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Pyrophosphito-Bridged Diplatinum Chemistry[†]

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Square-planar platinum(II) complexes have long been known to exhibit metal–metal interactions in the solid state.[1] These intermetallic interactions can be sufficiently strong that even ions of the same charge can associate in solution media of high dielectric constant. Although unbridged oligomeric metal complexes are not found exclusively in platinum chemistry, they do occur mainly for square-planar metal ions, because the vacant axial coordination sites allow the metal centers to approach each other closely. Assuming that the ligands lie in the *xy* plane, the relative d-orbital energies are d_{xy}, $(d_{xz}, d_{yz}) < d_{z^2} \ll d_{x^2-y^2}$ in a planar d^8 monomer containing π acceptor ligands.[2] Approach along the axial direction causes the valence d_{z^2} orbitals to overlap to give bonding ($d\sigma$) and antibonding ($d\sigma^*$) orbitals. The orbital energy level diagram shown in Figure 1 has been useful in interpreting the ground- and excited-state properties of binuclear rhodium(I), iridium(I), and platinum(II) complexes.[3]

Intermetallic interactions in platinum complexes can extend beyond dimers into materials that exhibit higher oligomeric units. Two of the better known properties associated with these chain interactions are the anisotropic conductivity of $K_2[Pt(CN)_4]Cl_{0.3}$ and the intense absorption of the platinum blues.[4] In each case, the chain axis stabilizes a complex that has partial valence at platinum. Such materials can be viewed as intermediate structures in the transition from a discrete complex to a metallic state.[5]

Both oxidation (to d^7–d^8 or d^7–d^7 complexes) and reduction (to d^8–d^8 $p\sigma^1$ or d^8–d^8 $p\sigma^2$ species) lead to enhanced metal–metal bonding in the dimeric units. Accordingly, the sulfato-bridged diplatinum(III) (d^7–d^7) complex, $K_2[Pt_2(SO_4)_4(H_2O)_2]$, exhibits a short (2.471 (1) Å) Pt–Pt distance. Other diplatinum(III) compounds with relatively short Pt–Pt bonds contain α-pyridone, hydrogen phosphate, or trifluoroacetate bridging groups.[6] Although individual Pt–Pt separations are primarily determined by the bridging bite angle of the equatorial ligands, the shortening in the Pt–Pt distance on going from d^8–d^8 to d^7–d^7 in the α-pyridone- and dithioacetate-bridged complexes supports the molecular orbital model.[7] Reviews of work on diplatinum complexes give further examples.[8] Structural data for the mixed-valence d^7–d^8 complexes are fewer, but those available show that there is again a shortening of the Pt–Pt distance from the d^8–d^8 precursor.[9]

The most widely studied diplatinum(II) complex is $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ (abbreviated Pt_2), which contains bridging (P,P-bonded) pyrophosphito ligands. The excited-state chemistry exhibited by Pt_2 is probably the richest of all d^8–d^8 complexes. Photophysical studies confirm that the properties of the photoactive excited state are a manifestation of d^8–d^8 metal–metal interactions. Here we will devote much attention to the photochemistry of Pt_2, because the observed reactions with substrates include rare examples of atom abstractions in addition to electron transfers and other

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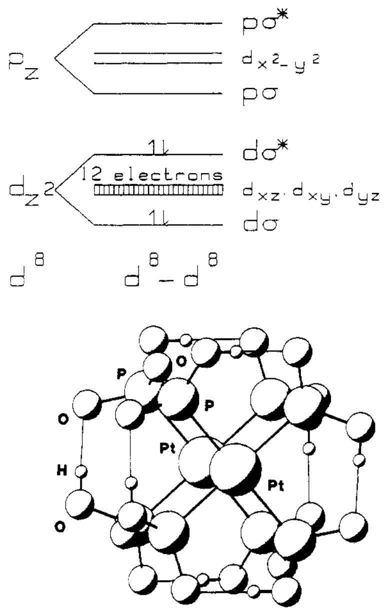

Figure 1. Orbital energy level diagram for interaction (face-to-face) of two d^8 square-planar units along the metal–metal axis. The structure of $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ (Pt_2) is shown.

well-studied inorganic excited-state processes.

