ^1H NMR spectra of these Co(II) heterosapphyrins show resonances in the range of −5 to 65 ppm that are clearly shifted to both higher and lower field than what is observed in the starting metal-free macrocycles. These large shifts confirm the presence of a high-spin tetrahedral Co(II) center in both **2** and **3**. This is because, depending on the position in space of a given proton, through-space dipolar interactions can lead to both upfield and downfield shifts such as those observed [10]. Although the spectra are too complicated for unambiguous signal assignment [11], the COSY spectrum of **2** could be recorded cleanly (fig 7). It shows the presence of four crosspeaks corresponding to four different ethyl groups. Thus, the presence of a symmetrical species in solution can be precluded. This information, coupled with the fact that the expected number of peaks is observed in the ^1H NMR spectra of **2** and **3** (vide supra), leads us to conclude that the structure of these complexes in solution is essentially the same as in the solid state. Consistent with this conclusion is the finding that there are no significant changes in the UV-vis spectra of the free-base oxa- or thiasapphyrins upon metallation with cobalt(II) or other transition metal species.

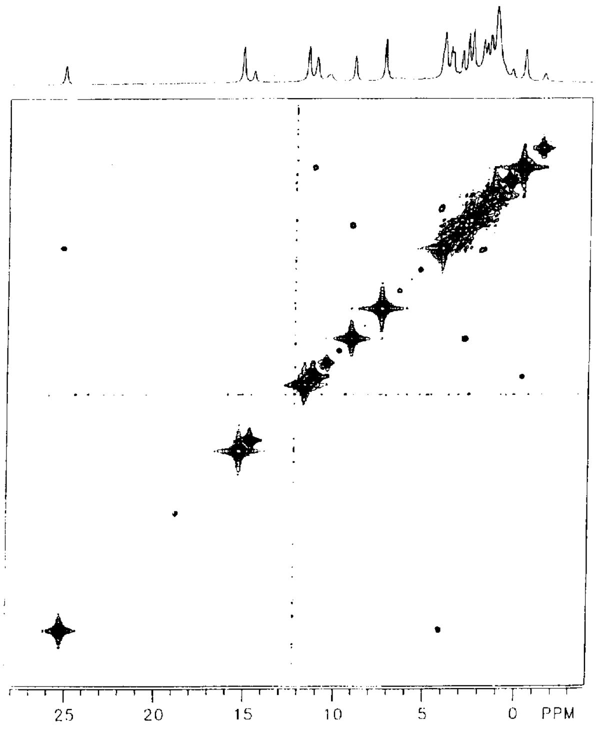


Fig 7. COSY spectrum of $(C_{36}H_{40}N_4O)Co(CH_3CO_2)_2$, **2**.

General properties of heterosapphyrin complexes

The metal chelation chemistry of heterosapphyrins and sapphyrins differs markedly from that of porphyrins. This is particularly apparent in the case of first row transition metal cations. Here, for heterosapphyrins the metal insertions are fast, while the analogous metallation reaction in the case of porphyrins often require long reaction times and high temperatures. On the other hand, in case of heterosapphyrins, the resulting complexes are much less stable than analogues species prepared from porphyrins. Indeed, metalloheterosapphyrin complexes involving first row transition metal cations are easily demetallated in the presence of acids such as HCl. This instability prevents the use of typical column chromatography techniques for the purification of complexes like **2** and **3**. Thus, the present representative Co(II) complexes could only be isolated in the solid state by a series of careful recrystallizations. In spite of the sensitivity of **2** and **3** towards demetallation, no oxidation of Co(II) ion was observed when these complexes or solutions of them were exposed to air. This is in sharp contrast to what is observed in the case of Co(II) porphyrin complexes. These are quickly oxidized by molecular oxygen to Co(III) species in solution. However, this behavior is not surprising if one considers the different coordination modes in porphyrins and heterosapphyrins. In-plane porphyrin cobalt complexes are always η^4-coordinated with the cobalt metal centers being coordinated to two imine-type nitrogens and two amine-type nitrogens. Thus, a square planar complex is formed. In the complexes described here, the cobalt atom is, in relation to the heterosapphyrin ligand, η^2-coordinated. Both bonds to the heterosapphyrin are of a coordinative (as opposed to covalent) nature, with two acetate or chloride ions covalently binding to the metal to form a tetrahedral complex. These strong ligands may help stabilize the cobalt(II) center against oxidation.

