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# Synthesis, chemical properties, and electrochemical behavior of a Pt(II) complex bearing a benzenediamide-derived ligand

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## ABSTRACT

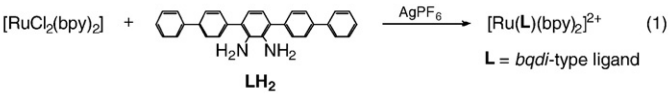
The reaction of [$PtCl_2$(cod)] (cod = 1,5-cyclooctadiene) with Ph-Ph′-Ph′(2,3-$NH_2$)-Ph′-Ph (**$LH_2$**) (Ph = phenyl; Ph′ = *p*-phenylene; Ph′(2,3-$NH_2$) = *p*-phenylene-2,3-diamine) gave a new platinum(II) complex bearing a π-conjugated Ph-Ph′-Ph′(2,3-NH)-Ph′-Ph (**L**, Ph′(2,3-NH) = *p*-phenylene-2,3-diamide) ligand, [Pt(**L**)(cod)], with the liberation of 2 HCl. The X-ray structure determination of the complex confirmed the coordination of the ligand to the platinum center in an *o*-benzenediamide form. The cyclic voltammogram of the complex showed reversible two-step $[\text{Pt-bda}]^0/[\text{Pt-sqdi}]^+$ and $[\text{Pt-sqdi}]^+/[\text{Pt-bqdi}]^{2+}$ redox couples (bda = *o*-benzenediamide, sqdi = *o*-semiquinone diimine, bqdi = *o*-benzoquinone diimine).

## Introduction

1,2-Phenylenediamines (pdas) serve as chelating ligands, and many reports have been published about pda-coordinated transition-metal complexes [1–10]. Quinonoid ligands, such as *o*-benzoquinone and *o*-benzoquinone diimine ligands, are called "*non-innocent ligands*", and the interesting chemical properties of metal complexes with these ligands have attracted much attention [11]. As shown in Scheme 1, pda undergoes the following acid–base reaction and reversible two-step redox electrochemical reactions, both as a free compound and as a ligand in metal complexes.

Such acid–base and electrochemical reactions have been investigated in detail using Ru complexes with this ligand [12,13]. However, electrochemical studies of Pt–pda complexes have received less attention [2–9]. Two examples of Pt–bda-type complexes have been reported [3a,10]; however, the electrochemical properties of the Pt–bda complexes have not been investigated.

Previously, we reported the synthesis of a new pda-type π-conjugated **$LH_2$** (cf. eq. 1), and the reaction of [$RuCl_2(bpy)_2$] with **$LH_2$** gave an Ru complex with a bqdi-type neutral ligand, Ph-Ph′-Ph′$(NH)_2$-Ph′-Ph (**L**) [13].



The presence of an expanded π-conjugation system in **L** lowered the LUMO level of the complex. π-Conjugated oligomers and polymers have been the subject of many studies, and transition-metal complexes with ligands having large π-conjugated systems are now attracting interest [14].

In this paper, we report the synthesis of a new platinum(II) complex, [Pt(**L**)(cod)] (cod = 1,5-cyclooctadiene), where **L** serves as a bda-type ligand in contrast to the bqdi-type coordination of **L** in [Ru(**L**)$(bpy)_2$]. Differences in electronic structures between [Ru$(bpy)_2$] and [Pt(cod)] seem to bring about such differences. The crystal structure of [Pt(**L**)(cod)] confirms the bda-type coordination mode of **L**, and optical and electrochemical properties of the complex have been revealed.

[Pt(**L**)(cod)] was prepared by the reaction of [$PtCl_2$(cod)] with **$LH_2$** in the presence of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) as a base in high yield (cf. Scheme 2). The reaction of $AgPF_6$-treated [$PtCl_2$(cod)] with diamine **$LH_2$** in 2-methoxyethanol gave [Pt(**L**)(cod)] in low yield.

