Synthesis, Crystal Structure and Spectroscopic Properties of Singly Bridged Dinuclear Platinum(II) Complex: $[Pt_2(terpyridine)_2(\mu\text{-}N,N\text{-}diethyldithiocarbamato)](PF_6)_3$

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Singly bridged dinuclear platinum(II) complex, $[Pt_2(trpy)_2(\mu\text{-}dtc)](PF_6)_3$ (trpy = 2,2':6',2"-terpyridine, dtc = *N,N*-diethyldithiocarbamate), was synthesized and structurally characterized. The compound is luminescent in the glassy solution of propylene carbonate.

Dinuclear platinum(II) complexes having doubly or quadruply bridged structures are well known for wide variety of bridging ligands. We have been interested in the effect of bridging ligands upon the Pt···Pt interaction. We described previously for the quadruply bridged platinum dimers that the bite distance of bridging ligands affects the Pt···Pt distance and may control the ease with which the platinum ions are oxidized to tervalent.[1-3] The extent of such effect may be perturbed by the number of bridging ligands as well as by the type of bridging ligands. Recently a number of singly bridged platinum dimers have been prepared by using 2,2':6',2"-terpyridine (trpy) as non-bridging in-plane ligands, though they are limited for N-N bridging ligands such as anions of arginine,[4] canavanine,[4] guanidine,[5] pyrazole,[6] and diphenylformamidine.[7] Since these N-N bridging ligands are uncommon in doubly or quadruply bridged platinum complexes, general properties of the singly bridged platinum dimers are still unknown. Furthermore for understanding the effect of bridging ligand toward the Pt···Pt interaction in singly bridged Pt dimers, it is important to prepare the complexes with different types of bridging ligands. We describe herein a new dinuclear platinum(II) complex of trpy using diethyldithiocarbamate (Et_2dtc) as a bridging ligand.

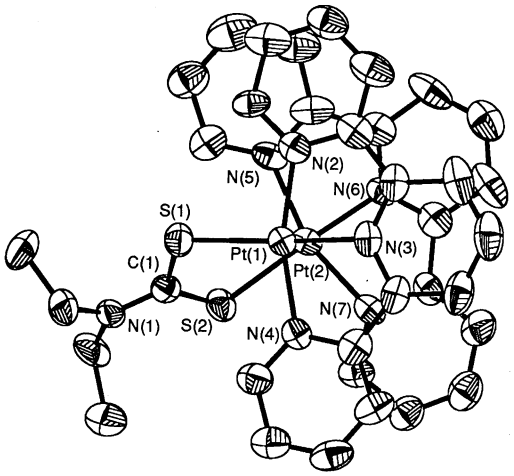

Figure 1. Molecular structure of **1**. Selected bond distances (Å) and angles (°): Pt(1)···Pt(2), 3.052(1); Pt(1)-S(1), 2.295(4); Pt(2)-S(2), 2.299(4); Pt(1)-N(2), 2.028(9); Pt(1)-N(3), 1.956(10); Pt(1)-N(4), 2.036(8); Pt(2)-N(5), 2.032(8); Pt(2)-N(6), 1.961(10); Pt(2)-N(7), 2.037(8); S(1)-C(1), 1.737(12); S(2)-C(1), 1.745(8); S(1)-Pt(1)-N(3), 176.2(2); N(2)-Pt(1)-N(3), 80.9(4); N(2)-Pt(1)-N(4), 161.4(4); N(3)-Pt(1)-N(4), 80.8(4); S(2)-Pt(2)-N(6), 176.0(2); N(5)-Pt(2)-N(6), 80.9(4); N(5)-Pt(2)-N(7), 160.8(4); N(6)-Pt(2)-N(7), 80.0(4); Pt(1)-S(1)-C(1), 110.4(4); Pt(2)-S(2)-C(1), 112.1(5); S(1)-C(1)-S(2), 124.0(8).

