Bull. Chem. Soc. Jpn., 70, 2179—2185 (1997)

Synthesis of Dichloro(phthalocyaninato)antimony(V) Perchlorate, Tetrafluoroborate, and Hexafluorophosphate and Electrochemical Reinvestigation on the New Complex Salts

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(Received April 22, 1997)

The titled new salts were synthesized by exchanging the unknown counter anion of $[Sb(pc)Cl_2]^+$ salt (pc^{2-} = phthalocyaninate, $C_{32}H_{16}N_8{}^{2-}$), which was the first product of the reaction of phthalonitrile with antimony(III) trichloride, with perchlorate, tetrafluoroborate, and hexafluorophosphate. Elemental analytical data and infrared spectra of the new salts confirmed that these complexes are composed of one $[Sb(pc)Cl_2]^+$ cation and one mononegative counter ion. The introduction of electrochemically inactive counter-anions exerted little effect on the electronic spectrum and the first and second pc-ring reduction potentials of the complex in dichloromethane, but has made it possible to observe the third and fourth reduction processes, which were not observed for the initial salt. Up to four successive reduction processes of a pc-ring were observed for the first time in a noncoordinating solvent. Although the ${}^1\Delta^2E_{1/2}$ (half-wave potential interval between the first and second reduction processes; 0.45 V), and ${}^3\Delta^4E_{1/2}$ (0.58 V) values for $[Sb(pc)Cl_2]^+$ were typical of those for the known phthalocyanines, the ${}^2\Delta^3E_{1/2}$ value (0.31 V) was much smaller. The anomaly in the spacing of the reduction processes for $[Sb(pc)Cl_2]^+$ is discussed in terms of the lack of a significant Jahn–Teller distortion of the pc-ring upon reduction.

The spectroscopic properties and redox characteristics of phthalocyanine and its derivatives, Pc's[1] and their metal complexes, MPc's, have attracted much attention in relation to the photochemically-induced electron-transfer reaction of phthalocyanine,[2—6] the photodynamic therapy of cancer,[7] synthetic metals[8—10] and semiconductors,[11] nonlinear optical properties,[12] electrochromic displays,[13] and fuel cells.[14] The spectroscopic properties (in particular, wavelengths of their characteristic Q-band maxima) and/or redox potentials of Pc's can be tuned to desired values by introducing substituents on the periphery of the macrocycle and/or varying the central metal in the cavity.[15] The latter seems less effective because a variation in the central metal does not change the spectral properties or redox potentials of the Pc's very much, although bismuth complexes have a significantly red-shifted Q-band (maximum wavelength = 716 nm).[16]

Recently, we reported that dichloro(phthalocyaninato)-antimony(V) complex cation, $[Sb(pc)Cl_2]^+$, where pc^{2-} = $C_{32}H_{16}N_8{}^{2-}$,[1] was synthesized and characterized in our laboratory.[17] This complex has quite unusual spectroscopic and electrochemical characteristics unlike the known MPc's: The Q-band maximum appeared at 726 nm in dichloromethane (hereafter abbreviated as DCM), which was red-shifted by ca. 1100 cm^{-1} with respect to those of the known unsubstituted MPc's; also, the first pc-ring reduction occurred at −0.22 V vs. ferrocenium$^+$/ferrocene (Fc^+/Fc), of which the value was the smallest of the known unsubstituted Pc's and MPc's by ca. 1.0 V. Quite recently, we reported unusual spectral characteristics of one-electron-reduced species of $[Sb(pc)Cl_2]^+$.[18] Thus, the complex cation as well as its reduced form is outstanding among the known MPc's reported so far in both its spectral and electrochemical characteristics. Although the composition of its chromophoric moiety has been confirmed to be $[Sb(pc)Cl_2]^+$, based on its FAB mass spectrum,[17] we had to assume the presence of hexachloroantimonate(V), $SbCl_6{}^-$, as an identified counter anion of the complex salt to explain the elemental analytical data. The presence of $SbCl_6{}^-$ has not yet been confirmed. In order to eliminate any ambiguity concerning the composition of this type of complex salt, we have tried to synthesize complexes with some counter anions, of which the sources are known, such as perchlorate, tetrafluoroborate, and hexafluorophosphate. The use of these anions yields the following advantages: 1) the presence of these anions can be readily evidenced by their characteristic infrared (IR) bands; 2) the complex salts are insoluble in acetonitrile (hereafter abbreviated as AN), whereas the initial salt is soluble, and hence desired salts can be obtained only by adding appropriate acids into AN solutions containing the initial salt. Furthermore, the introduction of the electrochemically inert counter anion did not give rise to any observable change in the electronic absorption spectrum and the first and second reduction potentials of the complex cation, but has made it possible to observe the third and fourth one-electron reduction processes (see below), which were not observed for the initial salt because of the appearance of irreversible reduction waves, probably due to a reduction of the electrochemically active $SbCl_6{}^-$.

An additional aspect of this work is to improve the best yield of the complex. When we first reported on the synthesis of the complex, the yield was very low: only 1% vs. the starting $SbCl_3$.[17] We have studied its yields under various conditions; the best yield has presently risen to 13.5% vs. starting $SbCl_3$.

In this communication, we wish to report on the syntheses of three new salts of the dichloro(phthalocyaninato)antimony(V) cation and reinvestigation of their electrochemistry.

