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Crystal of *meso*-*p*-tolyl-porphyrinato copper(II) Cu(tptp) and di-cation ion-pair complex $[H_4tptp]^{2+}[CF_3SO_3]_2^{-}$ formation during the reaction of $Cu(CF_3SO_3)_2$ with *meso*-*p*-tolyl-porphyrin in $CDCl_3$

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Abstract

In the NMR and ESR time-scale of this experiment, an attempt was made to prepare the copper sitting-atop (SAT) species $[Cu(H_2tptp)]^{2+}$ by the reaction of $Cu(CF_3SO_3)_2$ with *meso*-*p*-tolyl-porphyrin (H_2tptp) in $CDCl_3$; however, this led to the formation of *meso*-*p*-tolyl-porphyrinatocopper(II) Cu(tptp) and the protonated porphyrin $[H_4tptp]^{2+}[CF_3SO_3]_2^{-}$ (**2a**). Previous researchers might have misinterpreted the SAT $[Cu(H_2tpp)]^{2+}$ complex as being a single component instead of a mixture of $[H_4tpp]^{2+}[CF_3SO_3]_2^{-}$ (**1**) and Cu(tpp) for a similar reaction between 5,10,15,20-tetraphenylporphyrin H_2tpp and $Cu(CF_3SO_3)_2$ in CH_3CN. This work determines the crystal structure of Cu(tptp) and its hyperfine constants $a_{Cu} = 94.0$ G and $a_N = 15.8$ G using ESR. The crystal structure of $[H_4tptp]^{2+}[CH_3SO_3]_2^{-}$ (**3**) is reported and employed to simulate the groupings of $[H_4tptp]^{2+}$ and $CF_3SO_3^{-}$ in the di-cation ion-pair complex **2a**.

Keywords: Crystal structures; Cu^{2+} porphyrin complexes; Protonated porphyrins; SAT complexes; Electron spin resonance; Nuclear magnetic resonance

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1. Introduction

Previously, Inada et al. [1,2] reported on the formation of the ‘sitting-atop’ (SAT) complex $[Cu(H_2tpp)]^{2+}$ via the reaction of $Cu(CF_3SO_3)_2$ with 5,10,15,20-tetraphenylporphyrin (H_2tpp) in acetonitrile under a dry nitrogen atmosphere. We have not been successful in synthesizing the complex $[Cu(H_2tpp)]^{2+}$ by repeating the previous work [1] using the same solvent acetonitrile. According to their suggestion, the reaction of $Cu(CF_3SO_3)_2$ with H_2tpp in $CHCl_3$ in the absence of a strong base should be easily arrested at the formation of the SAT complex because of the low donor number (DN) of $CHCl_3$. It is known that the donor number of chloroform (DN = −) is less than that of acetonitrile (DN = 14.1) [3]. Hence, we did not investigate the reaction in the same solvent, i.e. chloroform. However, the SAT complex $[Cu(H_2tpp)]^{2+}$ is not detected in the reaction of $Cu(CF_3SO_3)_2$ with H_2tpp in $CDCl_3$ under a dry N_2 atmosphere; instead, a mixture (A) consisting of Cu(tpp) and $[H_4tpp]^{2+}[CF_3SO_3]_2^{-}$ (**1**) is observed. The proton NMR spectrum (^{1}H NMR) for the Cu(tpp) in mixture A in $CDCl_3$ shows a broad multiplet at 7.50 ppm for *meta*-hydrogens and at 7.64 ppm for *para*-hydrogens (see Fig. 1 and Table 1). The ^{1}H NMR values are quite close to those of 7.48 ppm (*meta*-H) and 7.62 ppm (*para*-H) for the compound Cu(tpp) reported by Godziela and Goff [4]. The ^{1}H NMR data for **1** in mixture A in $CDCl_3$ at 24°C (see Fig. 1 and Table 1) showed a singlet at 8.73 ppm (8H) for β-pyrrole protons, a doublet at 8.61 ppm (8H) for *ortho*- protons and a multiplet at 8.00 ppm (12H) for *meta*- and *para*- protons, and a singlet at −1.84 ppm (with 4H) for the N-H protons. Our interpretation of these data differs from that of Inada et al. [1,2]. Inada et al. [1,2] might have misinterpreted the mixture A as the SAT complex $[Cu(H_2tpp)]^{2+}$. The ^{1}H NMR data for their SAT complex in CD_3CN at room temperature (see Table 1) showed a singlet at 8.77 ppm (4H)