In the case of the Rh(I) thiasapphyrin complex, **4**, the metal ion environment is analogous to that of related porphyrin systems [9a-b]. In both cases two rhodium(I) metal cations form out-of-plane complexes with the macrocycle with η^2-coordination to the linked pyrroles presumably playing a role in helping to stabilize an overall square planar coordination environment. Thus, in **4**, the sulfur does not take part in metal ion coordination. This behavior was already observed in the case of the bisrhodium(I) dicarbonyl complex of the parent all-aza sapphyrin system [4a]. Interestingly, like these latter congeners, complex **4** proved quite stable. In particular, while out-of-plane Rh(I) porphyrin complexes are transformed easily into in-plane Rh(II) or Rh(III) porphyrin complexes [12], the heterosapphyrin system **4** and its all-aza analogues do not display this kind of reactivity. Indeed, all attempts to convert these out-of-plane sapphyrin complexes into in-plane 1:1 complexes have so far proved unsuccessful.

The reason for the above stability remains something of a mystery at present. The relatively high ν(CO) values recorded for **4** and its all-aza analogues has led us to consider that at least one of the carbonyl groups bound to the η^2-chelated rhodium center should be easily displaced. To date, however, we have not been able to effect either photolytic or thermal loss of CO from these kind of complexes. Further, as was true for the corresponding pentapyrrolic sapphyrin systems [4a], complex **4** displays a remarkable stability under oxidizing conditions (eg, methyl iodide or acetic anhydride) that is not seen in the case of porphyrins [13]. On the other hand, reagents such as HCl will cleave off both the metal centers to yield the diprotonated form of the starting thiasapphyrin. For instance, molecular iodine reacts but slowly with **4**, removing one of the metal carbonyl moieties to afford a mono Rh(I) dicarbonyl thiasapphyrin complex, as confirmed by mass spectrometry.

Conclusions

The present results show that heterosapphyrins may be used to stabilize η^2-ligated, four coordinate metal complexes with both first and second row transition metal cations. In the case of the second row metal Rh(I), the reaction conditions needed to form the dinuclear, bis-Rh(I) complex are similar to those used to prepare the corresponding porphyrin complexes [9c]. However, weak base (eg, triethylamine) was necessary to accomplish complete deprotonation and metal insertion in the case of the heterosapphyrin. The fact that such an approach proved successful was unexpected in view of the lack of acidity observed in the corresponding all-aza sapphyrin system (treatment of the latter with aqueous sodium hydroxide solution, for instance, fails to effect a complete deprotonation [2h]).

In the case of the first row metal, Co(II), the formation of complexes by heterosapphyrins is even more facile than it is with Rh(I). In fact, no base is required to effect metal insertion. In this instance, the requisite coordination site is formed by tautomeric shifts of protons within the macrocycle core. Such shifts produce two imine-like nitrogens on adjacent pyrrole rings that then coordinate to the transition metal atom. Since no deprotonation is involved, the coordination environments produced actually resemble more closely those formed using classic bis-ligating ligands, such as 2,2′-bipyridines or 2,2′-biimidazoles, than those formed using porphyrinato dianions.

A similar situation was observed in the case of a Zn(II) complex of another expanded aromatic macrocycle (porphocyanine) reported recently by Dolphin and coworkers [14]. In this instance, as for complexes **2** and **3**, the coordination geometry is tetrahedral rather than square-planar. This coordination mode was also observed in the case of cobalt(II) amethyrin, a potentially hexadentate ligand, that with this first-row transition metal cation serves only to fill partially the coordination sphere of the bound four-coordinated ion [15].

Of particular interest in the present study is the finding for the first row transition metal cation Co(II) that the η^2-binding mode is apparently more stable than the η^4-binding mode. While noteworthy, this conclusion is perhaps not too far fetched if one considers that an expanded porphyrin is involved. First, the use of an expanded porphyrin, such as a heterosapphyrin, provides a large macrocyclic core that can accommodate a first row transition metal *with accompanying ancillary ligands* in a more or less in-plane fashion. This is something that is not possible with porphyrins. Secondly, the presence of additional alternative π-conjugation pathways in expanded porphyrins (at least relative to porphyrins) permits proton rearrangements to take place that allow neighboring pyrrole rings to coordinate to a transition metal cation without deprotonation. This, in turn, allows a transition metal to adopt a favorable

Table I. Crystallographic data[a] for $(C_{36}H_{40}N_4O)Co(CH_3CO_2)_2$ **2**, $(C_{36}H_{40}N_4S)CoCl_2$ **3**, and $(C_{36}H_{38}N_4S)Rh_2(CO)_4$ **4**.

