Highly Ruffled Manganese(III) Complexes of *meso*-Tetra(*tert*-butyl)porphyrin

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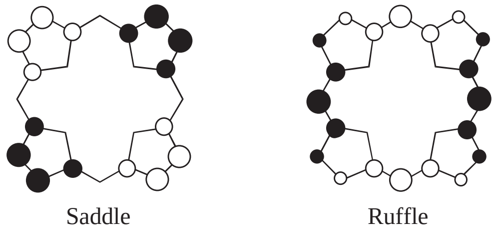
Extraordinarily ruffled acetato[5,10,15,20-tetra(*tert*-butyl)porphinato]manganese(III) has been prepared. The ^{1}H NMR spectra have revealed that the inversion barrier of the porphyrin ring exceeds 66 kJ mol^{-1} and that the spin densities are quite different between the diastereotopic β-carbon atoms.

Nonplanar porphyrin rings have attracted much attention because they serve unique ligand field to the central metal ions and modulate the physicochemical properties of the complexes such as spin state, electron configuration, redox potential, etc.[1] Among several deformation modes, saddled and ruffled porphyrin rings shown in Scheme 1 are frequently found not only in the model systems but also in naturally occurring heme proteins.[2,3] Typical examples showing the saddled and ruffled conformations are Ni(OETPP) and Ni(T^{i}PrP), where the β and *meso* carbon atoms deviate from the mean porphyrin plane by 1.24 and 0.74 Å, respectively.[4–6] Introduction of paramagnetic metal ions into these porphyrins could give the complexes whose electronic structures are quite different from those of typical planar complexes. In fact, we have shown on the basis of the characteristic NMR spectra and other spectroscopic and magnetic data that highly deformed Fe(OETPP)(THF)$_2^+$ and Fe(T^{i}PrP)(THF)$_2^+$ exhibit an essentially pure intermediate-spin ($S = 3/2$) state.[7] It is then expected that the NMR spectra of extraordinarily ruffled complex M(T^{t}BuP)$^{n-2}$ with paramagnetic metal ion(M^{n+}) should exhibit unique electronic structures due to the specific metal–porphyrin orbital interactions. Actually however, only one example, Cu(T^{t}BuP), classified into this category has been reported though the spectroscopic studies except UV–vis have not been carried out.[5,8,9] Here, we report the first example of the NMR study of paramagnetic Mn(T^{t}BuP)(OAc)(**1**) and compare the results with those of Mn(T^{i}PrP)(OAc)(**2**) and Mn(TPP)(OAc)(**3**).

Mn(T^{t}BuP)Cl was prepared by the addition of methanol solution of MnCl$_2$ into the refluxing chloroform solution of (T^{t}BuP)H$_2$ under aerobic condition. Because of the low solubility of Mn(T^{t}BuP)Cl, we have replaced the chloride with acetate by washing the CH$_2$Cl$_2$ solution with 10% aq CH$_3$COONa. Crude **1** was purified by chromatography on basic and then on neutral alumina (both activity IV). The green band obtained by the elution with CHCl$_3$ was washed with 10% aq CH$_3$COONa. The organic layer, after being dried over CH$_3$COONa, was evaporated to give pure **1**. UV–vis (CH$_2$Cl$_2$, λ/nm): 407, 434, 493, 566, 625, 664. ^{1}H NMR (CD$_2$Cl$_2$, 298 K, δ/ppm): −28.3 (4H, Py-H), −2.9 (4H, Py-H), 3.2 (36H, *tert*-butyl), 15.4 (broad, 3H, ligand). FAB-MS: $m/z = 589$, Mn(T^{t}BuP)$^+$. Effective magnetic moment (CH$_2$Cl$_2$, 298 K): 4.7 μ_B.



Scheme 1. The saddled and ruffled conformations. Filled and open circles indicate displacement above and below the porphyrin ring.

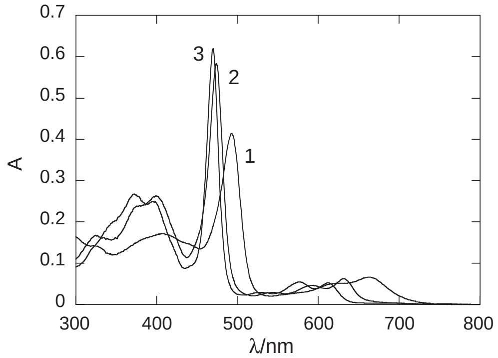


Figure 1. UV–vis spectra of **1**, **2**, and **3** taken in CH$_2$Cl$_2$ solution at ambient temperature.