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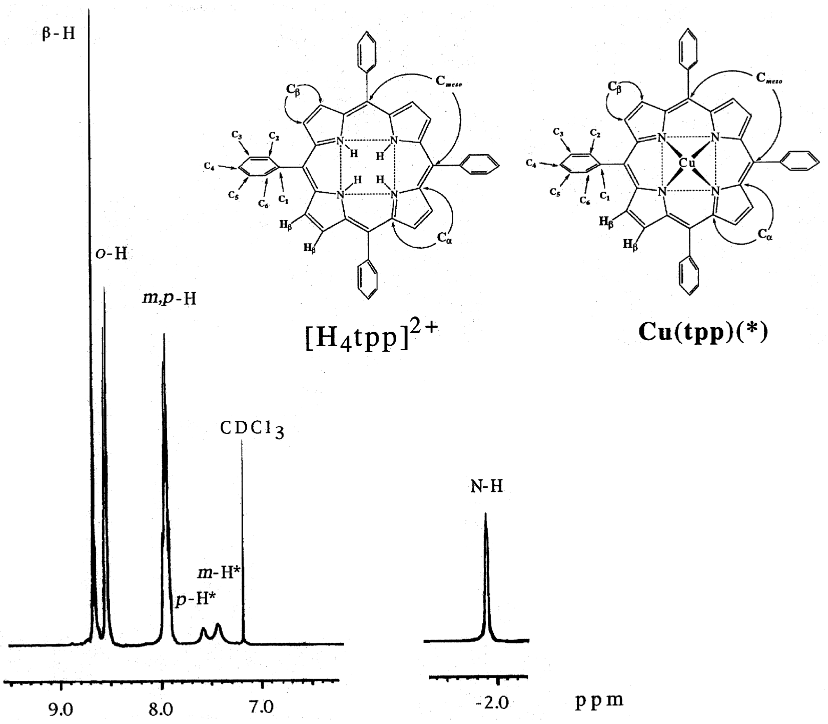


Fig. 1. 400.13 MHz ^{1}H NMR spectrum for the mixture A consists of Cu(tpp) and $[H_4tpp]^{2+}[CF_3SO_3]_2^-$ (**1**) in $CDCl_3$ at 24°C. Resonances due to Cu(tpp) are labeled with an asterisk (*).

Table 1
Proton chemical shifts (δ) for copper and protonated porphyrins in $CDCl_3$ at 24°C

Porphyrin	β-H	o-H	m-H		p-H	p-CH_3	NH	CH_3SO_3
H_2tptp	8.84	8.08 (7.8) [a]	7.54 (7.7)			2.69	−2.79	
$[H_4tptp]^{2+}[CH_3SO_3]_2^-$ (**3**) [b]	8.71	8.60 (7.6)	7.86 (7.2)			2.77	−2.22	2.65
$[H_4tptp]^{2+}[CF_3SO_3]_2^-$ (**2b**) [c]	8.68	8.50 (8)	7.83 (8)			2.78	−1.74	
Cu(tptp)[4]		7.48	7.30			2.52		
2a in mixture B [d]	8.66	8.48 (6.1)	7.62 (6.0)			2.77	−1.76	
Cu(tptp) in mixture B			7.30			2.53		
Free ionic $CH_3SO_3^-$ [19]								2.80
H_2tpp	8.89	8.25–8.27		7.74–7.81			−2.73	
$[H_4tpp]^{2+}[CF_3SO_3]_2^-$ (**1**) [c]	8.74	8.60 (7.2)		8.00 (m) [f]			−1.84	
Cu(tpp)[4]			7.48		7.62			
$[Cu(H_2tpp)]^{2+}$ in CD_3CN[1]	8.66(NH) 8.77(N)	8.10–8.12		7.31–7.50			−2.05	
1 in mixture A [e]	8.73	8.61 (6.9)		8.00 (m)			−1.84	
Cu(tpp) in mixture A			7.50		7.64			

[a] ^3J(H–H) coupling constant.
[b] Compound **3** was obtained by protonation of H_2tptp with CH_3SO_3H.
[c] Compound **2b** (or **1**) was obtained by protonation of H_2tptp (or H_2tpp) with CF_3SO_3H.
[d] Mixture B = **2a** + Cu(tptp).
[e] Mixture A = **1** + Cu(tpp).
[f] m = multiplet.

for the coordinating β-pyrrole protons, a doublet at 8.66 ppm (4H) for the uncoordinating β-pyrrole protons, one multiplet at 8.10–8.12 ppm for *ortho*-phenyl protons and another multiplet at 7.31–7.50 ppm for the *meta*- and *para*-phenyl protons, and a singlet at −2.05 ppm (2H) for pyrrole N-H [1,2]. If the doublet centered at 8.61 ppm is due to the long-range coupling of β-protons with a nitrogen-bonded proton of the same pyrrole ring, the ^4J(H–H) coupling constant should be less than 4 Hz [5,6]. However, the coupling constant of 6.9 Hz is reasonably assigned to adjacent ^{1}H–^{1}H coupling, ^3J(H–H). Furthermore, the doublet at 8.61 ppm remains unchanged on irradiating the NH proton at δ −1.84 ppm. In addition, the doublet for the *ortho-* protons becomes a singlet on irradiating the *meta-* and *para*-phenyl protons at 8.00 ppm. Thus the ^{1}H NMR spectral data support the composition of mixture A proposed by us and disagree with the SAT complex reported previously [1,2].

