# Modulation of axial coordination in N-confused porphyrin–antimony(v) dibromide complex by proton stimulus

Jia-Cheng Liu,[a] Tomoya Ishizuka,[a] Atsuhiro Osuka[a] and Hiroyuki Furuta*[abc]

[a] Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan
[b] Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 812-8581, Japan. E-mail: hfuruta@cstf.kyushu-u.ac.jp
[c] PRESTO, Japan Science and Technology Corporation (JST), Japan

The change of the axial bond length in the antimony(v) N-confused tetraphenylporphyrin dibromide complex was demonstrated by protonation and confirmed from X-ray single crystal analyses.

N-Confused porphyrins (NCPs), the isomers of porphyrins by the *confusion* of the pyrrole rings, exhibit unusual physical and chemical properties, which greatly differ from those of normal porphyrins.[1–3] In particular, NCPs possess a peripheral nitrogen that could be used as an inlet or outlet for the flow of *molecular communication*. An external stimulus, such as protonation or metal coordination, at this position may cause a change in the electronic states of the NCP or the metal largely because it is directly related to the intrinsic properties of NH tautomerism[4] and multivalency[5] of NCP ligands, either dianionic (HNCP[2−]) or trianionic (NCP[3−]), while normal porphyrins exist only as dianionic (P[2−]). These anionic modes of NCP depend on a number of factors including the central metal ion and its oxidation state.[6] To clarify such effects, we have examined an antimony NCP complex because of its axial coordination, good stability and the facile comparison to normal porphyrins.[7] In this communication, we report the syntheses and crystal structures of a neutral and protonated antimony(v) N-confused tetraphenylporphyrin (NCTPP) complex bearing two bromide atoms as axial ligands. For reference, the X-ray crystal structure of antimony(v) tetraphenylporphyrin (TPP) complex is also presented herein.†



NCP[2−]          NCP[3−]          P[2−]
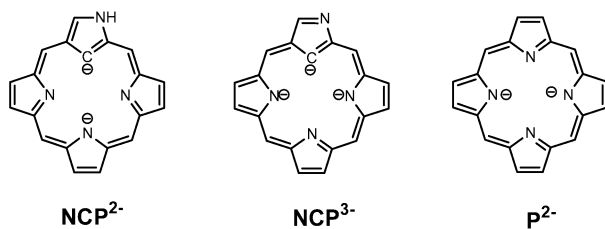
NCTPP was metallated with antimony by using a modification of the previous method.[8] A dried pyridine solution of free base NCTPP and 10 equiv of antimony(iii) bromide was stirred for four days under argon, then evaporated to dryness *in vacuo*. The reaction mixture was filtered through Celite with dried CH$_2$Cl$_2$, purified by silica-gel column chromatography. The products [Sb(HNCTPP)Br$_2$]$^+$Br$^-$ (**1**) in fractions of CH$_2$Cl$_2$–THF were collected, dried under vacuum, recrystallized from CH$_2$Cl$_2$–hexane to give crystals, in 42% yield. When a slight excess of pyridine was added to a CH$_2$Cl$_2$ solution of **1**, the complex Sb(NCTPP)Br$_2$ (**2**) was quantitatively obtained. On the other hand, the corresponding TPP complex, [Sb(TPP)Br$_2$]$^+$ Br$_3^-$ (**3**), was synthesized from the oxidation of [Sb(TPP)]Br with *ca.* 2 equiv of pyridinium tribromide in CH$_2$Cl$_2$ at room temperature in 76% yield.[7] (Scheme 1)

The $^1$H NMR spectrum of **1** in CDCl$_3$ showed a broad peak ascribable to the outer NH resonance at 16.20 ppm, the position of which is downfield-shifted compared to those in the Ni$^{II}$ complex (10.03 ppm),[2] and Pd$^{II}$(NCTPP) (9.95 ppm),[9] probably due to hydrogen bonding with the Br$^-$ anions, but the neutral

complex **2** was lacking the outer NH signal. The outer α-CH proton signals in the *confused* pyrrolic unit appeared at 10.09 and 10.07 ppm for **1** and **2**, respectively, suggesting the proton charge is delocalized in **1**. In addition, the absence of any inner protons (NH or CH) signals in **1**, **2** and **3** indicated that antimony(v) was equatorially four-coordinated by the NCTPP and TPP core.

