Photophysical Properties and X-Ray Crystal Structure of a Luminescent Platinum(II) Dimer $[Pt_2(2,2':6',2''\text{-terpyridine})_2(Gua)](ClO_4)_3 \cdot H_2O$ (Gua = guanidine anion)

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A new luminescent d^8–d^8 dinuclear Pt^{II} polypyridyl complex $[Pt_2(2,2':6',2''\text{-terpyridine})_2(Gua)]^{3+}$ is synthesised and characterized by X-ray crystallography; its spectroscopic and photoredox properties are investigated.

Broadly speaking, there are two main categories of luminescent metal complexes, which are widely studied in the field of inorganic photochemistry. The first category is composed of metal complexes containing polypyridine ligands. Representative examples are $[Ru(bipy)_3]^{2+}$,[1a] (bipy = 2,2′-bipyridine) and cyclometallated Pt^{II} complexes.[1b] Polymetallic metal complexes, which belong to the second category, are well-exemplified by the complexes $[Pt_2(P_2O_5H_2)_4]^{4-}$,[2a] and $[Rh_2(1,3\text{-diisocyanopropane})_4]^{2+}$.[2b] We describe herein a new luminescent dinuclear d^8–d^8 complex with polypyridine ligand $[Pt_2(trpy)_2(Gua)](ClO_4)_3$,[3] here abbreviated as $\mathbf{1}\cdot(ClO_4)_3$ (trpy = 2,2′:6′,2″-terpyridine; Gua = guanidine anion), which possesses the essential features of the two categories. An interesting aspect of **1** is that it may serve as a model for understanding the solid-state metal–metal and excimeric interactions of Pt^{II}–(α-diimine) complexes.[4–6]

The complex cation **1** was prepared by refluxing [Pt(trpy)Cl]Cl with 0.5 equiv. of guanidine carbonate in water for 24 h.[3] Addition of $LiClO_4$ to the solution gave $\mathbf{1}\cdot(ClO_4)_3$, which could be recrystallized from acetonitrile.

Fig. 1 shows the perspective views of the two independent complexes.† Both cations are mainly composed of two slightly staggered planar [Pt(trpy)] units (torsion angle = 28.6° and 22.1°), which are nearly parallel to each other (dihedral angle = 12 and 9°). The intramolecular Pt–Pt separations are 3.090(1) and 3.071(1) Å, which are close to that of 2.922 Å found in $[Pt_2(P_2O_5H_2)_4]^{4-}$.[2a] The crystal lattice of $\mathbf{1}\cdot(ClO_4)_3$ is composed of three columns of the dinuclear complexes stacking along the *z* axis and in a head-to-tail manner. This results in an off-axis intermolecular alignment of the Pt atoms. The ^{13}C NMR spectrum‡ of **1** consists of nine peaks only, suggesting the equivalence of the two [Pt(trpy)] units in solution.

Fig. 2 displays the absorption and emission spectra of $\mathbf{1}\cdot(ClO_4)_3$ in degassed acetonitrile at room temperature. The intense absorption peaks at 246 nm (ε 5×10^4 cm^{-1}), 271 nm (ε 4.1×10^4 cm^{-1}), 310 nm (ε 1.8×10^4 cm^{-1}), 328 nm (ε 1.3×10^4 cm^{-1}) and 342 nm (ε 1.2×10^4 dm^3 mol^{-1} cm^{-1}) are assigned to the intraligand π–π* transition of trpy. This assignment is based on the similarity of these peaks to the π–π* transition found in $Ir(trpy)_2^{3+}$.[7] Apart from these transitions, there is also a broad absorption centred on 483 nm (ε 2.7×10^3 dm^3 mol^{-1} cm^{-1}) with a shoulder around 440 nm. The 483 nm band which is absent in the monomeric $[Pt(trpy)Cl]ClO_4$ complex (480 nm, ε 194 dm^3 mol^{-1} cm^{-1}), arises from the Pt–Pt and/or ligand–ligand π–π interaction. With reference to previous work on Pt^{II}–(α-diimine) complexes,[4–6] the 480 nm transition is tentatively assigned to be the $^1[d\sigma^* \rightarrow \sigma(\pi^*)(trpy)]$ transition. Here, the dσ* orbital is formed by the antibonding interaction of the two Pt d_{z^2} orbitals and σ(π*) and σ*(π*) are formed by bonding and