Crystals of [Pt**L**(cod)] suitable for X-ray diffraction analysis were obtained from a $CH_2Cl_2$–hexane solution. Fig. 1 shows the molecular structure of [Pt(**L**)(cod)] determined by X-ray crystallography [15]. [Pt(**L**)(cod)] has a distorted square-planar geometry around the metal center. The bond lengths of N1–C1 and N2–C2 are 1.377(2) and 1.389(2) Å, respectively, which are longer than those in Pt-sqdi-type complexes (1.331(9)–1.368(7) Å) [4b,4d,5,8b], and shorter than those in [$Pt(pda)_2$]$Cl_2$ (1.450(2) Å) [8a], indicating that the ligand in [Pt(**L**)(cod)] coordinates to Pt as a bda-type dianionic ligand, and the complex is a Pt(II) complex (not a Pt(0) complex). The Pt1–N1 and Pt1–N2 lengths are 1.974(2) and 1.9652(19) Å, respectively, which are slightly shorter than those of [$Pt(pda)_2$]$Cl_2$ (2.0402(17) Å) [8a]. The five benzene rings are twisted, and the dihedral angles are similar to those of $[Ru(\mathbf{L})(bpy)_2]^{2+}$ [13].

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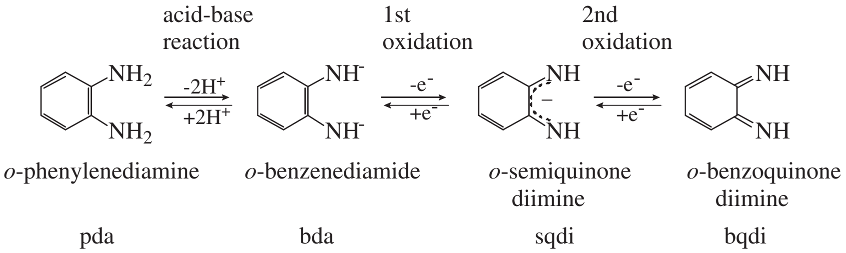
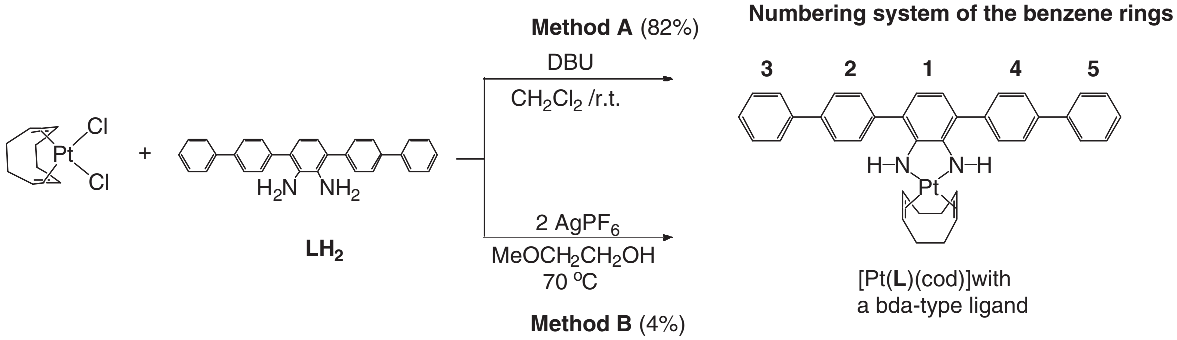


**Scheme 1.** Redox behavior of *o*-phenylenediamine.



**Scheme 2.**

The $^1$H NMR spectrum of [Pt(**L**)(cod)] shows the expected signals for the cod and aromatic ligands; six independent signals were observed in the aromatic region, and two cod-originated olefinic and aliphatic peaks were observed at $\delta$ 3.81 and 2.48, respectively.