When the porphyrin group (tpp) was substituted using *meso-p*-tolyl-porphyrin (tptp), a mixture B consisting of *meso-p*-tolyl-porphyrinatocopper(II) Cu(tptp) and the protonated porphyrin $[H_4tptp]^{2+}[CF_3SO_3]_2^-$ (**2a**) was formed via the reaction of $Cu(CF_3SO_3)_2$ with H_2tptp in $CDCl_3$. Cu(tptp) was crystallized out in mixture B and its X-ray structure is reported here. Both Cu(tptp) and **2a** in mixture B were characterized using ESR, ^{1}H, ^{13}C and ^{19}F NMR methods.

2. Experimental

2.1. Preparation of mixture B consisting of Cu(tptp) and $[H_4tptp]^{2+}[CF_3SO_3]_2^-$ (2a)

H_2tptp (0.5 mmol) and $Cu(CF_3SO_3)_2$ (1 mmol, from TCI) were dissolved in $CDCl_3$ (15 cm^3, 99.8% from Aldrich) under a nitrogen atmosphere and the mixture was stirred at room temperature for 12 h. After the removal of unreacted $Cu(CF_3SO_3)_2$ through filtration, the filtrate consisting of Cu(tptp) and **2a** (i.e. the mixture B) was studied using NMR (Fig. 2) and ESR (Fig. 3) spectroscopy. Meanwhile, a blue–purple crystal of Cu(tptp) was grown by slow evaporation of $CDCl_3$ from the solution of mixture B.

2.2. Preparation of $[H_4tptp]^{2+}[CH_3SO_3]_2^-$ (3) and $[H_4tptp]^{2+}[CF_3SO_3]_2^-$ (2b)

Compound **3** (or **2b**) was obtained by protonation of H_2tptp (1 mmol) with 3 mmol of CH_3SO_3H (or CF_3SO_3H) in $CHCl_3$. Compound **3** was dissolved in $CHCl_3$ and layered with benzene. After 2 weeks, blue–green and equant shape crystals of complex **3** were obtained for single-crystal X-ray analysis. ^{1}H (or ^{13}C, or ^{19}F) NMR data for **2b** and **3** are shown in Table 1 (or Table 2), respectively.

2.3. NMR spectra

^{1}H and ^{13}C NMR spectra in $CDCl_3$ were recorded at 400.13 and 100.61 MHz, respectively, on a Bruker AM-400 spectrometer. The ^{19}F NMR spectra were measured in $CDCl_3$ at 376.76 or 282.40 MHz, on a Varian Mercury-400 or Bruker MSL-300 spectrometer. The reference peaks in ^{1}H NMR and ^{13}C NMR are relative to $CHCl_3$ at 7.24 ppm and the center line of $CDCl_3$ at 77.0 ppm, respectively. ^{19}F data are externally relative to $CFCl_3$.

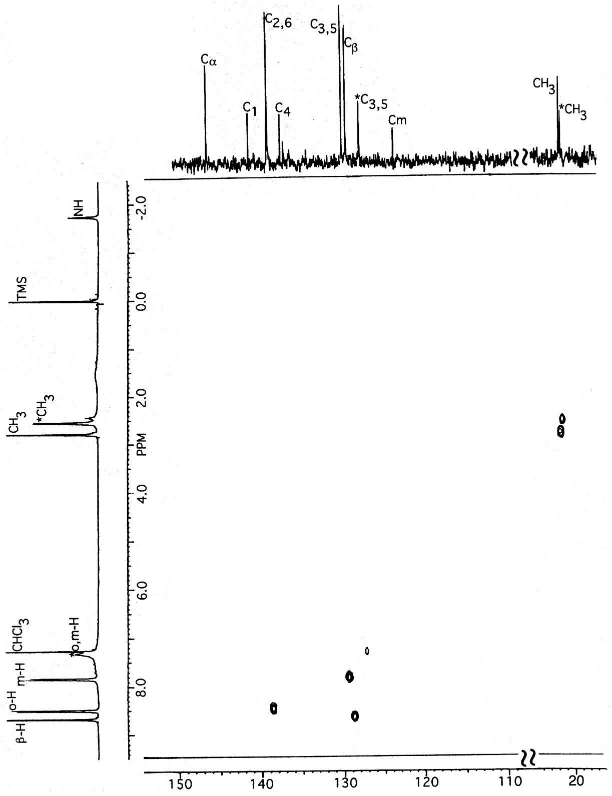


Fig. 2. The C-H COSY spectrum for the mixture B consists of Cu(tptp) and complex **2a** in $CDCl_3$ at 24°C. Resonances due to Cu(tptp) are labeled with an asterisk (*).

