Proc Indian Natn Sci Acad, **70, A,** No. 2, March 2004, pp. 391-398
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RECEPTOR PROPERTIES OF OXA CORROLES AND OXA SMARAGDYRINS

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(Received 10 October 2002 ; Accepted 25 October 2002)

Porphyrins and corroles are important ring systems involved in diverse biological functions. Recent research has concentrated on exploitation of these macrocycles as anion and cation receptors. In this overview, an account of receptor properties of two modified corroles namely oxa corrole and expanded oxacorrole (smaragdyrin) is described. Specifically it has been shown that they bind transition metals such as Rh(I) and Ni(II) in their free base form, while in the protonated form they act as anion receptors for anions like F$^-$, Cl$^-$, AMP$^-$ etc. The details of the binding of anions and cations are highlighted here.

Key Words : Corrole; Smaragdyrin; Porphyrin; Receptors; Anion and Cation Complexes

Introduction

Porphyrin and corrole rings are ubiquitous in natural systems performing diverse biological functions[1-3]. Even though, both ring systems contain 18p electrons, structurally, corrole is different from porphyrin. Specifically, corrole contains one less methane bridge than porphyrin resulting in the formation of a direct pyrrole-pyrrole link. Addition of an extra pyrrole ring to a porphyrin skeleton leads to a new 22p sapphyrin ring system[4] (Scheme 1). Sapphyrin is one of the early members of the "*expanded porphyrin family*"[1,2,5] which exhibit diverse chemistry such as receptors for anions[6,7], a potential ligand for transition metal binding[8] in addition to certain biomedical applications[8a,9].

Removal of one meso carbon from a sapphyrin skeleton leads to a new ring system with 22p electrons, which has been christened as smaragdyrin[4] or nor-sapphyrin[10] in the literature. The structural relationship between sapphyrin and smaragdyrin is analogous to that between a porphyrin and a corrole. The chemistry of smaragdyrins are not as well developed as their sapphyrin analogues because of the difficulties encountered in the synthesis as well as its inherent instability. Even though, Johnson and coworkers were successful in synthesis of partially b-substituted smaragdyrin, its instability towards acid and light prevented them from pursuing further studies. Only in 1997, Sessler and coworkers[11] found that the stability of smaragdyrin skeleton can be increased by substituting all the b position by alkyl substituents. They were successful in synthesizing a stable isomer of b-substituted smaragdyrin[12]. Recent work from this laboratory[13] has shown that it is possible to synthesize stable meso aryl smaragdyrins by an oxidative coupling reaction of modified tripyrrane and dipyrromethane. Further more, both corrole and smaragdyrin form metal complexes with transition metals and anion complexes in the protonated form with anions such as F$^-$, Cl$^-$ etc. In this paper, we wish to give an overview of receptor properties of corrole and smaragdyrin towards transition metal cations as well as anions such as F$^-$, Cl$^-$ AMP$^-$ etc. It is observed that both oxa corrole **1** and oxa expanded corrole **2** form stable complexes with Ni(II), Rh(I) in different binding modes through the formation of Metal-Nitrogen covalent bond. On the other hand in the protonated forms **1** and **2** binds to F$^-$ and Cl$^-$ anions through weak N-H–Cl and N-H—F$^-$ bonding interactions. The binding constants evaluated for **2** in solution with different anions vary as F$^-$ > AMP$^-$ » Cl$^-$.

Results and Discussion

The details of the synthesis of **1** and **2** and their spectral and structural characterization are described in our earlier work[13b, 13c].

(a) Interaction of Metal Cations with 1 and 2

Reaction of Rh(I) in the form of di-m-chloro-bis dicarbonyl rhodium(I) and Ni(II) chloride with **1** and **2** in alcohol free chloroform and subsequent work up gave the corresponding Rh(I) and Ni(II) metal corroles, **3** and **4** in good yields (Scheme 2 and 3).