Fig. 2 shows the UV–vis spectrum of [Pt(**L**)(cod)] in $CH_2Cl_2$; the complex shows three absorption bands with peaks at $\lambda_{max} = 261$ ($\varepsilon = 46{,}500$), 353 ($\varepsilon = 28{,}500$), and 427 nm ($\varepsilon = 17{,}500$). The absorption band at $\lambda_{max} = 261$ nm is assigned to an intraligand $\pi$–$\pi^*$ transition of **L**. The other absorption bands were assigned by time-dependent density functional theory (TD-DFT) calculations [16]. Table 1 shows a summary of selected calculated singlet excited-state transitions for [Pt(**L**)(cod)]. Three-dimensional plots of the frontier orbitals of [Pt(**L**)(cod)] and its molecular orbitals (MO) are shown in Fig. 3 using GaussView 4.1 [17]. HOMO, HOMO-1, and HOMO-3 possess contributions of the d orbitals of Pt, π-orbitals of the bda (HN–C=C–NH) unit, and the π-orbitals of *p*-quinquephenyl in **L**. The HOMO-2 and LUMO-2 orbitals are primarily localized on **L**, and LUMO has some metal character. The TD-DFT calculation of [Pt(**L**)

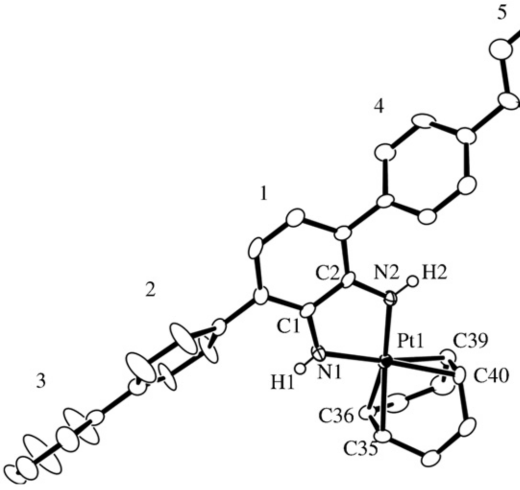


**Fig. 1.** ORTEP drawing of [Pt**L**(cod)] at 50% ellipsoidal level. Benzene ring 4 is disordered. H atoms except H1 and H2 are omitted for simplicity. Selected bond lengths (Å) and dihedral angles (°): Pt1–N1 1.974(2); Pt1–N2 1.9652(19); Pt1–C35 2.165(2); Pt1–C36 2.151(2); Pt1–C39 2.142(2); Pt1–C40 2.143(2); N1–C1 1.377(2); N2–C2 1.389(2); C1–C2 1.416(3); C2–C3 1.406(2); C3–C4 1.396(3); C4–C5 1.377(3); C5–C6 1.401(3); and C1–C6 1.397 (2); Plane1$_{(C1–C6)}$–Plane2$_{(C7–C12)}$ 49.97(8); Plane1$_{(C1–C6)}$–Plane3$_{(C13–C18)}$ 17.43(10); Plane1$_{(C1–C6)}$–Plane4$_{(C19–C24)}$ 75.02(13); Plane1$_{(C1–C6)}$–Plane4′$_{(C19,C22,C25–28)}$ 52.89(16); Plane1$_{(C1–C6)}$–Plane5$_{(C25–C30)}$ 70.09(10); Plane2$_{(C7–C12)}$–Plane3$_{(C13–C18)}$ 33.39(10); Plane2$_{(C7–C12)}$–Plane4$_{(C19–C24)}$ 26.82(13); Plane2$_{(C7–C12)}$– Plane4′$_{(C19,C22,C25–28)}$ 102.45(17); Plane2$_{(C7–C12)}$–Plane5$_{(C25–C30)}$ 119.30(11); Plane3$_{(C13–C18)}$–Plane4$_{(C19–C24)}$ 59.58(10); Plane3$_{(C13–C18)}$–Plane5$_{(C25–C30)}$ 85.95(12); Plane3$_{(C13–C18)}$– Plane4′$_{(C19,C22,C25–28)}$ 69.07(17); Plane4$_{(C19–C24)}$–Plane5$_{(C25–C30)}$ 145.10(15); Plane4′$_{(C19,C22,C25–28)}$–Plane5$_{(C25–C30)}$ 17.25(18).