Experimental

Materials. Antimony trichloride, phthalonitrile, perchloric acid, tetrafluoroboric acid, and hexafluorophosphoric acid were of reagent grade and were used without further purification. Reagent-grade AN, which had preliminary been distilled over diphosphorus pentaoxide twice and stored over molecular sieves (Merck, 4A), was distilled over fresh molecular sieves (Merck, 4A) just prior to use. The other solvents were of reagent grade and used as received unless noted. Tetrabutylammonium perchlorate (TBAP), tetrafluoroborate (TBAT), and hexafluorophosphate (TBAH) were of reagent grade and were recrystallized twice from ethyl acetate/hexane prior to use.

Modified Preparation of Dichloro(phthalocyaninato)antimony(V) Hexachloroantimonate(V), $[Sb(pc)Cl_2]SbCl_6$. The hexachloroantimonate(V) salt was prepared essentially according to a literature method,[17] which was modified as below. A mixture of 10.0 g of antimony trichloride and 11.2 g of phthalonitrile (1 : 2 in molar ratio) was fused at 150 °C with stirring under an argon atmosphere. A green solid of 0.8 g of $[Sb(pc)Cl_2]SbCl_6\cdot CH_2Cl_2$ was isolated from 5 g of the crude product. Anal. Found: C, 35.15; H, 1.67; N, 10.49%. Calcd for $C_{33}H_{18}N_8Cl_{10}Sb_2$: C, 35.24; H, 1.61; N, 9.97%. Yield; 13.5% vs. the starting $SbCl_3$. For the following anion exchange, another portion of hexachloroantimonate(V) salt was obtained in this way and was directly subject to the succeeding steps without further purification.

Preparation of Perchlorate Salt, $[Sb(pc)Cl_2]ClO_4$. We dissolved 10 g of crude hexachloroantimonate(V) salt, which had been preliminary washed with a small amount of DCM, into 350 ml of AN with sonication (it should be noted that when unpurified AN was used, a considerable amount of blue solid precipitated and hence yields of the desired salt significantly lowered; the blue solid was characterized as a mixture of $[Sb(pc)Cl_2]^+$, its radical anion, and H_2pc by infrared and electronic absorption spectra). Upon filtration, 220 ml of perchloric acid was slowly added to the AN solution until a small amount of green solid began to precipitate. After an additional 10 ml of the same acid was added, the solution was allowed to stand over night to precipitate a yellow-green microcrystalline solid. This was collected by filtration and recrystallized from DCM/hexane. Yields; 96 mg (1.1% vs. the starting $SbCl_3$ assuming that the yield of the initial hexachloroantimonate(V) is 13.5%). Anal. Found: C, 47.39; H, 2.02; N, 13.73%. Calcd for $C_{32}H_{16}N_8O_4Cl_3Sb$: C, 47.76; H, 2.00; N, 13.93%.

Preparation of Tetrafluoroborate, $[Sb(pc)Cl_2]BF_4$. An AN solution containing the crude product was prepared as above (5 g in 780 ml). Upon filtration, 65 ml of tetrafluoroboric acid was slowly added to 850 ml of the AN solution until a small amount of green solid began to precipitate. A yellow-green solid of $[Sb(pc)Cl_2]BF_4$ was similarly obtained as described above. Yields; 40 mg (1.0 % vs. the starting $SbCl_3$). Anal. Found: C, 48.48; H, 1.98; N, 14.08 %. Calcd for $C_{32}H_{16}N_8BF_4Cl_2Sb$: C, 48.52; H, 2.04; N, 14.15 %.

Preparation of Hexafluorophosphate, $[Sb(pc)Cl_2]PF_6$. An AN solution containing the crude product was prepared as above (2.5 g in 780 ml). Upon filtration, 19 ml of hexafluorophosphoric acid was slowly added to 780 ml of the AN solution until a small amount of green solid began to precipitate. A yellow-green solid of $[Sb(pc)Cl_2]PF_6$ was similarly obtained as described above. Yields; 26 mg (1.2% vs. the starting $SbCl_3$). Anal. Found: C, 44.80; H, 1.92; N, 13.02%. Calcd for $C_{32}H_{16}N_8PF_6Cl_2Sb$: C, 45.20; H, 1.90; N, 13.18%.

Measurements. The IR spectra were recorded on a JASCO FT/IR-8000 spectrometer (600—4000 cm^{-1} region) in KBr media by a diffuse-reflectance method. Measurements of the electronic absorption spectra were carried out using either a Shimadzu UV-160A or a Hitachi U-3500 spectrometer.

All of the cyclic voltammetry (CV) experiments were performed 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. 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 a 0.01 M (1 M = 1 mol dm^{-3}) $AgNO_3$/Ag-wire and 0.1 M TBAP in AN, 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 ferrocenium$^+$/ferrocene (Fc^+/Fc) redox couple as an internal standard. Hereafter, all of the potentials are referred to the Fc^+/Fc couple unless otherwise noted. All of the measurements were carried out at room temperature (24±1 °C).

