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Headline Articles

Pd(II)- and Pt(II)-Linked Tetranuclear Complexes as Assembly Units for Higher Ordered Structures

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The formation of ···Pt(II)···Br–Pt(IV)··· mixed-valence complexes was utilized for the assembly of square compounds, $[(en)M(4,4'\text{-bpy})]_4(NO_3)_8$ ($\mathbf{1}\cdot(NO_3)_8$; **a**: M = Pt(II), **b**: M = Pd(II), 4,4′-bpy = 4,4′-bipyridine), into higher ordered infinite complexes. The reaction of $\mathbf{1}^{8+}$ with cationic Pt(IV) complex, $[PtBr_2(en)_2]^{2+}$ ($\mathbf{2}^{2+}$), afforded a 1 : 3 complex $\mathbf{1a}\cdot(\mathbf{2})_3{}^{14+}$. Crystallographic analysis of this complex showed that two moieties of $\mathbf{2}^{2+}$ bridged at the cis corner of $\mathbf{1a}^{8+}$ making a stair-like infinite network, whereas another moiety of $\mathbf{2}^{2+}$ was accommodated in the cavity of $\mathbf{1a}^{8+}$. On the other hand, complexation of **1b** with anionic Pt(IV) complex, $PtX_6{}^{2-}$ ($\mathbf{3}^{2-}$; **a**: X = Cl, **b**: X = Br), afforded a 1 : 4 complex $\mathbf{1}\cdot(\mathbf{3})_4$. UV-vis observations suggested the formation of a linear tube structure, in which each corner of $\mathbf{1}^{8+}$ is bridged by the linear X–Pt–X motif of $\mathbf{3}^{2-}$.

Pd(II)- and Pt(II)-linked square complexes such as $\mathbf{1}^{8+}$ are prototypical compounds among a family of tetranuclear square complexes in which transition metals provide 90 degree angles at every corner of the square.[1] A way of modifying this structure into an organic soluble one has been developed recently.[2a] Introduction of functional groups such as chiral biphenyls, calixarene, porphyrins, nucleic acids, and crown ether units into the square is also reported.[2b,3] A Pd(II)–Re(I) bimetallic square shows luminescent property.[4] However, the simple square structure has never been employed as a building block for higher dimensional structures except 4,4′-bpy bridging coordination grids.[5] Thus, we studied the accumulation of square complexes $\mathbf{1}^{8+}$ into higher ordered infinite complexes via formation of ···Pt(II)···X–Pt(IV)··· (X: halogen) mixed-valence complexes. Mixed-valence one-dimensional materials, easily obtained by mixing $M(II)L_4$ and $M(IV)L_4X_2$ salts, are of special interest because of their specific physical properties such as conductivity and non-linear optical activities.[6] We describe here how the complexes $\mathbf{1}^{8+}$ assemble into stair and tubular networks upon complexation with Pt(IV) species $\mathbf{2}^{2+}$ and $\mathbf{3a}^{2-}$ or $\mathbf{3b}^{2-}$ respectively (Chart 1).

Results and Discussion

Reaction of $\mathbf{1a}^{8+}$ with Pt(IV) Complex $[PtBr_2(en)_2]Br_2$ ($\mathbf{2}\cdot Br_2$). It is well-known that the reaction of $(en)_2Pt^{2+}$ with $\mathbf{2}^{2+}$ gives mixed-valence one-dimensional $\{[(en)_2Pt][PtBr_2(en)_2]\}_n{}^{4n+}$. Thus it is anticipated that $\mathbf{1a}^{8+}$ will react with $\mathbf{2}^{2+}$ in a 1 : 4 stoichiometry, giving a one-dimensional tubular network. However, when $\mathbf{1a}\cdot(NO_3)_8$ was treated with four equivalents of $\mathbf{2}\cdot Br_2$ in 5 M $NaNO_3$ aqueous solution (1 M = 1 mol dm^{-3}), these components reacted in a 1 : 3 stoichiometry, giving complex $[\mathbf{1a}\cdot\mathbf{2}_3](NO_3)_{14}\cdot 6H_2O$ (**4**) as yellow crystals (64% isolated yield). The ratio of molecular components of **4** has been determined by elemental analysis and ^{1}H NMR. Even the use of larger amount of $\mathbf{2}\cdot Br_2$ (6 equiv) resulted in the formation of the same product in 91% isolated yield. Solid state UV-vis spectrum of **4** shows a new absorption band at 420 nm which was not observed in solution. Thus, this absorption indicates a possible charge transfer interaction between Pt(II)–Pt(IV) through the halogen atoms.