Synthesis and Spectroscopy

The diplatinum(II) complex $K_4[Pt_2(\mu\text{-}P_2O_5H_2)_4]$, which is often referred to as "platinum pop", is prepared from K_2PtCl_4 and phosphorous acid.[10] The initially formed P-bonded complex $Pt(OP(OH)_2)_4H_2$ undergoes intermolecular condensation at 100 °C in the reaction mixture to give the bridged *P,P*-pyrophosphito complex $K_4[Pt_2(\mu\text{-}P_2O_5H_2)_4]$ (reaction 1). Heating to 170 °C gives a higher oligomer $\{K_4[Pt_2(\mu\text{-}P_2O_5H_2)_4]\}_n$, although this product has not been fully characterized. The single-crystal X-ray structure of $K_4[Pt_2(\mu\text{-}P_2O_5H_2)_4]\cdot 2H_2O$ shows the anion with an eclipsed "lantern" type structure having planar platinum(II) centers linked by $\mu\text{-}P_2O_5H_2^{2-}$ groups. The anion has a Pt–Pt separation of 2.925 (1) Å with no ligands bonded to the axial sites.[11] The complex is a dibasic acid (pK_{a1} 2.24, pK_{a2} 6.95).[12] Replacement of the potassium cations with tetra-*n*-butylammonium or bis(triphenylphosphine)nitrogen(1+) (PPN^+) gives salts of $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ that are soluble in nonaqueous solvents.

$$2K_2PtCl_4 + 8H_3PO_3 \rightarrow 2Pt(OP(OH)_2)_4H_2 + 4KCl + 4HCl \rightarrow K_4[Pt_2(\mu\text{-}P_2O_5H_2)_4] + 8HCl + 4H_2O \quad (1)$$

The Pt_2 complex has electronic absorption bands at 367 (log ε 4.54) and 435 nm (log ε 2.04) that are attributable to singlet and triplet dσ* → pσ transitions, respectively.[13] An unusual feature of the complex is that aqueous solutions show an intense green emission at 514 nm at ambient temperature. This phosphorescence at 514 nm ($\tau \sim 9\ \mu s$) from a triplet excited state is accompanied by a shorter lived fluorescence (8–40 ps) at 407 nm (Figure 2).[13,14]

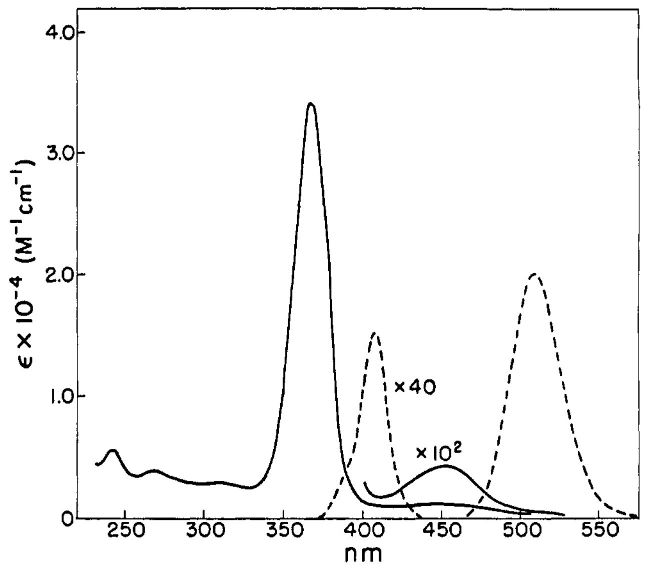

Figure 2. Absorption (—, ε scale) and corrected emission (---) spectra of Pt_2 (K^+ salt in aqueous solution at 25 °C).[13]

Extensive spectroscopic experiments on Pt_2 have further elucidated the dσ* → pσ excited states.[13-18] Examination of the low-temperature phosphorescence shows that the $^3A_{2u}$ level is split into a lower A_{1u} and a higher energy E_u state separated by ~42 cm^{-1}.[13,15] The application of a magnetic field (0–4 T) causes both a blue shift of the phosphorescence wavelength and an increase in peak intensity.[14] The electronic structure and spectra of Pt_2 have been calculated by using a nonempirical self-consistent extended Hückel method.[19] The calculation supports the spectral assignments but suggests that an electronic structural model involving only Pt orbitals is not adequate for a quantitative rationalization of the properties of Pt_2.

