3212 © 1994 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 67, 3212—3215(1994) [Vol. 67, No. 12

Redox Potentials of Bromo- and Chloro(phthalocyaninato)bismuth(III) Complexes

Hiroaki ISAGO*,# and Yutaka KAGAYA#
National Research Institute for Metals, 3-12, 2-Chome, Nakameguro, Meguro-ku, Tokyo 153

(Received March 3, 1994)

The redox potentials of the titled complexes, [Bi(pc)X] (pc^{2-}=phthalocyaninate, $C_{32}H_{16}N_8{}^{2-}$, and X=Cl^- and Br^-), in *N,N*-dimethylformamide solutions have been determined by cyclic voltammetry for the first time as phthalocyanine complexes of group-15 elements. The voltammograms of [Bi(pc)Cl] consisted of one oxidation ($E_{1/2}$=0.36 V vs. ferrocene/ferricinium$^+$) and two reduction couples (ca. −1.2 and ca. −1.0 V), each of which was a quasi-reversible one-electron process. The voltammograms of [Bi(pc)Br] were quite similar to those obtained with [Bi(pc)Cl], with the exception of the appearance of an additional irreversible anodic peak at 0.30 V, which could be attributable to the oxidation of non-ligand bromide, suggesting the dissociation of [Bi(pc)Br] into $[Bi(pc)]^+$ and Br^- in DMF. This is the first case in which [M(pc)X]-type (M=trivalent metal) complex dissociated into $[M(pc)]^+$ and X^- in solution.

The electrochemistry of phthalocyanines and porphyrins has attracted much attention in relation to the photosensitization,[1)] electrocatalytic properties,[2)] electrochromic properties,[3)] semiconductivity,[4)] and so on. The redox potentials of a number of metallophthalocyanines (MPcs) have been determined so far.[5—8)] However, nothing is known concerning the electrochemistry of complexes of group-15 elements, although the electrochemistry of phosphorus(V)–porphyrin complexes (possessing a similar tetrapyrrole ring skeleton) have been intensively investigated.[9)] This was because no complex had been isolated until the authors isolated the titled bismuth complexes.[10)] This paper describes the redox characteristics of the titled complexes for the first time as an MPc of group-15 elements.

In a previous work,[10)] the bismuth complexes showed anomalous solubility characteristics for MPcs: Being insoluble in non-polar solvents, which had been used for the usual MPcs, but being relatively soluble in polar solvents. In this paper, the following accessible explanation for the anomaly is given: [Bi(pc)X] dissociates into $[Bi(pc)]^+$ and X^- in polar solvents.

Experimental

Details concerning the preparation of the [Bi(pc)X]s, (pc^{2-}=phthalocyaninate, $C_{32}H_{16}N_8{}^{2-}$, and X=Cl^- and Br^-), are described elsewhere.[10)] Bismuth(III) bromide (Kojundo Chemical Laboratory Co., Ltd., 99.99%) was used as received. Tetrabutylammonium bromide (TBAB), perchlorate (TBAP), tetrafluoroborate (TBAT), and hexafluorophosphate (TBAH) were prepared by conventional methods.[11)] Commercially available ferrocene was sublimed twice prior to use. Reagent-grade *N,N*-dimethylformamide (DMF) was dried over molecular sieves (0.4 nm) overnight and then distilled under a vacuum below 70 °C just prior to use.

All of the cyclic voltammetry experiments was 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. 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 appropriate supporting electrolyte in DMF). 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 oxidation (controlled-potential coulometry) of [Bi(pc)X] was carried out in a DMF solution containing 0.05 M TBAP by using a Hokuto Denko (HA-501) potentiostat/galvanostat connected to a Hokuto Denko (HF-201) coulometer. In this case, 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.

Electronic absorption (UV) and magnetic circular dichroism (MCD) spectra were recorded at ambient temperature on a Shimadzu (UV-160A) spectrophotometer and a JASCO (J-720) spectropolarimeter equipped with a 0.45-T permanent magnet, respectively.

