

## Short Communication

### Preparation and spectral and electrochemical properties of the nickel(II), palladium(II) and platinum(II) complexes of 2,3,9,10,16,17,23,24-octapropyltetrapyrzino-*porphyr*azine

Kazuhiro Takahashi\*, Yasuyoshi Aoki,  
Tomoyuki Sugitani, Futoshi Moriyama,  
Yasuhiro Tomita, Makoto Handa, Kuninobu  
Kasuga

Department of Chemistry, Faculty of Science, Shimane  
University, Matsue, Shimane 690 (Japan)

and Kunihisa Sogabe

Department of Chemistry, Faculty of Education, Shimane  
University, Matsue, Shimane 690 (Japan)

(Received March 13, 1992; revised June 15, 1992)

#### Abstract

The Ni(II), Pd(II) and Pt(II) complexes with 2,3,9,10,16,17,23,24-octapropyltetrapyrzino-*porphyr*azine were prepared. Their absorption spectra and cyclic voltammograms (CV) in CH<sub>2</sub>Cl<sub>2</sub> were measured. The two absorption bands corresponding to the Q and B bands of metallophthalocyanines are observed in the 500–660 and 270–400 nm ranges, respectively. The two redox couples indicating reversible one-electron transfer processes appear in the reduction side of the CV. Irreversible oxidation with decomposition of the complex molecule was confirmed by a controlled-potential electrolysis experiment. The spectral and electrochemical properties of these complexes reflect the energy gap between the highest occupied and lowest unoccupied molecular orbitals of the ligand.

#### Introduction

While tetrapyrzino-*porphyr*azine (Tpz) was reported as a phthalocyanine (Pc) analog compound in 1937 [1], its derivatives and metal complexes have not been well studied [1, 2] in contrast to extensively investigated Pcs. In the field of coordination chemistry, the lack of study of Tpz complexes is thought to be due to their virtual insolubility. This characteristic has caused serious

difficulties in purification and measurements of properties in solution. Recently, the octaalkyl-substituted Tpz (H<sub>2</sub>RTpz) and their complexes have been reported [3–5]. H<sub>2</sub>RTpz are fairly soluble in some alkyl halides [5]. Thus we have attempted to develop a series of soluble Tpz–transition metal complexes using H<sub>2</sub>RTpz so as to investigate the chemical and physical properties of the complex molecules in solution. In this study, we have prepared the title complexes, [M<sup>2+</sup>(PrTpz<sup>2-</sup>)] (M = Ni (1), Pd (2), Pt (3) (Fig. 1)), where H<sub>2</sub>PrTpz denotes 2,3,9,10,16,17,23,24-octapropyltetrapyrzino-*porphyr*azine. The spectral and electrochemical properties of these complexes in CH<sub>2</sub>Cl<sub>2</sub> have been studied by means of absorption spectra and cyclic voltammetry, respectively. Their properties are compared with those of divalent metal complexes of phthalocyanines. To obtain further information on the electrooxidation of these complexes, controlled-potential electrolysis and ESR measurements were performed.

#### Experimental

##### Materials

The starting material, 2,3-dipropyl-5,7-diimino-6*H*-pyrolo-[3,4-*b*]-pyrazine (pipz), was derived from 2,3-dicyano-5,6-dipropylpyrazine (pcpz). We obtained pcpz in a good yield by the following method without employing the standard literature procedure [5]. The reaction mixture of an ethanol solution (40 ml) containing 4,5-octanedione (4.31 g, 30 mmol), diaminomaleonitrile (2.70 g, 25 mmol) and a few drops of conc. HCl was refluxed for 2 h, treated with activated charcoal, and filtered. The filtrate was reduced in volume (c. 20 ml), water (30 ml) was added, and it was cooled in an ice bath. The crude pcpz obtained was recrystallized from an ethanol–water (2:3 vol./vol.) solution (yield 4.53 g (85%)). Following the literature method [6] and using 2.01 g of pcpz, pipz was obtained as a blue powder (yield 1.88 g (86%)). *Anal.* Found: C, 62.79; H, 7.43; N, 29.98. *Calc.* for C<sub>12</sub>H<sub>17</sub>N<sub>5</sub>: C, 62.31; H, 7.41; N,

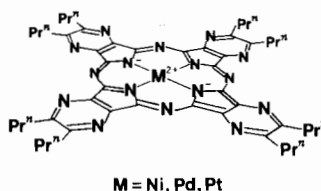


Fig. 1. Schematic drawing of [M<sup>2+</sup>(PrTpz<sup>2-</sup>)].