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† *Crystal data*: $(C_{15}H_{11}N_3Pt)_2(NH)_2CNH_2 \cdot 3ClO_4 \cdot H_2O$, $M = 1231.21$, space group $P\bar{1}$ (No. 2), $a = 12.804(3)$, $b = 14.615(5)$, $c = 20.273(5)$ Å, $\alpha = 104.06(2)°$, $\beta = 90.42(2)°$, $\gamma = 90.87(2)°$, $U = 3680(1)$ Å^3, $Z = 4$, $D_c = 2.22$ g cm^{-1}, μ(Mo-Kα) = 79.69 cm^{-1}, $F(000) = 2352$, no. of variables (*p*) 680, no. of unique data measured 17939, no. of observed data with $|F_o| \geqslant 6\sigma(|F_o|)$ (*n*) 11483, $R_F = 0.075$, $R_G = 0.084$. The residual extremes in the final difference map were +1.15 to −1.10 eÅ^{-3}. Raw intensities collected on a Nicolet R3m/V four-circle diffractometer at 294 K were processed with profile fitting procedure of Diamond and corrected for absorption using ψ-scan data. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ *NMR data*: Δ% < 0.2. ^1H NMR (270 MHz, CD_3CN, 25 °C): δ 4.59 (s, 2H, 2N*H*-C), 5.58 (s, 2H, NH_2–C), 7.56 (m, 4H), 7.94 (m, 8H), 8.17 (m, 4H), 8.32 (t, 2H) and 8.42 (dd, 4H)-terpyridine protons. ^{13}C NMR (270 MHz, CD_3CN, 25 °C): δ 125.2, 126.7, 130.4, 143.6, 143.8, 152.7, 154.9, 157.7(trpy), 167.5(Gua).