Results

The cyclic voltammograms (CVs) of [Bi(pc)Cl] in DMF ([complex]=ca. 0.1 mM) over the range +0.7 — −1.5 V consisted of one oxidation (Ox1) and two reduction couples (Red1 and Red2), each of which was a quasi-reversible one-electron process. A typical CV is shown in Fig. 1a. The averaged half-wave potentials ($E_{1/2}=(E_{pa}+E_{pc})/2$) of the couples at scan rates of 50, 100, and 200 mV s^{-1} (below 30 mV s^{-1}, the CVs observed were too shallow to analyze) are listed in Table 1. These values are almost constant, irrespective of the supporting electrolytes studied. With the exception of the appearance of an additional irreversible oxidation wave (Oxirr) at 0.30 V, the CVs of [Bi(pc)-Br] ([complex]=ca. 0.1 mM) were quite similar to those obtained with [Bi(pc)Cl] (Fig. 1b). The UV and MCD spectra of [Bi(pc)Br] in DMF (Fig. 2) are identical with those of [Bi(pc)Cl], and are characteristic of the usual-

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#Present address: National Research Institute for Metals, 1-2-1, Sengen, Tsukuba, Ibaraki 305.

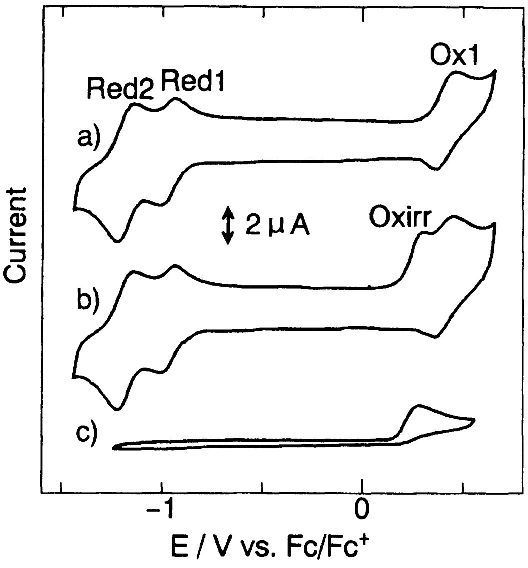

Fig. 1. Typical cyclic voltammograms of a) [Bi(pc)-Cl], b) [Bi(pc)Br], and c) TBAB in DMF solutions containing 0.1 M of TBAP at a scan rate of 100 mV s^{-1}([complex]=ca. 2×10^{-4} M).

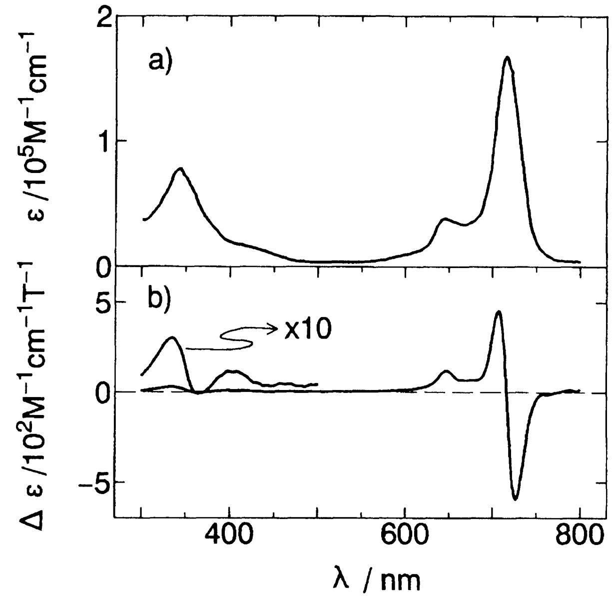

Fig. 2. The electronic absorption (a) and MCD spectra (b) of [Bi(pc)Br] in DMF .

