Crystalline Polymorphism of Bis[*o*-semibenzoquinonediimine(1−)]platinum(II)

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A platinum complex with a non-innocent ligand, $[Pt^{II}(L)_2]$ (**1**), where L is *o*-semibenzoquinonediimine monoanion, has two polymorphs. In one polymorph, molecules related by translation are arranged in the same orientation along the *c* axis, while in the other, molecules related by a *c*-glide plane are aligned alternately in different orientation.

Transition-metal complexes with non-innocent ligands, such as dioxolexes[1] and dithiolenes,[2] display attractive properties: valence tautomerism, high conductivity, magnetism, and so on. It has been established that *o*-phenylenediamine (H_2L) can coordinate to transition-metal ions via deprotonation and become a non-innocent ligand adopting three different oxidation states: *o*-phenylenediamide dianion (L^{2-}), *o*-semibenzoquinonediimine monoanion (L^{1-}), and neutral *o*-benzoquinonediimine (L^0).[3,4] The reaction of H_2L, or its substituted derivatives, with divalent metal ions (e.g. Ni^{II}, Pd^{II}, and Pt^{II}) in the presence of a base and air affords the neutral, planar, and diamagnetic complexes, $[M^{II}(L)_2]$, where L represents *o*-semibenzoquinonediimine, or its substituted-derivative monoanions.[4] These neutral complexes undergo four reversible one-electron redox steps to give five-membered species, $[M^{II}(L)_2]^z$ with $z = 2-, 1-, 0, 1+, 2+$. All the redox steps are ligand-centered, and the central metal ions formally retain the divalent state. These neutral complexes exhibit an intense absorption band ($\varepsilon > 10^4\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$), assigned to a ligand-to-ligand charge-transfer (LLCT) transition,[5] in the visible and near-IR region. The oxidation state of the ligand can be assigned by X-ray crystallography because the bond distances of the ligand reflect its oxidation state.[4e] So far, two crystal structures of the unsubstituted-ligand complexes, $[Ni(L)_2]$[6] and $[Pt(L)_2]$[7] (**1**), have been reported. The protonation and oxidation states of these complexes, however, were structurally ambiguous due to the poor quality of the diffraction data. For the complex $[Ni(L)_2]$, the authors reported the presence of a polymorph with its cell parameters as the footnote.[6] The polymorph of $[Ni(L)_2]$ is probably isostructural to the reported crystal structure of **1**,[7] hereafter called the α-phase. Another polymorph of **1**, hereafter called the β-phase, exists and is isostructural to $[Ni(L)_2]$, of which the full structure has been reported in the literature.[6] In this study, we have performed single-crystal X-ray analysis on fifteen crystals of **1** and have found four crystals belonging to the β-phase. Here, we report the β-phase structure of **1**. We have also redetermined the α-phase structure of **1** at low temperature to correctly assign the oxidation state of the ligand and to compare the crystal packing of both phases.

Complex **1** crystallizes in the monoclinic space group $P2_1$ for the α-phase and $P2_1/c$ for the β-phase. The phase was independent of the external crystal shape. The two phases can be distinguished from the cell parameters c and β after indexing on a diffractometer. In the α-phase, an averaged value of the β parameter was 92.57(2)° for three crystals of which the cell parameters were determined by the cell-refinement after the measurement of the intensity data at 153 K. On the other hand, in the β-phase, the averaged β value was 90.62(7)° for the four crystals under the same conditions as that of the measurement of the α-phase. The two values are clearly different. In addition, diffraction images that were collected on an area detector (Imaging Plate detector) had no reflections with an index of $l = n + 1/2$ in the α-phase; however, in the images of the β-phase, there were many strong or moderate reflections with an index of $l = 2n + 1$. The reciprocal vector $\boldsymbol{c}_{\alpha\text{-phase}}^{*}/2$ is not the reciprocal lattice unit cell one of the α-phase, and in the latter, the reciprocal vector $\boldsymbol{c}_{\beta\text{-phase}}^{*}$, corresponding to $\boldsymbol{c}_{\alpha\text{-phase}}^{*}/2$, is the reciprocal lattice unit cell one of the β-phase. Therefore, the α- and β-phases can be easily distinguished by indexing. A refinement in the space group $P2_1$ and a false cell, halved by applying the matrix $(1\ 0\ 0/0\ 1\ 0/0\ 0\ \frac{1}{2})$ to the correct cell was attempted for the β-phase crystal, but it was unsuccessful. These results show that the α-phase is not a false phase obtained by mistake from the β-phase by halving the correct cell.

