Syntheses and Characterization of Bromo- and Chloro(phthalocyaninato)bismuth(III) Complexes

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By the reactions of BiX_3 ($X=Cl^-$, Br^-, I^-, and NO_3^-) with Li_2(pc) (pc=phthalocyaninate dianion, $C_{32}H_{16}N_8^{2-}$) in dimethyl sulfoxide, *N*,*N*-dimethylformamide, acetonitrile, and acetone, [Bi(pc)X] complexes have been produced. These complexes were also produced by heating a mixture of BiX_3 and phthalonitrile. Among them, [Bi(pc)Cl] and [Bi(pc)Br] were isolated for the first time as a phthalocyanine complex of group-15 elements and successfully characterized by elemental analyses, solution chemistry, electronic and IR spectroscopy. The latter two complexes were soluble in polar solvents, but were insoluble in nonpolar solvents. In solutions, bismuth(III) in [Bi(pc)X] was labile and was readily expelled from a pc ring by a trace amount of water, acids, and bases, and it was replaced by a divalent transition metal upon the addition of MSO_4 (M=cobalt(II), nickel(II), copper(II), and zinc(II)) forming [M(pc)]. The electronic and IR spectra of the [Bi(pc)X]s were characteristic of the usual metallophthalocyanines, except that a hyper metal-to-ligand charge-transfer band appeared in their electronic spectra.

Although phthalocyanine complexes of almost all of the metallic elements in the periodic table are known,[1] complexes of semi-metal elements (in particular of group-15 elements) have been less investigated.[2] In recent years, porphyrin (possessing a similar tetrapyrrole ring skeleton) complexes of group-15 elements (phosphorus,[2—7] arsenic,[2,4] antimony,[2,5,6,8] and bismuth[2,4,5]) have been intensively investigated. In contrast, up to now, only a few reports have been devoted concerning studies of the phthalocyanine complexes of these elements.[2] Gouterman and coworkers studied the spectroscopic properties of phosphorus complexes whose chemical compositions were unknown.[2,7] Rutter, Jr., et al. reported on the preparation of an arsenic complex in solution and its visible absorption maximum (580 nm),[9] which was anomalous for the usual metallophthalocyanines.[10] Linstead and coworkers have prepared two kinds of antimony complexes which were only characterized by elemental analyses.[11] Two research groups reported on a bismuth derivative in which the bismuth was identified as an anomalous divalent ion by only elemental analysis[12] and mass spectroscopy.[13] That is, essentially nothing is known about the phthalocyanine complexes of group-15 elements. The present investigation of bismuth–phthalocyanine complexes was undertaken with the intention of obtaining information concerning the spectroscopic and chemical properties of phthalocyanine complexes of group-15 elements and of comparing the properties to those of the usual-type metallophthalocyanines.

Another interest stems from whether the bis(phthalocyaninato)bismuthate(III) species will form or not. Since remarkable electrochromic properties of bis(phthalocyaninato)lanthanoids(III) were first reported by Moskalev and Kirin,[14] a number of studies have been published concerning the applications of these materials to electrochromic display devices.[15] Moreover, increasing attention has been paid in recent years to these lanthanoid(III) complexes from various view points of both pure and applied chemistry.[16] Bismuth(III) resembles lanthanoids(III) as follows: (1) its ionic radius with the same coordination number is close to those of the lanthanoids(III);[17] (2) it prefers a large coordination number, such as eight or nine, to smaller ones;[18] and (3) the trivalent oxidation state is most stable. Therefore, bis(phthalocyaninato)bismuthate(III), which is similar to lanthanoid complexes, are likely to form if the coordination geometry of the phthalocyanines around a given central metals would be determined by only the valence and ionic radius of the metal.[19] The authors have attempted to synthesize the bis(phthalocyaninato)bismuthate(III) species by conventional synthetic methods using bismuth(III) salts and either dilithium phthalocyaninate (Li_2(pc); pc represents phthalocyaninate dianion, $C_{32}H_{16}N_8^{2-}$) or phthalonitrile. However, at present, there has been no experimental evidence concerning the formation of the desired species. As described below, only mono(phthalocyaninato) species were obtained as the main products.

This paper describes the first case in which phthalocyanine complexes of group-15 elements were isolated and characterized.

