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## 双脂肪胺钌卟啉的合成、结构表征和晶体结构

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本文讨论了一系列双脂肪胺钌卟啉配合物, 包括  $Ru^{II}(Por)(H_2NR)_2$  和  $Ru^{II}(Por)(HNR_2)_2$  [Por = 四苯基卟啉(TPP), 中位-四(对甲苯基)卟啉(TTP), 中位-四(对氯苯基)卟啉(4-Cl-TTP); R = 叔丁基, 异丙基, 环己基, 正辛基, 正十二烷基, R' = 甲基和乙基]的合成, 结构表征和晶体结构测定。钌羰基卟啉与间-氯过苯甲酸的反应混合物用过量的脂肪胺处理, 得到高收率的双脂肪胺钌卟啉配合物。所有的新配合物经核磁共振光谱, 红外光谱, 紫外光谱以及元素分析得到证实。其中, 配合物  $Ru^{II}(Por)(H_2NBu-t)_2$  的结构已由 X-射线晶体结构测定。在  $Ru^{II}(Por)(H_2NBu-t)_2$  分子中, Ru-N(Por)和 Ru-N(H<sub>2</sub>NBu-t)键长分别为 2.041 Å 和 2.175 Å。

关键词: 脂肪胺 钌卟啉 配合物 合成 结构表征 晶体结构测定

BIS(ALIPHATIC AMINE)RUTHENIUM(II) PORPHYRINS SYNTHESIS,  
SPECTROSCOPY AND CRYSTAL STRUCTURE

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The synthesis, characterization and reactivities of a series of ruthenium porphyrins including  $Ru^{II}(Por)(H_2NR)_2$  and  $Ru^{II}(Por)(HNR_2)_2$  [Por = tetraphenyl porphyrinato (TPP), *meso*-tetrakis(*p*-tolyl)porphyrinato (TTP), *meso*-tetrakis(4-chlorophenyl) porphyrinato (4-Cl-TTP); R = *tert*-butyl, isopropyl, cyclohexyl, *n*-octyl, *n*-dodecyl, R' = methyl, ethyl are described. The reaction of  $Ru(Por)(CO)(MeOH)$  with *m*-chloroperoxybenzoic acid (*m*-CPBA) followed by treatment of the reaction mixture with excess aliphatic amines readily gave bis(aliphatic amine) ruthenium(II) porphyrins in high yields. All the new complexes have been characterized by <sup>1</sup>H NMR, IR, and UV-Visible spectroscopy. The X-ray crystal structure of  $Ru(TTP)(H_2NBu^t)_2$  has been determined. The Ru-N(Por) and Ru-

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N(H<sub>2</sub>NBu') distances in Ru(TTP)(H<sub>2</sub>NBu')<sub>2</sub> are 0.2041 nm and 0.2175 nm, respectively.

Keywords: aliphatic amine ruthenium porphyrin synthesis characterization  
crystal structure determination

## 0 Introduction

Although the chemistry of transition metal amine complexes has been intensively studied, relatively few reports have been made on the bis(amine) adducts of metalloporphyrins, and such reports have mainly concentrated on aromatic amines axial ligands, such as pyridine and imidazole<sup>[1]</sup>. The first bis(aliphatic amine) metalloporphyrin, [Rh(Etio)(HNMe<sub>2</sub>)<sub>2</sub>]<sup>+</sup>, was generated in a peculiar manner by Gouterman and co-workers in 1973, in which the dimethylamine ligand comes originates from the decarbonylation of the solvent N, N-dimethylformamide (DMF)<sup>[2]</sup>. Latter, Buchler and coworkers prepared Os(OEP)(NMe<sub>3</sub>)<sub>2</sub> from the reaction of Os(OEP)(N<sub>2</sub>)(THF) with trimethylamine<sup>[2]</sup>. However, as we are aware, no metalloporphyrins containing primary amines (RNH<sub>2</sub>) as the sole axial ligands have been isolated and well characterized prior to our previous communication<sup>[1]</sup>. The importance of bis(aliphatic amine) ruthenium(II) porphyrins is obvious; (1) Oxidative deprotonation of bis(tert-butylamine) ruthenium porphyrins generates the intriguing tert-butylimido ruthenium(VI) complexes<sup>[1]</sup>, which are the first examples of alkylimido metalloporphyrins that have been well characterized by <sup>1</sup>H NMR, IR and UV-Visible spectroscopy<sup>[1]</sup>, (2) Oxidation of ruthenium(II) porphyrin adducts with secondary amines, such as diphenylamine and dimethylamine, is expected to afford novel dialkylamido ruthenium porphyrins. In this contribution we present the synthesis, characterization of various bis(aliphatic amine) ruthenium(II) porphyrins, together with the structure of [*meso*-tetrakis(*p*-tolyl)porphyrinato]bis(tert-butylamine)ruthenium(II) [Ru(TTP)(H<sub>2</sub>NBu')<sub>2</sub>].