Results and Discussion

Synthesis of $[Sb(pc)Cl_2]SbCl_6$. The yields of $[Sb(pc)Cl_2]SbCl_6$ have been studied based on the reaction temperature and various molar ratios of the reactants. The effects of the reaction temperature on the yields are summarized in Table 1. The yields increased with an increase in the reaction temperature up to 150 °C, but drastically decreased to less than 0.1% above 180 °C (below 120 °C, no reaction occurred). At 180 and 200 °C, a blue solid formed as a crude product, which was less soluble in DCM than $[Sb(pc)Cl_2]SbCl_6$; also, the DCM solution showed a Q-band-like absorption band at around 750 nm in its electronic ab-

Table 1. Effects of Reaction Temperature and Molar Ratios of the Starting Materials on Yields of $[Sb(pc)Cl_2]SbCl_6$

T/°C	t/h	Molar Ratio[a)]	Yield (vs. $SbCl_3$)
120	10	6	0.2
	24	6	2.8
150	6	6	2.3
	10	12	1.8
		6	2.1
		2.3	10.1
		2	13.5
		1	< 0.1[b)]
	18	6	2.9
	24	6	3.0
180	3	6	< 0.1[b)]
	10	6	< 0.1[b)]
200	3	6	< 0.1[b)]

a) Molar ratios of starting reactants; phthalonitrile/$SbCl_3$.

b) Blue solid formed (λ_{max} = 750 nm in DCM).

sorption spectrum. The experiments at 150 °C showed that although the yield increased upon lengthening the reaction time to some extend, too much was not effective. The effects of the molar ratios of the reactants on the yields are also summarized in Table 1. The yields vs. the starting $SbCl_3$ increased with a decrease in the molar ratios of the starting phthalonitrile to $SbCl_3$ when the ratios were larger than 2. However, at a ratio of unity, the yield decreased to less than 0.1% and a blue solid formed, of which the soluble component in DCM showed an electronic absorption spectrum similar to that of the product at 180 °C. These data indicate that there are some unfavorable succeeding chemical changes above 180 °C or in the presence of an excess amount of $SbCl_3$ (note that the stoichiometric ratio for one $[Sb(pc)Cl_2]SbCl_6$ molecule is 2). Thus, the initial product, $[Sb(pc)Cl_2]^+$, was consumed in one or more unknown reactions with unreacted $SbCl_3$. It is of interest that a similar species formed as a product of the reaction of phthalonitrile with $SbBr_3$ under the same conditions, where the best yield (13.5%) for $[Sb(pc)Cl_2]SbCl_6$ was achieved (e.g., phthalonitrile/$SbBr_3$=2; at 150 °C). The product was sparingly soluble in DCM and the solution showed an absorption maximum at around 750 nm in its electronic spectrum. The reaction with $SbCl_3$ may be very slow and can be negligible below 150 °C. In fact, $[Sb(pc)Cl_2]^+$ did not react with $SbCl_3$ in DCM at room temperature.

Another characteristic aspect of this complex formation is a change in the valence of the antimony species. Although the trivalent antimony compound was used as the starting material, the product contained the pentavalent antimony species. Air-oxidation of the starting antimony(III) is quite unlikely because the starting materials were allowed to react under an argon atmosphere. Although a trace amount of oxygen can oxidize some antimony(III) species, oxidation of up to 27% (one $[Sb(pc)Cl_2]SbCl_6$ has two antimony(V) ions) of the starting $SbCl_3$ by the oxygen alone is impossible. An alternative possibility, that the $SbCl_3$ used could have contained a considerable amount of pentavalent antimony species as impurities, is much less likely because the reaction of $SbCl_5$ with phthalonitrile did not yield $[Sb(pc)Cl_2]^+$ under the same conditions. The most reasonable explanation is that the starting $SbCl_3$ played a role not merely as either a template for cyclic tetramerization of phthalonitrile or as a central metal ion but also as a two-electron reductant. For a cyclic tetramer of phthalonitrile to be a phthalocyaninate, pc^{2-}, the tetramer must be reduced by two electrons. The starting trivalent antimony can play a role as an electron-donor subsequently to be a pentavalent species. In order to study this possibility, we tentatively calculated the change in the Gibbs' free energy (ΔG) for the formation of $Sb^{V}(pc^{2-})$ from $Sb^{III}(pc^{0})$ (the cyclic tetramer can be regarded as a pc^{0}). The half-wave potentials of the pc^{0}/pc^{-} and pc^{-}/pc^{2-} processes for the known (normal) MPc's and Pc's are 1.11 and 0.65 V vs. SCE,[15b,20] respectively. Hence, the ΔG values for the following half-cell reactions, $pc^{-}+e=pc^{2-}$ and $pc^{0}+e=pc^{-}$, are $\Delta G=-0.65F$ and $-1.11F$, respectively, where the factor F denotes the Faraday constant. Thus, the ΔG value for the following half-cell reaction is $\Delta G=-1.76F$; $pc^{0}+2e=pc^{2-}$. The half-wave potential of the $Sb^{V}Cl_6^{-}/Sb^{III}Cl_6^{3-}$ process in the presence of a large excess amount of HCl in aqueous solutions is known (0.58 V vs. SCE).[19,20] Although there was only a trace amount of hydrogen ion in the reaction mixture, since there was likewise a trace amount of water and a large amount of chloride, we tentatively employed this value for that of Sb^{V}/Sb^{III} process in this reaction. Thus, the ΔG value for the following half-cell reaction is $\Delta G=0.58F\times 2=1.16F$; $Sb^{V}+2e=Sb^{III}$. The ΔG value for the following reaction, $pc^{0}+Sb^{III}=pc^{2-}+Sb^{V}$, is $-1.76F+(-1.16F)=-2.92F$. Since the intramolecular charge-transfer reaction, $Sb^{III}(pc^{0})=Sb^{V}(pc^{2-})$, has a large negative ΔG value, the $Sb^{V}(pc^{2-})$ species is much more thermodynamically favored than $Sb^{III}(pc^{0})$. The above calculation suggests that $SbCl_3$ can act as an electron-donor in this complex formation.