The geometries of the molecule are almost identical in both phases. Figure 1 shows the molecular structure of **1** in the β-phase. The neutral molecule of **1** is essentially planar, and the central Pt atom is coordinated to four N atoms of two bidentate chelate ligands. Selected bond distances are listed in Table 1. The geometries of the five-membered chelate rings are in good agreement with those of the *N*-substituted analogue bis[*N*-phenyl-*o*-semibenzoquinonediimine(1−)]platinum(II), $[Pt^{II}(L^{N\text{-Ph}})_2]$.[4e] The C–C distances of the carbon six-membered rings of the ligand essentially display a quinoid-type distortion. Thus, these results clearly show that the ligand is a *o*-semibenzoquinonediimine monoanion, although the protonation and oxidation states of the ligand were ambiguous in the previous reports.[6,7]

As shown in Fig. 2, the marked difference in the crystal

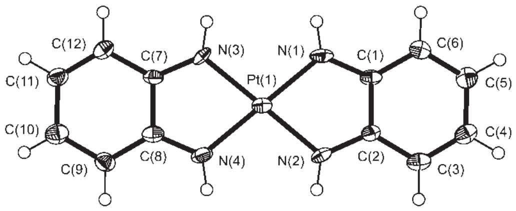

Fig. 1. Molecular structure of the neutral complex **1** in the β-phase with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms.

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packing between the two phases is the molecular orientation in the arrangement along the *c* axis. In the α-phase, the neutral molecules related by translation are arranged in an AAAA$\cdots$ pattern along the *c* axis, and in the β-phase the ones related by a *c*-glide plane are aligned in an ABAB$\cdots$ pattern along the *c* axis. Along the *b* axis, on the other hand, the molecules related by a two-fold screw axis are arranged in the same pattern in both phases. The dihedral angle between the molecular planes having the different orientation is almost identical in both phases [57.71(5)° in the α-phase and 57.56(13)° in the β-phase]. The molecular arrangements in the *ab* plane are similar to each other, but the stacks of the molecular sheets in the direction of the *c* axis are different.

Experimental

Preparation. Complex [Pt(L)$_2$] (**1**) was prepared by the procedure reported by Sidorov and Katser.[7] [PtCl$_2$(H$_2$L)] (0.267 mmol, 100 mg), prepared according to the literature method,[8] and H$_2$L (0.534 mmol, 58 mg) were dissolved in DMF (40 mL) under ultrasonication and then filtered. Purple plate-like crystals with metallic luster were obtained from the filtrate by very slow evaporation for two months. Yield 42 mg (39%). Vis–NIR absorption ($\nu_{\max}$/cm^{-1} (ε/dm^3 mol^{-1} cm^{-1}), DMSO): 14000 (97000). Found: C, 35.41; H, 3.01; N, 13.82%. Calcd for $C_{12}H_{12}N_4Pt$: C, 35.38; H, 2.97; N, 13.75%. Elemental analysis was carried out by Laboratory of Organic Elemental Analysis, Department of Chemistry, Graduate School of Science, The University of Tokyo.

Table 1. Selected Bond Distances (Å) for **1** in the α- and β-Phase

	α-Phase	β-Phase
Pt(1)–N(1)	1.960(3)	1.962(9)
Pt(1)–N(2)	1.963(3)	1.962(8)
Pt(1)–N(3)	1.967(3)	1.962(10)
Pt(1)–N(4)	1.965(3)	1.970(10)
N(1)–C(1)	1.352(4)	1.358(15)
N(2)–C(2)	1.351(4)	1.366(15)
N(3)–C(7)	1.346(4)	1.336(14)
N(4)–C(8)	1.353(4)	1.342(16)
C(1)–C(2)	1.435(4)	1.405(15)
C(2)–C(3)	1.422(4)	1.416(16)
C(3)–C(4)	1.371(5)	1.375(19)
C(4)–C(5)	1.424(5)	1.420(18)
C(5)–C(6)	1.382(5)	1.375(16)
C(1)–C(6)	1.407(5)	1.426(15)
C(7)–C(8)	1.441(4)	1.440(15)
C(8)–C(9)	1.407(5)	1.412(17)
C(9)–C(10)	1.378(4)	1.407(19)
C(10)–C(11)	1.425(6)	1.432(18)
C(11)–C(12)	1.368(5)	1.361(16)
C(7)–C(12)	1.414(4)	1.433(15)

Physical Measurements. Vis–NIR absorption spectra were recorded using a JASCO V-530 spectrophotometer.