## 1 Experimental

UV-Visible spectra were measured on a Mitton Roy Spectronic 3000 Array spectrometer. <sup>1</sup>H NMR spectra were recorded on either a JEOL Model FX 90Q spectrometer (90 MHz) or JEOL JNM-GSX 270 FT NMR spectrometer (270 MHz), and the chemical shifts ( $\delta$ , ppm) were reported relative to tetramethylsilane(TMS). Infrared spectra were obtained using a Nicolet 20 SXC FT-IR spectrometer or a Shimadzu IR-470 spectrometer (Nujol mulls).

### 1.1 Materials

Dodecacarbonyltriruthenium(0), Ru<sub>3</sub>(CO)<sub>12</sub> was from Adrich Chem. Co. *m*-Chloroperoxybenzoic acid (*m*-CPBA)(55%), isopropylamine (H<sub>2</sub>Ni<sup>i</sup>), cyclohexylamine (H<sub>2</sub>NCyhex), *n*-octylamine(H<sub>2</sub>NOct<sup>n</sup>), *n*-dodecylamine(H<sub>2</sub>NDodec<sup>n</sup>), dimethylamine(HNMe<sub>2</sub>), diethylamine(HNEt<sub>2</sub>),

were used without further purification. *tert*-Butylamin ( $H_2NBu'$ ) was freshly distilled prior to use. *meso*-Tetraphenylporphyrin  $H_2TPP$ , *meso*-tetrakis (*p*-tolyl) porphyrin  $H_2TTP$ , and *meso*-(4-chlorophenyl)porphyrin  $H_2(4-Cl-TPP)$ , were prepared by a literature method<sup>[5]</sup>. The complexes  $Ru(Por)(CO)(MeOH)(Por=TPP, 1a; TTP, 1b; 4-Cl-TPP, 1c)$  were synthesized from the reaction of  $Ru_3(CO)_{12}$  with corresponding free base porphyrins,  $H_2(Por)$ , in refluxing toluene under nitrogen followed by recrystallization of the purified  $Ru(Por)(CO)$  in dichloromethane-methanol<sup>[6]</sup>. Other complexes  $Ru(Por)(O)_2(Por=TPP, 2a; TTP, 2b; 4-Cl-TPP, 2c)$  were synthesized according to literatures procedures<sup>[7]</sup>.

### 1. 2 Synthesis

Preparation of bis(primary amine) ruthenium(II) porphyrins,  $Ru(Por)(H_2NR)_2$  ( $Por=TPP$ ,  $R=Bu'$ , **3a**;  $Pr'$ , **4a**; cyhex, **5a**; Oct<sup>n</sup>, **6a**.  $Por=TTP$ ,  $R=Bu'$ , **3b**;  $Pr'$ , **4b**; cyhex, **5b**; Oct<sup>n</sup>, **6b**; Dodec<sup>n</sup>, **7b**.  $Por=4-Cl-TPP$ ,  $R=Bu'$ , **3c**;  $Pr'$ , **4c**; cyhex, **5c**; Oct<sup>n</sup>, **6c**; Dodec<sup>n</sup>, **7c**: A solution of  $Ru(Por)(CO)(MeOH)(Por=TPP, 1a; TTP, 1b; 4-Cl-TPP, 1c)$  (50 mg) in dichloromethane or chloroform (20 mL) was treated with *m*-CPBA (150 mg) for several minutes. A large excess of an aliphatic amine was then introduced to afford a brown solution within two minutes. The solution was stirred for an additional 15 minutes, then concentrated to ca. 2 mL and next chromatographed on alumina with dichloromethane containing a small amount of the corresponding amine as the eluent. The leaving yellowish brown band was collected. *n*-Heptane was added to the eluate and the solvent volume was reduced until the product precipitated. The solid was collected by filtration, washed with heptane, and dried.

Bis (secondary amine) ruthenium(II) porphyrins,  $Ru(Por)(HNR_2)_2$  ( $Por=TPP$ ,  $R=Me$ , **8a**; Et, **9a**.  $Por=TPP$ ,  $R=Et$ , **9b**.  $Por=4-Cl-TPP, 9c$ ): The complexes were synthesized according to produces of bis(primary amine) ruthenium(II) porphyrins.

All new complexes have been characterized by <sup>1</sup>H NMR, IR, UV-Visible spectra and elemental analysis.

### 1. 3 X-ray structure determination

Crystals of  $Ru(TTP)(H_2NBu')_2$  (purple needles) suitable for X-ray crystallographic studies were obtained from slow evaporation of a solution of  $Ru(TTP)(H_2NBu')_2$  (**3b**) in dichloromethane-hexane containing a small amount of *tert*-butylamine. Crystal data:  $C_{36}H_{38}N_8Ru$ ,  $M=916.19$ , monoclinic, space group  $P2_1/n$ ,  $a=1.3808(3)$  nm,  $b=0.9672(3)$  nm,  $c=1.7880(6)$  nm,  $\beta=103.24(2)^\circ$ ,  $V=232.44(1)$  nm<sup>3</sup>,  $D_c=1.30$  g/cm<sup>-3</sup>,  $Z=2$ ,  $R=0.036$ ,  $R_w=0.050$ ,  $F(000)=948$ ,  $\mu=3.7$  cm<sup>-1</sup>, measured data is 4270, unique data is 3066. Diffraction measurement were made at room temperature on an Enraf-Nonius CAD4 diffractometer using Mo-K $\alpha$ (0.071073 nm) radiation. The intensity data were corrected for Lorentz and polarization effects, and absorption corrections were applied empirically on the basis of azimuthal scan of four strong reflections. All computations were performed on a Micro VAX II computer using the Enraf-Nonius SDP program. The structure was solved by heavy-atom methods. The position of the Ru atom in **3b** was located at the crystallographic center of symmetry. The coordinates of all the remaining non-hydrogen atoms were determined from subsequent Fourier maps. All non-hydrogen atoms refined by least squares anisotropical-

