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Facile Reduction of Dichloro(phthalocyaninato)antimony(V) Cation

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Antimony(V)-phthalocyanine, $[Sb(pc)Cl_2]^+$ (where pc^{2-} = phthalocyaninate, $C_{32}H_{16}N_8{}^{2-}$), has been prepared and characterized for the first time. Of the metallophthalocyanines without any substituent groups so far reported, it has the Q-band at the longest wavelength and the smallest first ring-reduction potential.

Metallophthalocyanines (MPcs) of almost all of metallic elements have been prepared and characterized so far.1) In particular, their redox characteristics have attracted much attention in relation to conductivity,2) photosensitization,3) electrocatalysis,4) and electrochromism.5) With regard to group-15 elements, essentially nothing had been known until bismuth complexes were prepared and characterized in our laboratory.6,7) In the course of studies concerning the other group-15 elements, the titled complex has been found quite reducible for a peripherally unsubstituted MPc. This paper communicates facile ring-reduction of the complex.

The titled complex was prepared by fusing a mixture of 6.0 g (26.3 mmol) of $SbCl_3$ (Kojundo Chemical, 99.9%) and 20.2 g (0.158 mol) of 1,2-dicyanobenzene at 150 °C for 10 h with stirring under an argon atmosphere. Crude product (25.7 g) was obtained as a viscous dark-green fluid and then solidified when allowed to cool to room temperature. The desired complex was successively extracted from 6.0 g of the crude product with dichloromethane (DCM) and was deposited as a yellow-green solid upon the addition of an equal volume of ether to the DCM solution. The solid was collected by filtration and again dissolved into 600 ml of DCM. Concentration of the solution into ca. 100 ml yielded a dark-blue needle-like microcrystalline solid of $[Sb(pc)Cl_2]SbCl_6 \cdot CH_2Cl_2$. This was collected by filtration, washed with a small amount of DCM/ether (1:2 in volume), and then dried. Yield; 1% based on the $SbCl_3$. Anal. Found: C, 34.24; H, 1.62; N, 9.86; Cl, 29.37%. Calcd for $C_{33}H_{18}N_8Cl_{10}Sb_2$: C, 35.24; H, 1.61; N, 9.97; Cl, 31.52%. In FAB mass spectrum (m-nitrobenzylalcohol/DCM matrix) shown in Fig. 1, $[Sb(pc)Cl_2]^+$ exhibited the desired parent ion peaks at around m/z 705 calculated from isotopic abundance. This complex was soluble in DCM, acetonitrile, chloroform, 1-chloronaphthalene, acetone, methanol, pyridine, THF, and DMF, although it turned bluish-purple in the latter five solvents.8)

All of the electrochemical experiments were performed at 25.0±0.5 °C in freshly distilled DCM containing tetrabutylammonium perchlorate (TBAP) as electrolytes under a nitrogen atmosphere using conventional three-electrode cells. A glassy carbon disk and a platinum wire were used as the working and the counter 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 working solutions by a fritted-glass junction bridge (0.1 M TBAP in DCM). The oxidation couple of ferrocene (Fc/Fc^+) was used as an internal standard. Hereafter, all potentials are referred to the Fc/Fc^+ couple.

The electronic (UV) and magnetic circular dichroism (MCD) spectra of the complex in DCM are shown in Fig. 2. The UV spectrum is typical of usual MPcs although the Q-band was shifted to the longest wavelength (726 nm) among the known MPcs without any peripheral substituents.$^{9)}$ A distinctive Faraday A-term centered at the Q-band was observed in the MCD spectrum, which indicated that the transition was orbitally degenerated,$^{9)}$ suggesting that the pc ring in the complex was approximately D_{4h} in symmetry. The IR spectrum of the complex in KBr media (not shown) was characteristic of the usual type MPcs. Thus, the complex seems "normal" as far as its spectroscopic properties are concerned.

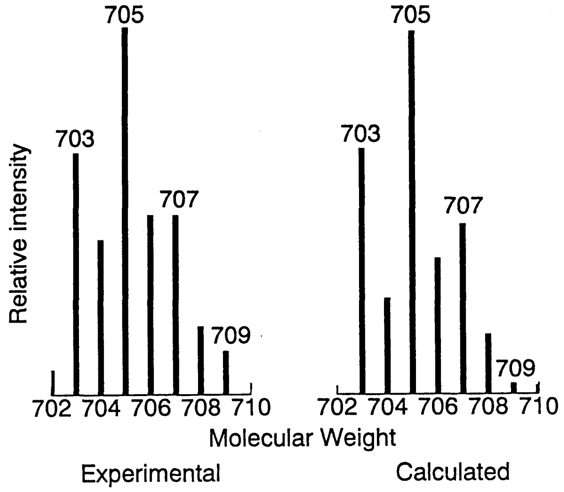

Fig. 1. Mass spectra around the peaks of the antimony complex.

