Facile Antimony(V/III) Interconversion in Phthalocyanine Complexes

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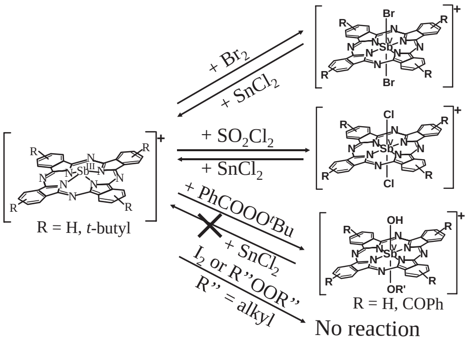
Facile antimony(V/III) transition has been found to occur in phthalocyanine complexes via oxidative addition/reductive elimination process.

Phthalocyanines have attracted much attention because of their similarities to compounds playing vital roles, supramolecular behaviors, applications in a wide variety of industrial and/or biomedical fields, etc.[1] Numbers of metal derivatives have so far been studied whereas those of group-15 elements, unlike porphyrin analogues,[2] were long ignored until we isolated the first bismuth[3] and antimony[4] derivatives. Nowadays, the presence of antimony ion, irrespective of its oxidation state (+3 or +5), in the cavity of phthalocyanine has proved to induce significant changes in properties of the ligand, e.g., a large red-shift in the main absorption band (Q-band),[4a–4c] J-aggregation (for $\mathrm{Sb^{III}}$ derivative),[4c] and so remarkably small reduction potentials as to oxidise elemental silver (for $\mathrm{Sb^{V}}$ analogue).[4a,4d–4f] However, both the $\mathrm{Sb^{III}}$ and $\mathrm{Sb^{V}}$ derivatives were prepared only by fusing mixtures of phthalonitriles and appropriate $\mathrm{Sb^{III}}$ salts.[4a–4c,4f,5] In this work, we wish to report facile, direct $\mathrm{Sb^{V/III}}$ interconversion in phthalocyanine complexes as shown in Scheme 1, unlike in porphyrin systems, where intermediate $\mathrm{Sb^{IV}}$ species can be involved.[2c]



Scheme 1. Summary of $\mathrm{Sb^{V/III}}$ interconversion in phthalocyanine complexes. See text for the details.

We prepared $[\mathrm{Sb(tbpc)Cl_2}]\mathrm{ClO_4}$[4b] and $[\mathrm{Sb(tbpc)}]\mathrm{I_3}$[4c] as described elsewhere and likewise prepared $[\mathrm{Sb(pc)}]\mathrm{I_3}$,[6] where $\mathrm{tbpc^{2-}}$ and $\mathrm{pc^{2-}}$ denote tetra-*t*-butyl substituted[7] and unsubstituted phthalocyaninate, respectively (i.e., $\mathrm{C_{48}H_{48}N_8}^{2-}$ and $\mathrm{C_{32}H_{16}N_8}^{2-}$). Oxidation of $[\mathrm{Sb^{III}(Pc)}]^+$ to $[\mathrm{Sb^{V}(Pc)L_2}]^+$, where Pc and L denote (unsubstituted or substituted) phthalocyaninate and monoanion, respectively, was performed by adding appropriate oxidant to solutions containing $[\mathrm{Sb^{III}(Pc)}]^+$ at room temperature. In a typical experiment, to a 20 mL of $\mathrm{CH_2Cl_2}$ solution containing $[\mathrm{Sb(tbpc)}]\mathrm{I_3}$ (119 mg, 0.96 mmol) was added dropwise a 0.4 mL of $\mathrm{Br_2}$ (7.7 mmol).[8a] The UV–vis spectrum of the solution immediately changed upon the addition of $\mathrm{Br_2}$; the Q-band blue-shifted and narrowed (Figure 1) and the resultant spectrum was characteristic of $[\mathrm{Sb^{V}(Pc)L_2}]^+$.[4a,4b,11] The ESI-MS of the product agreed well with theoretical pattern for $[\mathrm{Sb(tbpc)Br_2}]^+$ based on natural isotope abundance (Figure 2). Unlike the starting $[\mathrm{Sb(tbpc)}]^+$ that does not emit fluorescence in the Q-region,[4c] the generated $[\mathrm{Sb(tbpc)Br_2}]^+$ emits feasible fluorescence ($\lambda_{\max} = 753\,\mathrm{nm}$, $\phi < 0.001$ ($\lambda_{\mathrm{ex}} = 670\,\mathrm{nm}$, $\mathrm{CH_2Cl_2}$)), as is the case for $[\mathrm{Sb^{V}(Pc)L_2}]^+$ complexes.[4b,11] We similarly prepared $[\mathrm{Sb(pc)Br_2}]\mathrm{IBr_2}$[8b] from $[\mathrm{Sb(pc)}]\mathrm{I_3}$ suspended in solvent. The same reaction proceeded also in benzene, chlorobenzene, $\mathrm{CHCl_3}$, and $\mathrm{CH_3CN}$, but solvent is not essential because direct reaction also yielded $[\mathrm{Sb(pc)Br_2}]\mathrm{IBr_2}$ (yield 60%).[8c]

