Spectroscopic Properties of One-Electron-Reduced Species of Dichloro(phthalocyaninato)antimony(V) Cation

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Electrochemical properties of the titled complex in dichloromethane (DCM) solutions have been investigated by cyclic and rotating-disk-electrode voltammetry. Two successive reversible one-electron reduction waves ($E_{1/2} = -0.23$ and -0.65 V vs. ferrocene/ferricinium$^+$, respectively) and one irreversible oxidation wave ($E_{pa} = 1.32$ V) have been observed. These were assigned as phthalocyaninate-ring-centered. Ring-reduced species of the titled complex was generated by both chemical and electrochemical reduction of the complex in DCM solutions and was characterized by electronic absorption (UV; 250—1100 nm), magnetic circular dichroism (MCD; 250—800 nm), and ESR spectroscopy. A quite sharp ESR signal was observed at $g = 2.0041$ (with a width of 0.5 mT) for the electrochemically-generated species, confirming the formation of monomer but not of dimer. The reduced species showed some prominent bands in its UV spectra, at 328 (B1; $\pi \rightarrow \pi^*$), 382 (LMCT), 553 ($n \rightarrow \pi^*$), 599 ($\pi^* \rightarrow \pi^*$), and 1059 nm (Q; $\pi \rightarrow \pi^*$). The MCD spectra showed sharp bands at 328 and 599 nm as Faraday *C*-terms, indicating that the ground state of the reduced species is orbitally degenerated. Thus the phthalocyanine-ring is not significantly Jahn–Teller-distorted and is approximately D_{4h} in symmetry even upon reduction.

The spectroscopic properties of phthalocyanines (Pcs) have attracted much attention in relation to photochemically-induced electron-transfer reactions of Pc-ring,[1—11] photodynamic therapy of cancer,[12] the synthetic metals,[13—16] semiconductors,[17] and electrochromic displays.[18] Electronic absorption (UV) and magnetic circular dichroism (MCD) spectra of metal complexes containing Pc dianion (hereafter referred to as pc^{2-}) have been intensively studied and were reviewed elsewhere.[19] Nevertheless, spectroscopic properties of Pcs other than pc^{2-}, in particular those of their reduced species, have been less investigated. This was because the reduced species were oxygen sensitive[20] and hence some special equipment was required to measure spectra of such species. Only a few research groups have reported the UV spectra of Pc-ring-reduced metallophthalocyanines (MPcs) so far.[20—24] Furthermore, MCD data for reduced species have been available only for a couple of radical anions, that is, pc^{3-} species.[22—24]

Stillman's group has reported UV and MCD spectra of MPc radical anions which were quite complicated; so many bands were observed and most of them were not isolated but overlapped with each other.[23,24] They attributed the complexity to the lowering of the Pc-ring in symmetry from D_{4h} to C_{2v} due to Jahn–Teller (JT) distortion upon reduction (because the electron will be charged into one of orbitally doubly degenerated LUMOs, $e_g(\pi^*)$) and nonsymmetric solvation of the Pc-rings (they measured the spectra in a coordinating solvent (DMF)). Such complexity in spectra has made the assignment of the observed bands difficult. They needed troublesome band-deconvolution procedure to assign each band.[24] Such lowering of the Pc-ring in symmetry will increase the number of dipole-allowed transitions and hence will make the spectra more complicated. Therefore, measuring spectra of such species in noncoordinating solvents, such as dichloromethane (DCM), would work to eliminate one cause which can lower symmetry of the Pc-rings due to nonsymmetric solvation. Quite recently, we have reported that the Pc-ring-reduction of the titled complex occurred at a potential higher than those of the known MPcs by ca. 1.0 V in DCM solutions.[25] Its one-electron-reduced species (e.g., pc^{3-} species) was stable enough to be submitted to spectroscopic measurements without any special equipment. Therefore, this complex is a good starting material to investigate spectroscopic properties of reduced Pcs in noncoordinating solvents (although the one-electron-reduced species of the titled complex has no charge, hereafter we will refer to the species as "radical anion" for easier comparison with the other literature).

Another advantage in employing this complex as starting materials is as follows: Since antimony(V) ion is a quite small cation, the central antimony in the complex must lie within the Pc-plane and hence the Pc-ring (particularly the internal 16-membered ring) should be more rigid than those of MPcs with central metal ions out of plane (as discussed below). Such coordination geometry of a Pc ligand around antimony could be able to reduce the JT-effect upon the reduced Pc-ring and therefore the radical anion of the complex could show UV and MCD spectra which are simple enough to allow us to assign the observed bands more easily.

According to expectation, both the UV and the MCD spectra of the radical anion of the titled complex observed in DCM solutions were much simpler than the spectra of the known

MPc radical anions. In this paper, we wish to report spectroscopic properties (UV, MCD, and ESR) of radical anion of the titled complex and also to try to assign the observed bands based on a simple molecular orbital model, assuming that the Pc-ring of the radical anion is D_{4h} in symmetry even upon reduction.

Experimental

Materials. The preparation of the dichloro(phthalocyaninato)antimony(V) hexachloroantimonate, $[Sb(pc)Cl_2]SbCl_6$ ($pc = C_{32}H_{16}N_8{}^{2-}$), was reported elsewhere.[25] Tetrabutylammonium perchlorate (TBAP) was prepared by conventional methods.[26] Tetrabutylammonium tetrahydroborate (as reductant; Tokyo Kasei Industry Co., Ltd.,) was used as received. Commercially available ferrocene (as an internal standard in electrochemical measurements) was sublimed twice prior to use. Reagent-grade DCM was dried over molecular sieves (4A) overnight and then distilled over fresh molecular sieves (4A) just prior to use.