Finally, the best yield of $[Sb(pc)Cl_2]SbCl_6$ has risen to 13.5% under the following conditions: phthalonitrile/$SbCl_3$ = 2 in molar ratio at 150 °C for 10 h.

Preparation and Spectral Characterization of $[Sb(pc)Cl_2]^+X^-$ ($X^-=ClO_4^-$, BF_4^-, and PF_6^-). By the anion-exchange procedure described above, three new analytically pure salts have been isolated. The isolation of the three new $[Sb(pc)Cl_2]^+X^-$ salts yielded unambiguous experimental evidence that the complex salts were composed of one $[Sb(pc)Cl_2]^+$ cation and one counter monoanion. Although we have confirmed the composition of the chromophoric moiety based on its FAB-MS spectrum, we had to assume the presence of $SbCl_6^-$ as a counter anion, of which the source was unknown, to explain the elemental analytical data for the initial $[Sb(pc)Cl_2]^+$ salt;[17,18] we did not use any antimony(V) species in the synthetic or purification procedures. In order to exclude any ambiguity concerning the composition of this type of complex, we tried to prepare analytically pure $[Sb(pc)Cl_2]^+$ salts with known counter anions, which were successfully isolated as perchlorate, tetrafluoroborate, and hexafluorophosphate. An advantage of employing these anions is as follows. The initial salt is soluble in AN while the new salts are insoluble; hence, a desired salt is obtained only by adding appropriate acid into an AN solution containing the initial salt. Another advantage is that the presence of these anions is readily confirmed by their characteristic IR bands: Figure 1 shows the IR spectra of the obtained complex salts. The spectrum of the initial salt (Fig. 1a) is typical of those of the known peripherally-unsubstituted MPc's.[21] Assuming that $SbCl_6^-$ is the counter anion, this is reasonable because $SbCl_6^-$ is transparent in this spectral region (600—1500 cm^{-1}).[22] Hence, we may consider that the spectrum is contributed from the complex cation alone. In contrast, the spectra of the other salts showed one or more additional prominent bands. For example, the perchlorate salt exhibited two additional bands at 1094 cm^{-1} (very strong) and 623 cm^{-1} (medium) as shown in Fig. 1b. The former and the latter are attributed to T_2 (stretching) and T_2 (bending) vibrations of ClO_4^- (which belongs to the T_d point group), respectively.[23] Therefore, the IR spectrum of the complex salt is a superposition of the spectrum of ClO_4^- and that

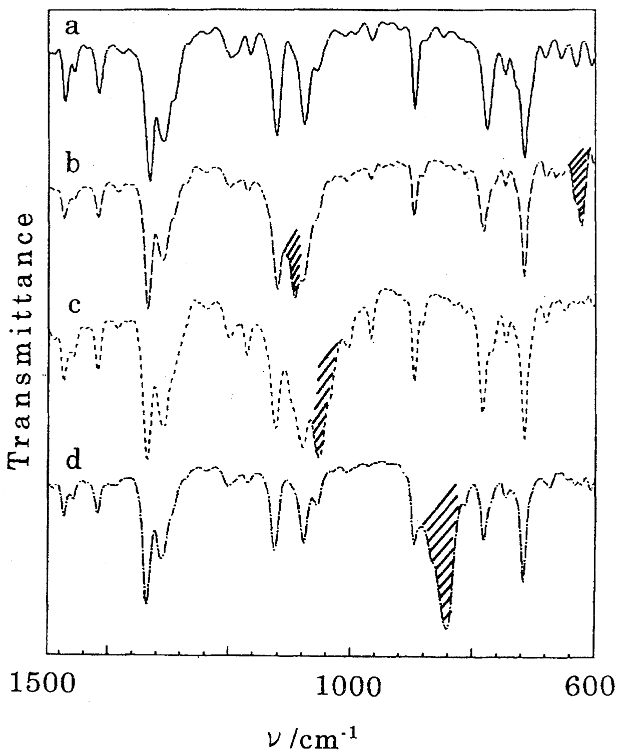

Fig. 1. Infrared spectra of $[Sb(pc)Cl_2]^+$ X^- salts; a) X^- = $SbCl_6^-$, b) ClO_4^-, c) BF_4^-, and d) PF_6^-. The shaded parts are absorption bands arising from the counter anions.

of $[Sb(pc)Cl_2]^+$, confirming the presence of perchlorate anion. Likewise, the intense 1053-cm^{-1} absorption band of the tetrafluoroborate salt (Fig. 1c) and the more intense 843-cm^{-1} band of the hexafluorophosphate salt (Fig. 1d) are attributed to a T_2 (stretching) vibration of BF_4^- (which belongs to the T_d point group) and a T_{1u} (stretching) vibration of PF_6^- (*Oh*), respectively.[23] Although BF_4^- is known to show a weak absorption band at around 760—780 cm^{-1},[23] the potential band was not observed, probably due to an overlap with more intense bands of the complex cation itself. Thus, the presence of the anions introduced was readily confirmed by the IR spectra.