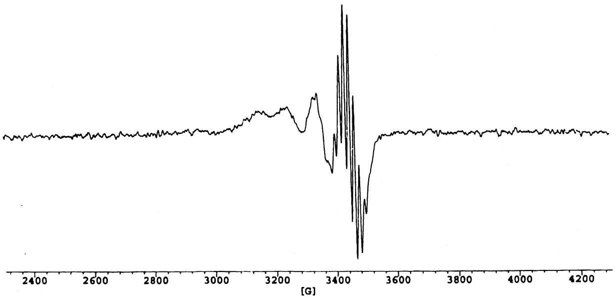


Fig. 3. The first derivative ESR spectrum for Cu(tptp) of mixture B in $CDCl_3$ at 24°C.

2.4. ESR spectra

ESR spectra were obtained with a Bruker EMX-10 X-band spectrometer system operating at 9.726 GHz with 100 kHz field modulation.

2.5. Crystallography

Table 3 presents crystal data and other information for Cu(tptp) and $[H_4tptp]^{2+}[CH_3SO_3]_2^-\cdot 2CHCl_3$ ($\mathbf{3}\cdot 2CHCl_3$). Measurements were taken on a Siemens SMART CCD diffractometer using monochromatic Mo Kα radiation

Table 2
^{13}C and ^{19}F NMR chemical shifts (δ) for $[H_4tptp]^{2+}[CF_3SO_3]_2^-$ (**2a**) and Cu(tptp) in mixture B in $CDCl_3$ at 24°C

Porphyrin	C_α	C_1	C_4	$C_{2,6}$	C_β	$C_{3,5}$	C_m	p-CH_3	CF_3SO_3	CH_3SO_3	CF_3SO_3 (^{19}F)
H_2tptp		139.4	137.4	134.6	131.1	127.4	120.1	21.5			
$[H_4tptp]^{2+}[CH_3SO_3]_2^-$ (**3**) [a]	145.8	141.0	136.9	139.0	128.5	129.4	123.1	21.6		38.0	
$[H_4tptp]^{2+}[CF_3SO_3]_2^-$ (**2b**) [a]	145.8	140.9	137.0	138.6	128.7	129.3	122.9	21.6	116.9 (320)		−81.1
2a in mixture B [b]	145.9	140.9	137.1	138.7	128.8	129.3	123.0	21.6	116.2 [c] (318) [d]		−81.2
Cu(tptp) in mixture B						127.1		21.4			
Free ionic $CF_3SO_3^-$ [19]									121.0 (321)		−78.7
Free ionic $CH_3SO_3^-$ [19]										41.3	

[a] The preparation of compounds **3** and **2b** is shown in Table 1.
[b] Mixture B = **2a** + Cu(tptp).
[c] Measured at −50°C.
[d] ^1J(C–F) coupling constant.

Table 3
Crystal data for Cu(tptp) and **3**·$2CHCl_3$

Empirical formula	$C_{48}H_{36}CuN_4$	$C_{52}H_{48}Cl_6N_4O_6S_2$
FW	732.3	1101.8
Space group	$P2_1/n$	$P4_32_12$
Crystal system	monoclinic	tetragonal
Crystal color, habit	black lamellar	blue equant
a (Å)	9.9271(4)	17.6633(3)
b (Å)	9.2107(4)	
c (Å)	20.9383(5)	16.8444(4)
β (°)	98.533(2)	
V (Å^3)	1893.3(6)	5255(1)
Z	2	4
D_{calc} (g cm^{-3})	1.285	1.392
μ(Mo Kα) (cm^{-1})	6.16	4.59
S	1.03	1.08
Crystal size (mm)	0.07×0.08×0.31	0.19×0.25×0.30
$2\theta_{max}$ (°)	56.0	55.8
T (K)	296	296
No. reflections measured	5636	19092
No. reflections observed ($I \geq 3.0\sigma(I)$)	1544	2916
R (%) [a]	4.57	5.27
R_w (%) [b]	4.95	5.55

[a] $R = [\Sigma||F_o| - |F_c||/\Sigma|F_o|]$.
[b] $R_w = [\Sigma w(||F_o| - |F_c||)^2/\Sigma w(|F_o|)^2]^{1/2}$; $w = A/(\sigma^2 F_o + BF_o^2)$.