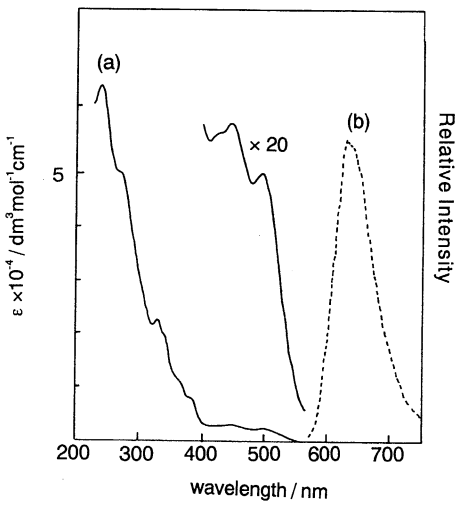

Figure 2. (a) UV-vis absorption spectrum of $\mathbf{1}\cdot(PF_6)_3$ in acetonitrile at room temperature and (b) emission spectrum of $\mathbf{1}\cdot(PF_6)_3$ in degassed propylene carbonate at 77K (λ_{ex} = 355 nm).

The complex cation $[Pt_2(trpy)_2(\mu\text{-}Et_2dtc)]^{3+}$ (**1**) was prepared as PF_6^- salt from $[Pt(trpy)Cl]^+$ and $Na(Et_2dtc)$.[8] Single crystals suitable for X-ray analysis were obtained by the recrystallization from DMF/ether.

Figure 1 shows the perspective view of the complex cation.[9] The two platinum centers are bridged by a diethyldithiocarbamate ligand with a Pt···Pt separation of 3.052(1) Å. Important structural data are summarized in Table 1 with those of other singly-bridged dinuclear Pt(II) trpy complexes. Since the bite distance of Et_2dtc (3.074(3) Å) is close to the Pt···Pt separation, two coordination planes defined by each three N atoms of trpy and an S atom of Et_2dtc are nearly parallel (dihedral angle, 9.0(1)°). It is noteworthy that in spite of the significantly shorter ligand bite distances the dpf and can complexes show similar Pt···Pt distances and dihedral angles of trpy N_3 planes to those of **1**. Accordingly, the donor atoms of dpf and can bridging ligand deviate towards one another from the coordination planes defined by three N atoms of each trpy ligand. These facts would suggest the existence of strong π-π interaction between trpy ligands. The actual planarity of the coordination plane is better for the complex of S-S bridging ligands compared with the complexes of N-N bridging ligand. Because of the extremely short ligand bite distance, the pz complex should be considered exceptionally. The average torsion angle of **1** along the Pt-Pt axis is 33.9° which is the largest among those of the complexes listed in Table 1.[10] It is suggested that the π-π interactions between aromatic molecules favors slipped geometry.[11] For singly bridged $\{Pt(trpy)\}_2$ systems, the slipped geometry is realized by a twist of the

Table 1. Structural data for $[Pt_2(trpy)_2(\mu\text{-}L)]^{3+}$ complexes [a]

bridging ligand (abbreviation, type[b])	*d*(Pt···Pt) (Å)	bite distance (Å)	dihedral angle (°)[i]
pyrazolate (pz, N-N)[c]	3.432(3)	1.335(7)	60.1(2) [52.7(4)]
guanidate (gua, N-N)[d,e]	3.090(1)	-	12
diethyldithiocarbamate (Et_2dtc, S-S)[f]	3.052(1)	3.074(3)	9.0(1) [9.0(4)]
diphenylformamidinate (dpf, N-N)[g]	3.049(3)	2.36(1)	16.8(2) [9.7(5)]
canavaninate (can, N-N)[e,h]	2.9884(7)	2.26(2)	21.9(3) [14.4(7)]

[a] The structural data of the reference compounds are recalculated for comparison in the same manner from the reported atomic coordinates. [b] Classified by the bridging atoms. [c] ref.6 [d] No atomic coordinates are given in ref.5. [e] The data are listed for one of the two independent complexes. [f] this work. [g] ref.7 [h] ref.4 [i] Those between the coordination planes defined by each four donor atoms. The data in bracket are those between the planes defined by each trpy N donor atoms.

coordination planes along the Pt-Pt axis. Judging from the long bite distance of Et_2dtc that allows flexible twisting of coordination planes, the structure of **1** may optimize the π-π interaction of trpy ligands. The crystal lattice of **[1]**·$(PF_6)_3$ is composed of three columns of the dimer pair of dimers stacking along the diagonal direction of *a* and *c* axes and in a head-to-tail manner as is also seen in the gua complex.[5] The intermolecular Pt(1)···Pt(1') (related by two fold axis) and Pt(2)···Pt(2") (inversion center) distances are 4.265(1) and 3.728(1) Å, respectively. The Pt(2)-Pt(1)-Pt(1') and Pt(1)-Pt(2)-Pt(2") angles are 150.44(2) and 162.62(2)°, respectively. The planarity of the coordination plane may affect to this columnar stacking which indicates the weak intermolecular Pt···Pt and/or π-π interactions in the solid state.