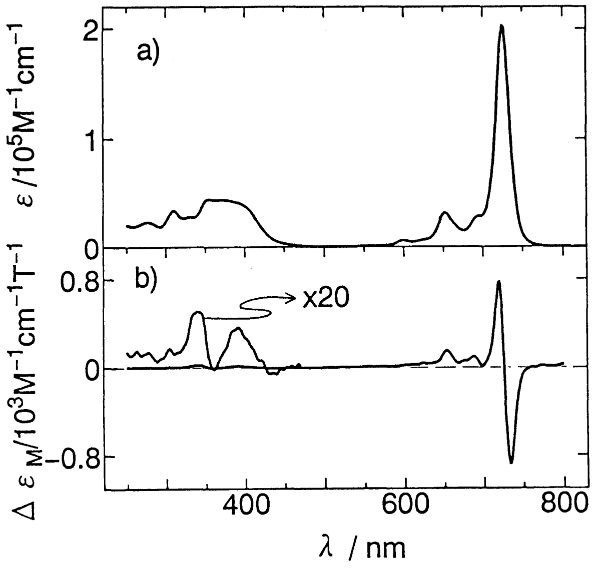

Fig. 2. UV and MCD spectra of the antimony complex.

However, this complex was quite easy to reduce. Figure 3 shows typical cyclic voltammograms (CVs) of the complex, consisting of two successive reduction couples (Red1 and Red2). Half-wave potentials of the Red1 and Red2 were -0.23 and -0.65 V, respectively. With regard to the Red1, peak current ratios ($i_p{}^a/i_p{}^c$) were essentially unity, irrespective of scan rates (v) in the 20 ~ 200 mV/s range; $i_p/v^{1/2}$ values were almost constant; and differential potentials (ΔE_p) between cathodic and anodic peaks were $65 < \Delta E_p/\mathrm{mV} < 75$ in the v range studied. Thus, the first reduction couple was a reversible diffusion-controlled one-electron process. Figure 4 shows the spectral changes during the controlled-potential electrolysis of the complex at -0.13 ~ -0.35 V (a platinum net was used as the working electrode). The intense 726-nm band lowered isosbestically in intensity as the reduction proceeded and new less intense bands coincidently grew in intensity at 554, 599, and 1050 nm. Retention of isosbestic points indicates occurrence of the reduction without any decomposition of the species. The drastic spectral changes both in intensity and peak positions and the similarity of the resultant spectrum to those of the hitherto reported anion-radical MPcs[10] indicate that the reduction is pc-ring centered.[11]

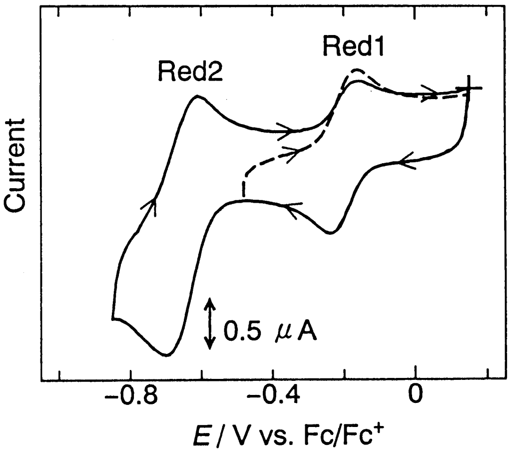

Fig. 3. Typical CVs of the antimony complex.

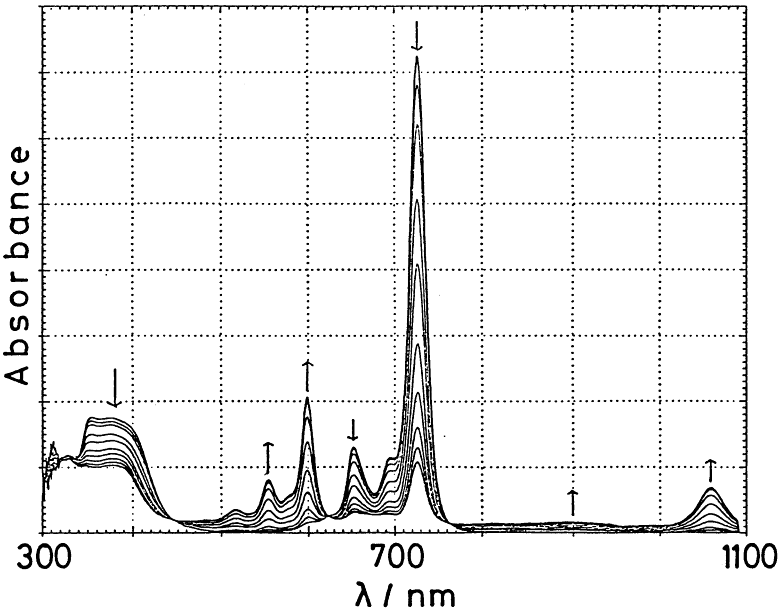

Fig. 4. Spectral changes during electrolysis of the antimony complex.

It is noteworthy that the first ring-reduction occurred at -0.23 V, of which the value is anomalously high for a ring-reduction potential of the usual type MPcs without any peripheral substituents. For example, the first ring-reduction occurred at ca. -1.4 V for the magnesium,[12] -1.44 V for the zinc,[13] and ca. -1.0 V for the bismuth complexes,[7] respectively. Lever has reported that the electron-withdrawing peripheral substituents (such as cyano group) made ring-reduction potentials more anodic.[14] However, the antimony complex in this study has no such substituents. By an analogy with the porphyrinate complex of antimony(V), which has likewise quite high ring-reduction potentials (-0.3 V),[15] the antimony ion in the complex in this study is tentatively assigned as pentavalent. Further characterizations are now in progress.

This complex may be a candidate of a new electron-acceptor for synthetic metals and catalysts of photo-oxidation and a good starting material for spectroscopic studies of anion-radical MPcs.

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