	2 $(C_{36}H_{40}N_4O)Co(CH_3CO_2)_2$	**3** $(C_{36}H_{40}N_4S)CoCl_2$	**4** $(C_{36}H_{38}N_4S)Rh_2(CO)_4$
a, Å	10.583(4)	17.455(6)	21.355(3)
b, Å	11.798(3)	15.857(6)	13.558(1)
c, Å	15.264(5)	12.482(5)	13.557(1)
α, °	87.12(2)	90.0	90.0
β, °	71.00(2)	107.61(3)	112.279(9)
γ, °	86.89(2)	90.0	90.0
V, Å^3	1798(1)	3293(2)	3632.2(7)
Z	2	4	4
fw	721.76	690.64	876.64
$F(000)$	762	1444	1776
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$C2/c$
T, °C	−100	−100	25
Radiation	Graphite monochromatized, Mo $K\alpha$ (λ = 0.71073 Å)		
ρ_{calc}, g/cc	1.33	1.39	1.60
μ, cm^{-1}	5.222	7.749	9.949
Transmission[b] coefficient	0.7578 → 0.9134	0.7482 → 0.9006	0.7561 → 0.8708
Crystal dimensions (mm)	0.12 × 0.20 × 0.80	0.06 × 0.32 × 0.32	0.16 × 0.30 × 0.47
Range of h,k,l	0 → 13, −14 → 14, −18 → 18	0 → 18, 0 → 17, −13 → 13	−25 → 27, 0 → 17, −17 → 17
Data collected	7657	4666	9124
Unique data	7251	4300	4205
Observed data $[F_o > 4(s(F_o))]$	4403	1757	3557
Scan range (2θ)	4–50°	4–45°	4–55°
Scan rate (°/min) (1.2° ω scans)	3–6	3–6	4–8
R_{int}	0.037	0.035	0.015
$R(F)^c$,$R(F)_{\text{all data}}$	0.072, 0.12	0.082, 0.19	0.027, 0.035
$R_w(F)$,$R_w(F)_{\text{all data}}$	0.074, 0.084	0.071, 0.082	0.036, 0.038
Goodness of fit	1.768	1.543	1.228
Parameters	297	213	231
Max $\lvert\Delta/\Sigma\rvert$	<0.1	<0.1	<0.1
Min, max peaks (e$^-$/Å^3)	−1.14, 1.22	−1.27, 1.19	−0.34, 0.52

[a] Data were collected on a Nicolet P3 diffractometer. Data for **2** and **3** were collected at −100 °C using a Nicolet LT-2 low-temperature delivery system. Lattice parameters were obtained from the least-squares refinement of 38 reflections with $15.1 < 2\theta < 22.8°$ for **2**, 30 reflections with $10.4 < 2\theta < 20.7°$ for **3** and 39 reflections with $18.5 < 2\theta < 22.4°$ for **4**. [b] Absorption correction was based on measured crystal faces. [c] $R(F) = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $Rw(F) = [\Sigma w(||F_o|-|F_c||)^2/\Sigma w(|F_o|)^2]^{1/2}$; where $w = 1/[\sigma(F_o))^2+(0.0004(F_o)^2)]$. Goodness of fit $= [\Sigma(w||F_o|-|F_c||)^2/(m-n)]^{1/2}$ where m is the number of observed reflections and n is the number of parameters refined.

coordination geometry without inducing changes in oxidation state.

The above hypotheses are, at present, based only on the results obtained with Co(II) and the oxa- and thiasapphyrin complexes described herein. However, preliminary results obtained with these same heterosapphyrins and Zn(II), Cu(II), and Ni(II) metal cations are consistent with the formation of complexes that appear to be structurally analogous to their better-characterized Co(II) analogues. Additionally, η^2/η^4-coordinated complexes of Zn(II) and Cu(II) have recently been recorded in the case of the newly synthesized expanded porphyrins porphocyanine [14] and amethyrin [15], respectively. Thus, the present results support the emerging contention that expanded porphyrins have a unique role to play in extending further the coordination chemistry of various transition and non-transition metal species. This is something we are continuing to explore.

Experimental section

Proton NMR spectra were recorded using either a Bruker AC-250 or a General Electric QE-300 instrument. Observed chemical shifts were referenced to TMS or to easily identifiable solvent signals. COSY spectra were acquired on General Electric GE GN500 instrument using 512 data points in F_1 and 1024 data points in F_2. The data were processed by using a sine bell window and zero filling to 1 K data points in both dimensions. High resolution mass spectra (HRMS) were obtained using a VG Analytical ZAB E/SE instrument and nitrobenzyl alcohol (NBA) as the matrix. Electronic spectra were recorded on a Beckman DU 640 spectrophotometer. Elemental analyses were performed by Atlantic Microlabs, Inc.