Experimental

Materials. Commercially available dilithium phthalocyaninate (Li_2(pc)) was recrystallized from dry acetone according to the literature.[20] Bismuth(III) salts (BiX_3; $X^-=Cl^-$, Br^-, and I^-, and $Bi(NO_3)_3\cdot 5H_2O$) were of reagent grade (99.99—99.9%) and used as received. Acetonitrile was dried over molecular sieves (0.3 nm) for 24 h and then distilled twice over phosphorus pentaoxide. Dimethyl sulfoxide (DMSO) and *N*,*N*-dimethylformamide (DMF) were dried over molecular sieves (0.4 nm) for 24 h and then distilled in a vacuum. Tetrahydrofuran (THF) was passed through an activated-alumina column and then distilled over molecular sieves (0.4 nm). All of the above-mentioned solvents were distilled just before use. The other solvents used were preliminary dried and purified by a method described in the literature.[21] All of the other chemicals were of reagent grade and were used without further purification.

Preparation of [Bi(pc)X] ($X=Cl^-$, Br^-, I^-, and NO_3^-) in Solution. The formation of the [Bi(pc)X] complex was initiated at room temperature by mixing two DMSO solutions severally containing a certain amount of BiX_3 and an appropriate amount of Li_2(pc). In a typical experiment, upon the addition of an equimolar amount of Li_2(pc) to a $BiCl_3$ solution, the solution immediately turned yellow-green. The resultant solutions, after being precisely diluted to a certain volume with DMSO, were immediately submitted to spectrophotometric measurements. The electronic spectrum of the reaction solution (Fig. 1) was characteristic of the usual metallophthalocyanines,[10] indicating the formation of the bismuth(III)–phthalocyanine complex.

Preparation of Bromo(phthalocyaninato)bismuth(III), [Bi(pc)Br] (Substitution Method). We dissolved 0.21 g (0.47 mmol) of $BiBr_3$ into 28 ml of acetonitrile. After filtration, the solution was added at room temperature to 25 ml of an acetonitrile solution containing 0.30 mmol of Li_2(pc). The resultant solution rapidly turned yellow-green, and then yellow-green microcrystalline solids precipitated within several minutes. The solids were collected by filtration with suction, washed with acetonitrile, and then dried under vacuum at 80 °C. All of the operations were performed in a glove box under a dry argon atmosphere. Yield; 95 mg (40% vs. Li_2(pc)). Anal. Found: C, 48.80; H, 2.16; N, 14.06%. Calcd for $C_{32}H_{16}N_8BiBr$: C, 47.95; H, 2.01; N, 13.99%. This complex was likewise prepared from corresponding acetone solutions. Yield; 91 mg (38% vs. Li_2(pc)). Anal. Found: C, 46.83; H, 2.03; N, 13.60%.

Preparation of Chloro(phthalocyaninato)bismuth(III), [Bi(pc)Cl] (Substitution Method). We dissolved 0.14 g (0.44 mmol) of $BiCl_3$ into 26 ml of an acetonitrile. After filtration, the solution was added at room temperature to 25 ml of acetonitrile solution containing 0.15 mmol of Li_2(pc). Yellow-green microcrystalline [Bi(pc)Cl] complexes were obtained in a similar manner as described above. Yield; 80 mg (70% vs. Li_2(pc)). Anal. Found: C, 49.45; H, 2.04; N, 14.54%. Calcd for $C_{32}H_{16}N_8BiCl$: C, 50.77; H, 2.13; N, 14.81%.

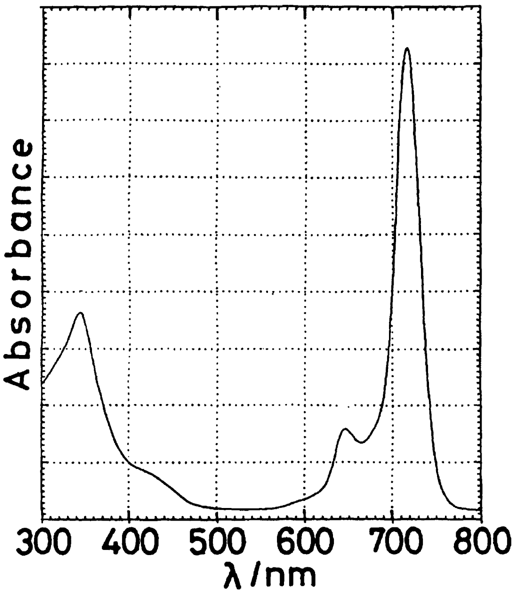

Fig. 1. Electronic absorption spectrum of [Bi(pc)Cl] produced by the reaction between $BiCl_3$ and Li_2(pc) in DMSO.