ly. Hydrogen atoms in calculated positions ( $C-H = 0.095$  nm) with assigned thermal parameters were not refined. At the end of the refinement, residual electron-densities in the final difference Fourier maps were in the range of  $-0.041$  to  $0.057$   $enm^{-3}$ . Final positional and equivalent isotropic thermal parameters are listed in Table 1. Selected bond lengths and angles are listed in Table 2.

Table 1 Atomic Coordinates and Equivalent Isotropic Temperature Factors of  $Ru(TTP)(H_2NBU)_2$  (3b)

atom	x	y	z	B(eq.)
Ru	0.0000	0.000	0.000	2.040(6)
N(1)	0.0955(2)	-0.0501(3)	-0.0675(2)	2.30(5)
N(2)	-0.0803(2)	-0.1756(3)	-0.0337(2)	2.23(5)
N(3)	0.0880(2)	-0.1401(3)	0.0839(2)	2.98(6)
C(1)	0.0930(3)	-0.1687(4)	-0.1108(2)	2.58(7)
C(2)	0.0216(3)	-0.2736(4)	-0.1178(2)	2.48(7)
C(3)	-0.597(2)	-0.2743(4)	-0.8330(2)	2.38(7)
C(4)	-1.363(3)	-0.3787(4)	-0.0946(2)	3.05(8)
C(5)	-0.2012(3)	-0.3436(4)	-0.0523(2)	3.10(8)
C(6)	-0.1668(2)	-0.21624(4)	-0.3129(2)	2.48(7)
C(7)	0.2132(2)	0.1451(4)	-0.0372(2)	2.56(7)
C(8)	0.1796(2)	0.0231(3)	-0.0746(2)	2.56(7)
C(9)	0.2281(3)	-0.0508(4)	-0.1254(2)	3.54(8)
C(10)	0.1765(3)	-0.1684(4)	-0.1468(2)	2.45(8)
C(11)	0.0321(2)	-0.3958(4)	-0.1668(2)	2.53(7)
C(12)	0.0210(3)	-0.3841(4)	-0.2457(2)	3.19(8)
C(13)	0.0323(3)	-0.4968(5)	-0.2902(2)	3.49(7)
C(14)	0.0546(3)	-0.6251(4)	-0.2582(2)	3.43(8)
C(15)	0.0650(3)	-0.6365(4)	-0.1790(2)	3.59(9)
C(16)	0.0549(3)	-0.5247(4)	-0.1341(2)	3.12(8)
C(17)	0.0686(4)	-0.7515(5)	-0.3050(3)	5.60(1)
C(18)	0.3107(3)	0.2038(4)	-0.0478(2)	3.07(8)
C(19)	0.3155(3)	0.3082(6)	-0.0987(3)	6.50(1)
C(20)	0.4060(4)	0.3633(6)	-0.1053(4)	7.50(1)
C(21)	0.4926(3)	0.3165(5)	-0.0631(3)	5.30(2)
C(22)	0.4883(3)	0.2095(8)	-0.0141(3)	6.70(1)
C(23)	0.3982(3)	0.1545(7)	-0.0061(3)	5.80(1)
C(24)	0.5906(4)	0.3795(7)	-0.0701(4)	8.20(2)
C(25)	0.1633(3)	-0.1138(4)	0.1579(2)	3.25(8)
C(26)	0.2522(3)	-0.0358(5)	0.1409(3)	5.10(1)
C(27)	0.1147(4)	-0.0295(5)	0.2113(3)	4.50(1)
C(28)	0.1978(4)	-0.2530(5)	0.1948(3)	4.50(1)

Table 2 Selected Bond Distances (nm) and Bond Angles( $^{\circ}$ ) (deg) in Ru(TTP)(H<sub>2</sub>NBu')<sub>2</sub>(3b)