X-ray experimental

Crystals were grown from a chloroform solution layered with methanol in the case of **4**, or hexanes in the case of **2** and **3**. Data were collected on a Nicolet P3 diffractometer with a graphite monochromator using Mo$K\alpha$ radiation (λ = 0.71073 Å). Crystallographic details are listed in table I. Data reduction and decay correction were performed using the SHELXTL-*Plus* software package [16]. The structures were solved by direct methods and refined by full-matrix least-squares [16] with anisotropic thermal parameters for the non-H atoms. All hydrogen atoms were calculated in idealized positions (C-H 0.96 Å, N-H 0.90 Å) with U_{iso} set to 1.2 × U_{eq} of the relevant atom.

Table II. Bond lengths (Å) and angles (°) for the non-hydrogen atoms of $(C_{36}H_{40}N_4O)Co(CH_3CO_2)_2$ **2**.

1	*2*	*3*	*1-2*	*1-2-3*
N1	Co	N8	2.023(5)	98.2(2)
N1	Co	O1A		107.3(2)
N8	Co	O1A	1.956(4)	126.8(2)
N8	Co	O1B		122.5(2)
O1A	Co	O1B	1.954(4)	99.3(2)
O1B	Co	N1	1.975(4)	98.4(2)
C2	N1	C5	1.356(7)	105.4(4)
C2	N1	Co		133.8(3)
C5	N1	Co	1.370(6)	120.7(4)
C3	C2	C27	1.446(8)	126.6(5)
C3	C2	N1		111.0(4)
C27	C2	N1	1.433(7)	122.3(5)
C4	C3	C30	1.384(7)	124.5(5)
C4	C3	C2		105.8(5)
C30	C3	C2	1.493(8)	129.1(4)
C5	C4	C31	1.419(8)	127.0(5)
C5	C4	C3		105.9(4)
C31	C4	C3	1.489(7)	127.0(5)
C6	C5	N1	1.402(7)	123.6(5)
C6	C5	C4		124.6(5)
N1	C5	C4		111.8(4)
C7	C6	C5	1.382(8)	130.4(5)
N8	C7	C11	1.380(7)	109.6(5)
N8	C7	C6		126.1(5)
C11	C7	C6	1.458(7)	124.3(5)
C9	N8	Co	1.364(7)	133.1(3)
C9	N8	C7		106.6(4)
Co	N8	C7		120.3(3)
C10	C9	C12	1.459(7)	120.8(5)
C10	C9	N8		110.0(5)
C12	C9	N8	1.401(8)	129.2(4)
C11	C10	C35	1.353(8)	127.4(5)
C11	C10	C9		107.0(5)
C35	C10	C9	1.496(7)	125.6(5)
C33	C11	C7	1.501(7)	125.0(5)
C33	C11	C10		128.2(5)
C7	C11	C10		106.8(4)
C13	C12	C9	1.388(7)	137.2(5)
O14	C13	C17	1.390(6)	109.0(4)
O14	C13	C12		126.4(5)
C17	C13	C12	1.396(8)	124.5(5)
C15	O14	C13	1.389(7)	105.6(4)
C16	C15	C18	1.387(8)	125.0(5)
C16	C15	O14		109.5(4)
C18	C15	O14	1.387(7)	125.6(5)
C17	C16	C15	1.355(7)	108.0(5)
C13	C17	C16		107.9(5)
C19	C18	C15	1.380(7)	139.4(5)
N20	C19	C23	1.370(8)	106.3(4)
N20	C19	C18		129.3(5)
C23	C19	C18	1.452(7)	124.5(5)
C21	N20	C19	1.383(6)	110.6(4)
C22	C21	C24	1.443(8)	126.3(5)
C22	C21	N20		106.2(5)
C24	C21	N20	1.367(9)	127.5(5)
C23	C22	C37	1.347(8)	127.8(6)
C23	C22	C21		108.5(5)
C37	C22	C21	1.503(7)	123.6(5)
C36	C23	C19	1.504(9)	124.5(5)
C36	C23	C22		127.2(5)
C19	C23	C22		108.3(5)
C25	C24	C21	1.407(8)	131.4(5)
N26	C25	C29	1.386(6)	107.3(5)
N26	C25	C24		123.6(6)
C29	C25	C24	1.417(9)	129.1(5)
C27	N26	C25	1.375(7)	109.6(5)
C28	C27	C2	1.431(8)	132.1(6)
C28	C27	N26		107.4(4)
C2	C27	N26		120.5(5)
C29	C28	C41	1.383(7)	123.7(5)
C29	C28	C27		107.5(6)
C41	C28	C27	1.497(10)	128.2(5)
C39	C29	C25	1.498(8)	124.4(5)
C39	C29	C28		126.8(6)
C25	C29	C28		108.2(5)
C32	C31	C4	1.521(10)	113.0(5)
C34	C33	C11	1.507(10)	114.5(5)
C38	C37	C22	1.536(11)	111.7(5)
C40	C39	C29	1.502(11)	112.9(5)
C1A	O1A	Co	1.196(9)	120.4(4)
C1A	O2A		1.223(7)	
C1A	C3A		1.562(9)	
O1A	C1A	O2A		128.8(6)
O1A	C1A	C3A		115.6(5)
O2A	C1A	C3A		115.5(7)
C1B	O1B	Co	1.236(9)	134.3(4)
C1B	O2B		1.219(8)	
C1B	C3B		1.531(9)	
O1B	C1B	O2B		125.2(6)
O1B	C1B	C3B		115.4(5)
O2B	C1B	C3B		119.4(7)