Neither BiI_3 nor $Bi(NO_3)_3{\cdot}5H_2O$ was available as a starting material due to their insolubility in these solvents.

Preparation of Chloro(phthalocyaninato)bismuth(III), [Bi(pc)Cl] (Nitrile Method). A mixture of 1.7 g (5.39 mmol) of $BiCl_3$ and 7.8 g (60.9 mmol) of phthalonitrile (1 : 11 in molar ratio) was fused under an argon atmosphere in a capped flask at 300 °C for 1 h with occasional stirring. Crude products were obtained as a viscous greenish fluid and then solidified when allowed to cool to room temperature. The solid was washed with dichloromethane for 72 h using a Soxhlet-extractor. The remaining solid was dissolved into DMSO. After filtration, the solution was chromatographed over a silica-gel column (Merck, Silica Gel 60, 30 cm long and 2.5 cm in diameter). The solution was separated into three chromatographic bands. After an uncharacterized yellow-brown band was eluted out, a light-blue band (minor fraction; [M(pc)]-like spectrum, $\lambda_{max}=672$ nm) and a yellow-green band containing [Bi(pc)Cl] (main fraction; $\lambda_{max}=716$ nm) were eluted out with DMSO in this order. A considerable amount of blue solids, which were identified as H_2(pc) by the electronic spectrum in 1-chloronaphthalene, precipitated both from the eluates and in the column bed as the [Bi(pc)Cl] band had passed by. Therefore, no pure [Bi(pc)Cl] was isolated by this method. Essentially, the same results were obtained when BiI_3 and $BiBr_3$ were used instead of $BiCl_3$.

Measurements. Measurements of the electronic spectra were carried out at room temperature using a Shimadzu UV-160A recording spectrophotometer (300—1100 nm region). The IR spectra of the solid materials were recorded at room temperature on a JASCO FT/IR-8000 spectrometer (650—4000 cm^{-1} region) by a diffuse reflectance method (KBr media). All of the measurements were carried out for materials whose elemental analytical data were known, unless otherwise noted.

Results and Discussion

Preparation. The reactions between BiX_3 and Li_2(pc) in DMF, DMSO, acetonitrile, acetone, and THF proceeded quite rapidly, even at room temperature. It is well known that the lithium ions in Li_2(pc) are readily replaced by other metals.[10] A similar substitution reaction, such as $BiX_3+Li_2(pc)\rightarrow[Bi(pc)X]+2LiX$, is considered to take place in the reaction. In order to determine the composition of the produced complex, the absorbance at 716 nm (the [Bi(pc)X] Q-band) was plotted as a function of the molar ratio (R) of Li_2(pc) to $BiCl_3$ (Fig. 2). The absorbance increases in proportion to the R values until R reaches 0.95, but remains almost constant beyond this value. Thus, the molar ratio of bismuth(III) to the pc ligand in the complex is unity. This was confirmed by elemental analyses for