Table 4
Selected bond distances (Å) and angles (°) for Cu(tptp) and **3**·$2CHCl_3$

Cu(tptp)	
Cu(1)–N(1)	2.000(4)
Cu(1)–N(2)	1.994(4)
Cu(1)–N(1)–C(2)	127.2(3)
Cu(1)–N(1)–C(5)	127.4(4)
Cu(1)–N(2)–C(7)	127.4(4)
Cu(1)–N(2)–C(10)	126.9(3)
N(1)–Cu(1)–N(1a)	180.0(1)
N(1)–Cu(1)–N(2)	90.0(2)
3·$2CHCl_3$	
S(1)–C(30)	1.748(8)
S(1)–O(1)	1.442(5)
S(1)–O(2)	1.433(5)
S(1)–O(3)	1.463(4)
N(2)–C(7)	1.390(7)
N(2)–C(10)	1.367(6)
N(1)–C(2)	1.390(7)
N(1)–C(5)	1.370(6)
C(30)–S(1)–O(1)	106.3(3)
C(30)–S(1)–O(2)	106.1(3)
C(30)–S(1)–O(3)	106.4(3)
O(1)–S(1)–O(2)	114.5(3)
O(1)–S(1)–O(3)	111.8(3)
O(2)–S(1)–O(3)	111.2(3)
C(7)–N(2)–C(10)	110.6(4)
N(2)–C(10)–C(11)	127.2(5)
N(2)–C(10)–C(9)	106.5(4)
N(2)–C(7)–C(6)	126.6(4)
N(2)–C(7)–C(8)	105.4(4)
C(7)–C(6)–C(5)	123.3(5)
C(7)–C(6)–C(16)	120.4(4)

($\lambda = 0.71073$ Å). Next, absorption corrections were based on 3191 (or 13717) symmetry-equivalent reflections using the SHELXTL-PC program package with $T_{min} = 0.481$, $T_{max} = 0.962$ or $T_{min} = 0.786$, $T_{max} = 0.942$ for Cu(tptp) and **3**·$2CHCl_3$, respectively. The structures were solved by direct methods (SHELXTL PLUS) and refined using full-matrix least-squares. All non-hydrogen atoms were refined with anisotropic thermal parameters, whereas all hydrogen-atom positions were located on a difference map (or were calculated using a riding model) and included in the structure factor calculation for Cu(tptp) and **3**·$2CHCl_3$. Table 4 outlines selected bond distances and angles for both complexes.

3. Results and discussion

3.1. Molecular structure of Cu(tptp)

Crystals of Cu(tptp) were obtained by slow evaporation of $CDCl_3$ from the mixture B. Fig. 4(a) illustrates the skeletal framework of complex Cu(tptp), with $P2_1/n$ symmetry. This

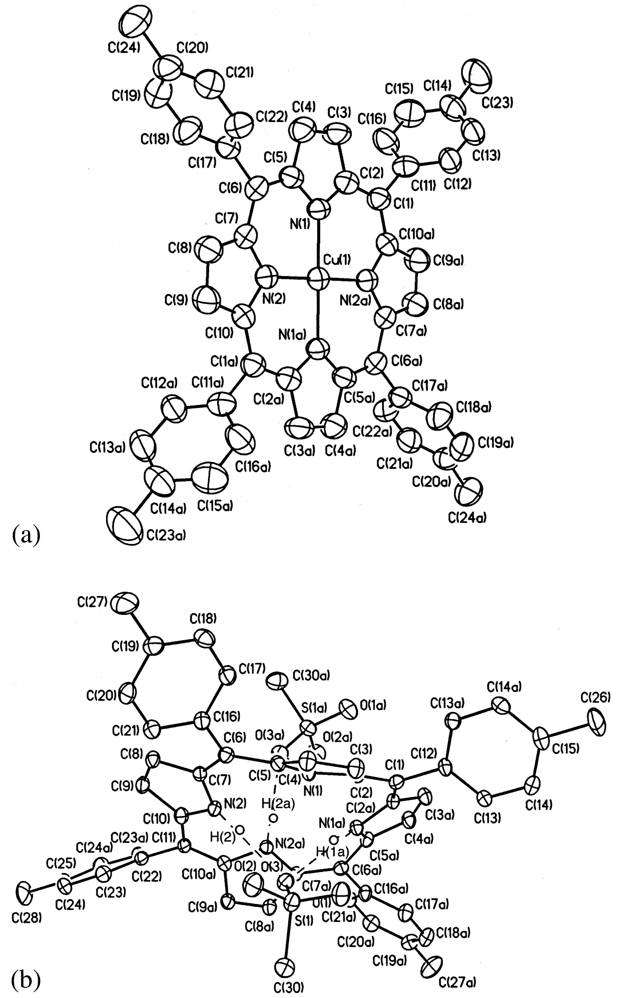


Fig. 4. Molecular configuration and atom-labeling scheme for (a) Cu(tptp) and (b) **3**·2CHCl$_3$, with ellipsoids drawn at 20% probability. The refined positions of the hydrogen atoms bonded to the pyrrole nitrogens are shown for **3**·2CHCl$_3$; all other hydrogen atoms for both compounds and solvents C(29)H(29a)Cl(1)Cl(2)Cl(3) for **3**·2CHCl$_3$ are omitted for clarity.