Single crystal structure determinations revealed that the complex **1** consists of [Sb(HNCTPP)Br$_2$]$^+$ cations and uncoordinated Br$^-$ anions, while **2**, Sb(NCTPP)Br$_2$, is a neutral molecule having no counter ion (Fig. 1a,b) Complex **3** should be formulated as [Sb(TPP)Br$_2$]$^+$ Br$_3^-$, since it consists of two crystallographically distinct [Sb(TPP)Br$_2$]$^+$ cations and two free Br$_3^-$ anions (Fig. 1c) The antimony atom lies in the mean plane of the porphyrin core defined by twenty C and four N atoms within the deviation of 0.086 Å for **1**, 0.042 Å for **2** and 0.194 Å for **3**, respectively. It is interesting to note that in **1**, there is a distance of 3.771(9) Å between the uncoordinated Br$^-$ anion and the protonated outer-N of NCTPP, which suggests a weak N–H⋯Br$^-$ hydrogen bonding interaction.[10] But in **3**, the shortest separation of the peripheral β-carbon and center Br atom in uncoordinated Br$_3$ is 3.90(1) Å, indicating the absence of hydrogen bonding interactions. In each compound, the central antimony(v) ion shows an elongated octahedral coordination with four donor atoms (N or C) originating from the porphyrin core and two long axial Br atoms. The equatorial planes were formed by three nitrogen atoms and a carbon atom with Sb–N and Sb–C average distances of 2.06(1) Å for **1** and 2.08(1) Å for **2**, respectively, and by four nitrogen atoms with Sb–N distances in the range of 2.074(8)–2.094(8) Å for **3**.

Interestingly, the bond distances between the central Sb and axial Br of three complexes differ distinctly, 2.533(2) Å for **1**, 2.565(2) Å for **2** and 2.518(1) Å for **3** (average), respectively. In general, the higher charge the metal cation has, the more strongly it interacts with coordinating anion, and the shorter the bond distance. The formal counting of the Sb(v) charge in the porphyrin core without axial ligands gives +3 in **3** and +2 in **2**, which is compatible with the result of Sb–Br bond lengths observed. The intermediate length of protonated NCP complex **1**, thus, suggests a partial proton charge distribution to the central Sb through the resonance form **II** shown in Scheme 2.

The control of the electronic properties of the metals in NCP by protonation,[11] resulting the change of axial bond length, is of
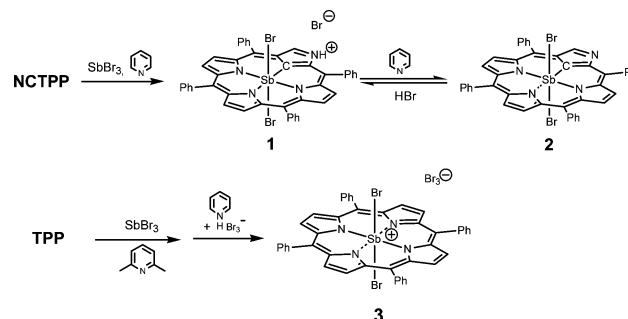