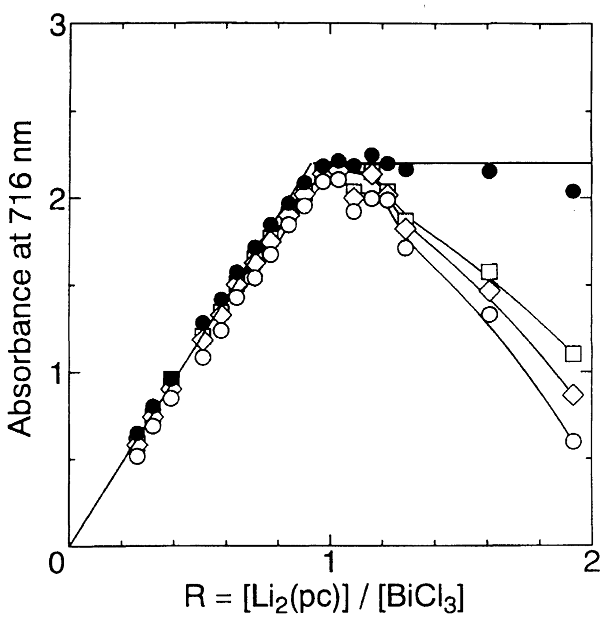

Fig. 2. Plots of the absorbance at [Bi(pc)Cl] Q-band in DMSO solutions containing $BiCl_3$ and $Li_2(pc)$ as a function of the initial molar ratios of $Li_2(pc)$ to $BiCl_3$ in solutions ($R=[Li_2(pc)]_0/[BiCl_3]_0$): just (●), two days (□), four days (◇), and seven days (○) after preparation. $[BiCl_3]_0=1.29\times10^{-5}$ mol dm^{-3}.

the solid materials ([Bi(pc)Cl] and [Bi(pc)Br]). When $BiBr_3$, BiI_3, and $Bi(NO_3)_3$ were used as the starting materials, virtually identical spectra as that in Fig. 1 were observed. Thus, a 1 : 1 complex forms in the reactions, irrespective of the starting bismuth salts studied. The same complexes were produced in DMF, acetonitrile, acetone, and THF; the absorption spectra in these solvents were the same as that in Fig. 1. However, in THF the reaction solution isosbestically turned blue due to the formation of $H_2(pc)$. In acetonitrile and acetone, the complexation was followed by the precipitation of yellow-green solids of [Bi(pc)X]. Regardless of the bismuth(III) salts and solvents studied, only the mono(phthalocyaninato) species were obtained as products of the reactions.

In the presence of excess $Li_2(pc)$, however, a prolonged reaction time (up to a week) appears to give rise to a quite slow succeeding reaction between the produced [Bi(pc)X] and $Li_2(pc)$. The absorbance at 716 nm gradually decreased in the $R>0.95$ region, although there was little decrease in the $R<0.95$ region (Fig. 2). New absorption bands at around 640 and 740 nm grew in intensity during the course of one week. One possible explanation for this observation is that bis(phthalocyaninato)bismuthate(III), $[Bi(pc)_2]^-$, was produced. However, a quite low yield and a difficulty in the chromatographic separation of this species has resulted in a further characterization at present. Attempts to accelerate the reaction by heating the solutions at 60 °C resulted in the decomposition of [Bi(pc)X] into $H_2(pc)$ and unknown bismuth compounds.

In the preparation of [Bi(pc)X], the choice and dehydration of the solvents are most important. At present, dehydrated acetonitrile is the most useful for the following reasons: (1) both $BiCl_3$ (or $BiBr_3$) and $Li_2(pc)$ are sufficiently soluble; (2) the formation of [Bi(pc)X] takes place quite rapidly; and (3) the produced [Bi(pc)-X] is sparingly soluble in the solvent. Acetone is also available for the preparation of [Bi(pc)Br] for the same reasons. Since [Bi(pc)X] complexes were deposited as soon as they were produced (within several minutes), they did not undergo unfavorable succeeding reactions. The [Bi(pc)X]s were also produced in DMSO and DMF. However, they were relatively soluble in these solvents which are quite labile, and hence a considerable amount of [Bi(pc)X] changed to $H_2(pc)$ and an uncharacterized [M(pc)]-like species ($\lambda_{max}=672$ nm) during the concentration procedure, even below 70 °C. In THF, the produced [Bi(pc)X] gradually changed to $H_2(pc)$ at a half-life time of about one hour at room temperature. Although Linstead et al. attempted to prepare bismuth(III) complexes in a similar manner using ethanol as a solvent, they reported that only $H_2(pc)$ was obtained.[11] This was probably due to the instability of the produced bismuth complex and/or moisture in the solvents used. The authors should note that when the acetonitrile used had been preliminary insufficiently dehydrated, the deposited complexes from the solvents were contaminated by a considerable amount of $H_2(pc)$.

The nitrile method was employed with the intention to prepare bis(phthalocyaninato) species. This was because a series of bis(phthalocyaninato)lanthanoids(III) have been prepared as the main products by similar methods.[14] However, only mono(phthalocyaninato) species formed as a main product, although no pure material was isolated in this study. A prolonged reaction time (up to 24 h) yielded virtually the same results.