The electronic absorption spectra of these new salts in DCM were essentially identical with that of the initial salt; the absorption peak wavelengths were exactly the same and the molar extinction coefficients at each peak were within 100±5 % of those for the initial salt.[17] This indicates that the introduced counter anions exerted little effect on the electronic structure of the complex cation.

Electrochemistry. The electrochemistry of the new salts was studied by cyclic voltammetry. Typical voltammograms of $[Sb(pc)Cl_2]BF_4$ in DCM showed four successive reduction processes (Fig. 2). This is reasonable because the LUMO of an MPc, which belongs to the point group D_{4h}, is orbitally doubly degenerate,[24] and, hence, up to four additional electrons can be readily accepted. The first wave was fully reversible in the range of scan rates studied (10—200 mV s^{-1}) while the second wave was irreversible below 100 mV s^{-1} although it seemed reversible at higher scan rates. These are the cases for the initial salt.[17,18] Furthermore, the third and fourth waves were clearly observed, which were not observed for the initial salt. This is because the appearance of more than one irreversible reduction waves at the negative of the second wave, probably attributable to a reduction of the electrochemically active counter-anion, $SbCl_6^-$, prevented observation of the higher reduction processes. That is, the introduction of the electrochemically inactive counter-anions has made it possible to observe the third and fourth reduction processes of the complex cation for the first time. This is the first case that up to four reduction processes were observed in a noncoordinating solvent; the other MPc's, of which up to the fourth reductions were known, have been studied in *N*,*N*-dimethylformamide (DMF). The third wave was likewise irreversible at scan rates lower than 100 mV s^{-1}, although it seemed to be reversible at higher scan rates. Therefore, the third reduction product is unstable even on the CV time scale, like the second reduction product. The fourth wave exhibited much poorer reversibility. The numbers of electrons involved in the first and second reductions are known to be unity.[18] Since the peak separations of the third and fourth waves were 65—85 and 100—110 mV, respectively, within the range of the scan rates studied, and since peak current heights of all four waves were nearly identical, all four reductions were one-electron processes. Although the first wave is known to involve a reduction of the pc-ring based on spectroelectrochemistry,[17,18] the origins of the other waves

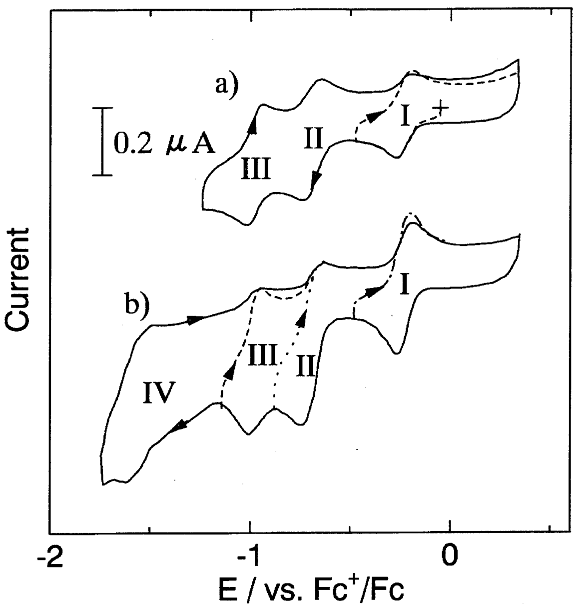

Fig. 2. Typical cyclic voltammograms of $[Sb(pc)Cl_2]BF_4$ in DCM containing 0.1 M TBAT as supporting electrolyte ($\nu = 200$ mV s^{-1}): The numbers, I, II, III, and IV represent the first, second, third, and fourth waves, respectively. a) Broken line; the first scan with the potential reversed at just negative of the first wave. Solid line; with the potential reversed at just negative of the third reduction wave. b) Solid, broken, dotted, and dot-dash lines show voltammograms with the potential reversed at just negative of the fourth, third, second, and first waves, respectively.

are unknown because of the chemical instability of the reduction products, even on the CV time scale. The possibility that some of the waves can involve a reduction of the central antimony(V) can not be completely excluded. However, we may assign these waves as pc-ring-centered reductions (e.g., pc^{3-}/pc^{4-}, pc^{4-}/pc^{5-}, and pc^{5-}/pc^{6-}) as well as the first wave, because such a reversible one-electron reduction of antimony(V) is not yet known. Voltammograms of perchlorate and hexafluorophosphate behaved in essentially the same manner. The use of TBAP or TBAH as a supporting electrolyte instead of TBAT gave rise to little change in the half-wave potentials or reversibility of all four waves. The half-wave potentials of the four reduction processes of these new salts are listed in Table 2 together with those for the other MPc's, of which up to the fourth reduction potentials are known. Irrespective of the counter anions, the half-wave potentials of the complex salts (including those of hexachloroantimonate(V) salt apart from the third and fourth reductions) were essentially identical. As stated earlier,[17,18] the ring reductions of $[\mathrm{Sb(pc)Cl_2}]^+$ occurred at higher potentials by ca. 1 V than those of the known MPc's.[15b,25] Surprisingly, the ring-reduction potentials of $[\mathrm{Sb(pc)Cl_2}]^+$ are even higher than those of octacyano-substituted MPc's,[26,27] although the complex cation does not have any electron-withdrawing substituent on its periphery; it is known that strong electron-withdrawing groups, such as a cyano group, on the periphery of an MPc gives rise to a significant anodic shift of the ring-reduction potentials.[28]