Adducts **2** and **3** are 1:1 complexes of metal-to-heterocycle, while **4** is a 2:1 complex. In **3**, the Co ion is disordered about two orientations with respect to the macrocycle. In one orientation, having 62.4(4)% occupancy, the Co ion is bound to N1 and N8 on one side of the macrocycle while, in the other, it is bound to N20 and N26. The Co ions are 1.92 Å apart. The thermal ellipsoids for the chloride ions are slightly elongated parallel to the Co-Co vector indicating some disorder in their positions as well. In spite of this latter indication, the difference in the Cl-ion positions actually proved too small to be resolved.

Table III. Bond lengths (Å) and angles (°) for the non-hydrogen atoms of $(C_{36}H_{40}N_4S)CoCl_2$ **3**.

1	*2*	*3*	*1-2*	*1-2-3*
Co2	Co1	Cl1	1.919(7)	65.3(2)
Cl1	Co1	Cl2	2.318(5)	127.7(2)
Cl1	Co1	N1		98.4(4)
Cl1	Co1	N8		112.8(4)
Cl1	Co1	S14		80.2(2)
Cl2	Co1	N1	2.273(5)	95.6(4)
Cl2	Co1	N8		113.4(4)
Cl2	Co1	S14		80.3(2)
N1	Co1	N8	2.010(11)	101.2(4)
N1	Co1	S14		173.2(4)
N8	Co1	S14	2.027(10)	85.4(3)
S14	Co1	Co2	2.720(5)	68.6(2)
Cl1	Co2	Cl2	2.311(7)	132.4(3)
Cl1	Co2	S14		80.8(2)
Cl1	Co2	N20		112.5(4)
Cl1	Co2	N26		92.8(4)
Cl2	Co2	S14	2.191(8)	82.2(2)
Cl2	Co2	N20		109.4(4)
Cl2	Co2	N26		99.1(4)
S14	Co2	N20	2.696(6)	83.8(3)
S14	Co2	N26		172.3(4)
N20	Co2	N26	2.037(12)	102.8(5)
N26	Co2	Co1	2.028(10)	103.5(4)
C2	N1	C5	1.36(2)	108.0(11)
C2	N1	Co1		132.7(10)
C5	N1	Co1	1.36(2)	118.5(8)
C3	C2	C27	1.43(2)	131.4(12)
C3	C2	N1		106.9(12)
C27	C2	N1	1.40(2)	121.7(12)
C4	C3	C30	1.33(2)	124.3(15)