distances			
Ru-N(1)	0.2040(4)	C(2)-C(11)	0.1499(6)
Ru-N(2)	0.2042(3)	C(3)-C(4)	0.1443(5)
Ru-N(3)	0.2175(3)	C(4)-C(5)	0.1342(6)
N(1)-C(1)	0.1379(5)	C(5)-C(6)	0.1445(5)
N(1)-C(8)	0.1390(4)	C(11)-C(12)	0.1387(5)
N(2)-C(3)	0.1372(5)	C(11)-C(16)	0.1384(5)
N(2)-C(6)	0.1387(5)	C(12)-C(13)	0.1380(6)
N(3)-C(25)	0.1505(4)	C(13)-C(14)	0.1372(6)
C(1)-C(2)	0.1401(5)	C(14)-C(15)	0.1396(6)
C(1)-C(10)	0.1444(6)	C(14)-C(17)	0.1517(6)
C(2)-C(3)	0.1402(5)		
angles			
N(1)-Ru-N(2)	90.5(1)	N(1)-C(1)-C(2)	125.4(3)
N(1)-Ru-N(3)	85.7(1)	N(1)-C(1)-C(10)	109.2(4)
N(2)-Ru-N(3)	82.3(2)	C(2)-C(1)-C(10)	125.5(3)
Ru-N(1)-C(1)	126.3(2)	C(1)-C(2)-C(3)	125.6(3)
Ru-N(1)-C(8)	126.8(2)	C(1)-C(2)-C(11)	117.6(3)
C(1)-N(1)-C(8)	106.7(3)	C(1)-C(10)-C(9)	107.4(4)
Ru-N(2)-C(3)	126.1(2)	C(2)-C(11)-C(12)	121.8(3)
Ru-N(2)-C(6)	126.8(2)	C(2)-C(11)-C(16)	120.4(3)
C(3)-N(2)-C(6)	107.1(3)	C(3)-C(25)-C(27)	109.5(3)
Ru-N(3)-C(25)	131.7(2)	C(26)-C(25)-C(27)	110.5(4)

## 2 Results and Discussion

### 2.1 Synthesis

The ruthenium ( I ) porphyrins Ru(Por)(L)<sub>2</sub> (L is a weakly coordinating ligand such as pyridine) are usually prepared from the carbonyl complexes Ru(Por)(CO) through photolytic decarbonylation in the presence of L<sup>[a]</sup>. However, no bis(aliphatic amine) ruthenium ( I ) porphyrins have been isolated by this method. Our extensive studies on the reaction between dioxoruthenium ( VI ) porphyrins and aliphatic amine revealed that sequential addition of *m*-CPBA and excess aliphatic amine to a solution of Ru(Por)(CO)(MeOH) in dichloromethane or chloroform would lead to the rapid reduction of the resulting Ru(Por)(O)<sub>2</sub> intermediate, with the bis(aliphatic amine) ruthenium ( I ) porphyrin being formed nearly quantitatively within several minutes. This synthetic route was found to be relatively simple. It is not necessary to isolate the pure dioxo ruthenium ( VI ) porphyrins before they are allowed to react with the aliphatic amines. The elemental analysis data of new complexes was listed in Table 3.

Table 3 Elemental Analysis of Bis (Aliphatic Amines) Ruthenium Porphyrins

complex	Formular	C(%)	H(%)	N(%)	yield(%)
Ru(TPP)(H <sub>2</sub> NBu <sup>t</sup> ) <sub>2</sub> (3a)	C <sub>52</sub> H <sub>50</sub> N <sub>6</sub> Ru	76.62 (72.47)	5.86 (5.73)	9.77 (9.23)	85
Ru(TTP)(H <sub>2</sub> NBu <sup>t</sup> ) <sub>2</sub> (3b)	C <sub>50</sub> H <sub>58</sub> N <sub>6</sub> Ru	73.2 (73.41)	6.47 (6.38)	9.10 (9.17)	84
Ru(4-Cl-TPP)(H <sub>2</sub> NBu <sup>t</sup> ) <sub>2</sub> (3c)	C <sub>52</sub> H <sub>46</sub> Cl <sub>2</sub> N <sub>6</sub> Ru	62.44 (62.59)	4.70 (4.65)	8.38 (8.42)	90
Ru(TPP)(H <sub>2</sub> NPr <sup>i</sup> ) <sub>2</sub> (4a)	C <sub>50</sub> H <sub>46</sub> N <sub>6</sub> Ru	72.18 (71.39)	5.57 (5.49)	10.10 (9.79)	86
Ru(TTP)(H <sub>2</sub> NPr <sup>i</sup> ) <sub>2</sub> (4b)	C <sub>54</sub> H <sub>54</sub> N <sub>6</sub> Ru	73.00 (73.03)	6.15 (6.13)	9.53 (9.46)	85
Ru(4-Cl-TPP)(H <sub>2</sub> NPr <sup>i</sup> ) <sub>2</sub> (4c)					89
Ru(TPP)(H <sub>2</sub> NCyhex) <sub>2</sub> (5a)					98
Ru(TTP)(H <sub>2</sub> NCyhex) <sub>2</sub> (5b)	C <sub>60</sub> H <sub>62</sub> N <sub>6</sub> Ru	74.25 (74.43)	6.49 (6.45)	8.50 (8.68)	90
Ru(4-Cl-TPP)(H <sub>2</sub> NCyhex) <sub>2</sub> (5c)	C <sub>58</sub> H <sub>50</sub> Cl <sub>2</sub> N <sub>6</sub> Ru	63.95 (64.06)	4.65 (4.80)	7.95 (8.00)	92
Ru(TPP)(H <sub>2</sub> NOct <sup>n</sup> ) <sub>2</sub> (6a)					84
Ru(TTP)(H <sub>2</sub> NOct <sup>n</sup> ) <sub>2</sub> (6b)	C <sub>64</sub> H <sub>74</sub> N <sub>6</sub> Ru	74.65 (74.75)	7.28 (7.25)	8.15 (8.17)	80
Ru(4-Cl-TPP)(H <sub>2</sub> NOct <sup>n</sup> ) <sub>2</sub> (6c)	C <sub>60</sub> H <sub>62</sub> Cl <sub>2</sub> N <sub>6</sub> Ru	64.83 (64.92)	5.43 (5.63)	7.37 (7.57)	86
Ru(TTP)(H <sub>2</sub> NDodec <sup>n</sup> ) <sub>2</sub> (7b)	C <sub>70</sub> H <sub>90</sub> N <sub>6</sub> Ru	75.77 (75.82)	7.89 (7.95)	7.23 (7.57)	70
Ru(4-Cl-TTP)(H <sub>2</sub> NDodec <sup>n</sup> ) <sub>2</sub> (7c)					74
Ru(TPP)(HNMe <sub>2</sub> ) <sub>2</sub> (8a)					94
Ru(TPP)(HNEt <sub>2</sub> ) <sub>2</sub> (9a)	C <sub>56</sub> H <sub>50</sub> N <sub>6</sub> Ru	72.62 (72.02)	5.86 (5.94)	9.77 (9.86)	88
Ru(TTP)(HNEt <sub>2</sub> ) <sub>2</sub> (9b)					85
Ru(4-Cl-TPP)(HNEt <sub>2</sub> ) <sub>2</sub> (9c)					89