Contrary to our expectation, no experimental evidence for the formation of the bis(phthalocyaninato) species could be obtained. It is of importance to point out that lanthanoids(III) readily formed bis(phthalocyaninato) species, whereas bismuth(III) did not under the same conditions. One possible explanation for the difference between the chemistry of the metals is that bismuth(III) has a lone-pair electron in the outer shell, whereas the lanthanoids(III) do not. It has been reported that the lone pair is stereochemically active and determines the coordination geometry around a bismuth ion.[18] In a number of bismuth(III) compounds, a stereochemically active lone pair lengthens (and hence weakens) the chemical bonds which are oriented toward the same direction as the lone pair.[18] In the case of [Bi(pc)X] complexes (which are approximately D_{4h} in symmetry) the lone-pair orbital is rich in the $6p_z$ character (the C_4-axis is chosen as a z-axis) and hence lies perpendicular to the pc plane. If another pc ligand would be ligated to the same bismuth ion, the chemical bonds would be oriented toward the same direction as the lone pair. It is therefore likely that the lone pair may prevent any close contact of another pc ligand to the coordination sphere of the bismuth(III) ion in [Bi(pc)X].

However, [Bi(pc)X] in DMSO and DMF appears to react with one more Li_2(pc), forming an unknown species which shows absorption bands at around 640 and 740 nm. A number of bis(phthalocyaninato)metal complexes have been reported to show similar absorption bands in this region.[19] Thus, the possibility that the bis(phthalocyaninato) species is produced in this reaction cannot be completely excluded. Further efforts to prepare the desired species are now in progress.

Solubility and Reactivity of [Bi(pc)X] Complexes. Like the usual metallophthalocyanines, both [Bi(pc)Cl] and [Bi(pc)Br] have limited solubility in common organic solvents. However, the complexes were relatively soluble in polar solvents, such as DMF, DMSO, acetone, pyridine, and THF, although in the latter two the complexes gradually changed to H_2(pc). Interestingly, these complexes were not soluble at all in nonpolar solvents, such as chloroform, dichloromethane, benzene, 1-chloronaphthalene, and 1,2,4-trichlorobenzene, which had been conventionally used as solvents for the usual phthalocyanines.[1]

Both [Bi(pc)Cl] and [Bi(pc)Br] were stable in dehydrated DMSO and DMF unless heated. No spectral change was observed, at least for a few weeks at room temperature. These complexes were also relatively stable even in solvents which had not been preliminary dehydrated. Neither a spectral change nor precipitation took place for a few days. On the other hand, in acetone, pyridine, and acetonitrile, the complexes were readily demetallated by moisture in the solvents, unless the solvents used were preliminary dehydrated. In particular, in THF [Bi(pc)X] gradually changed to H_2(pc), even in solvents which had been preliminary dehydrated over molecular sieves (0.4 nm) and were distilled just prior to use. Although the proton source in THF is unknown at present, even careful purifications of the solvent used in the experiments leaves trace amount of water and/or other impurities able to generate protons.

Both [Bi(pc)Cl] and [Bi(pc)Br] complexes were air-stable, but quite unstable against water and acids in both the solid state and solution. The addition of a small amount of either water, glacial acetic acid, nitric acid, or hydrochloric acid into either DMF or DMSO solutions containing [Bi(pc)X] gave rise to a rapid precipitation of H_2(pc). These complexes reacted with some bases in either DMF or DMSO solutions (as mentioned below). The addition of a small amount of anhydrous hydrazine also caused a rapid precipitation of H_2(pc), probably due to its protic nature. A reaction with either triethylamine or pyrrole at first gave rise to the rapid formation of an unknown species showing a [M(pc)]-like Q-band at 710 nm, followed by a slow isosbestical change to [M(pc)]-like species whose spectrum (λ_{max} = 665 nm) was virtually identical with that of metal-free pc^{2-},[10] indicating that a bismuth ion was expelled from the pc ligand. Imidazole did not react with [Bi(pc)X] at all.