Electrochemistry. All of the cyclic voltammetry (CV) experiments were carried out by using a Hokuto Denko HA-501 potentiostat/galvanostat connected to a Hokuto Denko HB-104 function generator and a Rika Denki RY-11 X–Y recorder. In rotating-disk-electrode voltammetry (RDE) experiments, a Yanaco P10-RE Mk-II disk rotator, which was connected to the above equipment, was used. Conventional three-electrode cells were used, in which a glassy carbon electrode and a platinum wire were used as the working electrode and the auxiliary electrode, respectively. A pseudo-reference electrode, consisting of an Ag-wire/0.01 M (1 M = 1 mol dm^{-3}) $AgNO_3$ and 0.1 M TBAP in acetonitrile, was separated from the working solution by a fritted-glass junction bridge (0.1 M TBAP in DCM). The redox potentials observed were calibrated by using a ferrocene/ferricinium$^+$ (Fc/Fc^+) redox couple as an internal standard. Hereafter, all of the potentials are referred to the Fc/Fc^+ couple. The electrochemical reduction (controlled-potential electrolysis) of $[Sb(pc)Cl_2]^+$ was carried out in DCM solutions containing 0.03 M TBAP by using a Hokuto Denko HA-501 potentiostat/galvanostat connected to a Hokuto Denko HF-201 coulometer, where a platinum mesh was used as the working electrode. All of the electrochemical experiments were carried out at 25.0±0.5 °C under a dry nitrogen atmosphere.

Electrochemical and Chemical Reduction. An apparatus for electrochemical reduction (controlled-potential electrolysis) experiments was described above. A portion of the working solution, which was electrolyzed at an appropriate potential, was pipetted and immediately submitted to spectroscopic measurements. Chemical reductions were carried out by titrating a DCM solution containing ca. 1 mM of tetrabutylammonium tetrahydroborate into a DCM solution containing ca. 0.01 mM of the antimony complex until no further significant spectral change was observed. Totally, ca. 1.2 equivalent of $BH_4{}^-$ was consumed.

Spectral Measurements. All of the UV spectra were recorded on a Shimadzu UV-160A spectrophotometer. Measurements of MCD spectra were carried out using a JASCO J-720 spectropolarimeter equipped with a 0.45-T permanent magnet under a nitrogen atmosphere. ESR spectra were measured by a JEOL JES-PE2XG (X-band) spectrometer under a nitrogen atmosphere. All of the spectral measurements were carried out at room temperature.

Results and Discussion

Electrochemistry. A typical cyclic voltammogram of $[Sb(pc)Cl_2]^+$ in a DCM solution is shown in Fig. 1a. Two successive reduction waves (Red1 and Red2) were observed, of which the half-wave potentials were −0.23 and −0.65 V, respectively, and one oxidation wave (Ox) was observed, of which the oxidation current peak potential was 1.32 V. With respect to the Red1, peak current ratios (i_{pa}/i_{pc}) were essentially unity, irrespective of scan rates (v) in the 20—200 mV s^{-1} range; $i_p v^{-1/2}$ values were almost constant; and differential potentials (ΔE_p) between cathodic and anodic peaks were $65 < \Delta E_p/\text{mV} < 75$ in the v range studied.[25] This redox couple is assigned as Pc-ring reduction because the electrolyses around the Red1 were accompanied with drastic changes in its UV spectrum both in peak positions and intensity (Fig. 2). Unlike the known dichloro(porphyrinato)antimony(V) complexes,[27] the first reduction was fully reversible. To the contrary, i_{pa}/i_{pc} values of the Red2 couple were not unity and decreased with a decrease in v; ΔE_p values were approximately 100 mV. Reduction of the complex at a rotating-disk electrode gave a current-voltage curve consisting of two successive waves as shown in Fig. 1b. The two waves were equal in magnitude of limiting currents (i_L). A study of i_Ls as a function of rotation rate (ω) showed that i_Ls of both the Red1 and Red2 were proportional to $\omega^{1/2}$, thus indicating that both the reductions were diffusion-controlled. Nernst-plots for each of the Red1 and Red2 waves gave a straight line with a slope of 59 mV, thus indicating that both the reductions were one-electron processes. Therefore, the Red2 was also a reversible diffusion-controlled one-electron process, although the second reduction product was unstable even on a CV time scale. As potential differences between the first and the second reduction couples of the known MPcs are about 0.4 V,[28] and as the Red2 is apart from the Red1 by 0.42 V, the Red2 is also attributable to Pc-ring reduction. Liu et al. have reported that, in both one-electron-reduced species (porphyrinate(3-)) and two-electron-reduced species (porphyrinate(4-)) of dichloro(porphyrinato)antimony(V) complex, intramolecular charge-transfer reactions from the reduced porphyrinates to the central antimony(V) took place to form (porphyrinato)antimony(III).[27] Similar intramolecular charge transfer reactions could occur in this case as well. The half-wave potentials of the Red1 and Red2 determined by RDE voltammetry were −0.22 and −0.65 V, respectively. These values are quite close to those values determined by CV.