Two applications of Pt_2 have been suggested. One is in the trace detection of platinum. The 514-nm emission intensity is linear with concentration, and emission has been detected at 77 K from solutions containing only 4 parts per trillion platinum.[20] A second possible use is in the fabrication of luminescent solar concentrators.[21]

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Oxidative Addition

The complex Pt_2 undergoes thermal two-electron two-center oxidative addition of halogens or alkyl iodides to give axially substituted diplatinum(III) complexes Pt_2X_2 (X = Cl, Br, I) or Pt_2RI (R = alkyl).[22] Mechanistic studies with methyl iodide show that the reaction follows an associative pathway and that the rate is unperturbed by added external nucleophile.[23] These diamagnetic Pt_2X_2 and Pt_2RI products have an intermetallic bond joining the diplatinum(III) centers.[22,24] Diplatinum(III) species of these types also can be synthesized by the oxidation of Pt_2 in the presence of excess halide ion. The chemical oxidants that have been used include Ce^{4+}, $IrCl_6^{2-}$, $PtCl_6^{2-}$, $Fe(CN)_6^{3-}$, $Co(EDTA)^-$, $Ru(NH_3)_6^{3+}$, and H_2O_2; electrochemical anodic oxidation also has been employed.[25] Kinetic studies show that the rate law for chemical oxidation is $k[Pt_2][X^-]$, where k increases with the nucleophilicity of X^-. This oxidation reaction is reversible, with Pt_2 being regenerated from Pt_2X_2 by the addition of H_2, H_3PO_2, SO_3^{2-}, or ascorbic acid or by cathodic reduction. When the reaction between Pt_2 and X^- is followed by UV-vis spectroscopy using an OTTLE cell, the reversible Pt_2/Pt_2X_2 conversion occurs with a single isosbestic point and no detectable intermediates.[26] The reactivity of Pt_2 to one-electron oxidants is exemplified by the reversible addition of NO_2 to give $Pt_2(NO_2)_2$ (reaction 2). The N-bonded adduct reverts to Pt_2 in

$$Pt_2 + 2NO_2 \rightleftarrows Pt_2(NO_2)_2 \qquad (2)$$

the absence of excess NO_2.[27] Chemical or anodic oxidation routes have been used to prepare $Pt_2(SCN)_2$, $Pt_2(H_2O)_2^{2+}$, $Pt_2(MeCN)_2^{2+}$, and $Pt_2(imidazole)_2^{2+}$.[28]

Mixed-Valence Complexes

Halogen addition occurs by a two-step reaction where the first product is the mixed-valence complex Pt_2X (X = Cl, Br, I), which can be isolated in the solid state. With excess halogen, Pt_2X_2 is formed. In aqueous solution, disproportionation of Pt_2X occurs.[12] The solid-state structure of $K_4[Pt_2Br]\cdot 3H_2O$ at ambient temperature shows an infinite Pt–Pt–Br linear chain with the bromide symmetrically bonded between Pt_2 units.[9] The Pt–Pt distance in Pt_2Br is intermediate between those found in Pt_2 and Pt_2Br_2. For $K_4[Pt_2Cl]\cdot 3H_2O$, however, the bridging chloride is disordered over two sites to give alternately short (2.367 (7) Å) and long (2.966 (8) Å) Pt–Cl bonds.[29] The low-temperature (19 K) structure of $K_4[Pt_2Br]$, however, also shows unequal Pt–Br distances (2.579 and 2.778 Å). Calculations on these mixed-valence complexes show that Peierls distortions are not as favored for chains of binuclear platinum units as they are for mononuclear chains.[30] The bromo complex has a high electrical conductivity in the semiconductor range ($\sigma_{\parallel} = 10^{-4}$–$10^{-3}\ \Omega^{-1}\ cm^{-1}$).[9] Dichroic or metallic green crystals of $[Pt^{II}(en)_2][Pt^{IV}(en)_2X_2][Pt^{III}{}_2X_2]$ also have been prepared from the reaction of $[Pt(en)_2X_2]X_2$ (X = Br, I) with Pt_2.[31]