Figure 1 shows the UV–vis spectrum of **1**–**3** taken in CH$_2$Cl$_2$ solution at ambient temperature. Each band showed a red shift on going from **3** to **2** and then to **1**, indicating the increase in nonplanarity of the porphyrin ring. Figure 2a shows the ^{1}H NMR spectrum of **1** taken in CD$_2$Cl$_2$ at 298 K. Two signals at δ −2.9 and −28.3 ppm were unambiguously assigned to the pyrrole signals on the basis of the ^{2}H NMR spectrum of the corresponding pyrrole-d_8 complex shown in the inset. The existence of the two pyrrole signals clearly indicates that the ring inversion of the ruffled porphyrin ring is slow on the ^{1}H NMR time scale. Figure 2b shows the ^{1}H NMR spectrum of **2** taken under the same condition. In contrast to the case of **1**, **2** exhibited a single pyrrole signal at −20.5 ppm, suggesting that the ring inversion is fast at 298 K. Figure 3 shows the Curie plots of the pyrrole-d signals of deuterated **1**–**3** taken in toluene (**1**) or in CH$_2$Cl$_2$ (**2** and **3**) solutions. All the complexes showed linear lines with correlation coefficients of 0.997–0.999. The ^{2}H NMR spectra of **1** were then taken at higher temperatures to determine the inversion barrier. No coalescence phenomenon was observed, however, even at 363 K, which indicates that the activation free energy for inversion is higher than 66 kJ mol^{-1} at 363 K.[10] By contrast, **2** maintained a single pyrrole signal even at 173 K though the signal broadened to a great extent; the half-height width at 173 K reached as much as 1100 Hz. The broad pyrrole signal in ruffled **2** could not necessarily be ascribed to the slow inversion because planar **3** also showed a broad

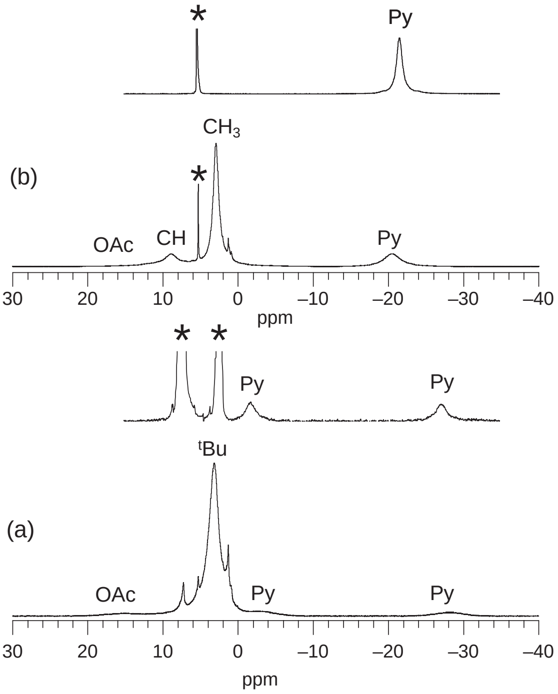


Figure 2. ^{1}H NMR spectra (CD_2Cl_2, 298 K) of (a) **1** and (b) **2**. ^{2}H NMR spectra of the corresponding pyrrole-d_8 complexes are given in the inset of (a) and (b). Toluene was used as a solvent for **1**-pyrrole-d_8. The asterisks * indicate the solvent peaks.

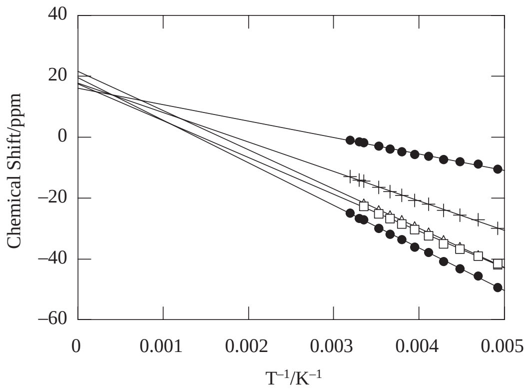


Figure 3. Curie plots of the pyrrole-d signals of **1** (●) taken in toluene solution, and those of **2** (△) and **3** (□) taken in CH_2Cl_2 solution. Averaged pyrrole-d shifts in **1** are given by (+).

signal at 173 K; the half-height width was 1300 Hz.

The chemical shifts of the pyrrole signals of **1**–**3** have been compared. The average positions of the two pyrrole signals in **1** is −15.6 ppm, which is more downfield than the pyrrole signals of **2** and **3**; they appeared at −20.5 and −22.7 ppm, respectively. Since the upfield shift of the pyrrole signal in high-spin ($S = 2$) Mn(III) complexes is caused by the Mn d_π and porphyrin $3e_g$ interaction,[11,12] the downfield pyrrole shift in **1** should be ascribed to the less effective interaction caused by the extraordinarily ruffled porphyrin core. Another notable feature in the ^{1}H NMR spectrum of **1** is a large difference in the isotropic shifts between the diastereotopic pyrrole protons; they are −11.9 and −37.3 ppm.[13] If we assume that the dipolar contribution to the isotropic shift is rather small in high-spin Mn(III) complexes,[12] the observed isotropic shift approaches to the contact shift. Thus, the ratio of the π spin densities between two diastereotopic β-carbon atoms should be close to 3:1.[14] The result suggests that the spin distribution on the porphyrin ring is greatly perturbed by the porphyrin deformation.

In conclusion, we have revealed that the extraordinarily deformed porphyrin ring affects the spin delocalization from the metal to the porphyrin ring, leading to the asymmetric spin distribution on the peripheral carbon atoms.

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