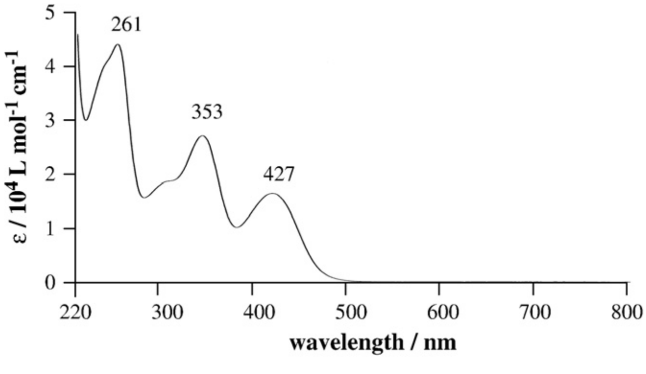


**Fig. 2.** UV–vis spectrum of [Pt(**L**)(cod)] in $CH_2Cl_2$.

**Table 1**
Selected calculated singlet excited-state transitions for [Pt**L**(cod)].

| Wavelength/nm | Oscillator strength | Assignment (% of major transition contributing to the band) |
|---|---|---|
| 453 | 0.1685 | HOMO → LUMO (71%) |
| 376 | 0.5416 | HOMO-1 → LUMO (85%)<br>HOMO → LUMO + 2 (4%) |
| 277 | 0.3269 | HOMO-3 → LUMO (82%)<br>HOMO-3 → LUMO + 1 (3%) |
| 259 | 0.2010 | HOMO-2 → LUMO + 2 (4%)<br>HOMO-1 → LUMO + 9 (44%) |

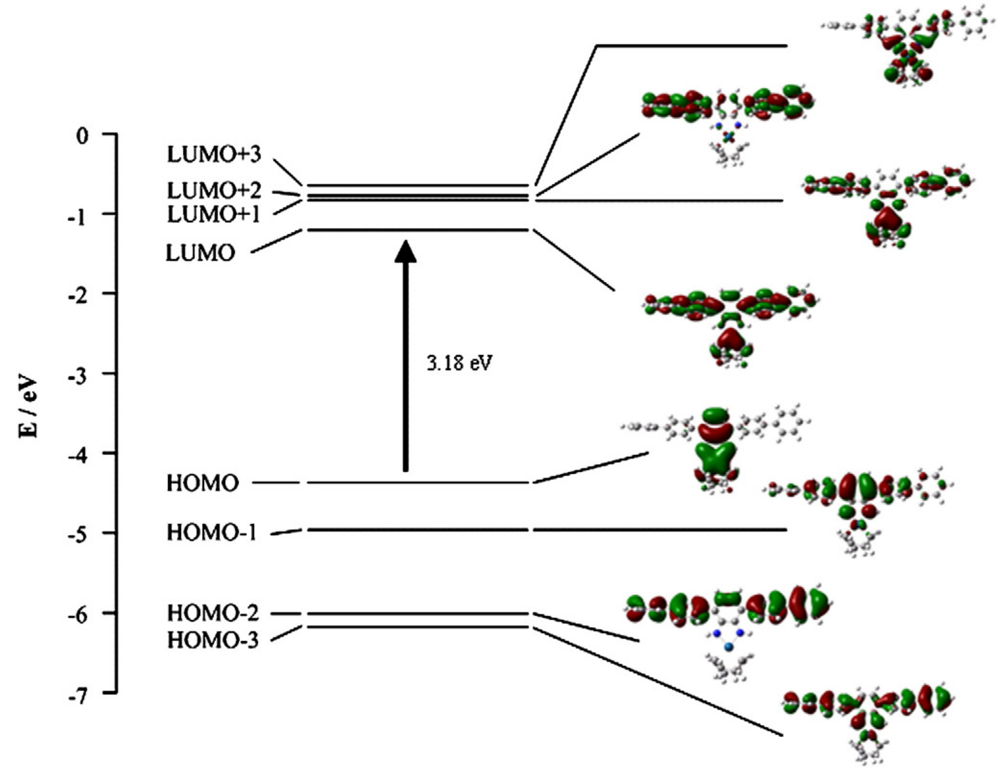


**Fig. 3.** Energy level diagram and graphic representation of frontier rbitals of [Pt**L**(cod)]. HOMO-1, HOMO-2, and LUMO + 1 are primarily localized in the **L** ligand.