An Anomaly in the Spacing of the Successive Ring-Reduction Processes for $[\mathrm{Sb(pc)Cl_2}]^+$. The half-wave potential intervals between the nth and $(n+1)$th reductions, ${}^{n}\Delta^{n+1}E_{1/2}$ $(=E_{1/2}{}^{n}-E_{1/2}{}^{n+1})$,[29] are listed in Table 3. The ${}^{1}\Delta^{2}E_{1/2}$ (0.45 V) and ${}^{3}\Delta^{4}E_{1/2}$ (0.58 V) values for $[\mathrm{Sb(pc)Cl_2}]^+$ are within the range of those for the other known MPc's. However, the ${}^{2}\Delta^{3}E_{1/2}$ value (0.31 V) alone seems to be much smaller. In order to explain this anomaly, we studied the ground-state configurations for pc$^{(m+2)-}$ ($m=0$, 1, 2, 3, and 4). Lever et al. have argued that an anomaly in the spacing of the successive ring-reduction processes for a given MPc could be related to the spin-multiplicity of the ground state for its pc^{4-} species.[15b] The ground-state configuration for pc^{4-} species is either ${}^{3}\mathrm{A}_{2g}$ or ${}^{1}\mathrm{B}_{1g}$, of which the latter can be stabilized by the Jahn–Teller (JT) effect with respect to the former. If an MPc has the pc-ring subject to a significant JT-

Table 2. Ring-Reduction Potentials of MPc's, of Which up to the Fourth Reduction Potentials are Known

MPc	$E_{1/2}$/V vs. Fc$^+$/Fc				Solvent	Ref.
	$E_{1/2}{}^{1}$ a)	$E_{1/2}{}^{2}$	$E_{1/2}{}^{3}$	$E_{1/2}{}^{4}$		
[Mg(pc)] b)	−1.31	−1.79	−2.55	−2.98	DMF	25
[Zn(pc)] b)	−1.26	−1.70	−2.25	−2.65	DMF	25
[Zn(ocpc)] b,c)	−0.55	−0.90	−1.50	−1.75	DMF	26,27
[Al(pc)Cl] b)	−0.93	−1.38	−1.82	−2.38	DMF	25
[Ni(pc)] b)	−1.25	−1.63	−2.41	−2.75	DMF	25
[Cu(pc)] b)	−1.24	−1.58	−2.41	−2.68	DMF	25
[Cu(ocpc)] b,c)	−0.6	−1.03	−1.48	−1.65	DMF	26,27
$[\mathrm{Sb(pc)Cl_2}]\mathrm{SbCl_6}$	−0.23	−0.65	—	—	DCM	17,18
$[\mathrm{Sb(pc)Cl_2}]\mathrm{BF_4}$	−0.22	−0.67	−0.97	−1.56	DCM d)	This work
$[\mathrm{Sb(pc)Cl_2}]\mathrm{PF_6}$	−0.23	−0.68	−0.99	−1.56	DCM d)	This work
$[\mathrm{Sb(pc)Cl_2}]\mathrm{ClO_4}$	−0.23	−0.67	−0.98	−1.56	DCM d)	This work

a) The $E_{1/2}{}^{n}$ ($n=1$,2,3, and 4) denotes the nth reduction potential. b) The original data were referred to SCE. c) The ocpc^{2-} denotes octacyanophthalocyaninate ligand. d) Containing 0.1 M TBAT as supporting electrolyte.

Table 3. Half-Wave Potential Interval, ${}^{n}\Delta^{n+1}E_{1/2}$, Values for the MPc's Listed in Table 2

MPc	${}^{n}\Delta^{n+1}E_{1/2}=E_{1/2}{}^{n}-E_{1/2}{}^{n+1}$/V			Solvent	Ref.
	${}^{1}\Delta^{2}E_{1/2}$	${}^{2}\Delta^{3}E_{1/2}$	${}^{3}\Delta^{4}E_{1/2}$		
[Mg(pc)]	0.48	0.75	0.44	DMF	25
[Zn(pc)]	0.44	0.55	0.40	DMF	25
[Zn(ocpc)] a)	0.35	0.60	0.25	DMF	26,27
[Al(pc)Cl]	0.45	0.44	0.56	DMF	25
[Ni(pc)]	0.38	0.78	0.34	DMF	25
[Cu(pc)]	0.30	0.83	0.27	DMF	25
[Cu(ocpc)] a)	0.43	0.45	0.17	DMF	26,27
$[\mathrm{Sb(pc)Cl_2}]\mathrm{X}$ b)	0.45	0.31	0.58	DCM	This work

a) The ocpc^{2-} denotes octacyanophthalocyaninate ligand. b) Averaged values for $\mathrm{X}^-=\mathrm{ClO_4}^-$, $\mathrm{BF_4}^-$, and $\mathrm{PF_6}^-$.

distortion upon ring-reduction, the ground state for its pc^{4-} species will be a singlet; otherwise it will be a triplet. An experimental investigation has shown it to be a singlet for pc^{4-} species of some known MPc's,[30] which were known to be significantly JT-distorted upon a one-electron ring-reduction based on electronic absorption and MCD studies.[31] In contrast, we have reported that the pc^{3-} species of $[Sb(pc)Cl_2]^+$ was unlikely to be subject to a significant JT-distortion based on its electronic absorption and MCD spectra.[18] Therefore, the ground state for the pc^{4-} species of the antimony(V) complex can be a triplet if the pc-ring maintains D_{4h} symmetry upon the addition of one more electron to the $e_g(\pi^*)$ LUMO.