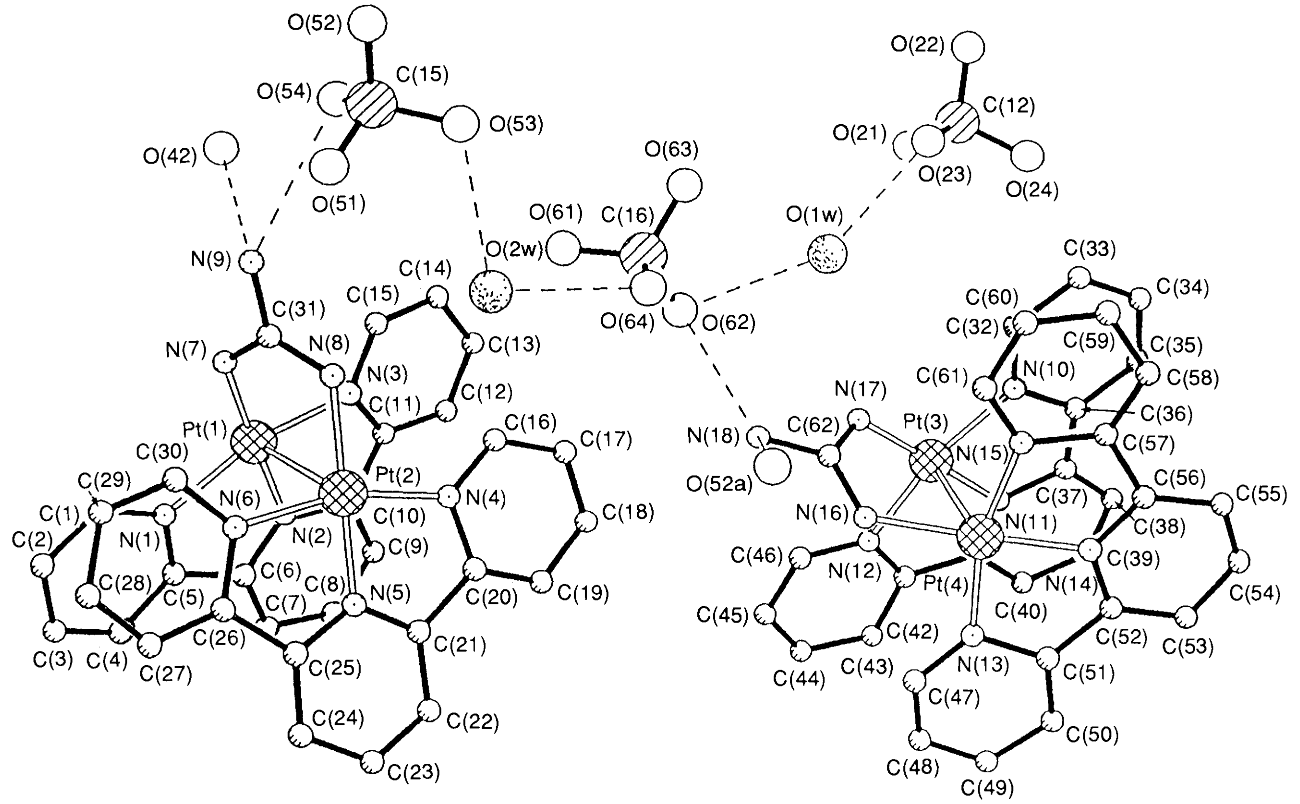


Fig. 1 A perspective view of the asymmetric unit of $[Pt_2(trpy)_2\text{-}(Gua)](ClO_4)_3{\cdot}H_2O$ with three of the ClO_4^- anions omitted. Pt(1)–Pt(2) 3.090(1), Pt(3)–Pt(4) 3.071(1), Pt(1)–N(1) 2.02(1), Pt(1)–N(3) 2.01(1), Pt(1)–N(2) 1.92(1), Pt(1)–N(7) 2.00(1) Å. Pt(2)–Pt(1)–N(1) 94.1(3), N(1)–Pt(1)–N(3) 161.0(4), N(1)–Pt(1)–N(2) 79.9(4), N(7)–Pt(1)–N(2) 177.4(5), N(2)–Pt(1)–N(3) 81.3(4), Pt(1)–N(7)–C(31) 127(1), N(7)–C(31)–N(8) 121(1)°.

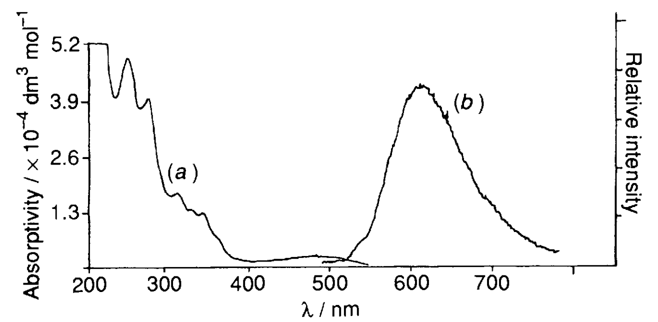
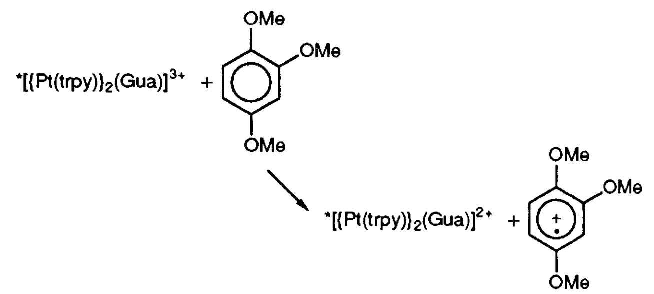


Fig. 2 (*a*) UV–VIS absorption spectrum of **1** $(ClO_4)_3$ in degassed acetonitrile and (*b*) emission spectrum of $\mathbf{1}{\cdot}(ClO_4)_3$ $(1.35 \times 10^{-4}$ mol dm$^{-3})$ in degassed acetonitrile at room temperature

antibonding interactions of π^* orbitals of the two trpy ligands. It should be noted that configurational mixing between the $6p_z$ orbital of Pt and $\sigma(\pi^*)$ orbital may exist. All the above-mentioned absorption bands obey the Beer Law in the concentration range of 10^{-6} to 10^{-3} mol dm^{-3} suggesting no dimerization or oligomerization of the metal complex occurs. This is further confirmed by conductivity measurement which shows that the complex remains as 1:3 electrolyte in the concentration range 10^{-6} to 10^{-2} mol dm^{-3}.