In solution, both [Bi(pc)Cl] and [Bi(pc)Br] reacted with divalent transition metals, even at room temperature, upon the addition of MSO_4 (M=cobalt(II), nickel(II), copper(II), and zinc(II)) forming corresponding [M(pc)]. For example, upon the addition of a DMSO solution containing $ZnSO_4 \cdot 7H_2O$ to a DMSO solution containing [Bi(pc)Br] (30 : 1 in molar ratio), [Bi(pc)Br] gradually and isosbestically changed to [Zn(pc)] (λ_{max}= 670 nm[10]) as shown in Fig. 3. Similar spectral changes were observed during a reaction with copper(II) sulfate. Thus, a bismuth(III) ion in [Bi(pc)X] was directly replaced by either zinc(II) or copper(II). On the other hand, the reaction of [Bi(pc)X] with cobalt(II) at first gave rise to a rapid formation of an unknown species showing a [M(pc)]-like Q-band at 710 nm, followed by a slow isosbestical change to [Co(pc)] (λ_{max}=667 nm[10]). Figure 4 shows the spectral changes of a DMSO solution containing [Bi(pc)Br] to which a DMSO solution containing $CoSO_4 \cdot 7H_2O$ (1 : 39 in molar ratio) was added. Similar spectral changes were observed during the reaction with nickel(II) sulfate, except that a Q-band of an intermediate was located at 712 nm. Details concerning the mechanisms of the reactions with

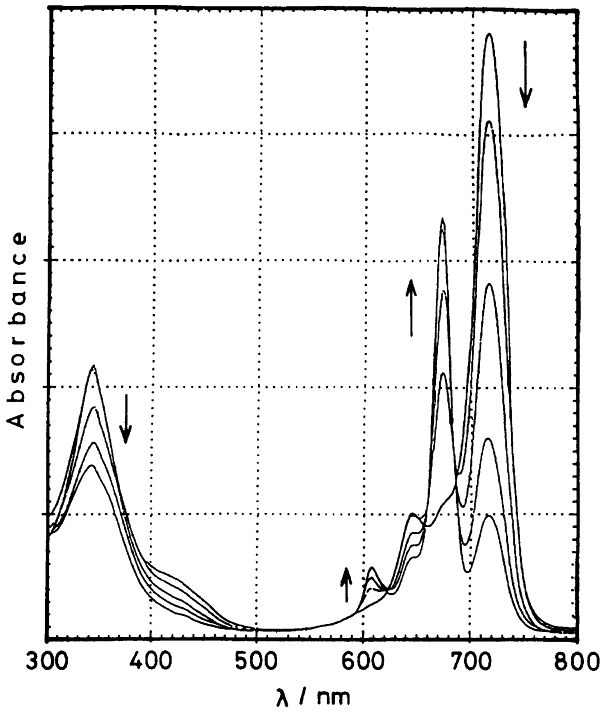

Fig. 3. Spectral changes during a reaction between [Bi(pc)Br] and $Zn(SO_4)$ in DMSO ($[Bi(pc)Br]_0$= ca. 1.82×10^{-5} mol dm^{-3}). The arrows indicate the direction of the spectral changes: just, 51 h, 102 h, 171 h, and 216 h after the addition of $Zn(SO_4)$.

Table 1. Electronic Spectral Data of [Bi(pc)X] Complexes in DMSO

X^-	λ_{max}/nm (molar coefficient constant/10^5 $dm^3\,mol^{-1}\,cm^{-1}$)			
Cl^-	716.0 (1.69),	645.0 (0.34),	415 (sh,[a] ca. 0.17),	343.0 (0.71)
Br^-	716.0 (1.68),	645.0 (0.34),	415 (sh, ca. 0.17),	344.0 (0.71)
I^- [b]	715.5 (1.00),	645.0 (0.20),	415 (sh, ca. 0.10),	343.0 (0.47)
NO_3^- [b]	716.0 (1.00),	645.0 (0.24),	415 (sh, ca. 0.10),	343.0 (0.48)

a) Sh; shoulder. b) As far as [Bi(pc)I] and [Bi(pc)(NO_3)] are concerned, the values in parentheses are relative intensity.