Table 1. Half-Wave Potentials of [Bi(pc)X] in DMF

Complex	Electrolytes	$E_{1/2}$/V vs. Fc/Fc$^+$ ($\Delta E_p$$^{a)}$/mV)			
		Red2	Red1	Oxirr$^{b)}$	Ox1
[Bi(pc)Cl]	TBAP	−1.19(80)	−1.01(70)	—	0.36(60)
	TBAT	−1.18(80)	−0.98(80)	—	0.38(60)
	TBAH	−1.17(80)	−0.96(60)	—	0.38(70)
[Bi(pc)Br]	TBAP	−1.18(80)	−0.97(80)	0.30	0.41(90)
	TBAT	−1.18(90)	−0.97(60)	0.31	0.42(100)
	TBAH	−1.18(80)	−0.96(60)	0.30	0.41(70)
TBAB	TBAP	—	—	0.30	—

a) ($E_p^a-E_p^c$)/mV. b) E_p^a.

type MPcs.[12] During the electrochemical oxidation of [Bi(pc)Br] at 20 mV above the anodic peak potential of Oxirr, little spectral change was observed, except for a slight decrease in the intensity of the Q-band. The number of electrons per molecule transferred during the oxidation was 1.16±0.06 for three independent experimental runs. The electrochemical oxidation of [Bi(pc)-X] at 50 mV above the anodic peak potential of Ox1 gave rise to the deposition of blue solids on the surface of the electrode, which were identified as being metal-free H_2(pc) based on the UV spectra in 1-chloronaphthalene.

Discussion

At present, DMF has been most useful for voltammetric measurements of [Bi(pc)X]. Under the same conditions, the use of dimethyl sulfoxide (DMSO) as a solvent, which had been preliminary dehydrated over molecular sieves (0.4 nm) and freshly distilled, yielded CVs consisting of only irreversible waves. This was probably due to the instability of the electrochemically generated species in DMSO, although [Bi(pc)X]s were considerably stable in the solvent, unless heated.[10] The other conventional electrochemically-useful solvents (e.g., THF, acetonitrile, dichloromethane, and dichlorobenzene) were not available due to the instability and/or limited solubility of the complexes in the solvents.[10]

Since the CVs of [Bi(pc)Cl] are characteristic of the usual-type MPcs, in which no metal-centered redox reaction occurs,[5] the three quasi-reversible redox couples are considered to be pc-ring-centered. Thus, Ox1, Red1 and Red2 are assigned to pc^{2-}/pc^{-}, pc^{3-}/pc^{2-}, and pc^{4-}/pc^{3-}, respectively. Although the $E_{1/2}$ values observed (Table 1) were typical of the usual-type MPcs,[5] the potential difference between the first ring oxidation and the first ring reduction (ΔE) was 1.36±0.02 V, the value of which was the smallest of the peripherally unsubstituted MPcs (Table 2). Since the first oxidation and reduction potentials of a given compound are related to an energy level of its HOMO and LUMO, respectively, the smallest ΔE values indicate the proximity of the pc HOMO and LUMO in energy. This is consistent with the considerably bathochromically-shifted Q-band of [Bi(pc)X]s,[10] which can be assigned based on the MCD spectra of [Bi(pc)X]s (Fig. 2b) as an excitation from an $a_{1u}(\pi)$ (HOMO) to an orbitally degenerated $e_g(\pi^*)$ (LUMO) in character,[12] for a peripherally unsubstituted MPc.

With the exception of Oxirr, the CVs of [Bi(pc)Br] were quite similar to those of [Bi(pc)Cl]. The electronic structure of [Bi(pc)X] is essentially the same irrespective of the sort of X studied,[10] suggesting that Oxirr

Table 2. The Potential Differences between First Ring Oxidation and First Ring Reduction (ΔE) in Various MPcs