The X-ray analysis of **4** showed that two moieties of $\mathbf{2}^{2+}$ bridged the cis corner of $\mathbf{1a}^{8+}$ forming a stair-like network. The third moiety of $\mathbf{2}^{2+}$ acted as a guest molecule and occupied the cavity of molecular square $\mathbf{1a}^{8+}$ (Figs. 1a and 1b). The geometry of $\mathbf{1a}^{8+}$ was similar to that of the corresponding Pd(II) complex $\mathbf{1b}^{8+}$ whose crystal structure was reported.[1d] The distance of Pt(II)–Br (3.22 and 3.37

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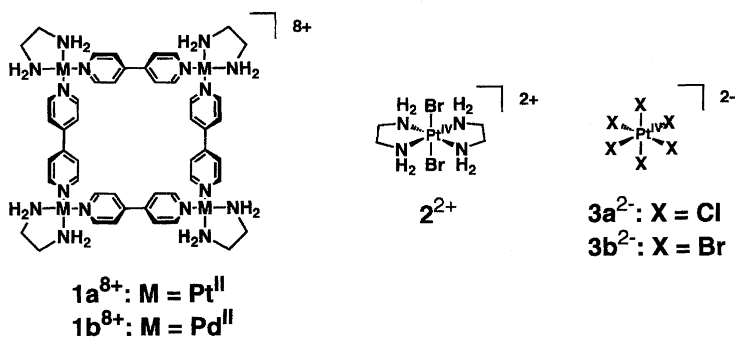

Chart 1.

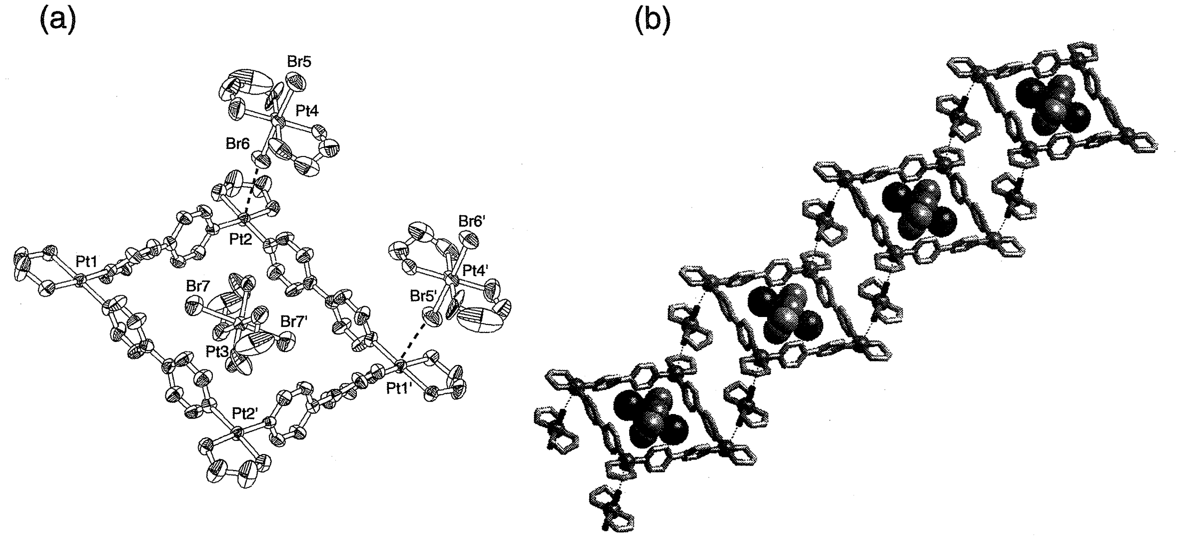

Fig. 1. (a) ORTEP drawing of **4**. Pt(1)–Pt(2), 11.09 Å; Pt(1)–Pt(2′), 11.12 Å; Pt(1)–Br(5), 3.22 Å; Pt(2)–Br(6), 3.37 Å; Pt(4)–Br(5), 2.43 Å; Pt(4)–Br(6), 2.44 Å; Pt(3)–Br(7), 2.43 Å. Counter ions and water molecules are omitted for clarity. (b) Stair-like structure of **4**.

Å) was slightly longer than that of typical $[PtBr_2(en)_2][Pt(en)_2]\cdot4(ClO_4)$ complex (3.006 Å),[6g] indicating a weaker interaction between Pt(IV) and Pt(II) through bromine atom. As a result of Pt(II)···Br–Pt(IV) interaction, a rectangular grid was formed which has no free space.