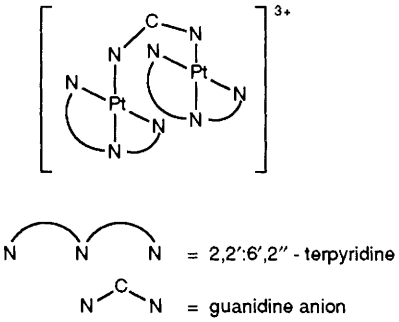
Photoexcitation of a degassed acetonitrile solution of **1** at 450 nm results in a phosphorescence centred around 620 nm (quantum yield = 1.27×10^{-4}; lifetime = 0.35 μs). Noticeably, **1** is a prototype example of a new class of d^8–d^8 complexes showing room temperature photoluminescence in solution. Complex $\mathbf{1}{\cdot}(ClO_4)_3$ also exhibits a very strong solid-state emission at around 620 nm with lifetime of 0.4 μs at room temperature. Upon cooling to 77 K, the emission intensity increases and the band width of the emission is reduced. We tentatively assign the emitting state to be $^3[d\sigma^*\sigma(\pi^*)]$. Similar assignment has been made for



Scheme 1

$Pt(bipy)(CN)_2$ and $[Pt(bipy)_2][Pt(CN)_4]$.[4] Notably, the solution emission and solid-state emission energies are nearly the same and close to that of the excimeric emission of Pt(α-diimine)$(CN)_2$ in solution.[5,6] This suggests that the solid-state intermolecular interaction in $\mathbf{1}{\cdot}(ClO_4)_3$ is negligible and the excited state is localized in individual dinuclear molecules. This is consistent with the X-ray structure of $\mathbf{1}{\cdot}(ClO_4)_3$ showing no intermolecular metal–metal interaction between adjacent $[Pt_2(trpy)_2(Gua)]^{3+}$ units. Thus, $\mathbf{1}{\cdot}(ClO_4)_3$ can be regarded as a model for further understanding of the solid-state and excimeric interactions of Pt^{II}–(α-diimine) complexes.

The cyclic voltammogram of **1** in acetonitrile shows two quasi reversible reduction couples at −0.98 and −1.26 V *vs.* $Cp_2Fe^{+/o}$ [ΔE_p *ca.* 80–90 mV and $i_{pc}/i_{pa} = 1$ for these two couples. Electrochemical studies on the $Ru(trpy)_2^{2+}$ and $Fe(trpy)_2^{2+}$[6] suggested that the ligand-centred reduction would occur at −1.9 *vs.* SSCE (saturated standard calomel electrode). We tentatively assign the −0.98 and −1.26 V reduction waves to be the $\mathbf{1}^{3+}/\mathbf{1}^{2+}$ and $\mathbf{1}^{2+}/\mathbf{1}^{+}$ couples, respectively.



With the 0–0 transition located at about 530 nm, the excited state reduction potential E° ($\mathbf{1}^{3+*}/\mathbf{1}^{2+}$) is estimated to be +1.20 V *vs.* Ag/$AgNO_3$. This clearly indicates that the $^3[d\sigma^*\sigma(\pi^*)]$ excited state of **1** is a very strong oxidant. In fact, the emission of **1** is quenched by 1,2,4-trimethoxybenzene with a rate constant of 1.4×10^9 dm^3 mol^{-1} s^{-1} at room temperature. The transient absorption spectrum recorded 10 μs after flashing a degassed acetonitrile of $\mathbf{1}\cdot(ClO_4)_3$ (2.4×10^{-4} mol dm^{-3}) and 1,2,4-trimethoxybenzene (1.3×10^{-3} mol dm^{-3}) shows intense absorption bands centred at 400 and 450 nm, which are due to the transitions of the 1,2,4-trimethoxybenzene radical cation.[9] This confirms the photochemical reaction shown in Scheme 1.

Given the fact that the photoredox properties of $[Pt_2(trpy)_2(Gua)]^{3+}$ can be tuned by adding substituent groups on the trpy ligand, the present study provides an entry to an entirely new class of luminescent d^8–d^8 complexes, which may have photochemistry as rich as $[Ru(bipy)_3]^{2+}$ and $[Pt_2(P_2O_5H_2)_4]^{4-}$.

We acknowledge financial support from the Croucher Foundation, the University of Hong Kong and Hong Kong Research Grants Council. H. K. Y. thanks the Croucher Foundation of Hong Kong for a Studentship.

Received, 1st June 1992; Com. 2/02869G

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