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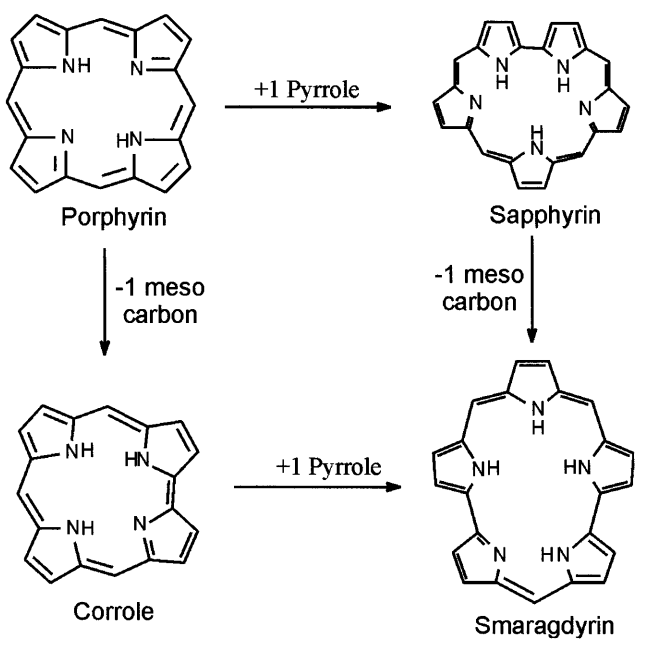
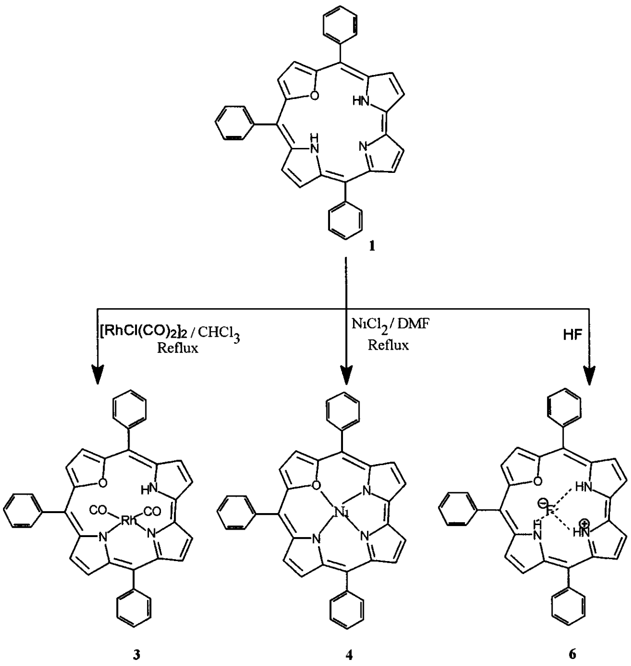


