Conductivity of Reduced Metallo-tetra-*N*-methyl-2,3-pyridinoporphyrazine Complexes

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Abstract

Tetra-*N*-methyl-2,3-pyridinoporphyrazine complexes of cobalt(II), nickel(II), copper(II) and zinc(II) were reduced by sodium dithionite in an aqueous solution. The central metal ions were reduced in the cobalt(II), nickel(II) and copper(II) complexes, whereas the ligand was reduced in the zinc(II) complex. Conductivities of the complexes significantly increased in reduction.

Introduction

Many studies have been reported on the electroconductivity of metallophthalocyanine (PcM) in the past decade: e.g. partial oxidations of PcM and polymer $(PcMX)_n$ complexes where X is a bridging ligand such as oxygen, halogen and cyanide anions [1, 2], intrinsic semiconductors of bis(phthalocyaninato)lutetium(III) and its alkyl chain derivatives [3–5]. The conductivity of the metallophthalocyanine complexes can also be increased by the partial reduction of the complexes but few studies have been reported; the $(PcSiO)_n$ polymer was reduced by potassium vapor in a sealed tube and the reduced species (unstable in air) showed semiconductivity at room temperature [6]. Recently, thin films of the reduced metallophthalocyanine complexes were also prepared by co-condensation of the complexes with potassium under high vacuum, and their conductivities were investigated [7].

To elucidate the conductivity of the reduced metallophthalocyanine complexes, a facial reduction of the complexes is desired. It has been reported that redox potentials of metal(II) complexes with tetra-*N*-methyl-2,3-pyridinoporphyrazine, TMPM(II), are shifted to more positive values compared with those of non-annelated metallophthalocyanine complexes [8, 9]. In this paper, TMPM(II) complexes where M = Co(II), Ni(II), Cu(II) and Zn(II) are reduced in mild conditions to investigate their conductivities (Fig. 1).

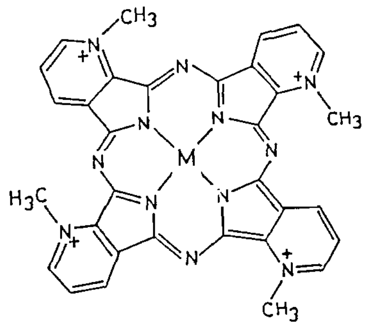

Fig. 1. Schematic representation of the TMPM(II) complex.

Experimental

Materials

The copper(II) complex was prepared according to the method of Iwashima and Sawada [10], and was methylated in a similar way to that described by Wöhrle *et al.* [8]; the mixture of urea, 2,3-pyridinedicarboxylic acid, anhydrous copper(II) chloride (4:4:1 mole ratio) and a catalytic amount of ammonium molybdate was heated at *c.* 250 °C for several hours. The crude product was ground and washed successively with warm sodium hydroxide solution (5% wt./vol.), warm water, warm dilute hydrochloric acid (3% vol./vol.) and finally with warm water. Subsequently, the product was reprecipitated from concentrated sulfuric acid by the addition of water (yield 18%).

The DMF solution containing the complex and dimethyl sulfate was allowed to stand overnight at 120 °C under nitrogen atmosphere. The dark purple precipitates obtained were dissolved in water. After filtration of the solution, the objective was obtained by the addition of adequate amounts of acetone

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TABLE 1. Elemental analyses

	Found (%)			Calculated (%)		
	C	H	N	C	H	N
TMPCo(I)·$1.5SO_4$·$0.5H_2O$	48.92	3.47	21.02	48.72	3.20	21.32
TMPNi(I)·$1.5SO_4$·$2.5H_2O$	46.52	3.59	20.45	46.61	3.55	20.39
TMPCu(I)·$1.5SO_4$·$3H_2O$	45.32	3.12	20.18	45.84	3.61	20.05

The result of an elemental analysis for the reduced zinc species was not satisfactory, but the C/N ratio (found, 2.69) was consistent with the calculated value (2.67).

(yield 47%). The complexes of cobalt(II), nickel(II) and zinc(II) were also prepared in a similar method to that described above. Their purities were determined by means of elemental analyses and electronic spectra.

Measurements

The electronic spectra in solution and the infrared spectra (KBr pellets) were measured on a Hitachi 200-20 spectrophotometer and a Hitachi 260-50 spectrophotometer, respectively. The ESR spectra were measured in the solid state at room temperature with a JEOL-1X spectrophotometer. Conductivity measurements of pressed pellets of the samples were carried out in the temperature range from –60 to 20 °C with a two probe method.

Results and Discussion

The purple precipitates were immediately obtained by the addition of sodium dithionite into an aqueous solution of the TMPNi(II) complex. The reduced complex scarcely dissolves in common organic solvents and water.