For dinuclear Pt(trpy) systems, there exists a characteristic band around 450-500 nm which is assigned to be $^1[d\sigma^*\text{-}\sigma(\pi^*)(trpy)]$.[4,5,12,13] The uv-vis absorption spectrum in acetonitrile at ambient temperature and emission spectrum in propylene carbonate at 77 K of **1** are shown in Figure 2. The characteristic band for the Pt(trpy) dimer appears at 495 nm (ε = 2390 $dm^3\ mol^{-1}\ cm^{-1}$) for **1**. Gray and co-workers mentioned that the characteristic absorption bands move to lower energy with decreasing Pt···Pt separation.[13] The band for **1** appeared around the expected position from the correlation for the absorption energy and Pt···Pt separation. The emission spectrum of **1** exhibits featureless band at 640 nm; the excited-state lifetime is 4.4 μs. Further details on the emission of **1** will be discussed elsewhere.

The cyclic voltammogram of **1** in acetonitrile shows two quasi-reversible reduction waves at -0.79 (ΔE_p = 60 mV) and -1.08 V (ΔE_p = 140 mV) vs. $Fc^{+/0}$ (i_{pc}/i_{pa} = 1 for these two couples). The corresponding reduction potentials of $[Pt_2(trpy)_2(gua)]^{3+}$ are ca. 0.2 V more negative,[5] which may indicate more electropositive platinum center of **1** with less electron donating S-ligand. The difference between the first and the second reduction potentials of **1** (0.29 V) is almost the same as that of $[Pt_2(trpy)_2(gua)]^{3+}$ (0.28 V). This fact indicates that the extent of π-π interaction of trpy ligands accompanying with Pt···Pt interaction in **1** is comparable with that in $[Pt_2(trpy)_2(gua)]^{3+}$.

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8 A mixture of [Pt(trpy)Cl]Cl·$2H_2O$ (107 mg, 0.2 mmol/10 ml H_2O) and $AgNO_3$ (68 mg, 0.4 mmol) was stirred for several hours, and then resulting AgCl was removed by centrifugal filtration. A minimum volume of aqueous solution of Na(Et_2dtc)·$3H_2O$ (23 mg, 0.1 mmol) was added to the filtrate with stirring at room temperature. Red purple solid obtained by addition of NH_4PF_6 to the solution was recrystallized from acetonitrile. Yield 49 mg (33.8 %). Anal. Calcd for $C_{35}H_{32}F_{18}N_7P_3Pt_2S_2$: C, 29.20; H, 2.24; N, 6.81; S, 4.45 %. Found: C, 29.29; H, 2.32; N, 6.92; S, 4.42 %.
9 Crystal data for **[1]**·$(PF_6)_3$·(C_3H_7NO): $C_{38}H_{39}F_{18}N_8OP_3Pt_2S_2$, FW=1512.95, monoclinic, space group *C*2/*c*; *a* = 31.751(3) Å, *b* = 19.038(3) Å, *c* = 19.074(3) Å, β = 122.01(1)°, *V* = 9776(2) $Å^3$, *Z* = 8, D_c = 1.96 g cm^{-3}, μ(MoKα) = 60.6 cm^{-1}. The structure was solved by heavy atom method using UNICS III. The final *R* value was 0.046 (R_w = 0.045) for 6290 reflections with $|F_o| \geq 6\sigma|F_o|$ measured on a RIGAKU AFC-5R diffractometer up to 2θ = 60° (Mo Kα radiation, λ = 0.71073 Å).
10 Average tortion angles of $[Pt_2(trpy)_2L]^{3+}$ about the Pt-Pt axis (L, deg): pz, 0; gua, 28.6; dpf, 7.4; can, 22.0.
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