Stair-like networks run along *b* axis and stack such that there was a herringbone pattern of **4** grids (Fig. 2). The inter-stair separation in the herringbone layer was 9.7 Å. Counter ions and water molecules were found in between stairs, forming an infinite hydrogen bond networks with NH_2 groups of $\mathbf{2}^{2+}$.

Interestingly, a cationic molecule $\mathbf{2}^{2+}$ was accommodated by cationic host $\mathbf{1a}^{8+}$ (Fig. 3). This unusual "cation-in-a-cation" structure may be stabilized by NO_3^- and H_2O

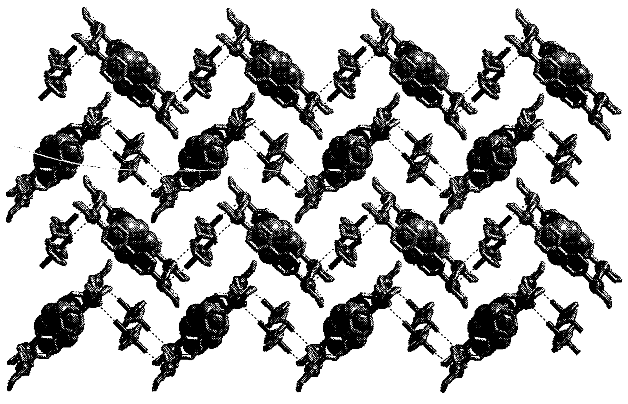

Fig. 2. Top view of the layer structure of **4**. NO_3^- and H_2O molecules were omitted because some of them are disordered.

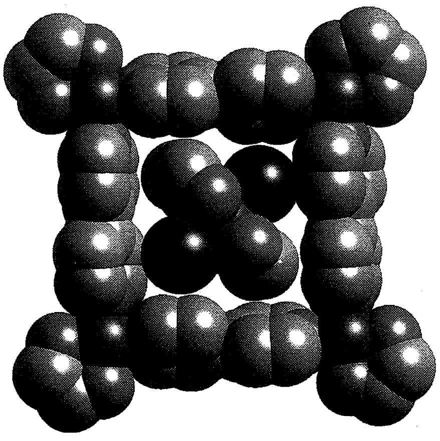

Fig. 3. Top view of the molecular square $\mathbf{1a}^{8+}$ with encapsulated cationic guest $\mathbf{2}^{2+}$.

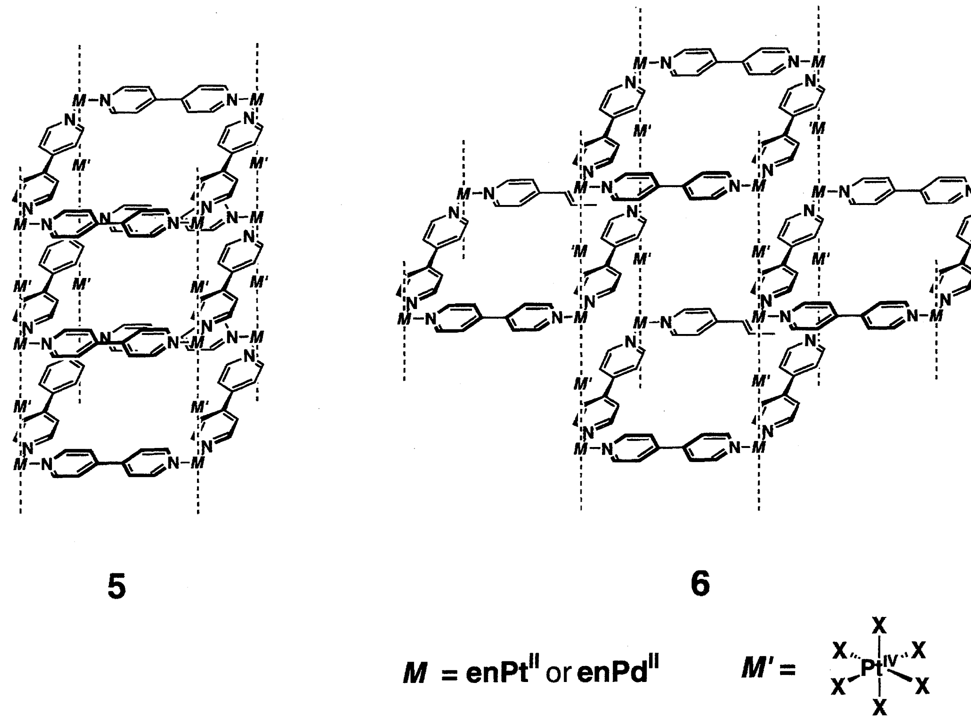

Chart 2.

networks existing in between the layers, though the details remain unclear due to the partial disorder of the counter ions and solvents. The perfect match of their shape and size, as found in Fig. 3, should be also important to override unfavorable electrostatic effect.[7] On the other hand, **1a**$^{8+}$ and **2**$^{2+}$ dissociated in the solution. The NMR measurement showed that the chemical shifts of **1a**$^{8+}$ and **2**$^{2+}$ prepared by dissolving crystal of **4** in D_2O were identical to those of sole compounds.