**Scheme 1** Syntheses of antimony(v) porphyrin complexes (**1–3**).
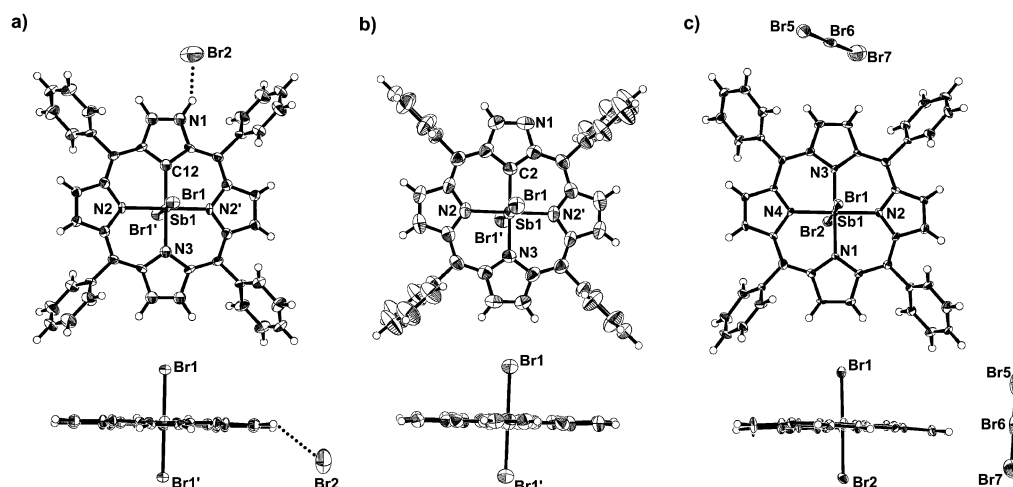
**Fig. 1** X-Ray structures of a) **1**, b) **2** and c) **3**. Due to the crystallographic pseudo-symmetry of **1** and **2**, a quarter and a half of the molecules appear as an asymmetric unit, respectively. Phenyl groups were omitted for clarity in side views. Selected bond lengths (Å) for **1**: Sb1–N2, 2.07(1); Sb1–N3, 2.05(1); Sb1–Br1, 2.533(2); N1–Br2, 3.766 (6); for **2**: Sb1–N2, 2.08(1); Sb1–N3, 2.073(7); Sb1–Br, 2.565(2); and for **3**: Sb1–N1, 2.079(8); Sb1–N2, 2.076(8); Sb1–N3, 2.074(8); Sb1–N4, 2.081(8); Sb1–Br1, 2.522(1); Sb1–Br2, 2.510(1). Dotted lines indicate the weak hydrogen bonding interactions in a).
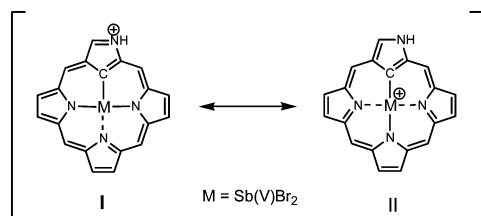


**Scheme 2** Two resonance forms (**I**, **II**) of the [Sb(HNCTPP)Br$_2$]$^+$ core.

interest and such fine-tuning of the metal coordination would be useful in designing axial ligand bridged NCP oligomers aiming for a molecular wire.[8]

The electronic spectral changes of **1** upon addition of pyridine in CH$_2$Cl$_2$ are shown in Fig. 2.[12] The Soret band at 464 nm for **1** was finally 8 nm blue-shifted with decreasing intensity. The longest wavelength Q-band of **1** (744 nm) gradually disappeared as pyridine increases and the absorption spectrum of the final product displayed Q-bands at 694.5, 609.5, 564.0 and 526.0 nm, which were identical to those of complex **2**. In contrast, when HBr was introduced into the solution of **2** in CH$_2$Cl$_2$, the absorption spectrum of **1** was completely recovered. Therefore, the protonation and deprotonation process are reversible and easily controlled by the addition of acid and base, respectively.

To summarize, two antimony(v) compounds with different electronic states for the coordinating NCP unit were synthesized and structurally characterized. The protonated Sb(v) NCP complex associates the bromide anion at the edge of the plane with hydrogen bonding interactions both in the solid and solution. Due to the labile axial ligand exchange reaction, only neutral NCTPP antimony(v) complexes were obtained with
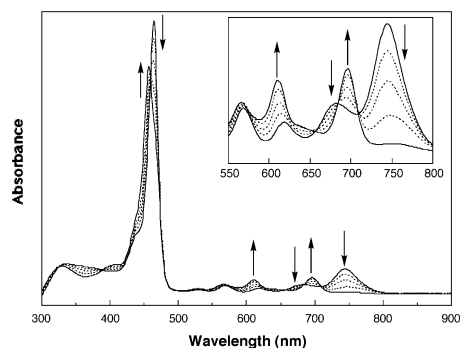
methoxy or ethoxy ligands.[8] Replacing HBr by another acid may influence the hydrogen bonding interaction, causing a large change in the charge distribution at the central Sb(v) metal. Further synthetic and structural studies of Sb(v) NCTPP complexes with variety of axial ligands are now in progress.

## Notes and references

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12 The addition of 2,6-lutidine gave the same spectral changes, which excludes the possibility of axial coordination of pyridine added.



**Fig. 2** Absorption spectral changes of **1** upon addition of pyridine in CH$_2$Cl$_2$, [**1**]: 1.35 × 10$^{-5}$ M, [pyridine]: 0, 0.25, 0.5, 0.8, 1.0 equiv.