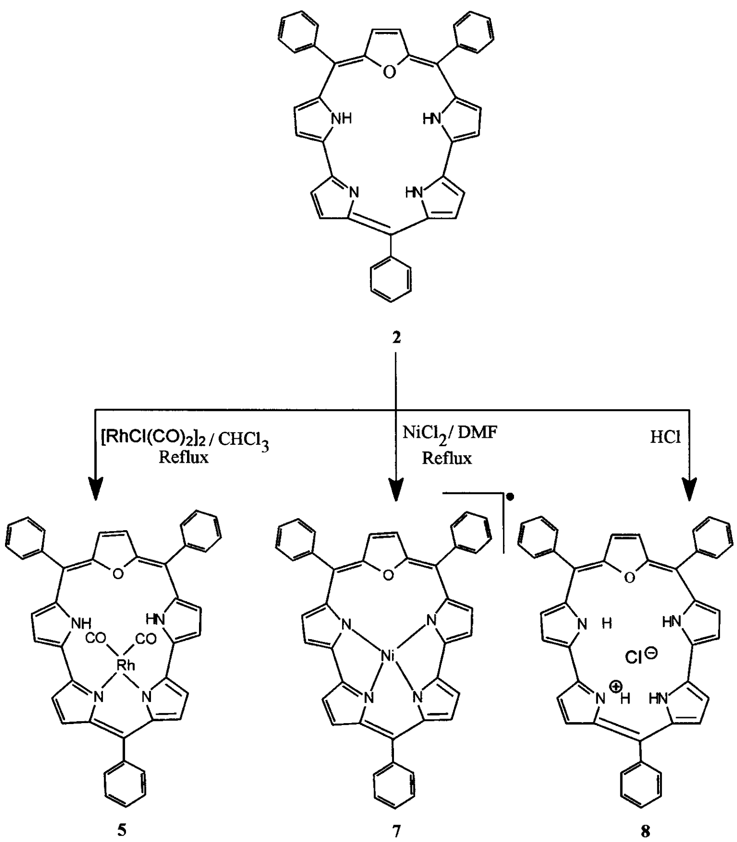
Scheme 1

Structural Relationship between Various Macrocyles



Scheme 2

Synthesis of Cation and Anion Complexes from Oxa Corrole



Scheme 3

Synthesis of Cation and Anion Complexes from Smaragdyrin

The crystal structure of Rh(I) corrole **3** is shown in the Fig. 1. According to the X-ray structure, the Rh(I) ion is located above the corrole plane and the geometry around the metal centre is close to square planar (C39-Rh1-N2 94.1(2)°, C38-Rh1-N3 94.4(2)°). One imino and one amino nitrogen of the macrocycle is coordinated to the Rh(I) ion and the other two coordination sites are occupied by carbonyl ligands. This is consistent with the earlier observation of requirement of one amino and one imino nitrogen for the stabilization of Rh(I) ion in the macrocyclic environment[14]. Eventhough monooxa corrole has one