C4	C3	C2		109.8(12)
C30	C3	C2	1.57(2)	125.2(13)
C5	C4	C31	1.43(2)	127.3(13)
C5	C4	C3		105.8(13)
C31	C4	C3	1.50(2)	126.9(13)
C6	C5	N1	1.40(2)	124.4(12)
C6	C5	C4		126.1(14)
N1	C5	C4		109.5(11)
C7	C6	C5	1.40(2)	132.2(13)
N8	C7	C11	1.37(2)	110.4(11)
N8	C7	C6		126.8(12)
C11	C7	C6	1.43(2)	122.8(14)
C9	N8	Co1	1.364(15)	137.4(10)
C9	N8	C7		106.4(11)
Co1	N8	C7		116.1(8)
C10	C9	C12	1.45(2)	122.0(11)
C10	C9	N8		109.3(12)
C12	C9	N8	1.35(2)	128.6(13)
C11	C10	C35	1.35(2)	126.8(13)
C11	C10	C9		107.2(11)
C35	C10	C9	1.50(2)	125.8(12)
C33	C11	C7	1.51(2)	128.1(12)
C33	C11	C10		125.2(12)
C7	C11	C10		106.7(12)
C13	C12	C9	1.41(2)	134.4(11)
S14	C13	C17	1.727(13)	107.8(11)
S14	C13	C12		123.0(10)
C17	C13	C12	1.40(2)	129.1(12)
C15	S14	Co1	1.700(15)	150.8(4)
C15	S14	Co2		111.2(4)
C15	S14	C13		94.2(7)
Co1	S14	Co2		41.51(15)
Co1	S14	C13		110.4(5)
Co2	S14	C13		151.0(5)
C16	C15	C18	1.40(2)	124.9(13)
C16	C15	S14		108.9(10)
C18	C15	S14	1.38(2)	125.8(10)
C17	C16	C15	1.36(2)	113.9(13)
C13	C17	C16		114.8(12)
C19	C18	C15	1.39(2)	131.4(12)
N20	C19	C23	1.40(2)	108.8(11)
N20	C19	C18		126.5(11)
C23	C19	C18	1.42(2)	124.7(12)
C21	N20	Co2	1.40(2)	113.5(8)
C21	N20	C19		107.2(10)
Co2	N20	C19		139.3(8)
C22	C21	C24	1.42(2)	125.1(12)
C22	C21	N20		107.5(11)
C24	C21	N20	1.36(2)	127.5(13)
C23	C22	C37	1.37(2)	126.1(13)
C23	C22	C21		109.5(13)
C37	C22	C21	1.50(2)	124.3(12)
C36	C23	C19	1.52(2)	125.8(12)
C36	C23	C22		127.3(13)
C19	C23	C22		106.9(13)
C25	C24	C21	1.38(2)	133.6(13)
N26	C25	C29	1.37(2)	106.6(13)
N26	C25	C24		125.0(11)
C29	C25	C24	1.43(2)	128.2(13)
C27	N26	Co2	1.39(2)	129.9(9)
C27	N26	C25		109.9(10)
Co2	N26	C25		115.4(9)
C28	C27	C2	1.44(2)	130.1(13)
C28	C27	N26		106.8(13)
C2	C27	N26		123.0(10)
C29	C28	C41	1.36(2)	123.0(12)
C29	C28	C27		107.0(12)
C41	C28	C27	1.50(2)	129.5(15)
C39	C29	C25	1.51(2)	122.4(15)
C39	C29	C28		128.0(13)
C25	C29	C28		109.2(12)
C32	C31	C4	1.47(2)	111.1(13)
C34	C33	C11	1.50(2)	112.8(13)
C38	C37	C22	1.53(2)	112.7(14)
C40	C39	C29	1.48(3)	105.6(14)

The complex in **4** lies on a crystallographic two-fold axis at 1/2, y, 1/4. The two-fold axis passes through the thiophene ring, and bisects the sulfur atom and the bipyrrole. The function, $\Sigma w(|F_o| - |F_c|)^2$, was minimized, where $w = 1/(\sigma(F_o))^2$ and $\sigma(F_o) = \{.5kI - 1/2[(\sigma(I))^2 + (0.02I)^2]^{1/2}\}$. The intensity, I, is given by $(I_{\text{peak}} - I_{\text{background}}) \times$ (scan rate); where 0.02 is a factor to downweight intense reflections and to account for instrument instability and k is the correction due to Lp effects, absorption and decay. The absorption correction was based on measured crystal dimensions. Data were checked for secondary extinction errors which were negligible. Sigma(I) was estimated from counting statistics; $\sigma(I) = [(I_{\text{peak}} + I_{\text{background}})^{1/2} \times$ (scan rate)]. Neutral atom scattering factors for the non-H atoms were taken from Cromer and Mann, with the anomalous-dispersion corrections taken from the work of Cromer and Liberman [17, 18]. The scattering factors for the H atoms were obtained from Stewart, Davidson and Simpson [19]. Values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography [21]. All figures were generated using SHELXTL-*Plus* [16]. Other computer programs used in this work are listed elsewhere [21].

Table IV. Bond lengths (Å) and angles (°) for the non-hydrogen atoms of $(C_{36}H_{38}N_4S)Rh_2(CO)_4$ **4**.