Reactions of 1 with $PtCl_6^{2-}$ (3a^{2-}) and $PtBr_6^{2-}$ (3b^{2-}). Reactions of **1**$^{8+}$ and anionic Pt(IV) complexes such as $PtCl_6^{2-}$ (**3a**$^{2-}$) and $PtBr_6^{2-}$ (**3b**$^{2-}$) were also attempted. An aqueous solution of **1**·$(NO_3)_8$ and an aqueous solution of potassium salts of **3**$^{2-}$ were mixed in 1 : 5 ratio. Immediately, colored insoluble powder precipitated. Elemental analysis of the product showed the formula of **1**·(**3**)$_4$, and yields of product were 92—97%. Even the use of large excess of **3**$^{2-}$ (16 equiv) resulted in the formation of the same products. The products were characterized by UV-vis and elemental analysis. The UV-vis spectrum showed new absorption bands which indicate the existence of interaction of Pd(II) and Pt(IV) (e.g., 390 and 490 nm for **1b**·(**3a**)$_4$) (Fig. 4), suggesting that each corner of **1**$^{8+}$ is bridged by the linear X–Pt(IV)–X motif of **3**$^{2-}$. From these observations, we propose the assembly of square **1**$^{8+}$ into polytube structures such as **5** and **6** or their hybrid that involve one-dimensional Pt(II)···X–Pt(IV)–X··· chains (Chart 2).

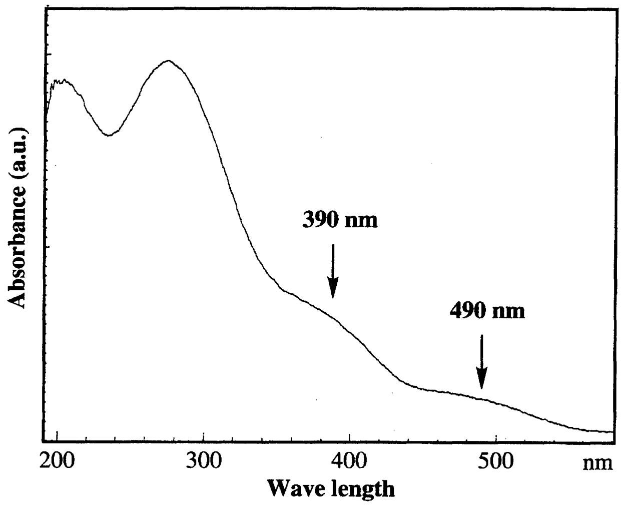

Fig. 4. UV-vis spectrum of **1b**·(**3a**)$_4$.

Conclusion

Novel stair-like and tubular structures were prepared by two stage self-assembly process. In first stage, $M(NO_3)_2(en)$ (M: Pt or Pd) and 4,4′-bpy are assembled into square complexes **1**$^{8+}$. In the second stage, the square **1**$^{8+}$ and $Pt^{IV}L_4X_2$ are assembled into higher dimensional supramolecular structure through M(II)···halogen–Pt(IV) interaction. Moreover, the present report demonstrated that formation of halogen-bridged mixed valence complex can be used for aggregation of metal containing supramolecules.

Experimental

Materials. Compound **1a**·$(NO_3)_8$[1a], **1b**·$(NO_3)_8$,[1c] and **2**·Br_2[6a] were prepared according to reported procedures. Potassium salts of **3a**$^{2-}$ and **3b**$^{2-}$ are commercially available.

Preparation of 4. An aqueous solution (1 cm^3) of **1a**·$(NO_3)_8$ (0.05 mmol) and **2**·Br_2 (0.2 mmol) was treated with $NaNO_3$ (425 mg) at room temperature. A trace amount of insoluble material was filtrated and the clear yellow solution was allowed to stand for 1 d. Yellow crystals which appeared were collected and dried in vacuo to give **4** in 64% yield. Mp 224—227 °C (decomp); ^{1}H NMR (500

MHz, D_2O, TMS as an external standard) $\delta = 8.90$ (d, $J = 5.6$ Hz, 16H, Py*Ha*), 7.86 (d, $J = 5.6$ Hz, 16H, Py*Hb*), 3.11 (t, $J = 13.7$ Hz, 24H, $-CH_2-$), 2.86 (s, 16H, $-CH_2-$); IR (KBr) 3449, 3045, 1618, 1385, 1173, 1138, 1053, 826 cm^{-1}; Elemental analysis: Calcd for $C_{60}H_{124}Br_6N_{42}O_{42}Pt_7 \cdot 6H_2O$: C, 17.81; H, 3.09; N, 14.54%. Found: C, 17.78; H, 3.05; N, 14.43%.