M in MPc[a)]	ΔE/V	Solvent	Ref.
[Bi(pc)Cl]	1.36±0.02	DMF	This work.
[Bi(pc)Br]	1.38±0.01	DMF	This work.
Pb(II)	1.39	DMF	5a)
Mg(II)	1.55	DMA[b)]	5c)
In(III)	1.55	DMF	5a)
Hg(II)	1.56	DMF	5a)
Al(III)	1.57	DMF	5a)
Th(IV)[c)]	1.58	PhCN[d)]	5d)
Ga(III)	1.60	DMF	5a)
U(IV)[c)]	1.62	PhCN	5d)
Ln(III)[c,e)]	1.62—1.68	DMSO	5f)
Zn(II)	1.68	DMA[b)]	5b)
Cd(II)	1.71	DMF	5a)
Si(IV)	1.89	CH_2Cl_2	5e)

a) Except for [Bi(pc)X]s, ligands other than pc^{2-}, if any, are omitted for clarity. b) DMA=*N*,*N*-dimethylacetamide. c) Mono(phthalocyaninato) complex. d) PhCN=cyanobenzene. e) Ln=Lanthanoids.

was not pc-ring-centered. This was confirmed by controlled-potential electrolysis experiments; little spectral change was observed during the electrolysis at 20 mV above the anodic peak potential of Oxirr, and the number of electrons per molecule transferred during the electrolysis was essentially unity. Metal-centered oxidation can also be excluded because no such wave was observed for [Bi(pc)Cl]. Hence, the most accessible explanation is that Oxirr is bromide-centered. For a comparison, a typical CV of TBAB, which was measured under the same conditions, is shown in Fig. 1c. An irreversible anodic wave appeared at 0.30 V, which was identical with the peak potential of the Oxirr. Thus, Oxirr can be attributable to the oxidation of bromide. However, the 0.30-V oxidation potential is quite low as those of bromides, which were ligated to metal ions; for example, 0.83 V for $BiBr_3$. This suggests that [Bi(pc)X] dissociates in DMF into $[Bi(pc)]^+$ and Br^-.

An alternative explanation for the appearance of the oxidation wave of free Br^- is that the bromide in [Bi(pc)Br] is replaced by perchlorate added as supporting electrolytes: e.g., $[Bi(pc)Br]+ClO_4^- \rightarrow [Bi(pc)ClO_4]+Br^-$ (this process, if any, can not be monitored spectrophotometrically because the electronic spectra of [Bi(pc)X]s are essentially identical with each other, irrespective of the sort of X^-[10)]). However, such replacement reactions are unlikely to occur, because the CVs obtained with [Bi(pc)Br] in either TBAT or TBAH solution also showed the irreversible oxidation wave of free Br^- (Table 1). If the Br^- in [Bi(pc)Br] were ligated to the bismuth ion in DMF, no oxidation wave of free Br^- would be observed in the solutions containing either TBAT or TBAH, because both BF_4^- and PF_6^- have poor coordination ability, and, hence, can not replace the bromide as a ligand. Therefore, the free Br^- is considered to be generated not by the replacement reaction, but by the dissociation of [Bi(pc)Br].

In a previous study,[10)] [Bi(pc)X]s showed anomalous solubility characteristics for the usual-type MPcs. That is, they were insoluble in non-polar solvents, such as dichloromethane and 1-chloronaphthalene, which had been conventionally used for MPcs whereas relatively soluble in polar solvents. These facts are consistent with the above speculation that [Bi(pc)Br] dissociates into $[Bi(pc)]^+$ and Br^-. It is noteworthy that bismuth(III) complexes of porphyrin (possessing a similar tetrapyrrole ring skeleton) are known to be ionic $[Bi(porphyrinate)]^+$.[13)]

With regard to [Bi(pc)Cl], it is unknown at present whether the complex dissociates into $[Bi(pc)]^+$ and Cl^- in DMF. If it dissociates, an oxidation wave of the free Cl^- is expected to be observed at around 0.7 V. Unfortunately, the limited solubility of the complex into DMF made it difficult to detect such an oxidation wave because of a steep increase in the base-line current in the CV beyond 0.6 V, as shown in Fig. 1. However, based on a similarity in the solubility characteristics and the spectroscopic properties between [Bi(pc)Cl] and [Bi(pc)Br],[10)] it is considered that [Bi(pc)Cl] also dissociates in DMF.