\*Author to whom correspondence should be addressed.

30.28%. The present complexes were prepared from an appropriate anhydrous  $MCl_2$  and pipz by the same procedure. The preparation of **3** was as follows. The 2-(diisopropylamino)ethanol suspension (5 ml) of  $PtCl_2$  (213 mg, 0.80 mmol) and pipz (605 mg, 2.62 mmol) was refluxed for 2 h. To the reaction mixture was added methanol (30 ml). The solid deposited was filtered off, washed with methanol, dissolved in  $CHCl_3$  (600 ml), and filtered. The filtrate was purified by column chromatography using 200 mesh activated alumina and  $CHCl_3$  as an eluent. The eluate of the blue chromatographic band containing **3** was fractionally collected under the check of the absorption spectra. The impure fractions of the tailing part showing absorption of  $H_2PrTpz$  [5] were purified again. The pure eluates were combined and reduced in volume. By adding a large quantity of n-hexane to this solution, **3** was obtained as dark violet fine needles (yield 30 mg (4%)). Complexes **1** and **2** were obtained as dark blue (yield 26%) and dark purplish blue needles (yield 11%), respectively. *Anal.* Found for **1**: C, 63.43; H, 6.19; N, 24.35; **2**: C, 59.40; H, 5.92; N, 22.68; **3**: C, 54.59; H, 5.30; N, 21.02. Calc. for  $C_{48}H_{56}N_{16}M$ : **1** (M=Ni): C, 62.96; H, 6.16; N, 24.47; **2** (M=Pd): C, 59.84; H, 5.86; N, 23.26; **3** (M=Pt): C, 54.79; H, 5.36; N, 21.30%.

#### Measurements

Absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. All electrochemical measurements were carried out under an Ar atmosphere in  $CH_2Cl_2$  solutions of the complexes containing  $[Bu^p_4N]ClO_4$  ( $0.1 \text{ mol dm}^{-3}$ ). Cyclic voltammograms were obtained with a Hokuto Denko potentiostat HA-501 and a function generator HB-104 using a glassy carbon disk working electrode (3 mm diam.), a Pt coil counter electrode and a saturated calomel reference electrode (SCE). Electrooxidation by controlled-potential electrolysis was performed with a Hokuto Denko HF-201 coulometer and an HA-501 using Pt mesh working and counter electrodes and SCE. ESR spectra were recorded on a JEOL-1X spectrometer.

#### Results and discussion

Figure 2 shows the absorption spectra of **1**, **2** and **3** in  $CH_2Cl_2$ . These spectra are similar to those of the divalent metal complexes of phthalocyanines ( $M^{II}Pcs$ ) [7]. From this spectral resemblance and the structural analogy between the present complexes and  $M^{II}Pcs$ , the two absorption bands observed in the ranges 500–660 and 270–400 nm can be assigned to the Q band and the B band, respectively. The absorption maxima of the Q and B bands in **1**, **2** and **3** are given in Table 1. The Q band is attributed to the  $\pi \rightarrow \pi^*$  electronic

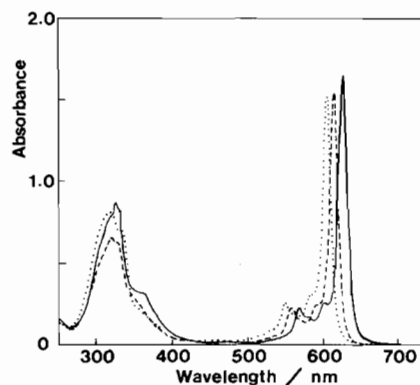


Fig. 2. Absorption spectra of **1** (—), **2** (---) and **3** (····) in  $CH_2Cl_2$  ( $1 \times 10^{-4} \text{ mol dm}^{-3}$  solutions).