By using $\mathrm{SO_2Cl_2}$ (0.6 mL, 7.4 mmol) in place of $\mathrm{Br_2}$, $[\mathrm{Sb(tbpc)}]^+$ has readily and almost quantitatively been converted to $[\mathrm{Sb(tbpc)Cl_2}]^+$, as evidenced by UV–vis ($\lambda_{\max}$(Q-band) =

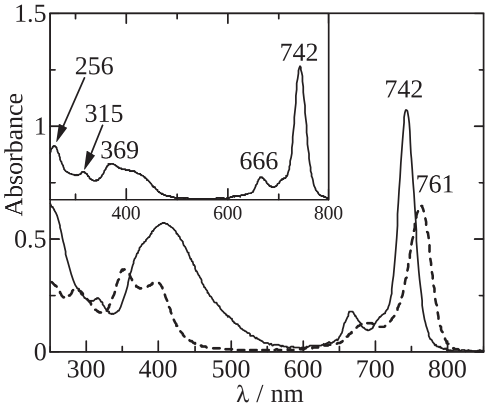


Figure 1. The spectral change of $\mathrm{CH_2Cl_2}$ containing $[\mathrm{Sb(tbpc)}]^+$ before (dashed line) and after (solid line) bromination; the inset shows the spectrum of $[\mathrm{Sb(tbpc)Br_2}]^+$ isolated as $\mathrm{IBr_2}^-$ salt.

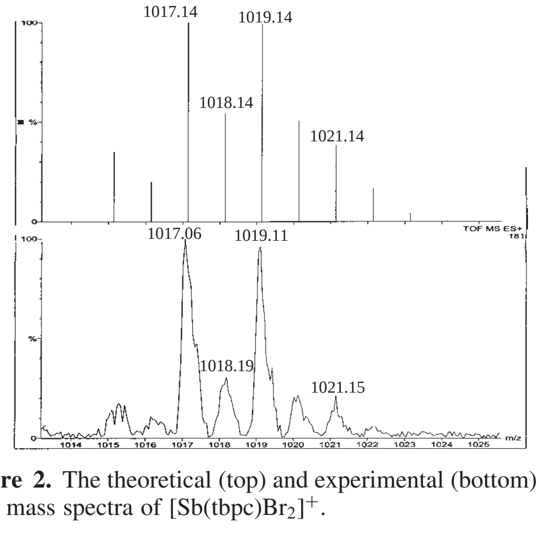


Figure 2. The theoretical (top) and experimental (bottom) ESI-TOF mass spectra of $[\mathrm{Sb(tbpc)Br_2}]^+$.

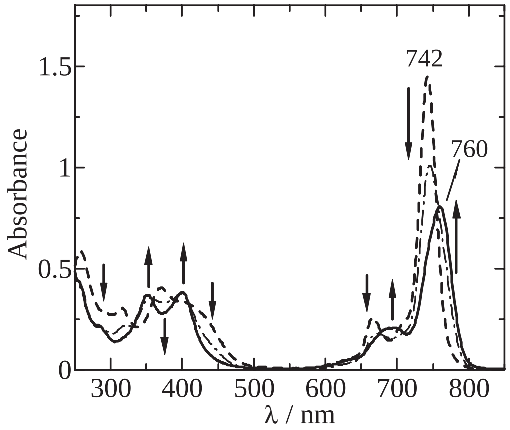


Figure 3. Spectral changes upon reduction of $[Sb(tbpc)Br_2]^+$ with $SnCl_2$ in CH_2Cl_2; (dotted line) before reduction, (dot-dash line) after 3.5 h, (solid line) after 17 h.

739 nm in CH_2Cl_2)[4b] and ESI-mass spectra. Action of *tert*-butyl perbenzoate or benzoyl peroxide to $[Sb(tbpc)]^+$ in CH_2Cl_2 have generated a mixture of $[Sb(tbpc)(OH)_2]^+$ and a small amount of $[Sb(tbpc)(benzoato)(OH)]^+$.[12] Dodecanoyl peroxide likewise oxidised $[Sb(tbpc)]^+$, but decomposition of tbpc ligand significantly lowered yields of the Sb^V species. Neither I_2 nor alkyl peroxide (di-*tert*-butyl- nor dicumyl peroxide) oxidised $[Sb(tbpc)]^+$ under the same conditions.

Reduction of $[Sb(tbpc)Br_2]^+$ and $[Sb(tbpc)Cl_2]^+$ with $SnCl_2$ in some solvents slowly and almost quantitatively generated $[Sb(tbpc)]^+$. In a typical experiment, when a CH_2Cl_2 solution (10 mL) containing $[Sb(tbpc)Br_2]^+IBr_2^-$ (ca. 10^{-5} M) was allowed to react with $SnCl_2$ (10 mg) with stirring at ca. 23 °C, slow conversion to $[Sb(tbpc)]^+$ was observed (Figure 3).[13] Reduction of $[Sb(tbpc)Cl_2]^+ClO_4^-$ occurred under more rigorous conditions (50 °C, 17 h, in chlorobenzene), but $[Sb(tbpc)(OH)_2]^+$ was not reduced under the same conditions. Hence, it seems that the weaker the bond between antimony and L (Sb–Br < Sb–Cl < Sb–O), the easier the reduction of antimony(V) is, indicating that a loss of the axial ligands is the rate-determining step. It should be noted that electrochemical[4a,4d,14] or chemical reduction of $[Sb^V(Pc)Cl_2]^+$ using BH_4^- or elemental silver[4d,4e] occurs first at the Pc-ligand to form the corresponding Pc^{3-} species.