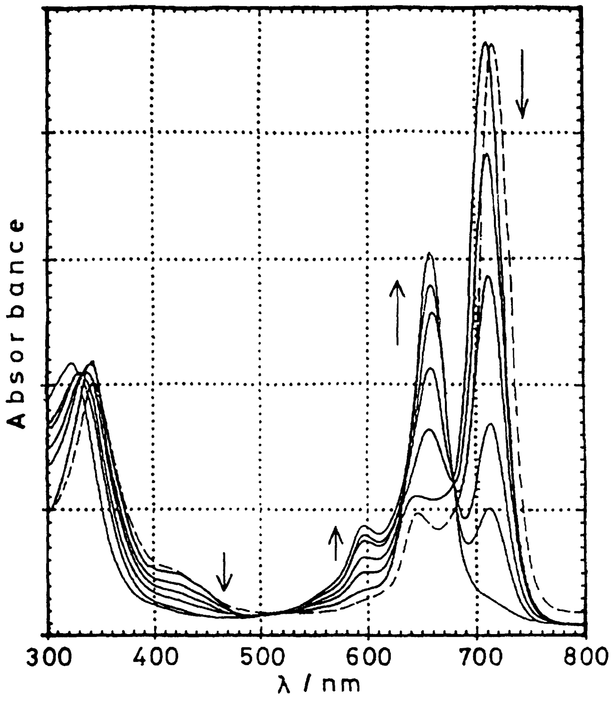

Fig. 4. Spectral changes during a reaction between [Bi(pc)Br] and Co(SO_4) in DMSO ($[Bi(pc)Br]_0$ = ca. 1.82×10^{-5} mol dm^{-3}). The arrows indicate the direction of the spectral changes: just, 24 h, 51 h, 171 h, 216 h, and 744 h after the addition of Co(SO_4). The broken line indicates the spectrum before the addition of Co(SO_4).

Table 2. IR Spectral Data of [Bi(pc)Br] and [Bi(pc)Cl]

ν/cm^{-1}			Assignment
[Bi(pc)Br]	[Bi(pc)Cl]	[Pb(pc)]	
723	725	723	γ(C–H)[b]
745	743	742	γ(C–H)
772	774	771	ν(C–N)[c]
785 sh[a]	781 sh	780	
818	816	815	
870 sh	870 sh	870	γ(C–H)
885	886	881	ρ(M–Np)[d]
953	955	951	
1005	1005	1002	
1060 sh	1060 sh	1059	β(C–H)[e]
1076	1076	1078	ν(C–N)
1117	1119	1114	β(C–H)
1163	1163	1160	ν(C–N)
1287	1287	1282	ν(C–C)[f]
1331	1333	1330	ν(C–N)
1412	1414	1404	ν(C–C)
1487	1489	1484	ν(C–C)

a) sh; shoulder. b) γ(C–H); out of plane C–H deformation. c) ν(C–N); C–N stretching vibration in pyrrole skeleton. d) ρ(M–Np); metal–nitrogen rocking vibration. e) β(C–H); in plane C–H deformation. f) ν(C–C); C–C stretching vibration in isoindole skeleton.

cobalt(II) and nickel(II) are unknown at present, and will be future subjects.

Thus, [Bi(pc)X]s are quite labile compared to the usual metallophthalocyanines. It is noteworthy that porphyrine analogues of bismuth(III) have been reported to be likewise labile.[5]

Neither [Bi(pc)Cl] nor [Bi(pc)Br] was volatile, even under a pressure of 0.0133 Pa up to 300 °C where the usual metallophthalocyanines sublime.[1] Above this temperature, both complexes began to decompose to H_2(pc)-like blue species and finally to phthalonitrile.