X-Ray Crystallographic Analysis of 4. Single crystals of **4** were obtained by slow diffusion of the aqueous solution (1 cm^3) of **1a**$\cdot(NO_3)_8$ (25 mM) and **2**$\cdot Br_2$ (100 mM) into an aqueous solution of $NaNO_3$ (10 M, 1 cm^3) at room temperature for 3 d. X-Ray data for **4**: $C_{60}H_{124}Br_6N_{44}O_{42}Pt_7 \cdot 12H_2O$, $M = 4190.80$, monoclinic, space group $P2_1/c$; $a = 20.648(4)$, $b = 16.205(3)$, $c = 19.397(3)$ Å, $\beta = 111.031(11)$, $V = 6057.8(18)$ Å^3; $\rho_{calc} = 2.278$ g cm^{-3}, $Z = 2$; $F(000) = 3956$; $\mu(Mo\,K\alpha) = 10.134$ mm^{-1}; crystal size = $0.4 \times 0.25 \times 0.25$ mm; temp 293 °C; 25113 reflections collected, 10175 ($I > 2\sigma(I)$) reflections observed; $R_1 = 0.0434$; $wR_2 = 0.1185$. The data were collected on a Siemens SMART/CCD diffractometer. Diffraction data were corrected for absorption using the SADABS[8] program. SHELXTL[9] was used for the structure solution and refinement was based on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed in calculated positions and refined isotropically with thermal parameters based upon the corresponding C-atoms [$U(H) = 1.2\ U_{eq}$ (C)]. Crystallographic data have been deposited at the CCDC, 12 Union Road. Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 134340. The complete data are deposited as Document No. 72041 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Preparation of 1a$\cdot$(3a)$_4$, 1a$\cdot$(3b)$_4$, 1b$\cdot$(3a)$_4$, and 1b$\cdot$(3b)$_4$. An aqueous solution (1.0 cm^3) of **1** (0.02 mmol) was added into an aqueous solution (10 cm^3) of **3** (0.1 mmol) at room temperature. Colored products were collected by filtration and dried in vacuo. The ratios of water were calculated from elemental analysis data.

1a$\cdot$(3a)$_4$: Brown solid, 95%, mp > 300 °C. IR (KCl) 3202, 1616, 1421, 1221, 1047, 820, 665 cm^{-1}. Elemental analysis: Calcd for $C_{48}H_{64}N_{16}Cl_{24}Pt_8 \cdot 13H_2O$: C, 16.42; H, 2.58; N, 6.38%. Found: C, 16.40; H, 2.58; N, 6.38%.

1a$\cdot$(3b)$_4$: Dark brown solid, 92%, mp 288—291 °C (decomp). IR (KBr) 3198, 1614, 1420, 1217, 1047, 816, 667 cm^{-1}. Elemental analysis: Calcd for $C_{48}H_{64}N_{16}Br_{24}Pd_4Pt_4 \cdot 20H_2O$: C, 12.26; H, 2.23; N, 4.76%. Found: C, 12.32; H, 2.01; N, 4.81%.

1b$\cdot$(3a)$_4$: Yellow powder, 96%, mp 284—287 °C (decomp). IR (KCl) 3213, 1612, 1418, 1219, 1059, 816, 658 cm^{-1}. Elemental analysis: Calcd for $C_{48}H_{64}N_{16}Cl_{24}Pd_4Pt_4 \cdot 13H_2O$: C, 18.27; H, 2.87; N, 7.10%. Found: C, 18.14; H, 2.73; N, 7.12%.

1b$\cdot$(3b)$_4$: Orange powder, 97%, mp 234—237 °C (decomp). IR (KBr) 3205, 1611, 1418, 1218, 1057, 814, 659 cm^{-1}. Elemental analysis: Calcd for $C_{48}H_{64}N_{16}Br_{24}Pd_4Pt_4 \cdot 14H_2O$: C, 13.59; H, 2.19; N, 5.28%. Found: C, 13.28; H, 1.82; N, 5.32%.

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