The ionic nature of the Bi–X bond in [Bi(pc)X] is unknown in the chemistry of [M(pc)X]-type complexes (the M represents a trivalent metal ion). However, this apparent anomaly in bismuth complexes can be rationalized as follows. Based on the similarity in the ionic radii of the central metals and spectroscopic properties of [Bi(pc)X]s and [Pb(pc)], the molecular structure of these complexes are considered to be close to each other.[10)] X-Ray crystallographic studies on [Pb(pc)] showed that the lead atom deviated by ca. 100 pm from the pc^{2-} plane and did not ligate any other ligands than the pc^{2-}.[14)] Since [Pb(pc)] and the $Bi(pc)^+$ moiety are isoelectronic with each other, it is not surprising that $Bi(pc)^+$ is likewise stable without any additional ligands. Furthermore, as discussed in a previous paper,[10)] the lone-pair orbital of the bismuth(III) ion in the $Bi(pc)^+$ moiety is rich in the $6p_z$ character (the C_4 axis is chosen as a z axis), and would be perpendicular to the pc^{2-} plane. In a number of bismuth(III) compounds, a lone-pair electron of bismuth(III) is known to be stereochemically active, and thus weakens the chemical bonds which are oriented in the same direction as the lone pair.[15)] If an axial ligand would be ligated to the bismuth ion in the $Bi(pc)^+$ moiety, the chemical bonds would be oriented in the same direction as the lone pair. It is therefore likely that the lone pair may prevent any close contact of the other ligand, particularly the axial ligand, to the coordination sphere around the bismuth ion in the $Bi(pc)^+$ moiety.

Conclusion

The redox potentials of the titled complexes have been determined for the first time as an MPc of group-15 elements. The CVs of [Bi(pc)Cl] were characteristic of the usual-type MPcs, in which no metal-centered redox reaction took place. The CVs of [Bi(pc)Br] were essentially the same as those of [Bi(pc)Cl], with the exception of an appearance of Oxirr, which could be attributable to the oxidation of non-ligand bromide, suggesting that [Bi(pc)Br] dissociates in DMF into $[\mathrm{Bi(pc)}]^+$ and Br^-. This is the first case in which [M(pc)-X]-type (M=trivalent metal) complex dissociates into $[\mathrm{M(pc)}]^+$ and X^- in solution. The smallest ΔE values (1.36 V) indicates the proximity of pc HOMO and LUMO in energy.

References

1) G. Ferraudi, "Phthalocyanines; Properties & Application," ed by C. C. Leznoff and A. B. P. Lever, VCH Publications, New York (1988), pp. 291—340.

2) A. P. B. Lever, M. R. Hempstead, C. C. Leznoff, W. Liw, M. Melnik, and P. Seymour, *Pure Appl. Chem.*, **58**, 1467 (1986), and references cited herein.

3) P. N. Moskalev and I. S. Kirin, *Zh. Fiz. Khim.*, **46**, 1778 (1972); Y. Liu, K. Shigehara, M. Hara, and A. Yamada, *J. Am. Chem. Soc.*, **113**, 440 (1991); H. Isago and R. Hasegawa, *Chem. Express*, **4**, 233 (1989); G. A. Corker, B. Grant, and N. J. Clecak, *J. Electrochem. Soc.*, **126**, 1339 (1979).

4) For example: P. Turek, P. Petit, J.-J. André, J. Simon, R. Eve, B. Boudjema, G. Guillaud, and M. Maitrot, *J. Am. Chem. Soc.*, **109**, 5119 (1987); Z. Belarbi, C. Sirlin, J. Simon, and J.-J. André, *J. Phys. Chem.*, **93**, 8105 (1989).