In brackets are the calculated values.

## 2.2 Spectroscopy <sup>1</sup>H NMR

All the bis(aliphatic amine) ruthenium( II ) porphyrins give well resolved <sup>1</sup>H NMR spectra indicating the complexes are diamagnetic (see table 4). For a certain porphyrinato ligand, the complexes with different axial aliphatic amines exhibit nearly the same porphyrin ring proton resonances. In many cases, even the N-H proton resonances of the axial amino group can be clearly observed, which appear as a broad peak at ca. -6.5 ppm. The other signals in the high field region deserve special attention since they are important for identifying the axial amine ligands. It is interesting to study the effect of porphyrin ring currents on the chemical shifts of the axial amine protons. Generally, the closer the protons are to the ring, the larger up-field shifts would be observed. This is in good agreement with our results obtained for bis(aliphatic amine) ruthenium( II ) porphyrins. In order to see how the proton resonances of the axial tert-butylamine, isopropylamine and diethylamine are af-

ected by the porphyrin ring current, we show here the  $^1\text{H}$  NMR spectra data of  $\text{Ru}(\text{TTP})(\text{H}_2\text{NBu}^t)_2$  (**3b**),  $\text{Ru}(\text{TTP})(\text{H}_2\text{NPr}^i)_2$  (**4b**), and  $\text{Ru}(\text{TTP})(\text{HNEt}_2)_2$  (**9b**), the tert-butyl group give a sharp singlet at -1.86 ppm. This is interesting since the expected bent  $\text{Ru}-\text{NH}_2-\text{C}$  geometry would result in different distances from tert-butyl protons to the ring plane and one would expect a broadened signal due to these protons. However, no such broadening has observed. This could be attributed to free rotations of the tert-butyl group around the N-C  $\sigma$  bond and its methyl groups around C-C  $\sigma$  bonds, which are likely to equalize all the protons of the tert-butyl group. For isopropylamine and diethylamine, their methyl proton resonances appear as a doublet at -1.52 ppm and a triplet at -1.58 ppm respectively. The chemical shift of the methyldyne protons for isopropylamine (-2.24 ppm) and that of the methylene protons for diethylamine (-2.30 ppm) are also nearly the same. It should be noted that, in complex **9b** the methylene proton resonances appear as a quasi-octet, which suggests that these proton resonances are coupled with those of the methyl and amino groups. Noteworthy is that while the replacement of  $\alpha$  methylene proton by a methyl group (from diethylamine to isopropylamine) only causes a small down-field shift of the methyl protons (-1.58  $\rightarrow$  -1.52 ppm), the further replacement of the other methylene proton by an additional methyl group (from isopropylamine to tert-butylamine) makes the methyl protons to shift up-field remarkably (-1.52  $\rightarrow$  -1.86 ppm). It is interesting to study the effect of porphyrin ring currents on the proton resonances of a long-chain alkyl group in the coordinated amine. Such a study has been reported<sup>[10]</sup> in the  $^1\text{H}$  NMR spectrum of  $\text{Ru}(4\text{-Cl-TPP})(\text{H}_2\text{NOct}^n)_2$ , all the methylene and methyl protons in the *n*-octyl group are completely resolved. The extent to which the proton resonances of the methylene groups are affected by the porphyrin ring current depends on the distances from these protons to the ring plane. It is evident that the observed up-field shift increases slowly from the 7th (the farthest) to the 4th methylene group but rapidly from the 4th to the 1th methylene (the nearest) groups.