Table I
Structural Data

complex	d(Pt–Pt), Å	d(Pt–X) axial, Å	ref
$K_4[Pt_2]\cdot 2H_2O$	2.925 (1)	-	11
$K_4[Pt_2Cl_2]\cdot 2H_2O$	2.695 (1)	2.407 (2)	22
$K_4[Pt_2Br_2]\cdot 2H_2O$	2.723 (4)	2.555 (5)	29
$[Bu_4N]_4[Pt_2Br_2)$	2.716 (1)	2.572 (1)	24
$K_4[Pt_2I_2]\cdot 2H_2O$	2.754 (1)	2.746 (1)	24
$K_2[Bu_4N]_2[Pt_2I_2]$	2.742 (1)	2.721 (1)	24
$K_4[Pt_2(NO_2)_2]\cdot 2KNO_2\cdot 2H_2O$	2.754 (1)	2.147 (6)	28
$Na_8[Pt_2(pop\text{-}H)_4(NO_2)_2]\cdot 18H_2O$	2.7333 (2)	2.153 (6)	27
$K_4[Pt_2(SCN)_2]\cdot H_2O$	2.760 (1)	2.466 (4)	28
$K_4[Pt_2(imidazole)_2]\cdot 7H_2O$	2.745 (1)	2.13 (2)	28
$K_4[Pt_2CH_3I]\cdot 2H_2O$	2.782 (1)	2.18 (3) (Pt–C), 2.816 (3) (Pt–I)	22
$[Bu_4N]_2[Pt_2(CH_3CN)_2]$	2.676 (1)	2.093 (10)	28
$K_4[Pt_2Cl]\cdot 3H_2O$	2.813 (1)	2.966 (8), 2.367 (7)	29
$K_4[Pt_2Br]\cdot 3H_2O$	2.793 (1)	2.699 (1)	9

Table II
Electronic Spectral Data[a]

complex	λ_{max}, nm	log ϵ	ref
Pt_2	367, 435	4.54, 2.04	13
$Pt_2^*(^3A_{2u})$	325, 460	–, –	13, 14, 43
Pt_2Cl	330	–	32
Pt_2Br	370	–	32
Pt_2SCN	390	–	32
Pt_2L	310	–	32
Pt_2H	~360	–	43, 45
Pt_2^+	310	4.88	32
Pt_2^-	420	–	37
Pt_2^{2-}	373, 413, 459	3.98, 4.00, 4.11	38
Pt_2Cl_2	282, 345, 390	4.68, 3.91, –	22
Pt_2Br_2	305, 345	4.74, 4.07	22
Pt_2I_2	338, 435	4.63, 4.20	22
Pt_2H_2	313	~4.5	48
$Pt_2(NO_2)_2$	312, 360, 470	4.34, 4.08, 2.81	28
$Pt_2(SCN)_2$	337, 480	4.64, 2.87	28
Pt_2BrCl	296, 350	4.59, 3.98	12, 25
Pt_2ICl	313	4.61	12, 25
Pt_2IBr	316	4.72	12, 25
$Pt_2Cl(H_2O)^+$	267	4.54	23
$Pt_2Br(H_2O)^+$	283	4.67	23
$Pt_2(H_2O)_2^{2+}$	245, 320	4.40, –	28
$Pt_2(MeCN)_2^{2+}$	211	4.67	28
$Pt_2L_2^{2+}$	250, 275, 304, 360	4.52, 4.24, 3.83, 2.60	28

[a] Units of ϵ are $M^{-1}\ cm^{-1}$; L = imidazole, 1-methylimidazole; see references for solvents and other conditions.

The mixed-valence complexes Pt_2X can be detected in solution as transients from either the oxidation of Pt_2 or the reduction of Pt_2X_2. Three routes used to prepare Pt_2^+ complexes are the oxidation of Pt_2 with hydroxyl radicals, the reduction of Pt_2X_2 with hydrated electrons, and the biphotonic ionization of Pt_2.[32]

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Intermetallic Bonding

The structural data for Pt_2X_2 show a shortening of the Pt–Pt separation from Pt_2 because of the presence of a Pt(III)–Pt(III) single bond in Pt_2X_2. Electron donation from the axial ligand X^- in Pt_2X_2 into the Pt–Pt $d\sigma^*$ orbital causes a variation of distance with axial ligand. The donor ability for X^- to platinum follows the sequence $SCN^- \sim I^- > NO_2^- > Br^- > Cl^-$, which correlates with the Pt–Pt distances (Table I).[22,24,27-29] The long Pt–X distances are due to the large trans influence of the Pt–Pt bond. This lengthening is expected, since the Pt orbitals involved in intermetallic bonding ($5d_{z^2}$ and $6p_z$) also are employed in the attachment of the axial ligand.