In the positive scan, an oxidation wave appeared alone at 1.32 V without any rereduction wave (Fig. 1c). Its peak current increased with an increase in v; however, no further analysis was carried out with respect to this oxidation wave because RDE voltammogram did not show any distinct wave in this region. By using Lever's empirical relations between the redox potentials of the known MPcs (M = main group elements) and charges and the ionic radii of central metals in the MPcs,[29] the potential difference between the first Pc-ring reduction and the first Pc-ring oxidation of the antimony complex can be estimated to be 1.56 V. Since the first Pc-ring reduction (Red 1) occurred at −0.23 V, the first oxidation wave is anticipated to appear at 1.33 V; this value is close to the E_{pa} of the Ox observed. Therefore, the wave can be

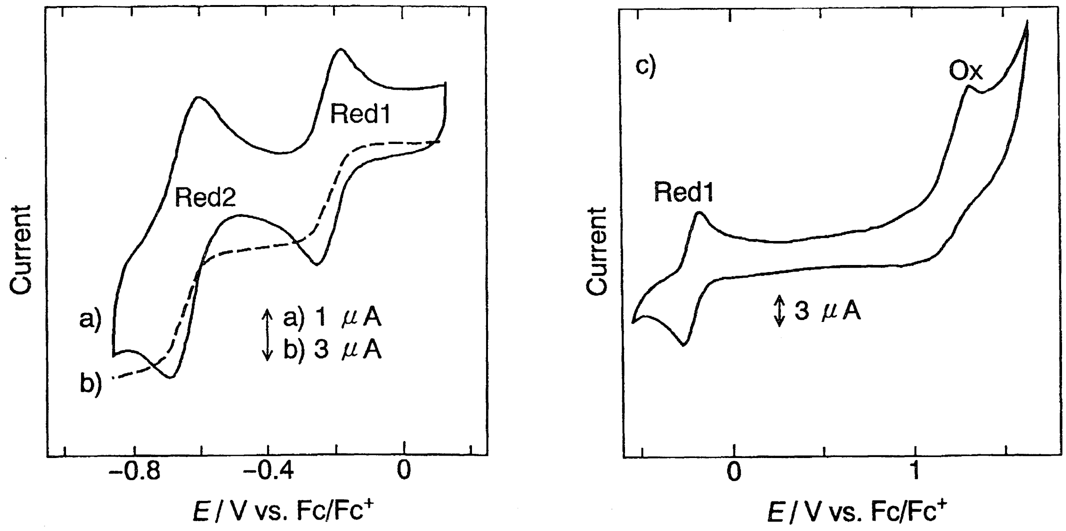

Fig. 1. Negative scans of a) cyclic ($v = 100$ mV s^{-1}) and b) RDE voltammograms ($v = 20$ mV s^{-1}; $\omega = 1600$ rpm) and c) positive scan of cyclic voltammogram ($v = 100$ mV s^{-1}) of $[\mathrm{Sb(pc)Cl_2}]^+$ (ca. 0.1 mM) in a DCM solution containing 0.1 M TBAP as supporting electrolytes.

attributed to Pc-ring oxidation. The oxidation potential is high enough to make its radical cation unstable. Actually, attempts to oxidize the complex with either bromine or nitrosyl tetrafluoroborate in DCM solutions were unsuccessful and resulted in no change in its UV spectrum.

Thus, with the exception of the anomalously facile Pc-ring-reduction of $[\mathrm{Sb(pc)Cl_2}]^+$, its electrochemical characteristics were typical of the known MPcs in which no metal-centered redox reactions occurred.[1,30—34] The facile reduction of $[\mathrm{Sb(pc)Cl_2}]^+$ is considered to arise from the high polarizability of the central antimony ion, which has a large positive charge of +5 and a small ionic radius.

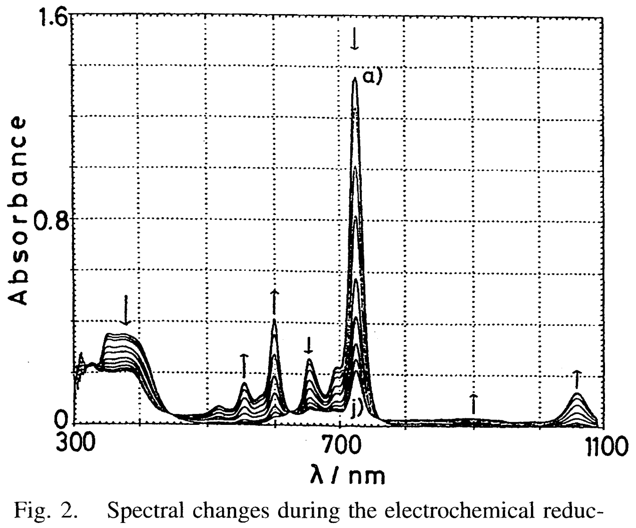

Fig. 2. Spectral changes during the electrochemical reduction of $[\mathrm{Sb(pc)Cl_2}]^+$ at a) −0.13, b) −0.15, c) −0.17, d) −0.19, e) −0.21, f) −0.23, g) −0.25, h) −0.27, i) −0.29, and j) −0.31 V in a DCM solution containing 0.03 M TBAP as supporting electrolytes. The arrows indicate the direction of the spectral changes. Initial [complex] = ca. 0.008 mM.