X-ray Crystallography. Each single crystal of **1** was mounted on a glass fiber. All measurements were made on a Rigaku R-AXIS RAPID Imaging Plate diffractometer with graphite-monochromated Mo Kα radiation (0.7107 Å) and with a Rigaku low-temperature device. Intensity data were measured at 153 K and corrected for Lorentz-polarization effects and analytical absorption factors from a multi-scan method. The structures were solved by conventional heavy-atom methods for the α-phase and by direct methods for the β-phase. The refinement was performed on F^2 by full-matrix least-squares methods with anisotropic displacement parameters for non-H atoms. The refinement of the α-phase in the non-centrosymmetric space group was done against 3275 unique reflections including 1253 Friedel pairs. The Flack parameter[9] [0.470(8)] shows that the measured crystal is a racemic twin. All H atoms were located at geometrically calculated positions and refined as riding. C–H and N–H bond distances were constrained to be 0.95 and 0.88 Å, respectively. H atom isotropic displacement parameters were set to be $1.2U_{\mathrm{eq}}$ of the parent atom. Programs used were *SHELXS*97[10] for solution, *SHELXL*97[10] for refinement, *ABSCOR*[11] for absorption correction and *ORTEP*-3[12] for drawing the structures.

The crystal data are as follows. α-Phase: $C_{12}H_{12}N_4Pt$, $M_r = 407.35$, monoclinic, $P2_1$, $a = 5.863(2)$, $b = 7.400(3)$, $c = 12.774(7)$ Å, $\beta = 92.55(2)°$, $V = 553.6(4)$ Å^3, $Z = 2$, $D_{\mathrm{calcd}} = 2.444$ g cm^{-3}, $T = 153$ K, $2\theta_{\max} = 64.1°$, 7467 measured reflections, 3275 independent reflections including 1253 Friedel pairs [$R_{\mathrm{int}} = 0.026$], 3214 observed reflections including Friedel pairs [$F_o{}^2 \geq 2\sigma(F_o{}^2)$], 156 parameters, $R[F_o{}^2 \geq 2\sigma(F_o{}^2)] = 0.0175$, $wR = 0.0416$, GOF = 1.116, Flack parameter: $x = 0.470(8)$. β-Phase: $C_{12}H_{12}N_4Pt$, $M_r = 407.35$, monoclinic, $P2_1/c$, $a = 5.787(3)$, $b = 7.429(4)$, $c = 25.779(14)$ Å, $\beta = 90.66(5)°$, $V =$

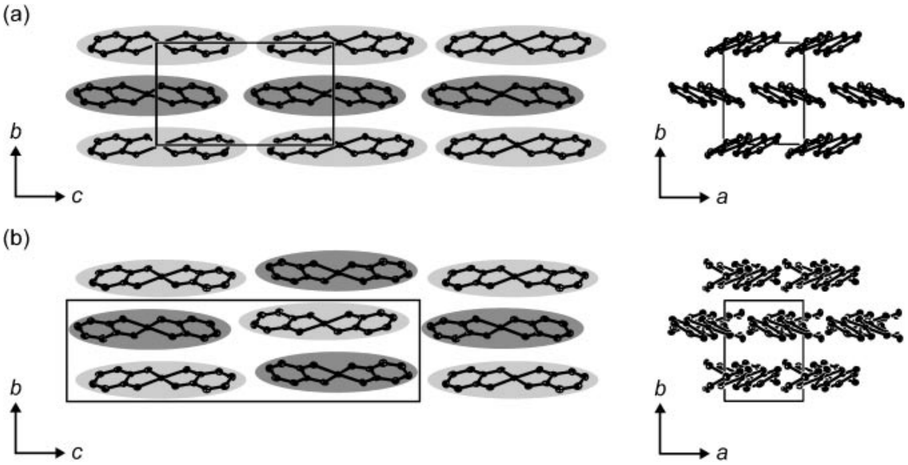

Fig. 2. Crystal packing of **1** in the α-phase (a) and the β-phase (b), viewed along the *a* axis (left) and the *c* axis (right). H atoms are omitted for clarity.

1108.4(10) Å^3, $Z = 4$, $D_{\text{calcd}} = 2.441\,\text{g cm}^{-3}$, $T = 153\,\text{K}$, $2\theta_{\text{max}} = 64.0°$, 11465 measured reflections, 3764 independent reflections [$R_{\text{int}} = 0.088$], 3507 observed reflections [$F_o{}^2 \geq 2\sigma(F_o{}^2)$], 155 parameters, $R[F_o{}^2 \geq 2\sigma(F_o{}^2)] = 0.0701$, $wR = 0.2183$, $\text{GOF} = 1.141$.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-604253 and CCDC-604254 for α- and β-phase, respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or form the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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