1	*2*	*3*	*1-2*	*1-2-3*
N1	Rh	N8	2.083(2)	88.09(8)
N1	Rh	C22		171.94(11)
N8	Rh	C22	2.083(2)	91.09(10)
N8	Rh	C24		177.21(12)
C22	Rh	C24	1.847(3)	88.26(12)
C24	Rh	N1	1.854(3)	92.17(11)
C2	N1	C5	1.363(3)	106.5(2)
C2	N1	Rh		129.8(2)
C5	N1	Rh	1.378(3)	119.2(2)
C3	C2	N1	1.445(3)	109.8(2)
C2′	C2	N1	1.434(4)	123.7(2)
C2′	C2	C3		126.3(2)
C4	C3	C16	1.361(3)	126.3(2)
C4	C3	C2		106.9(2)
C16	C3	C2	1.503(4)	126.1(2)
C5	C4	C17	1.435(4)	124.5(2)
C5	C4	C3		106.8(2)
C17	C4	C3	1.500(4)	128.5(3)
C6	C5	N1	1.387(3)	124.4(2)
C6	C5	C4		125.7(2)
N1	C5	C4		109.9(2)
C7	C6	C5	1.381(4)	128.2(2)
N8	C7	C11	1.382(3)	110.0(2)
N8	C7	C6		124.2(2)
C11	C7	C6	1.441(3)	125.8(2)
C9	N8	Rh	1.371(3)	129.5(2)
C9	N8	C7		106.0(2)
Rh	N8	C7		118.2(2)
C10	C9	C12	1.449(3)	122.3(2)
C10	C9	N8		110.1(2)
C12	C9	N8	1.400(3)	126.5(2)
C11	C10	C21	1.358(4)	128.1(2)
C11	C10	C9		106.7(2)
C21	C10	C9	1.507(4)	125.2(2)
C19	C11	C7	1.503(4)	124.0(3)
C19	C11	C10		128.7(2)

C7	C11	C10		107.0(2)
C13	C12	C9	1.388(3)	130.9(3)
C14	C13	S15	1.418(4)	109.1(2)
C14	C13	C12		123.6(2)
S15	C13	C12	1.746(3)	126.7(2)
C13′	S15	C13		92.8(2)
C14′	C14	C13	1.354(6)	114.4(2)
C18	C17	C4	1.521(6)	114.2(3)
C20	C19	C11	1.522(6)	112.6(3)
O23	C22	Rh	1.125(4)	176.3(3)
O25	C24	Rh	1.135(3)	175.7(3)

Atoms labeled with a prime (′) are related by $1 - x$, y, $1/2 - z$.

Synthesis

The ligands, 3,7,18,22-tetraethyl-2,8,17,23-tetramethyl-27-oxasapphyrin and 3,7,18,22-tetraethyl-2,8,17,23-tetramethyl-27-thiasapphyrin, were synthesized as described previously [2b, 22].

Cobalt(II)-3,7,18,22-tetraethyl-2,8,17,23-tetramethyl-27-oxasapphyrin diacetate, **2**

In a 100 mL three-necked round-bottomed flask 32 mg (0.059 mmol) of 3,7,18,22-tetraethyl-2,8,17,23-tetramethyl-27-oxasapphyrin was dissolved in 5 mL chloroform. A solution of cobalt(II) diacetate tetrahydrate, 40 mg (0.16 mmol) in 1 mL methanol, was added. The resulting solution was stirred for 10 min and shaken with 5 mL water. Next, the organic layer was separated off, filtered, and layered with 20 mL hexanes. In this way green crystals were obtained that, after one week, were collected by filtration, washed with hexanes, and dried in vacuo to give 27 mg (63% yield) of complex **2**.

^{1}H NMR ($CDCl_3$, 250 MHz): δ −5.45, −1.91, 1.05, 1.26, 1.43, 1.74, 1.84, 2.90, 4.05, 4.30, 4.51, 5.14, 5.41, 5.85, 6.20, 6.64, 7.61, 8.65, 9.81, 10.01, 10.48, 12.33, 13.46, 13.88, 19.01, 20.05, 20.89, 22.24, 23.09, 23.61, 26.80, 29.00, 30.09, 30.30.

LRMS (FAB, NBA): 603 (calc for $C_{36}H_{40}N_4OCo^{+2}$: 603).

UV-vis ($CHCl_3$): 464, 478 (Soret bands), 627, 651, 721 nm (Q-bands).

Cobalt(II)-3,7,18,22-tetraethyl-2,8,17,23-tetramethyl-27-thiasapphyrin dichloride **3**

In a 100 mL three-necked round-bottomed flask, 98.7 mg of 3,7,18,22-tetraethyl-2,8,17,23-tetramethyl-27-thiasapphyrin (0.176 mmol) was dissolved in 15 mL chloroform and mixed with a solution comprised of 22.8 mg (0.176 mmol) of anhydrous $CoCl_2$ in 2 mL methanol. The resulting mixture was stirred for 20 min and the solution was then evaporated to dryness. The residue was taken up in 2 mL chloroform, filtered and evaporated again. After recrystallization from a dichloromethane/hexanes (10:90) mixture, 48 mg (0.069 mmol) of product was obtained (39% yield).