Spectroscopy of the Radical Anion. The spectral changes during the controlled-potential electrolysis of this complex at potentials around the half-wave potential of Red1 have already been described in the previous paper[25] and are shown in Fig. 2 in more detail. New bands at 328, 553, 559, and 1059 nm grew and the 726-nm Q-band of $[\mathrm{Sb(pc)Cl_2}]^+$ lowered in intensity as the electrolysis proceeded. The drastic spectral changes both in intensity and peak positions confirms that the Red1 is Pc-ring reduction. A Nernst-plot for the spectral changes (using absorbance at 726-nm Q-band of $[\mathrm{Sb(pc)Cl_2}]^+$ instead of current) gave a straight line with a slope of 66 mV and a half-wave potential of −0.22 V; these values are very close to those determined by CV and RDE voltammetry. Thus, the electrochemical reduction produces a one-electron-reduced radical anion of $[\mathrm{Sb(pc)Cl_2}]^+$. This was confirmed by its narrow ESR signal at $g = 2.0041$ with a bandwidth of 0.5 mT (Fig. 3), which is characteristic of an unpaired electron delocalized over an extended π system.[1,5,6,23,24,35] The electrolysis proceeded isosbestically (Fig. 2) without any decomposition of the complex, but did not achieve quantitative reduction as is usual for bulk electrolysis. Figure 4 shows the UV and MCD spectra of electrochemically generated radical anion. The MCD spectrum of the electrochemically-generated radical anion was very simple and showed two intense positive peaks at 328 and 599 nm (Fig. 4b). A distinctive Faraday *A*-term centered at 726 nm was observed. The signal is attributable to residual $[\mathrm{Sb(pc)Cl_2}]^+$ because neither absorption band at 726 nm in the UV spectrum nor Faraday *A*-term in the MCD spectrum of the chemically-generated radical anion was observed, as described below. Thus, the MCD spectrum is simply described only by the 328- and 599-nm bands (the radical anion marker band at 1059 nm was out of the range of the spectropolarimeter used). The presence of the ESR signal confirms the doublet multiplicity and hence the lack of dimerization (the possibility of an equilibrium mixture of

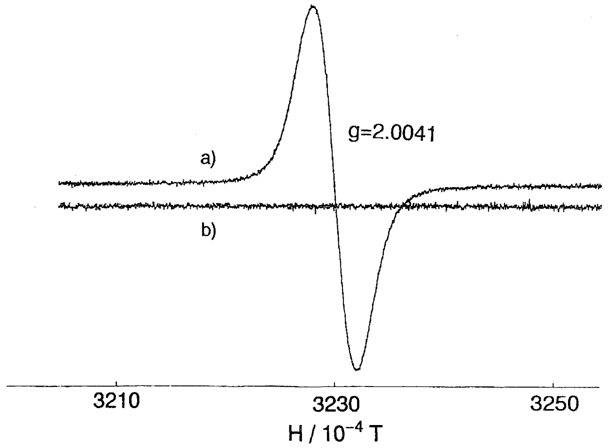

Fig. 3. The ESR spectra of a) the electrochemically-generated radical anion of $[Sb(pc)Cl_2]^+$ and b) $[Sb(pc)Cl_2]^+$ before reduction in a DCM solution containing 0.03 M TBAP as supporting electrolytes. Instrumental conditions: at room temperature, modulation amplitude = 0.1 mT (100 kHz), power = 1 mW. Initial [complex] = ca. 0.05 mM.

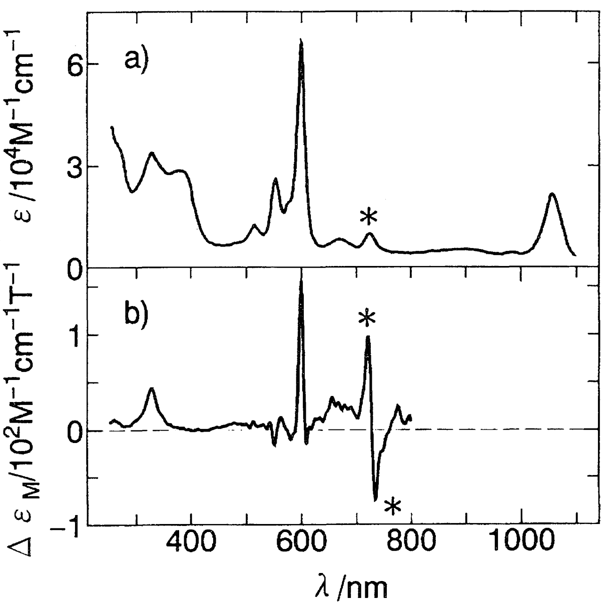

Fig. 4. The a) UV and b) MCD spectra of the electrochemically-generated radical anion of $[Sb(pc)Cl_2]^+$ in a DCM solution containing 0.03 M TBAP as supporting electrolytes. The asterisked signals are attributable to the Q-band of residual $[Sb(pc)Cl_2]^+$.

monomer and dimer can be excluded based on the simplicity of the UV and MCD spectra, as is seen in Fig. 4; if there were a considerable amount of dimer, some additional peaks arising from the dimer would be observed).

The chemical reduction of $[Sb(pc)Cl_2]^+$ using tetrahydroborate, BH_4^-, as a reductant apparently proceeded in two stages. At the first stage, the spectral changes were isosbestical and the 328-, 553-, 599-, and 1059-nm bands grew in intensity, as was the case of the electrolysis, but two additional broad bands grew in intensity in the 800—1000-nm region as is seen in Fig. 5. However, at the second stage,