Electronic spectral data for Pt_2X_2 and $Pt_2L_2^{2+}$ complexes are collected in Table II. Each complex shows an intense absorption ($\log \epsilon \approx 4.34–4.8$) in the UV region. For Pt_2X_2, where X is an anionic ligand, this absorption band is primarily due to an LMCT ($X \rightarrow Pt$) transition. For $Pt_2L_2^{2+}$ complexes, with neutral ligands L, the axial ligand is a poorer donor, and the absorption bands are due to the $d\sigma \rightarrow d\sigma^*$ transition of the Pt–Pt bond. These spectroscopic data give a donor order to platinum(III) of $SCN^- \sim I^- > NO_2^- > Br^- > Cl^-$, the same as that found from the structural data. X-ray photoelectron spectroscopy shows a 1-eV increase in Pt $4f_{7/2}$ binding energies on going from Pt_2 to Pt_2X_2.[28]

The aqueous-solution Raman spectra of Pt_2X_2 exhibit strong bands due to ν(Pt–Pt) and ν(Pt–X) (X = Cl, Br, I). Under resonance Raman conditions, long, nearly harmonic progressions are seen in ν(Pt–Pt); indeed, for Pt_2I_2, the progression reaches as far as 12ν.[33] Force-field analyses using both two-center (Pt_2) and four-center (Pt_2X_2) models suggest minimal intermetallic bonding in Pt_2 and a single Pt–Pt bond in Pt_2X_2. The small force constants for the Pt–X stretch are consistent with the long Pt–X distances. The Pt–Pt distance in the triplet excited state (Pt_2^*) is estimated by using Badger's rule to be 2.75 Å.[34] This value agrees with those estimated from analyses of the vibrational fine structure of the low-temperature absorption (367 nm) and emission (514 nm) bands and from a time-resolved Raman experiment.[14,15,35] This distance corresponds closely with those found in Pt_2X_2; the increased intermetallic bonding in Pt_2^* is readily rationalized, since the excited state arises from transfer of an electron from an antibonding ($d\sigma^*$) to a bonding ($p\sigma$) level.

Conversion of Pt_2 into Pt_2X_2 causes an upfield shift of 40 ppm in the ^{31}P NMR resonance and a decrease in ^1J(PtP) of 1000 Hz. Spectral simulation indicates much larger ^1J(PtPt) values (~9000 Hz) in Pt_2X_2 than in Pt_2 (800 Hz). This increased value of ^1J(PtPt) in Pt_2X_2 is due to the stronger intermetallic bond.[36]

Table III
Rate Constants for the Reactions of Amines with Pt_2^*

amine	$E_{1/2}$(ox), V	k_q,[a] $M^{-1}\ s^{-1}$
N,N,N′,N′-tetramethyl-1,4-benzenediamine	0.11	1.2×10^{10}
N,N,N′,N′-tetramethyl-(1,1′-biphenyl)-4,4′-diamine	0.36	3.0×10^9
N,N-trimethylbenzenamine	0.71	3.9×10^7
N,N-dimethylbenzenamine	0.78	1.2×10^7
N,N-diphenylbenzenamine	0.92	1.5×10^6

[a] In MeOH at 25 °C; ref 40.

Reduced Pt_2 Species

Aqueous solutions of Pt_2 react with hydrated electrons to give the one-electron-reduced complex, Pt_2^- (λ_{max} 420 nm).[37] This reduced complex presumably has the electronic configuration $(d\sigma)^2(d\sigma^*)^2(p\sigma)^1$. Reaction of Pt_2 with chromous ion also has been reported, but the product has not been identified.[38]

Ligand Substitution

Aqueous solutions of halogens X_2 (X = Cl, Br) react with Pt_2 to give the mixed aquo/halide complexes $Pt_2X(H_2O)^+$ (reaction 3).[23] The mixed Pt_2XY ($X \neq Y$ = Cl, Br, I) complexes are prepared in acid solution by a complementary redox reaction between Pt_2X_2 and Y_2 (X = I, Br, Y = Cl; X = I, Y = Cl, Br) (reaction 4).[12]

$$Pt_2 + X_2 + H_2O \rightarrow Pt_2X(H_2O)^+ + X^- \qquad (3)$$

$$Pt_2 + Y_2 + X^- \rightarrow Pt_2XY + Y^- \qquad (4)$$

Alternatively, Pt_2ICl is prepared from Pt_2CH_3I and $IrCl_6^{2-}$ with Cl^- (reaction 5).[23] These complexes undergo disproportionation at higher pH to Pt_2X_2 and Pt_2Y_2.