structure has a four-coordinate copper with four nitrogen atoms of the porphyrinato group. Bond distances are Cu(1)–N(1) = 2.000(4) and Cu(1)–N(2) = 1.994(4) Å. The $C_{20}N_4$ core is essentially planar. The Cu(1) sits at the inversion center, so the angles N(1)–Cu(1)–N(1a) and N(2)–Cu(1)–N(2a) are 180.0(1)°. The dihedral angles between the mean plane of the skeleton ($C_{20}N_4$) and the planes of the phenyl groups are 68.4° (C(14)) and 87.5° (C(20)).

The radius of the central hole ($C_{t'}\cdots N$, the distance from the geometrical center $C_{t'}$ of the mean plane of the 24-atom core to the porphyrinato-core N atoms) is 1.997 Å (or $\sim$2.00 Å) which is similar to the value of $\sim$2.01 Å suggested by Collins and Hoard [7]. Hence, the copper(II) atom is bonded and centered in a porphyrinato core ($C_{20}N_4$) with 'radial strain' being minimized. The average distance of 1.997 Å in Cu(tptp) is comparable with the observed Cu–N distances of 1.981 Å in Cu(tpp) [8], 1.998 Å in Cu(oep) (H_2oep = octaethylporphyrin) [9], 1.997 Å in Cu(oetpp) (H_2oetpp = octaethyltetraphenylporphyrin) [10], 1.984 Å in CutTEtpp (H_2tTEtpp = 2,3,12,13-tetraethyl-5,10,15,20-tetraphenylporphyrin), 1.975 Å in CucTEtpp (H_2cTEtpp = 2,3,7,8-tetraethyl-5,10,15,20-tetraphenylporphyrin) and 1.980 Å in CuHEtpp (H_2HEtpp = 2,3,7,8,12,13-hexaethyl-5,10,15,20-tetraphenylporphyrin) [11]. Interestingly, the structure of Cu(tptp) is also isomorphic to that of *meso-p*-tolyl-porphyrinatozinc(II) Zn(tptp) [12].

3.2. The crystal structure of $[H_4tptp]^{2+}[CH_3SO_3]_2^-\cdot 2CHCl_3$ *(**3**·2CHCl$_3$)*

Each porphyrin nucleus is associated with two complex anions $CH_3SO_3^-$ (Fig. 4(b)). First, the contacts between the porphyrin nitrogen atoms N(2) (or N(1a)) and O(3) of the anion are 2.866 (or 2.927 Å), and these are short enough to permit hydrogen bonding of the type N–H···O. The mean N···O distance in these types of hydrogen bonds is calculated as 2.90 Å. Second, the H···O distances (based on the refined hydrogen atom positions) are 1.94 Å for O(3)···H(2) and 1.98 Å for O(3)···H(la). The mean H···O distance in hydrogen bonds is calculated as 2.60 Å. Third, the values of N–H···O angles are close to linear values with 171.5° for N(2)–H(2)···O(3) and 163.2° for N(la)–H(1a)···O(3). All these results indicate that two triflate anions are hydrogen bonded to the pyrrole hydrogens in a monodentate bridging fashion, with one O(3) (or O(3a)) bonded to two opposite N-H protons, i.e. H(2) and H(la) (or H(1) and H(2a)), on the same face of the porphyrin [13]. The four phenyl group–porphyrin dihedral angles in **3**·2CHCl$_3$ are 35.4° (C(15)), and 31.4° (C(19a)), 40.0° (C(25)) and 31.4° (C(l9)). These dihedral angles are quite acute, averaging only 34.6°. They are slightly larger than the average 27° in $[H_2tpp]$-$[ClO_4]_2$ but smaller than 63° (or 75°) in $[H_4tmp][ClO_4]_2$ [14]. The distortion ($C_{20}N_4$) of **3**·2CHCl$_3$ is saddle shaped. Fig. 5 depicts the displacement (in Å) of each atom of the