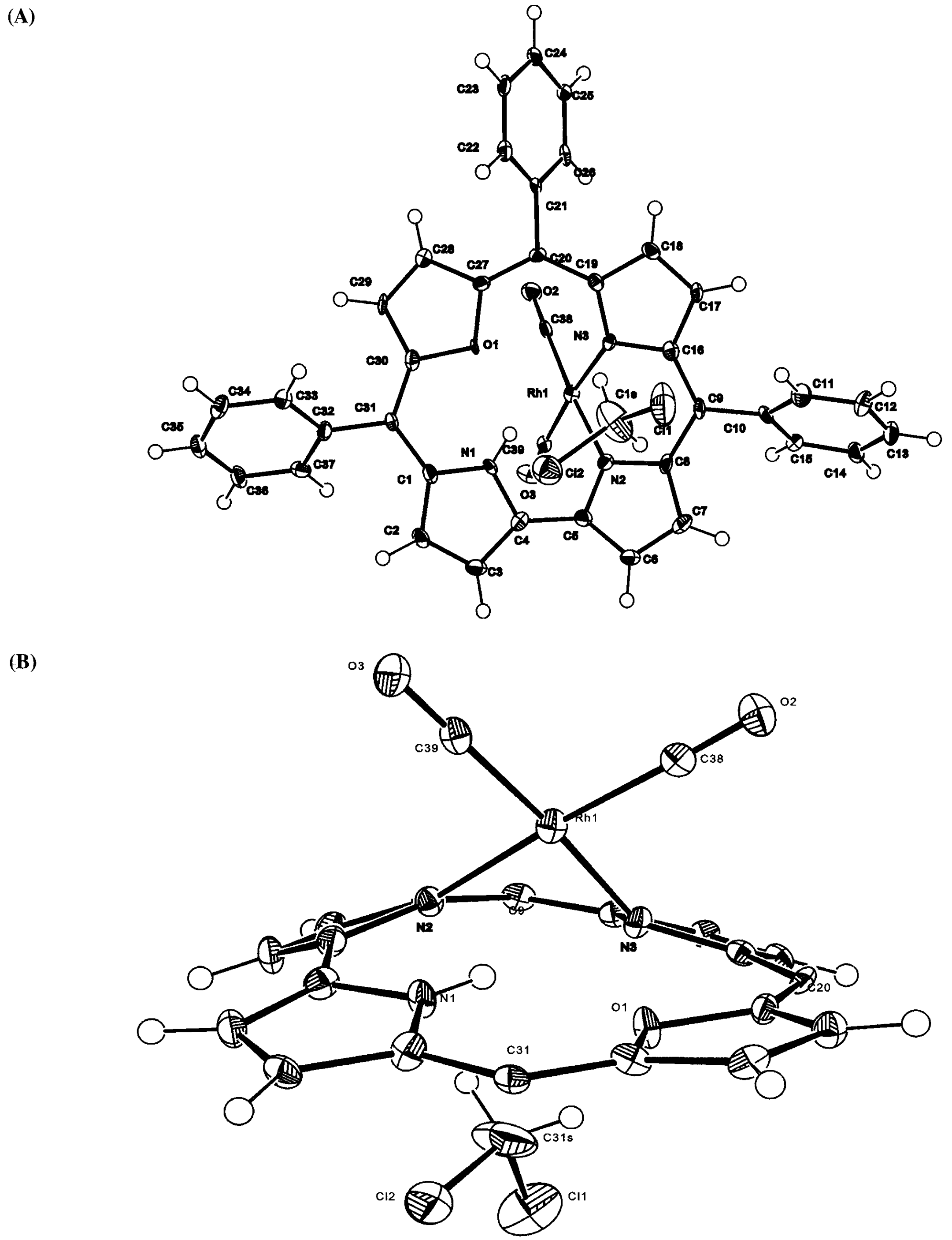


Fig. 1 ORTEP diagram for **3** (a) Top: Plane view (b) Bottom: Side view(phenyl rings are omitted for clarity)[13b]

imino (N2) nitrogen which is between the two amino (N1 and N3) nitrogens, the coordination of Rh(I) takes place only at N2 and N3 nitrogen atoms. This is probably due to the fact that this type of coordination will avoid strain in the molecule which otherwise will happen due to the direct C4-C5 link. Also there are strong intramolecular hydrogen bonding between the N1-H—O1 (2.63 Å, 122.35°) and N1-H—N2 (2.67 Å, 106.82°). Due to the out of plane coordination of Rh(I) ion, the pyrrole rings containing N2 and N3 are twisted above the mean corrole plane by an angle of 23.51° and 19.69° respectively. The angle between the plane containing the Rh(I) with its coordinated atoms and the mean corrole plane is 62.64°. The macrocycle is nonplanar and this is reflected in the increase of the nonbonded heteroatom distances relative to freebase monooxa corrole (O1-N3: 3.068 Å, O1-N1: 2.631 Å, N1-N2: 2.668 Å, N2-N3: 2.654 Å).

The structure of **4** revealed a flattened corrole macrocyle upon Ni(II) complexation (Fig. 2). There