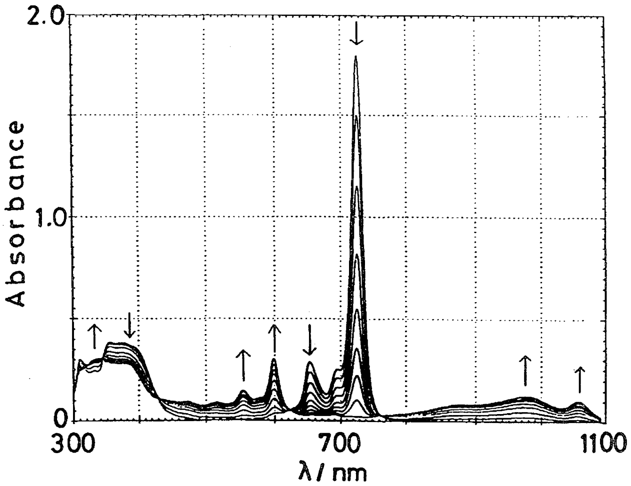

Fig. 5. Spectral changes (the first stage) during the chemical reduction of $[Sb(pc)Cl_2]^+$ with tetrabutylammonium tetrahydroborate in a DCM solution (initial [complex] = ca. 0.01 mM). The arrows indicate the direction of the spectral changes. Totally, ca. 1.2 equivalent of BH_4^- was consumed. Following the final spectrum, the two broad bands in the 800—1000-nm region started to lower in intensity.

the latter two bands were not related to the isosbestic points because the two bands lowered in intensity as the reaction proceeded. Therefore, we attributed the two bands to one or more unknown by-products. Mack and Stillman reported that broad absorption bands in the near-infra-red region were observed unless they took special care in photocheimcal reduction of [Zn(pc)].[24] The 726-nm Q-band of $[Sb(pc)Cl_2]^+$ completely disappeared in the chemical reduction. In turn, a pair of absorption bands were observed at 670 and 695 nm in the resultant spectrum, which were attributable to split Q-bands of $H_2(pc)$. As the first and second reduction potentials are close to each other, it is likely that some $[Sb(pc)Cl_2]^+$ molecules were reduced by the strong reductant (BH_4^-) to form pc^{4-} species, which is unstable even on a CV time scale. Liu et al. have reported that, in reduced species of the dichloro(porphyrinato)antimony(V) complex, intramolecular charge-transfer reactions from the ring-reduced porphyrinate to the central antimony(V) took place to form (porphyrinato)antimony(III) which underwent further reduction and then demetallation.[27] Similar reactions might occur also in this case. As there are several proton sources (CH_2Cl_2, BH_4^-) in the system, the metal-free pc^{2-} is likely to pick up protons from them to form $H_2(pc)$. Figure 6 shows the UV and MCD spectra of chemically-generated radical anion. The ESR spectrum of the chemically-generated radical anion was essentially the same as that of electrochemically-generated species ($g = 2.0043$; bandwidth = 0.6 mT).

The UV spectrum of the chemically-generated radical anion (Fig. 6a) is essentially the same as that of the electrochemically-generated species (Fig. 4a) except for the presence of a pair bands at 670 and 695 nm (attributable to $H_2(pc)$) and a pair of broad bands in the 800—1000-nm region (attributable to the other unknown by-product(s)) and the lack of the 726-nm band (attributable to residual $[Sb(pc)Cl_2]^+$) in the former

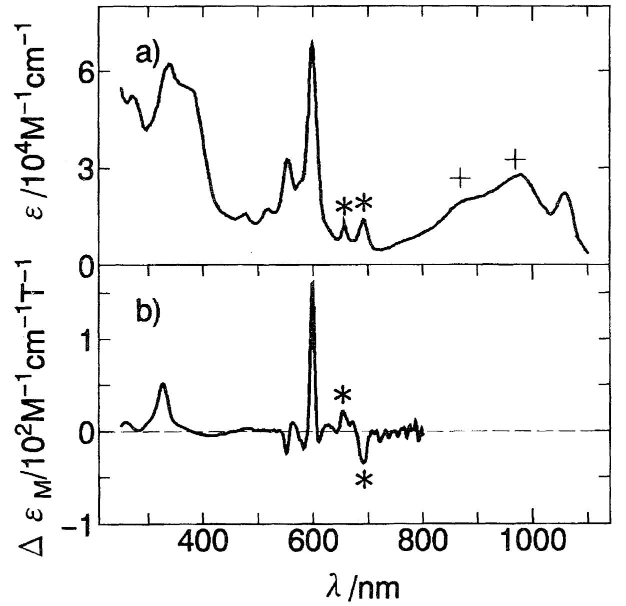

Fig. 6. The a) UV and b) MCD spectra of the chemically-generated radical anion of $[Sb(pc)Cl_2]^+$ in a DCM solution. The asterisked and daggered signals are attributable to the Q-band of $H_2(pc)$ as a by-product and absorption bands of the other unknown by-product(s), respectively.

spectrum. Thus, both the electrochemical and chemical reductions of $[Sb(pc)Cl_2]^+$ gave the same species. However, since the chemically-generated species was contaminated with some by-products, hereafter we will refer to the spectra of electrochemically-generated species when describing the spectral feature of the radical anion, unless otherwise noted.