5) a) A. B. P. Lever and P. C. Minor, *Inorg. Chem.*, **20**, 4015 (1981); b) T. Nyokong, Z. Gasyna, and M. J. Stillman, *Inorg. Chem.*, **26**, 548 (1987); c) E. Ough, T. Nyokong, K. A. M. Creber, and M. J. Stillman, *Inorg. Chem.*, **27**, 2724 (1988); d) R. Guilard, A. Dormond, M. Belkalem, J. E. Anderson, Y. H. Liu, and K. M. Kadish, *Inorg. Chem.*, **26**, 1410 (1987); e) T. M. Mezza, N. R. Armstrong, G. W. Ritter, II, J. P. Iafalice, and M. E. Kenny, *J. Electroanal. Chem.*, **137**, 227 (1982); f) A. Iwase and K. Tanaka, *Electrochim. Acta*, **35**, 1707 (1990).

6) H. Konami, M. Hatano, N. Kobayashi, and T. Osa, *Chem. Phys. Lett.*, **165**, 397 (1990); F. Castanede, C. Piechocki, V. Plichon, J. Simon, and J. Vaxiviere, *Electrochim. Acta*, **31**, 131 (1986); N. A. Ovchinnikova, L. G. Tomilova, N. B. Seregina, V. V. Minin, G. M. Larin, and E. A. Luk'yanets, *Zh. Obshch. Khim.*, **62**, 1631 (1992).

7) A. B. P. Lever, *Inorg. Chim. Acta*, **203**, 171 (1993); A. B. P. Lever and J. P. Wilshire, *Inorg. Chem.*, **17**, 1145 (1978); K. M. Kadish, L. A. Bottomley, and J. S. Cheng, *J. Am. Chem. Soc.*, **100**, 2371 (1978); A. B. P. Lever, P. C. Minor, and J. P. Wilshire, *Inorg. Chem.*, **20**, 2550 (1981); G. Fu, Y. Fu, K. Jayaraj, and A. B. P. Lever, *Inorg. Chem.*, **29**, 4090 (1990).

8) N. Kobayashi, H. Lam, W. A. Nevin, P. Janda, C. C. Leznoff, and A. B. P. Lever, *Inorg. Chem.*, **29**, 3415 (1990); W. A. Nevin, W. Liu, S. Greenberg, M. R. Hempstead, S. M. Marcuccio, M. Melnik, C. C. Leznoff, and A. B. P. Lever, *Inorg. Chem.*, **26**, 891 (1987); W. A. Nevin, M. R. Hempstead, W. Liu, C. C. Leznoff, and A. B. P. Lever, *Inorg. Chem.*, **26**, 570 (1987).

9) C. A. Marrese and C. J. Carrano, *J. Chem. Soc., Chem. Commun.*, **1982**, 1279; *Inorg. Chem.*, **22**, 1858 (1983); **23**, 3961 (1984).

10) H. Isago and Y. Kagaya, *Bull. Chem. Soc. Jpn.*, **67**, 383 (1994).

11) D. T. Sawyer and J. L. Roberts, Jr., "Experimental Electrochemistry for Chemists," Wiley-Interscience, New York (1974).

12) M. J. Stillman and T. Nyokong, "Phthalocyanines; Properties & Applications," ed by C. C. Leznoff and A. B. P. Lever, VCH Publications, New York (1988), pp. 133—289.

13) P. Sayer, M. Gouterman, and C. R. Connell, *J. Am. Chem. Soc.*, **99**, 1082 (1977).

14) K. Ukei, *Acta Crystallogr., Sect. B*, **29**, 2290 (1973); Y. Iyechika, K. Yakushi, I. Iwamoto, and H. Kuroda, *Acta Crystallogr., Sect. B*, **38**, 766 (1982).

15) For example: R. D. Rodgers, A. H. Bond, S. Aguinaga, and A. Reyes, *J. Am. Chem. Soc.*, **114**, 2967 (1992); R. D. Rodgers, A. H. Bond, and S. Aguinaga, *J. Am. Chem. Soc.*, **114**, 2960 (1992).