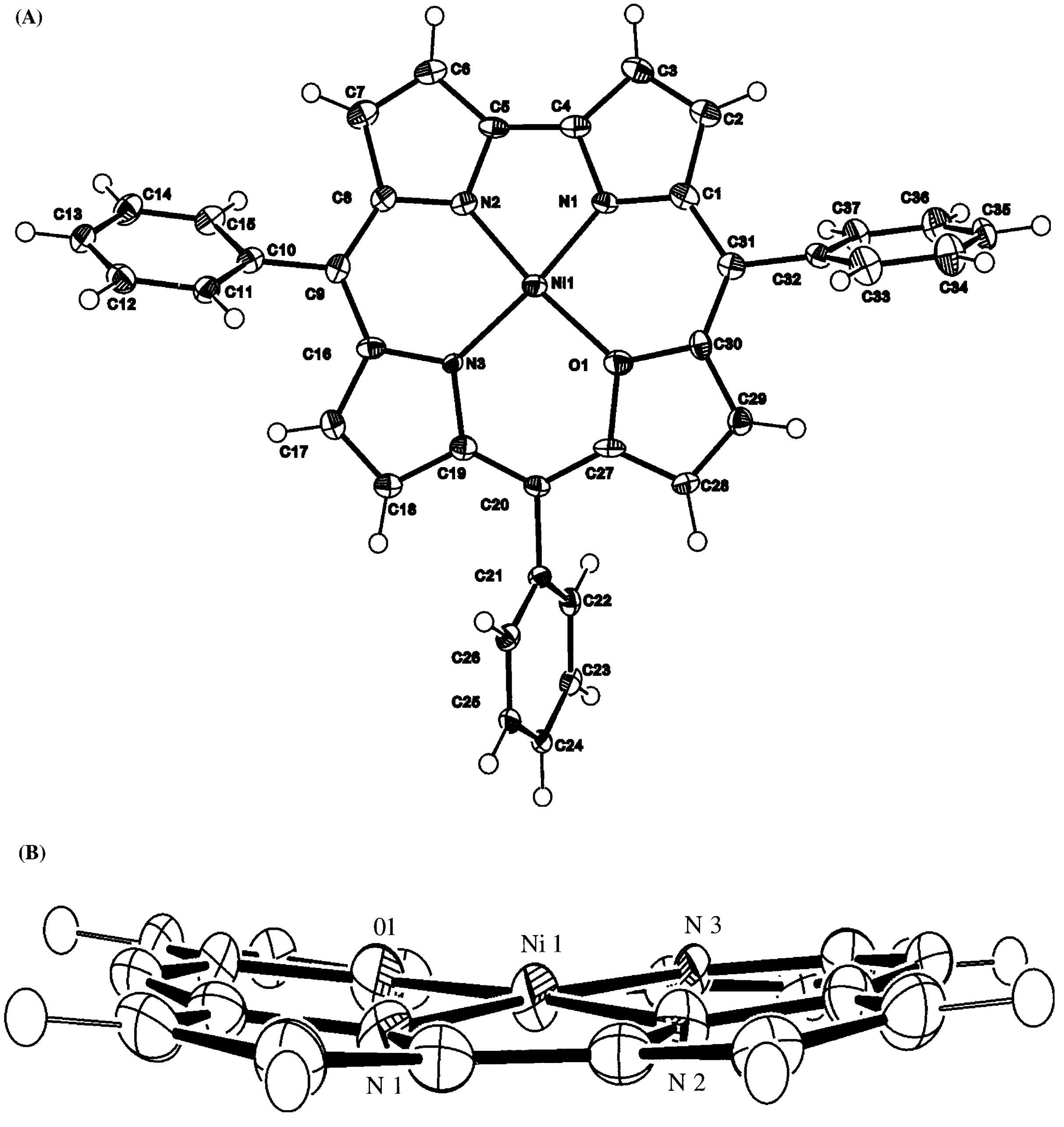


Fig. 2 ORTEP diagram for **4** (a) Top: Plane view (b) Bottom: Side view(phenyl rings are omitted for clarity)[13 b]

are two ionisable protons and hence the metal is expected to be in the oxidation state of +2 unlike in the case of b-substituted corroles[15]. The Ni(II) atom acquires a distorted square planar conformation which is due to the direct C4-C5 link. (N1-Ni-N2: 82.76(12)°). The Ni atom lies above the mean plane of the macrocycle by only 0.008 Å. The deviation of the heterocyclic ring from the mean plane of the corrole ring are O1 5.90, N1 4.95, N2 6.47, N3 8.00° and for the free base they are 5.48, 7.40, 6.09, 7.74° respectively. A comparison of Ni-N and Ni-O distances show that they are shorter when compared to the corresponding distances of porphyrins[16] thus reflecting reduced core size in oxa corroles. As expected, the two shortest Ni-N bonds are those involving nitrogens adjacent to Ca -Ca link, and this is typically observed for metallo corroles[15,17]. The incorporation of the metal ion decreases the N1-N2 (2.419 Å) and N3-O1 (2.815 Å) nonbonding distances and increases the N1-O1 (2.655 Å) and N2-N3 (2.647 Å) nonbonding distances.