In order to focus our attentions on the difference between our spectra and those of the known MPc radical anions, let us briefly refer to the UV and MCD spectra of radical anion of zinc-phthalocyanine which were reported by Mack and Stillman (see Fig. 3 in Ref. 24). The UV spectrum is typical of the known MPc radical anions.[20] The most outstanding difference was seen in the 550—650-nm region. The UV spectrum of the radical anion of the zinc complex shows a pair of bands with almost the same intensity at 635 and 570 nm. The two bands have almost the same intensity also in the MCD spectrum but are oppositely signed; the lower and higher energy bands are negatively and positively signed, respectively, thus showing a pseudo *A*-term. The spectral feature of radical anion of magnesium-phthalocyanine is essentially the same.[23]

On the contrary, in our case, both the UV and the MCD spectra showed a sharp band at 599 nm, which was well isolated from the other bands (Fig. 4). The 599-nm MCD band is contributed from either Faraday *B*-term alone or dominated by Faraday *C*-term. Between the two possibilities, the former is unlikely because obviously there is no negative MCD band that can cancel the positive 599-nm band (transitions into closely linked Jahn–Teller (JT)-split states would be expected to give rise to coupled pairs of oppositely signed Faraday *B*-terms in the MCD spectrum.[36] For pairs of states, which are relatively isolated, the resulting *B*-terms would be *x*- and *y*-polarized and would sum to zero.[36] The MCD spectra of radical anions of zinc- and magnesium-phthalocyanine complexes are this case[23,24]). For the same reason, the 328-nm band is also considered to be dominated by Faraday *C*-term. Therefore, we may conclude that the MCD spectrum is dominated by Faraday *C*-terms although measurements under cryogenic conditions should be helpful for deducing a more explicit conclusion. The appearance of the Faraday *C*-terms indicates that the ground state of this radical anion is orbitally degenerated. Since reduction of a Pc-ring is equal to charging an electron into its LUMO and the LUMO of Pc-ring is orbitally doubly degenerated ($e_g(\pi^*)$) according to the Gouterman's Four Orbital Model,[37] the ground state of MPc radical anion should be orbitally degenerated unless the Pc-ring is significantly JT-distorted upon reduction. Therefore, we conclude that the Pc-ring of the radical anion of $[Sb(pc)Cl_2]^+$ is approximately D_{4h} in symmetry even upon reduction.

Our observations may seem contradictory to those of Stillman's group[23,24] but are consistent with theirs in that our results are complementary with theirs: That is, they reported the UV and MCD spectra of MPc radical anions, which were JT-distorted; while we report here the spectra of a radical anion without significant JT-distortion. As a matter of fact, Stillman's group predicts that the lowest energy transitions of MPc radical anions without significant JT-distortion would show a Faraday *C*-term in the MCD spectra.[24] Our observation is exactly this case.

It is unknown at present why both magnesium- and zinc-phthalocyanine radical anions are subject to significant JT-distortion while antimony(V)-phthalocyanine radical anion is not. However, this can be rationalized in terms of the difference in their molecular structures and the rigidity of their internal 16-membered rings. Although the molecular structure of the $[Sb(pc)Cl_2]^+$ is unknown, the central antimony ion is considered to lie within a plane composed of the four pyrrole-nitrogens (Nps) as is the case of a tin(IV) ion in $[Sb(pc)Cl_2]$ complex.[38] This is because the $Sb(pc)Cl_2$ moiety is isoelectronic with the $[Sn(pc)Cl_2]$ complex and furthermore because the ionic radius of antimony(V) is smaller than that of Sn(IV) with the same coordination number.[39] It is noteworthy that the antimony(V) ions in some porphyrinato complexes, which have similar tetrapyrrole macrocycles, are known to lie within its four-Nps plane.[40] On the other hand, the molecular structure of magnesium-phthalocyanine complex with a water molecule as an apical ligand has been crystallographically determined and the magnesium ion is known to lie above its four Nps plane by ca. 50 pm.[41] With regard to zinc complex, although the zinc ion in [Zn(pc)] complex without any other ligand is known to be located essentially within its four-Nps plane,[42] the zinc ion in zinc-phthalocyanine complex with an *n*-hexylamine molecule as an apical ligand is known to lie above its four-Nps plane by 48 pm.[43] As the UV and MCD spectra of both of zinc- and magnesium-phthalocyanine radical anions were measured in a coordinating solvent (DMF),[23,24] both of the complexes must have a DMF molecule as an apical ligand and hence the central metals must lie above their planes. Quite recently, Cory et al. have reported stable structures of magnesium-phthalocyanine radical anion on the basis of their calculations.[44] In that work, they reported that the JT-effect on this radical anion would distort a square composed of the four-Nps rather than another one which is composed of the four aza nitrogens. Let us consider which is more rigid against JT-distortion, a Pc-ring with its central metal ion within its four-Nps plane or one with its central metal ion out of its four-Nps plane. The former must be much more rigid than the latter because the vibrations within the four-Nps plane of the former must be more significantly inhibited by the presence of the central metal ion than that of the latter. Therefore, the MPc moiety in the $[Sb(pc)Cl_2]^+$ must be approximately D_{4h} in symmetry even after reduction, because its planarity makes its internal four-Nps square more rigid, while those in both the zinc and magnesium complexes in a coordinating solvent must be subject to significant JT-distortion upon reduction because their non-planarity would make their internal four-Nps squares less rigid. This speculation suggests that the [Zn(pc)] complex, if reduced in a noncoordinating solvent (e.g., DCM), could show different UV and MCD spectra from those reported in DMF.[24]

Band Assignments. As is seen in Figs. 4 and 6, both the UV and MCD spectra of the radical anion of $[Sb(pc)Cl_2]^+$ were very simple and, unlike the spectra of magnesium-[23] and zinc-phthalocyanine radical anions,[24] no complexity was observed. When describing the spectral feature of the radical anion of $[Sb(pc)Cl_2]^+$, we will refer to the spectra of electrochemically-generated species unless otherwise noted because the chemically-generated species was contaminated with some by-products. Each band was well isolated from the others, and therefore we may consider that each band arises from a monoelectronic transition. A molecular orbital diagram of the antimony(V)-phthalocyanine radical anion is shown in Fig. 7.