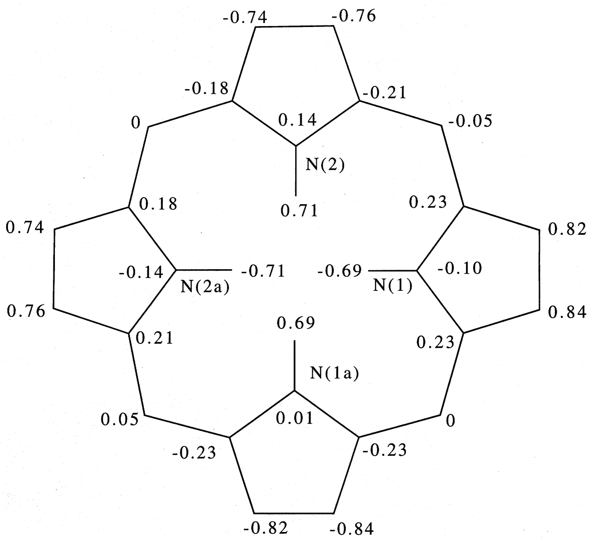
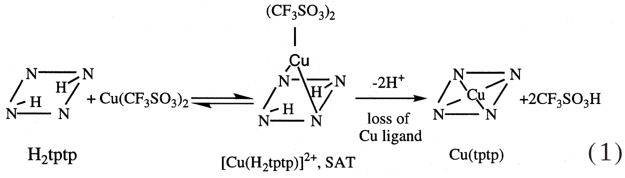


Fig. 5. Schematic diagram of the porphyrin core ($C_{20}N_4$) and four inner hydrogen atoms of **3**·2CHCl$_3$ in which each atom symbol is replaced by a number showing the displacement (in Å) of that atom from the mean plane of the porphyrin ($C_{20}N_4$) with a typical esd of 0.003 Å.

porphyrin from the porphyrin mean plane ($C_{20}N_4$) as well as displacements of the four central hydrogen atoms. The pyrrole NH protons are alternately displaced above and below the 24-atom mean plane by −0.69 Å for H(1), 0.71 Å for H(2), −0.71 Å for H(2a), and 0.69 Å for H(1a). The out-of-plane displacements of the inner hydrogen atoms help to relieve steric strain [15]. The groupings of $[H_4tptp]^{2+}$ and $CH_3SO_3^-$ of **3** in $CDC1_3$ retain their basic properties when bonded together by hydrogen bonds called an ion-pair. Although the structures of Cu(tpp) [8], Cu(oep) [9], Cu(oetpp) [10], CutTEtpp [11], CucTEtpp [11], CuHEtpp [11] and the di-cation of tetraarylporphyrin species $[H_4por](ClO_4)_2$ [14], $[H_4por](TFA)_2$ (TFA = trifluoroacetate) [15], and $[H_4por](OAc)_{3/2}(TFA)_{1/2}$ [15] (por = tpp, oep, oetpp) have already been published, Cu(tptp) and **3** are two new crystal structures with different porphyrin (tptp) and counter ion ($CH_3SO_3^-$).

3.3. NMR spectra of Cu(tptp) and $[H_4tptp]^{2+}[CF_3SO_3]_2^-$ (2a) in mixture B

The net reaction of $Cu(CF_3SO_3)_2$ with H_2tptp in $CDCl_3$ is known by Eqs. (1) and (2), where **2a** is a di-cation ion-pair complex [16].



(1)

$$H_2tptp + 2CF_3SO_3H \rightarrow \underset{(\mathbf{2a})}{[H_4tptp]^{2+}[CF_3SO_3]_2^-} \quad (2)$$