transition from HOMO (highest occupied molecular orbital ( $\pi$ )) to LUMO (lowest unoccupied molecular orbital ( $\pi^*$ )) of the ligand, and the B band is attributed to the deeper  $\pi$  levels  $\rightarrow$  LUMO ( $\pi^*$ ) transitions [7]. The absorption maxima of the Q band in  $M^{II}Pcs$  are ordinarily observed in the 650–690 nm range [7]. The Q band in the present complexes is considerably shifted to shorter wavelength compared with that in  $M^{II}Pcs$ . This blue shift implies that the energy gap between HOMO and LUMO of the  $Tpz^{2-}$  ring is larger than that of the  $Pc^{2-}$  ring. Such a remarkable shift is not found for the B band. The Q band in **1**, **2** and **3** shifts to shorter wavelength in that order, and the shapes of the B band in **1**, **2** and **3** differ from each other. These facts indicate that the  $\pi$  electron system of the  $Tpz^{2-}$  ring is affected by the replacement of the central metal ion, that is, the energy gap between HOMO and LUMO of the  $Tpz^{2-}$  ring is widening in the order,  $Ni^{2+} \rightarrow Pd^{2+} \rightarrow Pt^{2+}$ .

The cyclic voltammograms (CV) of **1** are shown in Fig. 3. Similar CV were observed for **2** and **3**. The CV of these complexes showed two redox couples in the reduction side (Red1 and Red2), and one anodic peak near the sweeping limit in the oxidation side (Ox). The redox potentials obtained from the CV are given in Table 1. The wave shapes and peak splitting values of Red1 and Red2 of **1**, **2** and **3** ( $60 < |E_{ap} - E_{cp}| < 70 \text{ mV}$ ) indicate reversible one-electron transfer processes. These complexes exhibit almost the same half-wave potentials of the reductions which seem to be ligand-centered as reported for most  $M^{II}Pcs$  [8]. The Ox of **1**, **2** and **3** are suggestive of an irreversible oxidation step. In the course of the oxidation by controlled-potential electrolysis (applied potential = 1.7 V versus SCE), the color of all the complex solutions faded away, and was only slightly reverted by the reverse reduction. No ESR signal arising from a trivalent metal ion or a ligand radical was observed for the oxidized solutions. From the above observations, it is confirmed

TABLE 1. Absorption maxima of the Q and B bands and redox potentials of 1, 2 and 3 in CH<sub>2</sub>Cl<sub>2</sub>

Complex	$\lambda_{\max}$ (nm) (log $\epsilon$ ) <sup>a</sup>		Redox potentials (V) vs. SCE		
	Q band	B band	$E_{1/2}^{\text{Red1}}$ <sup>b</sup>	$E_{1/2}^{\text{Red2}}$ <sup>b</sup>	$E_{\text{ap}}^{\text{Ox}}$ <sup>c</sup>
1	625 (5.21)	326 (4.93)	-0.52	-0.92	+1.55
2	612 (5.19)	320 (4.81)	-0.50	-0.91	+1.60
3	603 (5.18)	318 (4.91)	-0.51	-0.93	+1.63

<sup>a</sup>These values were obtained from  $1 \times 10^{-4}$  mol dm<sup>-3</sup> solutions. at the peak of Ox.