Spectroscopy. The electronic spectra of [Bi(pc)X] (X^-=Cl^-, Br^-, I^-, and NO_3^-) in DMSO were virtually identical with each other and with that shown in Fig. 1. The spectra are characteristic of the usual metallophthalocyanines.[10] Their spectral data are listed in Table 1. The same spectra were observed in DMF, acetone, acetonitrile, THF, and pyridine solutions, although the absorption bands arising from H_2(pc) were observed in the latter two solvents. Hence, the electronic structure of the complexes is essentially the same, irrespective of the solvents and sort of X^- studied. An intense Q-band appeared at 716 nm, which is an excitation from a HOMO ($a_{1u}(\pi)$) to a LUMO ($e_g(\pi^*)$)[22] of the pc ligand in character.[10,23] The [Bi(pc)X] Q-band is the most bathochromically shifted of the peripherally unsubstituted metallophthalocyanines ever known,[10] indicating the proximity of the pc HOMO and LUMO in energy. A broad band appeared at 340 nm, which corresponded to a B-(Soret) band. An additional band was observed at around 415 nm, which gave rise to the green cast of the complexes. A quite similar absorption band was reported for the (phthalocyaninato)lead(II) complex, [Pb(pc)],[2,23] which was assigned as an excitation from an $a_{2u}(6p_z)$ orbital of lead(II) to a pc $e_g(\pi^*)$ orbital (that is, a hyper metal-to-ligand charge-transfer (MLCT) band in character) by the analogy with (porphyrinato)lead(II).[23] Phthalocyanine complexes of germanium(II) and phosphorus(III), which have a lone-pair electron in the outer shell, also showed a similar extra band in this region.[2] Therefore, the extra 415 nm band of [Bi(pc)X] can be assigned as a hyper MLCT band, which is an excitation from an $a_{2u}(6p_z)$ orbital of bismuth(III) to a pc $e_g(\pi^*)$ orbital in character.

The IR spectra of [Bi(pc)Cl] and [Bi(pc)Br] are identical with each other. Thus, the molecular structure of [Bi(pc)X] is almost the same, irrespective of the sort of X^-. The peak positions of the prominent bands are listed in Table 2 along with the spectral data of [Pb(pc)][25] for a comparison. The spectra are characteristic of the usual metallophthalocyanines.[26—28] An empirical assignment of the IR bands is proposed (Table 2) according to the literature.[27,28] The IR bands at around 900 cm^{-1} have been assigned as a metal-pyrollic nitrogen (M–Np) rocking vibration (ρ(M–Np)), and are considered to be related to the strength of the M–Np bonds.[28] The corresponding bands were observed at 887 cm^{-1} for [Bi(pc)Cl] and 885 cm^{-1} for [Bi(pc)Br], respectively. These values are lower than those of transition-metal complexes.[28] The low frequencies of ρ(M–Np) in [Bi(pc)X] appear to reflect the weakness of the bismuth–nitrogen bonds.

The electronic and IR spectra of the [Bi(pc)X] complexes resemble those of [Pb(pc)],[2,23,25] which is likewise labile.[29] This is not surprising, since the $Bi(pc)^+$ moiety and [Pb(pc)] are isoelectronic with each other. Based on the similarity in the ionic radii of the central metals (Pb^{2+}; 98 pm as four-coordinate and Bi^{3+}; 96 pm as five-coordinate)[17] and in the IR spectra, the molecular structure of [Bi(pc)X] is considered to be close to that of [Pb(pc)]. X-Ray crystallographic studies on [Pb(pc)] showed that the lead atom deviated by ca. 100 pm from the pc plane.[30] Likewise, the bismuth atom in [Bi(pc)X] is anticipated to lie above the pc ligand. This nonplanarity is considered to signify their lability.

The spectroscopic characteristics of [Bi(pc)X]s presented here significantly differ from those of the bismuth(II)–phthalocyanine complex reported by Snow and Jarvis.[12] Although only the peak positions are described without intensity data in the literature, both the electronic and IR spectra of the latter seem to be close to those of H_2(pc), rather than to those of the usual metallophthalocyanines. It is lilkely that the bismuth(II) derivative was contaminated with a considerable amount of metal-free phthalocyanine, even though some bismuth derivatives would have been produced. In addition, such a stable bismuth(II) species is unknown.

Conclusion

The [Bi(pc)Cl] and [Bi(pc)Br] complexes have been prepared and isolated for the first time as phthalocyanine complexes of group-15 elements. Both nitrile and substitution methods, which are conventional synthetic methods for metallophthalocyanines, have mainly produced mono(phthalocyaninato) species. No experimental evidence for the formation of the bis(phthalocyaninato) species was obtained. The complexes were quite labile compared to the usual metallophthalocyanines, and were readily demetallated by water, acids, and bases. The complexes also react with some divalent transition metals in solutions, forming the corresponding metallophthalocyanines.

The spectroscopic properties of the complexes were characteristic of the usual metallophthalocyanines, apart from the appearance of a hyper MLCT band in the electronic spectra. The bathochromically shifted Q-band (716 nm) in electronic spectra indicates the proximity of the HOMO and LUMO of the pc ligand in energy.

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