^{1}H NMR ($CDCl_3$, 300 MHz): δ −1.34 (1H), −0.37 (3H), 0.30 (1H), 1.22, 1.56, 1.96, 2.51, 2.78, 3.10, 4.04 (3H),7.36 (3H), 9.07 (2H), 11.16 (2H), 11.62 (3H), 14.63 (1H), 15.32 (3H), 25.24 (2H), 64.25 (1H).

HRMS: 618.225 (calc for $C_{36}H_{39}N_4SCo^+$: 618.223).

UV-vis ($CHCl_3$): 491 (Soret), 642, 665, 744 (Q-bands) nm.

Bisrhodium(I)-3,7,18,22-tetraethyl-2,8,17,23-tetramethyl-27-thiasapphyrin tetracarbonyl **4**

The deprotonated form of 3,7,18,22-tetraethyl-2,8,17,23-tetramethyl-27-thiasapphyrin (50 mg, 0.09 mmol) was obtained by dissolving the free ligand in 15 mL dichloromethane containing 0.5 mL triethylamine. To this solution, $[RhCl(CO)_2]_2$ (40 mg, 0.1 mmol) was added. The resulting solution was then stirred at room temperature for 12 h. Residual solvent and excess triethylamine was then removed in vacuo and the residue taken up in dichloromethane. Filtration through celite, followed by chromatographic purification on silica gel using dichloromethane as the eluent afforded the dirhodium complex **4** (66 mg) in 83% yield.

IR (KBr): 2 053, 1 977 (CO), 2 874, 2 939, 2 969, 3 445 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.40 (t, 6H, $J = 7.6$ Hz), 1.97 (t, 6H, $J = 7.6$ Hz), 3.45 (s, 6H), 3.80 (m, 2H), 3.80 (m, 2H, $J = 7.6$ Hz), 3.83 (s, 6H), 3.91 (q, 2H, $J = 7.6$ Hz), 4.10 (m, 2H, $J = 7.6$ Hz), 4.22 (m, 2H, $J = 7.6$ Hz), 10.36 (s, 1H), 10.38 (s, 1H), 11.2 (s, 1H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ 12.5, 14.1, 16.8, 17.8, 18.0, 19.6, 20.1, 108.2, 108.3, 111.9, 126.5, 135.6, 136.5, 136.6, 138.2, 141.4, 141.9, 143.9, 152.5, 153.6, 153.7, 176.1, 177.2, 177.9, 178.9.

LRMS (FAB, NBA): M^+ 877 (calc for $C_{36}H_{38}N_4S)Rh_2(CO)_4$: 877), HRMS: found 877.080 (calc 877.080).

UV-vis (CH_2Cl_2): λ_{max} (log ε) 512 (5.13), 617 (3.12), 676 (3.68), 734 (3.91) nm.

Supplementary material

Tables of crystallographic data collection procedures and parameters, complete atomic coordinates and thermal parameters, bond distances and angles, torsion angles, and least square planes (121 pages).

Supplementary material data have been deposited with British Library, Document Supply Centre at Boston Spa, Wetherby, West Yorkshire, LS23 7BQ, UK, as supplementary publication N° = SUP 90425 and are available on request from the Document Supply Centre.

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22 For the synthesis of 3,7,18,22-tetraethyl-2,8,17,23-tetramethyl-27-thiasapphyrin the following modification of our earlier reported [3] procedure was used: 4,4′-diethyl-5,5′-diformyl-3,3′-dimethyl-2,2′-bipyrrole (145 mg, 0.53 mmol) was dissolved in 20 mL methanol. 2,5-Bis(4-ethyl-3-methylpyrrol-2-ylmethyl)thiophene (220 mg, 0.53 mmol) was then added before the mixture was diluted with 480 mL dichloromethane. *p*-Toluenesulfonic acid monohydrate (484 mg, 2.1 mmol) was added and the resulting mixture was stirred for 18 h at room temperature. Then, DDQ (5,6-dichloro-2,3-dicyanoquinone) (120 mg, 0.53 mmol) was added and the mixture was stirred for 30 min. The solvents were then removed in vacuo. The resulting residue was taken up in dichloromethane and purified by column chromatography, using increasingly polar dichloromethane/methanol mixtures containing a few drops of TFA (trifluoroacetic acid) as the eluent. The dark green fractions, eluting with dichloromethane/methanol (4%)/TFA (0.1%), were collected and taken to dryness in vacuo. This yielded the thiasapphyrin product as a dark blue solid (80 mg, 26%).