In summary, $[Sb^{III}(Pc)]^+$ complexes have readily been converted to the corresponding $[Sb^V(Pc)L_2]^+$ via oxidative addition process while the ease of the reverse process depends on the type of L. It should also be noted that as all the new compounds obtained in this study have intense absorption in 700–800 nm region, this work should be intriguing not only for chemists studying chemistry of phthalocyanines or group-15 elements, but also for those working for application to optical disks, photodynamic therapy of tumours, etc.

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References and Notes

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5 Any attempts to prepare phthalocyanine ligand first and then to insert antimony ion into its cavity have been unsuccessful.
6 Although we could not isolate $[Sb(pc)]I_3$ in an analytically pure form due to its poor solubility in common solvents, the main product has been confirmed to be the desired compound based on its ESI-mass ($m/z = 633$ ($^{121}Sb(pc)$) and 635 ($^{123}Sb(pc)$) and UV–vis spectra (in CH_2Cl_2) that was similar to that of $[Sb(tbpc)]^+$.
7 A mixture of four regioisomers.
8 a) The mixture was allowed to react for 1 h and then was evaporated to dryness. After the residue was again dissolved into CH_2Cl_2 (ca. 2 mL) and filtered, hexane (8 mL) was added to the solution to precipitate crude $[Sb(tbpc)Br_2]IBr_2{\cdot}2CH_2Cl_2$. The solid was collected by centrifugation and recrystallized from CH_2Cl_2/hexane (1/4). The counter anion, IBr_2^-, is the oxidation product of I_3^- with Br_2 (Raman; 162 cm^{-1} (expected value[9] = 168 cm^{-1}). Yield; 90% vs $[Sb(tbpc)]I_3$. Anal. Found: C, 40.53; H, 3.52; N, 7.64%. Calcd for $C_{50}H_{52}N_8Cl_4Br_4ISb$: C, 40.71; H, 3.55; N, 7.60%: $\lambda_{max} = 742$ nm (Q-band; $\log(\varepsilon/M^{-1}\,cm^{-1}) = 5.19$), 369 nm (4.65), 256 nm (4.99) in CH_2Cl_2. b) Yield; 42% vs $[Sb(pc)]I_3$. Anal. Found: C, 35.54; H, 1.50; N, 10.16%. Calcd for $C_{32}H_{16}N_8Br_4ISb$: C, 35.56; H, 1.49; N, 10.37%: $\lambda_{max} = 729$ nm (Q-band; 5.30), 370 nm (4.78), 258 nm (4.83) in CH_2Cl_2 (it is known that IBr_2^- shows an absorption peak around 258 nm ($\log \varepsilon = 4.32$)[10]). The IBr_2^- salt has easily been converted to PF_6^- salt by treating with $^nBu_4NPF_6$ in CH_2Cl_2 and precipitating by adding EtOAc: Yield; 71% vs $[Sb(pc)Br_2]IBr_2$. Anal. Found: C, 40.75; H, 1.77; N, 11.77%. Calcd for $C_{32}H_{16}N_8Br_2PF_6$: C, 40.93; H, 1.72; N, 11.93%. $\lambda_{max} = 729$ nm (Q-band; 5.30), 370 nm (4.74). c) It should be noted that only fusing mixtures of phthalonitriles and $SbBr_3$ under conditions, where $[Sb^V(Pc)Cl_2]^+$ formed,[4–6] produced $[Sb^{III}(Pc)]^+$ alone but not $[Sb^V(Pc)Br_2]^+$.
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12 Their counter anions are unknown; $m/z = 891$ ($^{121}[Sb(tbpc)(OH)_2)]^+$), 893 ($^{123}[Sb(tbpc)(OH)_2)]^+$), $\lambda_{max} = 723.5$ nm (Q-band; in CH_2Cl_2): $m/z = 995$ ($^{121}[Sb(tbpc)$ $(benzoato)(OH)]^+$), 997 (^{123}Sb counterpart). A considerable amount of H_2tbpc formed as by-product in case of benzoyl peroxide.
13 The generated $[Sb(tbpc)]^+$ was readily reconverted to $[Sb(tbpc)Br_2]^+$ by oxidation with Br_2.
14 The first reduction ($pc^{2-/3-}$) potential of $[Sb(pc)Br_2]PF_6$ has been determined by cyclic voltammetry to be −0.21 V (vs Fc^+/Fc) in CH_2Cl_2 (0.1 M $^nBu_4NPF_6$), of which the value is essentially the same as that of $[Sb(pc)Cl_2]PF_6$ (−0.22 V).[5]

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