As shown in Fig. 2, the absorbance at 600 nm attributable to the Q band of the TMPNi(II) complex disappeared in the reduced species, a new band appearing at 510 nm.

In the IR spectra, bands at 1410, 1200, 960 and 890 cm^{-1} disappeared on reduction, and a new band appeared at 1100 cm^{-1} tentatively assignable to a stretching vibration of sulfate anion. The same results were obtained for the other metal(II) complexes.

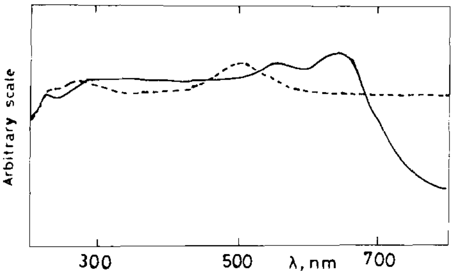

Fig. 2. Reflectance spectra of the TMPNi(II) complex:—— TMPNi(II); – – –its reduced species.

From elemental analyses (Table 1), the reduced species are identified as one-electron reduced species consistent with the results of ESR measurements described below.

In the ESR spectra, the signal of the TMPCo(II) complex at $g = 2.169$ (linewidth = 33 G) disappeared in the reduced species consistent with the result of reduction by ascorbic acid [11]. The signal of the TMPCu(II) complex at $g = 2.056$(250 G) also disappeared in the reduced species. On the other hand, the reduced species of the TMPNi(II) complex showed the broad signal centered at $g = 1.999$(380 G) which was not observed in the starting TMPNi(II) complex. The reduced species of the TMPZn(II) complex showed the sharp signal at $g = 2.001$ (5 G) which was ascribed to that of an organic radical species. It was reported that the π system of the TMPZn(II) complex was reduced by ascorbic acid [8]. That is, in the TMPCo(II), TMPNi(II) and TMPCu(II) complexes, the central metal ions were reduced, whereas the π system was reduced in the TMPZn(II) complex.

Although the conductivities of the starting TMPM(II) complexes are in the range of 10^{-7} to 10^{-10} S cm^{-1} at room temperature, those of the reduced species increased in the range of 10^2 to 10^4 (Table 2).

TABLE 2. Conductivities at room temperature (S cm^{-1})

M	TMPM(II)	Reduced species	E_a of the reduced species (eV)
Co	3.8×10^{-10}	8.8×10^{-8}	0.35
Ni	3.0×10^{-9}	7.9×10^{-5}	0.21
Cu	2.8×10^{-7}	1.8×10^{-5}	0.26
Zn	4.3×10^{-9}	7.0×10^{-6}	0.30

Of the reduced species, the nickel and copper complexes showed the higher conductivities consistent with their smaller activation energies. In the solid

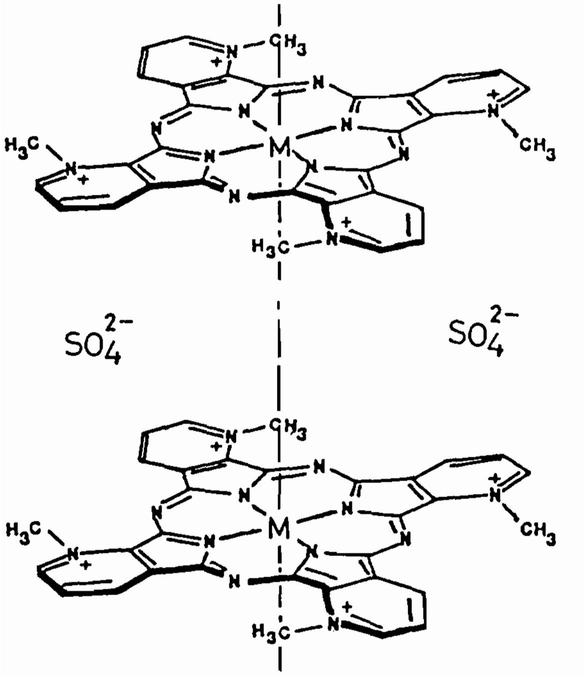

Fig. 3. Proposed column structure of the complexes sandwiched by sulfate anions.

state, two anions must be sandwiched between the positive TMPM(II) complexes as shown in Fig. 3 [12].

Nevertheless, the reduced species showed high conductivities, which might support the fact that the distance between the two macro rings does not significantly affect the conductivity, but the relative ring–ring staggering angle is important [13]. The conductivity of the reduced column of the TMPM(II) complexes with some other anions will be further studied to elucidate a conductivity mechanism of the reduced phthalocyanine analogues.

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