Let us compare the ground-state energies for a non-JT-distorted system with those for a JT-distorted system. The largest difference between the two systems will be seen between the second and third reduction. Both the first and second reductions involve the addition of an electron into the same orbital (for JT-distorted system) or into doubly degenerate $e_g(\pi^*)$ orbitals of which the energies are the same (Fig. 3). Thus, even though the pc-ring might be JT-distorted upon a ring-reduction or not, the orbital energies related to both reduction processes will be the same. This is also the case for the third and fourth reduction processes. On the other hand, the second and third reduction processes are related to the JT-stabilized and JT-destabilized orbitals, respectively, in the JT-distorted system, while both processes are again related to doubly degenerate orbitals for the non-JT-distorted system (Fig. 3).

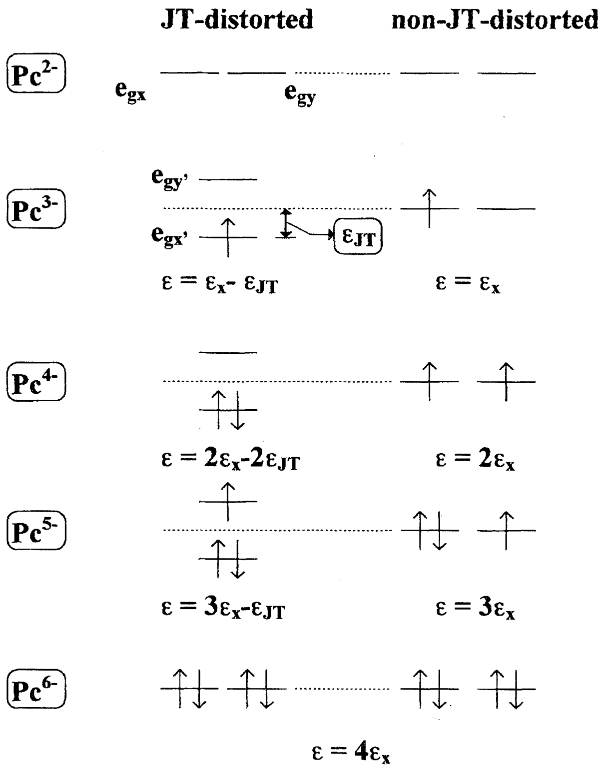

Fig. 3. Schematic diagrams of the ground-state configurations for JT-distorted and non-JT-distorted $pc^{(m+2)-}$ ($m = 1$, 2, 3, and 4) anions, where ε_i denotes the energy of an orbital i. Subscripts x and y represent e_{gx} and e_{gy}, respectively. ε_{JT} represents the JT-stabilization energy.

We even reproduced the mathematical expressions of the ground-state energies for $pc^{(m+2)-}$ ($m = 1$, 2, 3, and 4) with two-electron integrals taken into consideration,[32] where we followed Minor, Gouterman, and Lever[33] in using symbols for the integrals and orbital energies. The ground-state energies for $pc^{(m+2)-}$ relative to that for pc^{2-} are:

$$\begin{array}{lll}
m=1 & (^2E_g); & \varepsilon_x \\
m=2 & (^3A_{2g}); & \varepsilon_x+\varepsilon_y+J_{xy}-K_{xy} \\
 & (^1B_{1g}); & \varepsilon_x+\varepsilon_y+1/2(J_{xx}+J_{yy})-K_{xy} \\
m=3 & (^2E_g); & 2\varepsilon_x+\varepsilon_y+2J_{xy}+J_{xx}-K_{xy} \\
m=4 & (^1A_{1g}); & 2\varepsilon_x+2\varepsilon_y+4J_{xy}+J_{xx}+J_{yy}-2K_{xy}
\end{array}$$

The J_{ij} and K_{ij} represent two-electron Coulomb and exchange integrals between the electrons in orbitals i and j, respectively; ε_i denotes the energy of an orbital i (Fig. 3). Subscripts x and y represent e_{gx} and e_{gy}, respectively. In D_{4h} symmetry, $\varepsilon_x=\varepsilon_y$, $J_{xx}=J_{yy}$, and $J_{xx}\fallingdotseq J_{xy}$.[32] The J_{xx} and K_{xy} are on the order of 4 eV and 0.1—0.2 eV, respectively.[32] The energy, ΔW_m, necessary to add an electron in the gas phase to $pc^{(m-1+2)-}$ are given by:

$$\begin{array}{ll}
\text{JT-distorted} & \text{non-JT-distorted} \\
\Delta W_1=\varepsilon_x' \quad (\varepsilon_x'=\varepsilon_x-\varepsilon_{JT}) & \varepsilon_x \\
\Delta W_2=\varepsilon_x'+J_{xx}-K_{xy} & \varepsilon_x+J_{xy}-K_{xy} \\
\Delta W_3=\varepsilon_y'+2J_{xy} \quad (\varepsilon_y'=\varepsilon_x+\varepsilon_{JT}) & \varepsilon_x+J_{xy}+J_{xx} \\
\Delta W_4=\varepsilon_y'+2J_{xy}+J_{yy}-K_{xy} & \varepsilon_x+2J_{xy}+J_{xx}-K_{xy}
\end{array}$$