### 2.3 IR

Bis(aliphatic amine) ruthenium(II) porphyrins generally exhibit N-H stretching bands with weak or medium intensities. Two well resolved sharp bands for primary amines or one sharp band for secondary amines are usually observed (see Figure 1). The frequency of the N-H stretches depends on the metal ion, the aliphatic amine, but also to a lesser extent on the substitution on the phenyl group of the porphyrin ring. For the ligand TTP, the  $\text{H}_2\text{N}$  stretching frequencies of the ruthenium(II) complexes were found to be 3301, 3241  $\text{cm}^{-1}$  for tert-butylamine, and 3320, 3268  $\text{cm}^{-1}$  for *n*-octylamine. For a certain axial amine ligand such as tert-butylamine, the  $\text{NH}_2$  stretching frequencies of ruthenium(II) complexes are observed to be 3301, 3241  $\text{cm}^{-1}$  for TTP, and 3300, 3236  $\text{cm}^{-1}$  for 4-Cl-TPP. As expected, coordination of aliphatic amines to ruthenium(II) or osmium(II) considerably lowers their N-H stretching frequencies. It is interesting to note that the bis(aliphatic amine) ruthenium(II) porphyrins generally show N-H stretching bands with higher frequency than the corresponding osmium(II) complexes. For instance,  $\text{Ru}(\text{TTP})(\text{H}_2\text{NBu}^t)_2$  and  $\text{Os}(\text{TTP})(\text{H}_2\text{NBu}^t)_2$  give  $\text{NH}_2$  stretching bands at 3301, 3241  $\text{cm}^{-1}$  and 3280, 3225  $\text{cm}^{-1}$  respectively. This can also be attributed to the stronger  $\text{M} \rightarrow \text{Por}$  back bonding in the osmium(II) porphyrins.

Table 4  $^1\text{H}$  NMR (90 MHz or 279 MHz) Spectral Data of Bis(Aliphatic Amine) Ruthenium

complex	$\text{H}_a$ (8H, s)	$\text{H}_b$ (8H, d)	$\text{H}_m$ (8H, s)	$\text{CH}_3$ (12H, s)	axial ligands
$\text{Ru}(\text{TPP})(\text{H}_2\text{NBu}^t)_2(3b)$	8.04	7.89	7.43	2.63	$\text{C}(\text{CH}_3)_2$ ; -1.86(18H, s)
$\text{Ru}(4\text{-Cl-TPP})(\text{H}_2\text{NBu}^t)_2(3c)$	8.07	7.94	7.63		$\text{C}(\text{CH}_3)_2$ ; -1.89(18H, s) $\text{NH}_2$ ; -6.67
$\text{Ru}(\text{TPP})(\text{H}_2\text{HPr}^t)_2(4a)$	8.05( $\text{H}_a, \text{H}_b$ ) (16H, m)		7.63( $\text{H}_m, \text{H}_p$ ) (12H, m)		$\text{CH}(\text{CH}_3)_2$ ; -1.63(12H, d) $\text{CH}(\text{CH}_3)_2$ ; -2.34(2H, br)
$\text{Ru}(\text{TPP})(\text{H}_2\text{NPr}^t)_2(4b)$	8.05	7.85	7.41	2.61	$\text{CH}(\text{CH}_3)_2$ ; -1.52(12H, d) $\text{CH}(\text{CH}_3)_2$ ; -2.24(2H, br)
$\text{Ru}(4\text{-Cl-TPP})(\text{H}_2\text{NPr}^t)_2(4c)$	8.03	7.94	7.62		$\text{CH}(\text{CH}_3)_2$ ; -1.66(12H, d) $\text{CH}(\text{CH}_3)_2$ ; -2.39(2H, br) $\text{NH}_2$ ; -6.55
$\text{Ru}(\text{TPP})(\text{H}_2\text{NCyhex})_2(5a)$	8.01( $\text{H}_a, \text{H}_b$ ) (16H, m)		7.63( $\text{H}_m, \text{H}_p$ ) (12H, m)		$\text{C}_6\text{H}_{11}$ ; 0.80(2H, br), 0.60(4H, m) -1.48(4H, m), -1.81(4H, m) -2.86(2H, m); $\text{NH}_2$ ; -6.46(4H, br)
$\text{Ru}(\text{TPP})(\text{H}_2\text{NCyhex})_2(5b)$	8.05	7.89	7.44	2.63	$\text{C}_6\text{H}_{11}$ ; 0.77(2H, m), 0.57(4H, m), -1.52(4H, m), -1.85(4H, m), -2.90(2H, m); $\text{NH}_2$ ; -6.51(4H, br)
$\text{Ru}(4\text{-Cl-TPP})(\text{H}_2\text{NCyhex})_2(5c)$	8.03	7.93	7.63		$\text{C}_6\text{H}_{11}$ ; 0.79(2H, m), 0.59(4H, m), -1.54(4H, m), -1.84(4H, m), -2.93(2H, m); $\text{NH}_2$ ; -6.59(4H, br)
$\text{Ru}(\text{TPP})(\text{HNMe}_2)_2(8a)$	8.09( $\text{H}_a, \text{H}_b$ ) (16H, m)		7.60( $\text{H}_m, \text{H}_p$ ) (12H, m)		$\text{CH}_2$ ; -2.23(2H, d),
$\text{Ru}(\text{TPP})(\text{HNEt}_2)_2(9a)$	8.02( $\text{H}_a, \text{H}_b$ ) (16H, m)		7.63( $\text{H}_m, \text{H}_p$ ) (12H, m)		$\text{CH}_2\text{CH}_3$ ; -1.56(12H, t), $\text{CH}_2\text{CH}_3$ ; -2.27, $\text{NH}_2$ ; -6.55
$\text{Ru}(\text{TPP})(\text{HNEt}_2)_2(9b)$	8.08	7.90	7.43	2.63	$\text{CH}_2\text{CH}_3$ ; -1.58(12H, t), $\text{CH}_2\text{CH}_3$ ; -2.30, $\text{NH}_2$ ; -6.50
$\text{Ru}(4\text{-Cl-TPP})(\text{HNEt}_2)_2(9c)$	8.60	7.93	7.62		$\text{CH}_2\text{CH}_3$ ; -1.57(12H, t), $\text{CH}_2\text{CH}_3$ ; -2.31, $\text{NH}_2$ ; -6.70