The SAT complex $[Cu(H_2tptp)]^{2+}$ has been proposed as an intermediate. Loss of the N-H protons and $CF_3SO_3^-$ ligand produces Cu(tptp) and CF_3SO_3H. Finally, protonation of the remaining H_2tptp produces the ion-pair complex **2a** between the *meso-p*-tolyl-porphyrin di-cation $[H_4tptp]^{2+}$ and triflate ($CF_3SO_3^-$). Only Cu(tptp) and complex **2a** are observed by ^1H NMR in our system. The ^1H NMR spectrum for Cu(tptp) in mixture B in $CDCl_3$ (see Table 1 and Fig. 2) shows *m*-phenyl signals at 7.30 ppm and methyl protons at 2.53 ppm. These values are quite close to the corresponding signals at 7.30 ppm for the *m*-phenyl protons and 2.52 ppm for the methyl protons in complex Cu(tptp) reported by Godziela and Goff [4]. The N-H signals are downfield shifted by ~1.03 ppm from −2.79 (for H_2tptp) to −1.76 ppm for complex **2a** by protonation. The similar downfield shift due to protonation is also reflected by observing a 4.2–4.7 ppm downfield shift of N-H at −2.588 and −2.672 ppm for H_2Cttp (**4**) (2-aza-21-carba-5,10,15,20-tetra-*p*-tolylporphyrin), compared to 2.034, 1.877 and 1.612 ppm for $[\mathbf{4}\text{-}H_2]^{2+}$ [17]. In complex **2a**, the integrated peak areas are 8:8:8:4 for the β-pyrrole:*o*-phenyl:*m*-phenyl:N-H protons, respectively. Owing to the paramagnetic copper(II) ion in Cu(tptp), the ^{13}C NMR spectrum of Cu(tptp) (see Fig. 2 and Table 2) shows only two peaks at 127.1 ($C_{3,5}$) and 21.4 ppm (p-CH_3). The ^{13}C, ^{19}F and ^1H NMR data for **2a** in mixture B shown in Tables 1 and 2 are consistent with those of $[H_4tptp]^{2+}[CF_3SO_3]_2^-$ (**2b**) obtained by protonation of H_2tptp using CF_3SO_3H. Notably, these consistencies suggest that complex **2a** is **2b**. Furthermore, the ^{13}C (or ^{19}F) resonance of $CF_3SO_3^-$ for compound **2a** at $\delta = 116.2$ ppm with ^1J(C–F) coupling constant 318 Hz (or −81.2 ppm) is different from that of free ionic $CF_3SO_3^-$, i.e. $Bu_4N^+CF_3SO_3^-$, with $\delta = 121.0$ and ^1J(C–F) = 321 Hz (or −78.7 ppm) at room temperature [18,19]. Hence, the mutual geometric arrangement of the $[H_4tptp]^{2+}$, $CF_3SO_3^-$ and the solvent $CDCl_3$ in complex **2a** is explained as ion pairs. The intramolecular electric fields in the ion-pair complex **2a** cause considerable upfield shifts of −4.8 ppm (from 121.0 to 116.2 ppm) for the triflate carbon and about −2.5 ppm (from −78.7 to −81.2 ppm) for the ^{19}F resonance in the same complex [20]. When the CF_3^- of **2a** was replaced by a CH_3^- group, the complex **2a** became $[H_4tptp]^{2+}[CH_3SO_3]_2^-$ (**3**). In the absence of the crystal structure of **2a**, the close resemblance of ^{13}C and ^1H data (shown in Tables 1 and 2) for the di-cation $[H_4tptp]^{2+}$ of **2b** and **3** indicates a similar structure for these two complexes. Two $CH_3SO_3^-$ anions axial and hydrogen-bonded to the pyrrole hydrogen in **3** (shown in Fig. 4(b)) suggest that two $CF_3SO_3^-$ might be located on the axial position of the porphyrin ring ($C_{20}N_4$) of **2a**. The upfield shift of about −3.3 ppm (from 41.3 (obtained from free $CH_3SO_3^-$, i.e. $Cs^+CH_3SO_3^-$) [19] to 38.0 ppm) for carbon of CH_3SO_3 in **3** is due to the same electric field as in complex **2a**. Nevertheless, the ^1H chemical shift of CH_3SO_3 in **3** experienced an upfield shift of −0.15 ppm from 2.8 (obtained from free $CH_3SO_3^-$) [19] to 2.65 ppm, being controlled by the ring current effect.

3.4. ESR spectra for Cu(tptp) in mixture B

Cu(tptp) are paramagnetic because of the d^9 configuration of Cu(II). The unpaired electron resides in the $d_{x^2-y^2}$ orbital, which leads to characteristic EPR spectra for Cu(tptp): four peaks due to the nuclear spin ($I = 3/2$) of the Cu and superhyperfine interaction with the four nitrogens ($I = 1$) of the porphyrin. Cu(tptp) in $CDCl_3$ exhibits a typical Cu(II) porphyrin EPR spectrum as shown in Fig. 3. The experimental spectrum yields $a_{Cu} = 94.0$ G and four nitrogens with $a_N = 15.8$ G. These data are similar to those reported, $a_{Cu} = 90.5$ G and $a_N = 15.8$ G for Cu(tpp) [21], $a_{Cu} = 90$ G and $a_N = 15$ G for Cu(oep) [9], or $a_{Cu} = 86.5$ G and $a_N = 14.4$ G for Cu(oetpp) [10].

4. Conclusions

Inada postulated that in the reaction of Cu(II) with H_2tpp in CH_3CN, an intermediate complex species forms,

$[Cu(H_2tpp)]^{2+}$, in which the metal stays above the tetra-aza plane. We have repeated the reaction using a slightly different porphyrin (H_2tptp) in less basic solvent $CDCl_3$, and have crystallized from the solution the Cu(tptp) and the doubly protonated ligand $[H_4tptp]^{2+}[CF_3SO_3]^-$ (**2a**), which demonstrates that the H_2tptp acts simultaneously as Cu^{2+} complexation and as a proton receptor.

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