Here, ε_{JT} denotes JT-stabilization energy (Fig. 3). Therefore, the half-wave potential intervals between the successive reduction steps, ${}^n\Delta^{n+1}E_{1/2}={E_{1/2}}^n-{E_{1/2}}^{n+1}$, are:

$$\begin{array}{rll}
 & \text{JT-distorted} & \text{non-JT-distorted} \\
-F^1\Delta^2E_{1/2} & =\Delta W_2-\Delta W_1+2\alpha & \\
 & =J_{xx}-K_{xy}+2\alpha & J_{xy}-K_{xy}+2\alpha \\
-F^2\Delta^3E_{1/2} & =\Delta W_3-\Delta W_2+2\alpha & \\
 & =2J_{xy}-J_{xx}+K_{xy}+2\varepsilon_{JT}+2\alpha & J_{xx}+K_{xy}+2\alpha \\
-F^3\Delta^4E_{1/2} & =\Delta W_4-\Delta W_3+2\alpha & \\
 & =J_{yy}-K_{xy}+2\alpha & J_{xy}-K_{xy}+2\alpha
\end{array}$$

($F=$ the Faraday constant and α=solvation energy[32])

Following Hush,[32] we assume that $J_{xy}\fallingdotseq J_{xx}\fallingdotseq J_{yy}$. Consequently, the $-F^2\Delta^3E_{1/2}$ value for the JT-distorted system will be larger by $2\varepsilon_{JT}$ than that for the non-JT-distorted system, while the same ${}^1\Delta^2E_{1/2}$ and ${}^3\Delta^4E_{1/2}$ values are expected for both JT-distorted and non-JT-distorted systems. This well explains the small experimental ${}^2\Delta^3E_{1/2}$ value observed for $[Sb(pc)Cl_2]^+$ relative to those for the other MPc's. In addition, it is reasonable that the ${}^2\Delta^3E_{1/2}$ value for $[Sb(pc)Cl_2]^+$ is close to the ${}^1\Delta^2E_{1/2}$ value, because the K values are small enough compared to the J values, as stated above. Therefore, the anomaly in the spacing of the successive reduction processes is explained by assuming the lack of a significant JT-distortion upon the ring-reduction of $[Sb(pc)Cl_2]^+$, suggesting that the ground state for doubly-reduced species of this complex can be a triplet. Unfortunately, the chemical instability of this species makes it impossible to confirm the above speculation. Efforts to make new complexes with various axial ligands are being made in our laboratory so that their doubly-reduced species could be sufficiently stabilized to be studied spectroelectrochemically.

Conclusion

Three new analytically-pure $[Sb(pc)Cl_2]^+$ complex salts have been synthesized by replacing the initial counter anion, $SbCl_6^-$, with ClO_4^-, BF_4^-, and PF_6^-, respectively. The composition of the antimony-phthalocyanine complex has been unequivocally confirmed. Therefore, the "counter-anion problem", which remains unsolved for the initial salt, is no longer present for these new salts.

All of the new salts showed essentially the same electronic absorption spectra and the first and second reduction potentials as those of the initial hexachloroantimonate(V) salt, indicating that the counter anions exerted little effect on the electronic structure of $[Sb(pc)Cl_2]^+$. However, the introduction of these electrochemically inactive counter-anions has made it possible to study the third and fourth reduction processes of $[Sb(pc)Cl_2]^+$ by cyclic voltammetry, which were not observed for the initial salt. The ${}^1\Delta^2E_{1/2}$ and ${}^3\Delta^4E_{1/2}$ values for $[Sb(pc)Cl_2]^+$ were normal for an MPc, whereas the ${}^2\Delta^3E_{1/2}$ value was much smaller than those for the known MPc's. The anomaly in the spacing of the reduction processes for $[Sb(pc)Cl_2]^+$ has been interpreted in terms of the lack of a significant JT-distortion of the pc-ring upon ring-reduction, suggesting that the ground state of two-electron-reduced species of $[Sb(pc)Cl_2]^+$ could be a triplet.

The formation of $[Sb(pc)Cl_2]^+$ was temperature-sensitive and dependent on the molar ratios of the reactants. The best yield has risen to 13.5% vs. the starting $SbCl_3$ under the following conditions: phthalonitrile/$SbCl_3$=2; 150 °C; 10 h.

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1) The "Pc" denotes a general expression for phthalocyanine and its derivatives and hence is used when we do not specify a kind of phthalocyanine ligand. Likewise, "MPc" is used when neither a kind nor valence of the central metal is specified. On contrast, the "pc^{2-}" represents phthalocyaninate ligand itself; that is, pc^{2-}= $C_{32}H_{16}N_8{}^{2-}$.

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