The "oxidation state marker" bands(OSMB) of bis(aliphatic amine) ruthenium( I ) have frequencies ranging from 997 to 999  $\text{cm}^{-1}$ . This is similar to those reported for bis(tert-butylamine) ruthenium( I ) and osmium( I ) complexes with TPP or 3,4,5-MeO-TPP<sup>2</sup>. It should be noted that the OSMB of the osmium( I ) complexes appear at slightly higher frequencies (1000-1001  $\text{cm}^{-1}$ ) than the ruthenium( I ) analogues. This seems interesting because the OSMB was assigned to a porphyrin deformation mode in the literature<sup>[11]</sup>. The phenomenon that a vibrational band is sensitive to the oxidation state of the metal center in a metalloporphyrin is rationalized in terms of changes in  $\pi$  back donation of electrons from the central metal atom to the porphyrin ring(i. e. the  $\text{M} \rightarrow \text{Por}$  back-bonding). It is believed that the  $\text{M} \rightarrow \text{Por}$  back-bonding leads to occupation of anti-bonding orbitals of the porphyrin ring by the  $d$  electrons of the metal center, resulting in weakening of bonds of the porphyrin skeleton and lowering of its vibration frequency<sup>1</sup>. Since the osmium( I ) complexes have stronger  $\text{M} \rightarrow \text{Por}$  back bonding than the ruthenium( I ) analogues, the former should be expected to show the OSMB at lower frequencies, which obviously contradicts our observation. However, we can also consider this from a different view. Generally, the frequency of the OSMB was found to in-

crease as the oxidation state of the metal center becomes higher. Since the  $M \rightarrow \text{Por}$  back-bonding draws electron density from the metal center to the porphyrin ring, the osmium(II) ion due to stronger  $\text{Os} \rightarrow \text{Por}$  back-bonding. This assumption can account for the observed difference in the  $^1\text{H}$  NMR spectra and the  $\text{NH}_2$  stretching frequencies between bis(aliphatic amine) ruthenium(II) and osmium(II) porphyrins. So the osmium(II) complexes should be expected to show the OSMB at higher frequencies, which is consistent with our observation.

#### 2.4 UV-Visible

The spectrum of a bis(aliphatic amine) ruthenium(II) porphyrin shows a five-band characteristic structure. For complexes (3a-9c), the five bands appear approximately at 265, 300, 330, 410(Soret) and 508 nm respectively. Besides these five bands, the  $\alpha$  bands usually appear at ca. 530 nm as a shoulder to the 508 nm band ( $\beta$  band). These unique characteristics can be used to distinguish the bis(aliphatic amine) ruthenium(II) porphyrins from other metalloporphyrins. Therefore, characterization of bis(aliphatic amine) ruthenium(II) porphyrins based on their UV-visible spectra is usually sufficiently convincing. The bis(aliphatic amine) osmium(II) porphyrins<sup>9</sup> also give unique UV-visible spectra, in which a four-band structure usually appears at ca. 300, 340, 407 (Soret) and 486 nm ( $\beta$  band) respectively.

Buchler and co-workers reported a "rule of bathochromism" for osmium(II) porphyrins which can be rationalized by the equatorial back-bonding( $M \rightarrow \text{Por}$ ) in those complexes. According to this rule, for the *meso*-tetraarylporphyrins, the stronger the  $M \rightarrow \text{Por}$  back-bonding, the larger the blue shift of the  $\beta$  band between bis(aliphatic amine) ruthenium(II) and osmium(II) porphyrins indicates that the osmium(II) complexes generally show considerably larger blue shifts of the  $\beta$  bands than the ruthenium(II) analogues. For example, the  $\beta$  bands of  $\text{Os}(\text{TTP})(\text{H}_2\text{NBu}')_2$  and  $\text{Ru}(\text{TTP})(\text{H}_2\text{NB}')_2$  appear at 487 and 506 nm respectively. This is consistent with the fact that there exists stronger  $M \rightarrow \text{Por}$  back-bonding in the osmium(II) porphyrins than in the ruthenium(II) analogues.