The expanded corrole **2** also bind Rh(I) and Ni(II) and the binding modes observed are similar to that observed for **1**. Specifically the structure of **5** (Fig. 3) reveals that the rhodium atom is attached to the smaragdyrin skeleton in a h^2 fashion involving one amino and one imino nitrogen of the dipyrromethane unit (N2 and N3). The other two coordination sites of the rhodium are occupied by the carbonyl groups. Thus Rh(I) metal forms an out-of-plane complex and the observed bond lengths and angles indicate an approximate square planar geometry about the metal centre with a metal plane at an angle of 57.69° to the plane of the smaragdyrin (Rh-N3 2.034 Å, Rh-N4 2.042 Å, Rh-C42 1.871 Å, Rh-C43 1.856 Å, N3-Rh-N4 82.45°, C42-Rh-C43 89.32°, N3-Rh-C42 93.73°, N4-Rh-C43 94.27°). This metal environment is analogous to that observed for the Rh(I) complexes of hetero sapphyrins[8c,8h,8i]. Eventhough both the dipyrromethane and the bipyrrole units have one amino and one imino nitrogens (N3, N2 for dipyrromethane and N3, N4 for bipyrrole unit) which are necessary for Rh(I) coordination[8c,8h,8i], only the dipyrromethane unit is bound to the Rh(I) ion. This is attributed to the fact that the formation of an out-of-plane square planar complex with bipyrrole unit having a direct a -a link may cause severe distortion destabilizing the complex.

(b) Interaction of Anions with 1 and 2

The protonation of pyrrole nitrogens in **1** and **2**, leads to the generation of a positive charge on the specific pyrrole nitrogen which is delocalized through out the ring because of conjugation. Hence, the protonated derivative is expected to bind anions. Thus, addition HF to **1** and HCl to **2** generates the corresponding fluoride, chloride complexes **6** and **8** respectively (Scheme 2 and 3).

The solid state structure of HCl complex **8**, (Fig. 4) clearly shows coordination of the chloride ion above the plane of the macrocycle. Specifically, out of the four pyrrole –NH groups available, only three –NH groups are involved in the N-H—Cl hydrogen bonds. The hydrogen bond distances N1-C11 3.0902(17), N2-C11 3.119(17) and N4-C11 3.1400(17) Å suggest that the chloride anion is bound strongly by only three N-H—Cl hydrogen bonds which are pointed towards the chloride atom. The pyrrole rings N1, N2, and N4