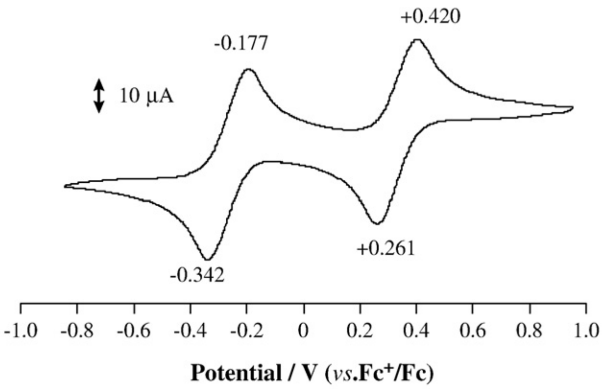


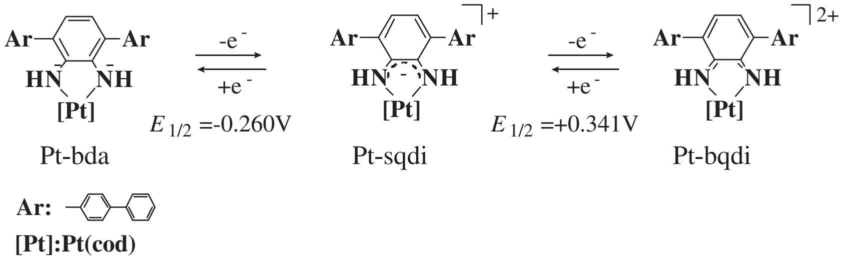
**Fig. 4.** Cyclic voltammogram of [Pt(**L**)(cod)] in $CH_2Cl_2$.

(cod)] indicates that a strong absorption at 353 nm, which is related to the 376 nm transition obtained by calculation (cf. Table 1), is dominated by an HOMO-1-to-LUMO transition, and a weaker peak at 427, which is related to the calculated 453 nm transition, originates from an HOMO-to-LUMO transition.

[Pt(**L**)(cod)] shows a weak luminescence at $\lambda_{EM} = 466$ nm when excited at $\lambda_{EX} = 293$ nm in $CH_2Cl_2$, though $\mathbf{LH_2}$ shows a strong luminescence at $\lambda_{EM} = 391$ nm ($\lambda_{EX} = 314$ nm) [18]. For [Pt(**L**)(cod)], the low energy band predicted to arise from the HOMO-to-LUMO (453 nm) transition matches the experimentally observed emission maximum.

The cyclic voltammogram (CV) of [Pt(**L**)(cod)] displays two quasi-reversible one-electron redox processes as shown in Fig. 4. The redox potentials for $E^1_{1/2}$ and $E^2_{1/2}$ are −0.260 V and +0.341 V (*vs.* $Fc^+$/Fc), respectively. No other peaks are observed in the range of +1.2 V to −2.5 V. These two reversible redox couples are based on the $[Pt(sqdi)]^+/[Pt(bda)]^0$ and $[Pt(bqdi)]^{2+}/[Pt(sqdi)]^+$ redox processes, as shown in Scheme 3. There has been no evidence of the generation of Pt(I) or Pt(III) species in the redox process, and the central Pt ion is thought to be divalent in all neutral, cationic, and dicationic forms. The $E^1_{1/2}$ of [Pt**L**(cod)] is more negative than those of Pt–catecholate (cat) complexes with a COD ligand [19]. This result indicates that the electron density of the bda ligand is higher than that of the cat ligand.

In summary, we have demonstrated the synthesis and electrochemical properties of a new Pt complex bearing the *p*-quinquephenyl-2″,3″-diamide ligand. The complex [Pt**L**(cod)] shows two-step reversible redox waves, which correspond to the $[Pt(sqdi)]^+/[Pt(bda)]^0$ and $[Pt(bqdi)]^{2+}/$



**Scheme 3.** Redox processes of [Pt**L**(cod)]. The negative charge on the **L** ligand is considered to be delocalized in the π-conjugated ligand.

$[Pt(sqdi)]^+$ reactions. This is the first example that clarifies the electrochemical properties of a di-deprotonated phenylenediamine-coordinated Pt complex.

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## Appendix A. Supplementary material

CCDC 793964 contains the supplementary crystallographic data for [Pt**L**(cod)]. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found in its online version at doi:10.1016/j.inoche.2010.11.018.

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