#### 2.5 X-ray structure of $\text{Ru}(\text{TTP})(\text{H}_2\text{NBu}')_2$

Fig. 2 shows the perspective drawing of 3b with atomic numbering scheme. Crystals of 3b consist of neutral molecules containing the Ru(II) ion N-chelated four pyrrole nitrogen atoms and two axial amine nitrogen atoms. The geometry of the  $\text{RuN}_6$  moiety can be best described as a distorted octahedron, which is elongated along the axial C<sub>2</sub> axis. The four equatorial pyrrole nitrogen atoms constitute a planar square at the center of which the ruthenium(II) ion is embedded. The N(3)-Ru-N(3)' axis is required to be linear by crystallographic symmetry, but it is not strictly perpendicular to

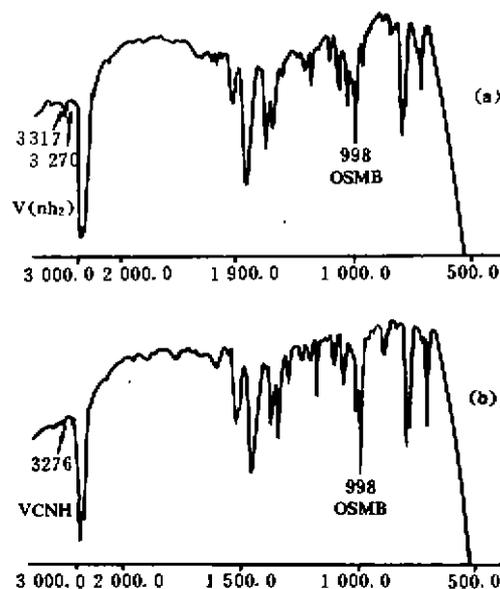


Fig. 1 IR spectra of (a)  $\text{Ru}(\text{TTP})(\text{H}_2\text{NMe})_2$  and (b)  $\text{Ru}(\text{TTP})(\text{HNMe}_2)_2$

the porphyrin ring plane probably due to the influence of the bulky tert-butyl group. The N(1)-Ru-N(3) and N(2)-Ru-N(3) angles [85.7(1)° and 82.3(2)° respectively] are different, which are smaller than those (both being 87.4(3)°) found for Rh(Etio)(HNMe<sub>2</sub>)<sub>2</sub>Cl · H<sub>2</sub>O<sup>2</sup>. This indicates a larger distortion in complex 3b. The axial Ru-N(amine) distance of 0.2175(3) nm is very similar to the Ru-N(pyridine) distances found in Ru(C6PBP)(CO)(py) (0.2173(6) nm)<sup>12</sup> and Ru(TPP)(CO)(py) (0.2193(4) nm), but the Rh<sup>3+</sup>-N(amine) distances (0.2090(8) nm) in Rh(Etio)(HNMe<sub>2</sub>)<sub>2</sub>Cl · H<sub>2</sub>O. The average Ru-N(pyrrole) distances average 0.2041(4) nm, which is very similar to those found in other ruthenium(II) porphyrins. For the axial tert-butylamine ligand, the N(3)-C-C angles and C-C-C angles give a mean value of 109.5(4)°, the C-C distances average 0.1527(7) nm, which is consistent with the C(sp<sup>3</sup>)-C(sp<sup>3</sup>) bond length. This indicates that Ru-N(3)-C(25) angles was equal to 131.7(2)°, which is considerably larger than the axial Rh-N-C angle (117(1)°) found in Rh(Etio)(HNMe<sub>2</sub>)<sub>2</sub>Cl · H<sub>2</sub>O. This difference could be ascribed to steric effect, since the tert-butyl group is much bulkier than the methyl group. In addition, the N(3)-C(25) distance (0.1505(4) nm) is slightly longer than the N-C distances (0.146(2) nm and 0.148(2) nm) in the axial dimethylamine ligand observed for Rh(Etio)(HNMe<sub>2</sub>)<sub>2</sub>Cl · H<sub>2</sub>O.

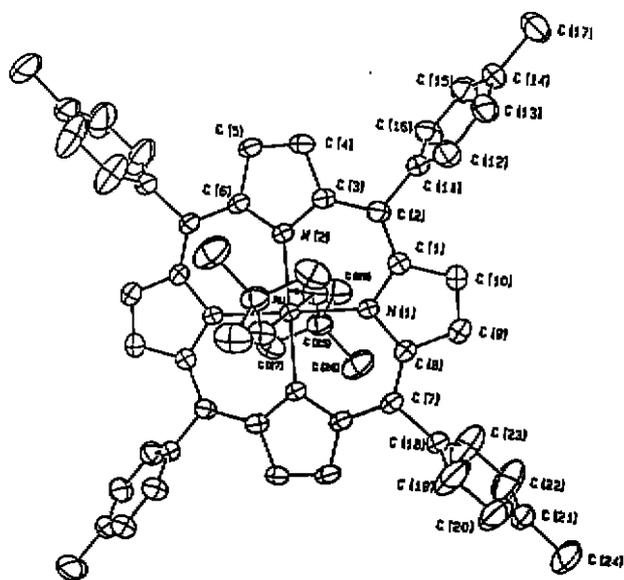


Fig. 2 Perspective drawing of Ru(TTP)(H<sub>2</sub>NBu')<sub>2</sub> (3b) with atomic numbering scheme

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