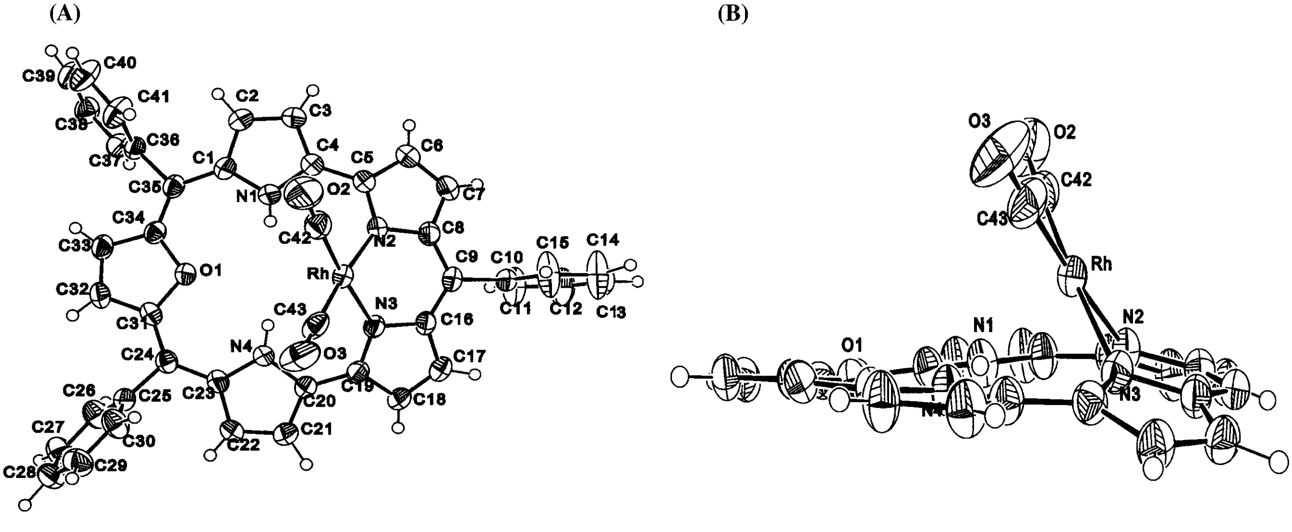


Fig. 3 ORTEP diagram for **5** (a) Top: Plane view (b) Bottom: Side view(phenyl rings are omitted for clarity)[13c]

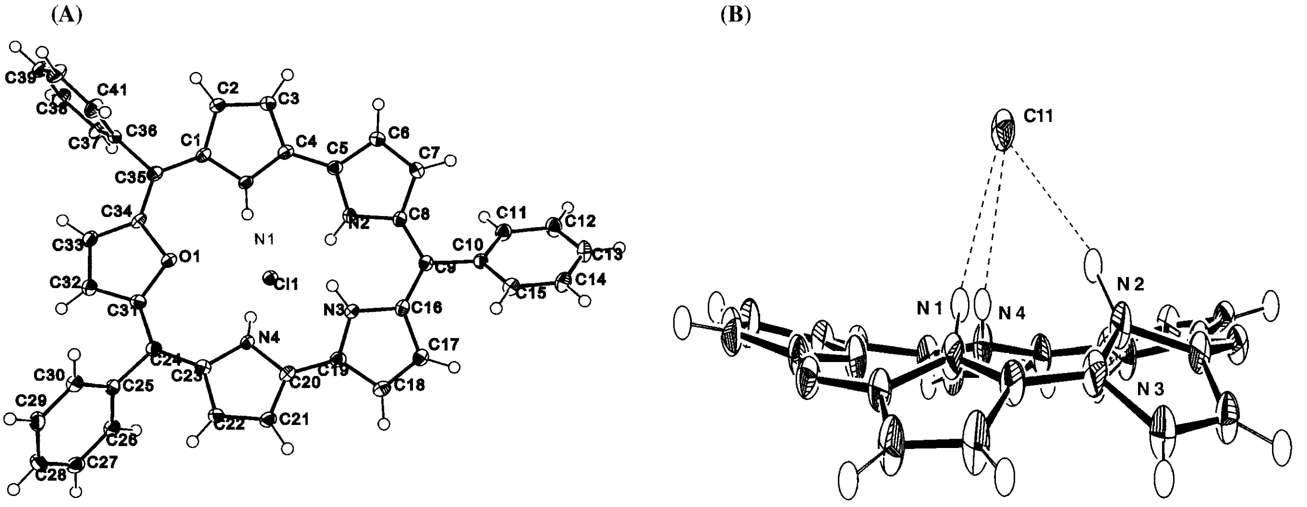


Fig. 4 ORTEP diagram for **8** (a) Top: Plane view (b) Bottom: Side view(phenyl rings are omitted for clarity)[13 c]

which are involved in the bonding are tilted above the plane of the macrocycle defined by the meso carbons while the pyrrole ring N3 is in the plane. This is reflected in the different torsional angles observed for the pyrrole rings in dipyrromethane unit; N2-C8-C9-C16 –14.4° and N3-C16-C9-C8 –6.4°. The hydrogen bonding distance compare well (3.176, 3.039, 3.200 Å)[6e] with that observed for the monoprotonated chloride salt of a b-substituted dioxasapphyrin. However, the binding seen here is slightly different from that observed for the monoprotonated chloride salt of smaragdyrin isomer where all the four nitrogens are involved in binding to the chloride anion[12].