<sup>b</sup>Half-wave potential estimated by  $E_{1/2} = (E_{\text{ap}} + E_{\text{cp}})/2$ . <sup>c</sup>Potential

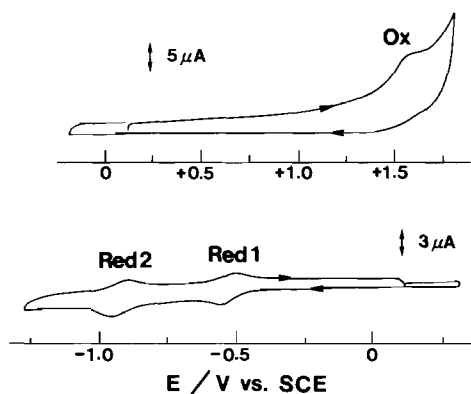


Fig. 3. Cyclic voltammograms of 1 ( $1 \times 10^{-4}$  mol dm<sup>-3</sup>; sweep rate = 100 mV s<sup>-1</sup>).

that the oxidation of the present complexes is irreversible and ligand-centered with decomposition of the complex molecule. The  $E_{\text{ap}}^{\text{Ox}}$  of 1, 2 and 3 is relatively high compared with the oxidation potential of the Pc<sup>2-</sup> ring in M<sup>II</sup>Pcs (<1.0 V versus SCE [8]), which is to be expected for the Tpz ring possessing eight electro-negative nitrogen atoms at 1,4,8,11,15,18,22,25 positions instead of carbon atoms of the Pc ring. The Ox shifts to positive direction in the order, 1 → 2 → 3, and the difference between  $E_{\text{ap}}^{\text{Ox}}$  and  $E_{1/2}^{\text{Red1}}$  slightly increases in the same order (1, 2.07; 2, 2.10; 3, 2.14 V). This order is the same as that of the blue shift of the Q band. If the oxidation and first reduction (at Red1) can be supposed to occur on HOMO and LUMO, respectively, of the Tpz<sup>2-</sup> ring, the potential separation between Ox and Red1 is considered to reflect the energy gap between HOMO and LUMO as well as the Q band.

In the present complexes, the replacement of the central metal ion, Ni<sup>2+</sup> → Pd<sup>2+</sup> → Pt<sup>2+</sup>, may cause HOMO to depress its energy level, but has little affect on LUMO.

### Acknowledgement

This work was partially supported by a Grant-in-Aid for Scientific Research No. 02740302 from the Ministry of Education, Science and Culture.

### References

- 1 R. P. Linstead, E. G. Noble and J. M. Wright, *J. Chem. Soc.*, (1937) 911.
- 2 E. G. Gal'pern, E. A. Luk'yanets and M. G. Gal'pern, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1973) 1976; K. Kasuga, K. Nishikori, T. Mihara, M. Handa, K. Sogabe and K. Isa, *Inorg. Chim. Acta*, 174 (1990) 153.
- 3 S. Tokita, S. Kojima, K. Kurogi and H. Nishi, *56th National Meet. Chemical Society of Japan, Tokyo, Japan, Apr. 1988*, Abstr. 2XIIIE35 and 2XIIIE36; S. Tokita, M. Shimada, N. Kai, M. Horiguchi, H. Matsutani and H. Nishi, *59th National Meet. Chemical Society of Japan, Yokohama, Japan, Apr. 1990*, Abstr. 2E504.
- 4 K. Ohta, T. Watanabe, T. Fujimoto and I. Yamamoto, *J. Chem. Soc., Chem. Commun.*, (1989) 1611.
- 5 S. Tokita, M. Kojima, N. Kai, K. Kurogi, H. Nishi, H. Tomoda, S. Saito and S. Shiraishi, *Nippon Kagaku Kaishi*, (1990) 219.
- 6 P. J. Brach, S. J. Grammatica, O. A. Ossanna and L. Weinberger, *J. Heterocycl. Chem.*, 7 (1970) 1403.
- 7 M. J. Stillman and T. Nyokong, in C. C. Leznoff and A. B. P. Lever (eds.), *Phthalocyanines, Properties and Applications*, VCH, New York, USA, 1989, Ch. 3.
- 8 A. B. P. Lever, S. Licoccia, K. Magnell, P. C. Minor and B. S. Ramaswamy, *ACS Symp. Ser.*, 201 (1982) 237; D. Wöhrle and V. Schmidt, *J. Chem. Soc., Dalton Trans.*, (1988) 549.