(1) 800—1100 nm Region: The 1059-nm band is diagnostic band of MPc radical anions,[20—24] however, this is significantly red-shifted as compared to the known MPc radical anions (for example, 960 and 948 nm for magnesium- and zinc-phthalocyanine radical anions, respectively[20]). Stillman's group assigned the marker bands in the near-infrared region as a Q-band of the radical anion (that is, a transition from its fully occupied $a_{1u}(\pi)$ orbital to the singly occupied $e_g(\pi^*)$ orbitals). Later Cory et al. supported this, based on their calculations.[44] We agree with them because the marker band of antimony(V)-phthalocyanine radical anion is significantly red-shifted (1059 nm) as compared to the known MPc radical anions as was the case for the Q-band (726 nm) of its parent $[Sb(pc)Cl_2]^+$ complex.[25] The weak bands observed at higher energy of the marker band (800—1000 nm) in the UV spectrum of the radical anion are considered to arise from the vibration structures of the Q-band.

(2) 650—800 nm Region: A weak band at 726 nm was observed in the UV spectrum of the radical anion and a distinctive Faraday *A*-term was observed at the center of the band in its MCD spectrum (Fig. 4). This band is attributable to the Q-band of residual $[Sb(pc)Cl_2]^+$ because the chemically-generated radical anion did not show any band at around 726 nm in its UV spectrum or any *A*-term in its MCD spectrum (Fig. 6). Thus, the absorption bands observed in this region did not arise from the radical anion of interest, but from something else.

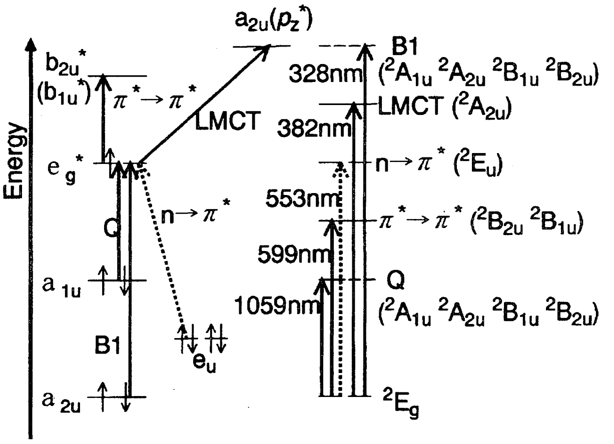

Fig. 7. Molecular orbital and state diagrams of the radical anion of $[Sb(pc)Cl_2]^+$ showing the transitions that are predicted to give rise to absorption bands in the 300—1100 nm range (energy level is arbitrary). The ground state is orbitally degenerated. The orbital ordering in the leftmost is based on references.[45] No accounts has been taken of changes in the energies of the molecular orbitals as a result of different orbital occupation upon reduction. The middle and the second right orbitals are the aza-nitrogen lone-pair orbitals and empty $6p_z^*$ of the central antimony(V) ion, respectively. The rightmost is the state diagram of the radical anion. The solid and dashed arrows indicate *x*,*y*-polarized and *z*-polarized transitions, respectively.

(3) 400—650 nm Region: A prominent narrow band and a less intense band were observed at 599 and 553 nm, respectively, in the UV spectrum. The former was prominent and narrow in the MCD spectra as well, but the latter was not. This is unusual for the known MPc radical anions but is explainable in terms of lack of significant JT-distortion as was described above. Unlike the antimony-phthalocyanine radical anion in this work, the UV spectra of the known MPc radical anions showed a pair of peaks with almost the same intensity in this region.[20] Stillman's group investigated the UV and MCD spectra of magnesium-[23] and zinc-phthalocyanine radical anions[24] and assigned the pairs of bands as transitions from singly occupied $b_1(\pi^*)$ ($e_g(\pi^*)$ in D_{4h} symmetry) to the $a_1(\pi^*)$ and $a_2(\pi^*)$ ($b_{1u}(\pi^*)$ and $b_{2u}(\pi^*)$, respectively) lowest empty orbitals.[23,24] However, this assignment seems inconsistent with our observations: If this is true, a pair of bands must be observed in our case also because the $b_{1u}(\pi^*)$ and $b_{2u}(\pi^*)$ are not orbitally degenerated whether the Pc-ring is JT-distorted or not, although they are close in energy to each other.[45]