A comparison of the twist of various pyrrole/ heterocyclic rings in free base of **2**, its Rh(I) complex **5** and its chloride complex **8** indicates different twist angles depending on the nature of the interactions and this is summarized in Table-I.

(c) Anion Complexes of Smaragdyrin in Solution

The complexation of anions by protonated form of smaragdyrin in solution is further probed by UV-Visible spectroscopy because of the strong absorption of the smaragdyrins. Three different anions; F^-, Cl^- and Adenosine Mono Phosphate (AMP^-) were chosen for study. In a typical experiment, a constant volume of smaragdyrin in its protonated form (~ $5.2X10^{-6}$ M) were taken in 10 ml volumetric flasks. An increasing amount of the required anion salt solution ($0.5X10^{-6}$ to $1X10^{-4}$M) in methanol was transferred to each flask. Then in each flask, 1 ml of 0.5M of 18-crown-6 was added so that the cation is complexed by the crown ether leaving the naked anion for binding. The remaining volume was make up with the solvent upto the mark. The solution was shaken well and immediately the absorption spectra of these solutions in the desired region were recorded. The addition of increasing amount of salt results in a small increase in the absorbance of the smaragdyrin due to complexation and this increase in the absorbance was analysed using the Nash equation[18] (1) to evaluate the binding constants.

$$1/C_A = \{(d^0/d^0\text{-}d)\ (K\text{-}(e_{AD}/e_D))\text{-}K\} \qquad ...(1)$$

Here 'd⁰' is the optical density of smaragdyrin at a particular wavelength in the absence of any salt while 'd' is the optical density of the anion complex of the smaragdyrin at a particular concentration of the salt

Table I

Deviation Angles (deg) between Plane Constructed with the Inner Periphery Atoms and the Plane of Individual Heterocyclic Rings

Heterocyclic rings	2	8	5
Furan ring	12.85	9.10	5.67
N1 Pyrrole ring	19.66	17.66	4.98
N2 Pyrrole ring	8.16	22.72	15.85
N3 Pyrrole ring	6.91	7.40	22.40
N4 Pyrrole ring	15.24	10.31	3.75

solution. C_A is the concentration of the anion, e_{AD} represents the molar absorptivity of the anion complex of smaragdyrin and K is the binding constant. The physical significance of this equation is quite clear when the reciprocal of acceptor concentration is plotted against (d^0/d^0- d). The intercept of the straight line should be negative of the binding constant and the slope is related to the molar absorptivity of the complex. The binding constants evaluated in solution for **2** vary as F^- (7.6×10^5 M^{-1}) > Cl^- (2.1×10^5 M^{-1}) ~ AMP^- (2.6×10^5 M^{-1}).

These values are approximately an order of magnitude lower relative to binding of the similar ions by protonated form of N5 sapphyrin reported by Sessler and coworkers[6d]. Relative to N5 sapphyrin, the oxasmaragdyrin **2** reported here is different in the following aspects; (a) the cavity size available for anion binding in the smaragdyrin is slightly smaller because of presence of two direct pyrrole-pyrrole links and the furan oxygen atom instead of pyrrole nitrogen, (b) The N5 sapphyrin reported by Sessler[6d] have b-alkyl substituents with free meso carbons while the smaragdyrins have meso phenyl substituents, (c) The number of hydrogen bonding sites which are mainly responsible for anion binding[6d] in the protonated form of oxasmaragdyrin is only four relative to five such sites in N5 sapphyrin. These structural differences probably could account for the small lowering of binding constants in the present study.

In summary, it has been shown that both corrole and expanded corrole form complexes with Rh(I) and Ni(II) in its freebase form and in protonated form they bind the anions. The X-ray structural characterization reveals that the metal ions are bound by covalent bonds where the anions are held by weak Hydrogen bonding interactions.

Acknowledgment

This work was supported by Department of Science and Technology (DST) and by the Council of Scientific and Industrial Research(CSIR), New Delhi, India.

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