Although we agree with them in that the single 599-nm band observed in our case is a $\pi^* \rightarrow \pi^*$ in origin, it is unknown to which empty π^* orbital the unpaired electron will be promoted. One possible explanation for this inconsistency is that the $b_{1u}(\pi^*)$ and $b_{2u}(\pi^*)$ are accidentally degenerated in our case. Although many theoretical models of pc^{2-} species have described $b_{2u}(\pi^*)$ as higher in energy than $b_{1u}(\pi^*)$,[45)] these two empty orbitals are considered to be close in energy to each other because they would be degenerated if the Pc-ring is an ideal cyclic polyene.[36)] Since the large positive charge (+5) of the central antimony ion would stabilize $b_{2u}(\pi^*)$ (with non-zero electron density on the four Nps[45b)]) more than $b_{1u}(\pi^*)$ (with no density on the Nps[45b)]), the two empty orbitals could be accidentally degenerated so far as no change in the ordering of the $b_{1u}(\pi^*)$ and $b_{2u}(\pi^*)$ orbitals as a result of different orbital occupation upon reduction is taken into consideration. An alternative explanation is that the 599-nm band is a transition from $e_g(\pi^*) \rightarrow b_{2u}(\pi^*)$ in character as Cory et al. suggested.[44)] They assigned the band of the lower energy band of the pair in the UV spectrum of magnesium-phthalocyanine anion radical as a transition from singly occupied $b_{3g}(\pi^*)$ ($e_g(\pi^*)$ in D_{4h} symmetry) to $a_u(\pi^*)$ ($b_{2u}(\pi^*)$ in D_{4h} symmetry) empty orbital and its higher-energy counterpart as an admixture of some monoelectronic transitions.[44)] Lack of significant JT-distortion in the radical anion of antimony complex will decrease the number of possible allowed transitions to be mixed and hence might significantly reduce the intensity of the counterpart. In addition, since $b_{2u}(\pi^*)$ would be stabilized by the large positive charge of the central antimony ion, as was stated above, the transition $e_g(\pi^*) \rightarrow b_{2u}(\pi^*)$ might be much isolated from the other transitions. Subsequently, only the transition to $b_{2u}(\pi^*)$ could be observed as a prominent 599-nm band. However, we must take care in employing Cory's model because their calculations were done on the assumption that the Pc-ring would be significantly JT-distorted upon reduction. In our case, the macrocycle is approximately D_{4h} in symmetry even upon reduction. In any case, there are some ambiguities concerning the ordering of the molecular orbitals upon reduction, making the assignment of this most prominent band ambiguous. Further theoretical study will be required to describe the spectral aspects of MPc radical anions.

The sets of weak bands at the blue edge of the 599-nm band can be assigned as vibronic progressions. A set of alternating positive and negative bands seen in the MCD spectrum clearly indicates that. However, the 553-nm band seen in the UV spectrum seems too intense as compared to the corresponding MCD band (Fig. 4). This band could be coupled with another electronic transition. In Schaffer's molecular orbital model,[45a)] e_u aza-nitrogen lone-pair orbitals (n) lie slightly above the $a_{1u}(\pi)$ HOMO of [Zn(pc)]. In spectroscopic studies of [Zn(pc)], Huang et al.,[46)] VanCott et al.,[47)] and Stillman et al.[48)] assigned the transitions, which were observed just blue to the Q-band, as a transition linking the nonbonding e_u orbitals to the $e_g(\pi^*)$ LUMOs. These are consistent with Schaffer's model. Since such an $n \rightarrow \pi^*$ transition ($e_u \rightarrow e_g(\pi^*)$ in character) is z-polarized as well as vibronic overtones are, both the transitions can be coupled with each other. Although such an $n \rightarrow \pi^*$ transition is unlikely to show significant intensity as the e_u lone-pair orbitals are orthogonal to the π molecular orbital system, the $n \rightarrow \pi^*$ transition can borrow intensity from the $\pi \rightarrow \pi^*$ transition at 599 nm via E_g vibrational modes[46)] (whether the 599-nm band might be a transition from $e_g(\pi^*)$ to $b_{1u}(\pi^*)$ or $b_{2u}(\pi^*)$ in character, the transition will be E_u in symmetry).

(4) 250—400 nm Region: Although two prominent bands were observed at 328 and 382 nm in the UV spectrum, only the former was observed in the MCD spectrum (Fig. 4). The former is assigned as a Soret band (B1: $a_{2u}(\pi) \rightarrow e_g(\pi^*)$ in character) because it has considerable intensity in the MCD spectrum and therefore should have considerable change in angular momentum.[36)] Stillman's group likewise assigned the bands observed in this region.[23,24)] The latter band is unlikely to be $\pi \rightarrow \pi^*$ or $\pi^* \rightarrow \pi^*$ in origin because the band has essentially no intensity in the MCD spectrum. Although the origin of this band is unknown at present, we tentatively assign this band as an LMCT transition from pc^{3-} to the central antimony(V) ion.[49)] The following transitions are dipole-allowed and x,y-polarized; $a_{1u}(\pi) \rightarrow e_g(5d_{xz/yz}{}^*)$, $a_{2u}(\pi) \rightarrow e_g(5d_{xz/yz}{}^*)$, and $e_g(\pi^*) \rightarrow a_{2u}(6p_z{}^*)$. Among them, the $e_g(\pi^*) \rightarrow a_{2u}(6p_z{}^*)$ is the most likely, because an intramolecular LMCT reaction is known to occur actually in the radical anion of dichloro(porphyrinato)antimony(V) complex to form (porphyrinato)antimony(III) species.[27)]

The assignments described above are summarized in Fig. 7 along with the molecular orbital and states diagram of the radical anion of $[Sb(pc)Cl_2]^+$.

Conclusion

The spectroscopic properties (UV and MCD spectra) of the radical anion of the titled complex in DCM solutions have been reported. This is the first case that both UV and MCD spectra of an MPc radical anion were measured in a noncoordinating solvent. Unlike the known MPc radical anions, both the UV and the MCD spectra of the antimony-phthalocyanine radical anion were very simple and showed that the transitions observed were orbitally degenerated in their ground states, indicating that the radical anion was not significantly JT-distorted. The absorption bands observed at 328, 382, 553, 599, and 1059 nm were assigned as $\pi \rightarrow \pi^*$ (Soret or B1 band), LMCT (from pc^{3-} to the central Sb^{5+}), $n \rightarrow \pi^*$, $\pi^* \rightarrow \pi^*$, and $\pi \rightarrow \pi^*$ (Q) transitions in origin, respectively.

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