$$Pt_2CH_3I + Cl^- + IrCl_6^{2-} \rightarrow Pt_2ICl + IrCl_6^{3-} + {}^{\bullet}CH_3 \qquad (5)$$

Kinetics of the anation reactions of $Pt_2X(H_2O)^+$ and the substitution reactions of Pt_2X_2 (X = Cl, Br) can be interpreted in terms of several mechanisms. The rate law for the reaction of $Pt_2X(H_2O)^+$ with anions Y^- (X = Cl, Br; Y = Br, I, SCN) (reaction 6) is $k[Pt_2X(H_2O)^+][Y^-]$. The rate is not accelerated by added Pt_2, and an interchange pathway has been proposed.[23] The replacement of X^- in Pt_2X_2 by Y^- follows three parallel pathways. The favored pathway is a Pt_2-catalyzed route with rate = $k[Pt_2X_2][Pt_2][Y^-]$. A less efficient pathway involves Y^- attack on the X^- ligand of Pt_2X_2. The least favored pathway involves X^- dissociation.[12] Aquation of the X^- ligands in Pt_2X_2 is not observed. The complex $Pt_2(H_2O)_2^{2+}$ (λ_{max} 248 nm) is prepared in solution by the oxidation of Pt_2.

$$Pt_2X(H_2O)^+ + Y^- \rightarrow Pt_2XY + H_2O \qquad (6)$$

Excited-State Electron Transfer

The triplet ($^3A_{2u}$) state of Pt_2 is a viable chemical reagent in part because of its long lifetime (9 μs) at ambient temperature and its high quantum yield (0.5) of formation. Triplet Pt_2^* is a one-electron reductant in aqueous solution. The phosphorescence quenching

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Table IV
Rate Constants for the Reactions of Pt_2*, *t*-BuO•, and Ph_2CO* with Hydrogen-Atom Donors[a]

substrate	$k_q(Pt_2^*)$	$k(t\text{-BuO}^\bullet)$	$k_q(Ph_2CO^*)$
$Et_3Si\mathit{H}$	2.0×10^4	5.7×10^6	–
$Ph_3Si\mathit{H}$	1.6×10^5	1.1×10^7	–
$Ph_3Ge\mathit{H}$	2.9×10^7	8.9×10^7	–
$Ph_3Sn\mathit{H}$	1.0×10^8	4.0×10^8	–
$Bu_3Sn\mathit{H}$	1.2×10^7	2.2×10^8	4.7×10^7
$Bu_3Sn\mathit{D}$	6.9×10^6	1.8×10^8	–
$Me_2C\mathit{H}OH$	$<1 \times 10^4$	1.8×10^6	1.3×10^6
$PhC\mathit{H}_3$	$<1 \times 10^4$	2.3×10^5	1.7×10^5
$Ph_2C\mathit{H}OH$	2×10^5	6.9×10^6	8.9×10^6

[a] See ref 49 and 45 for solvents and other conditions (temperatures are all near 25 °C); k in $M^{-1}\ s^{-1}$.

by the 1,1′-bis(2-sulfoethyl)-4,4′-bis(pyridinium inner salt) (BSEP) gives $BSEP^-$ (λ_{max} ~610 nm) and Pt_2^+.[13] Similar reactions occur with nitric acid to give Pt_2^+ and HNO_3^-, and with vesicle-bound *N*-alkyl-*N*-methyl-4,4′-bipyridinium ions.[39] Both the quenching reaction and the bimolecular back electron transfer rates are near the diffusion limit. Nicotinamide and $OsCl(NH_3)_5^{2+}$ are also reduced by Pt_2*, thereby making the $^3A_{2u}$ state a stronger reductant ($E°(3-/4-*) < -1$ V vs NHE) than $Ru(bpy)_3^{2+}$* ($E° = -0.88$ V vs NHE).[13] The $^3A_{2u}$ state is also a one-electron oxidant (Table III). Reductive quenching of Pt_2* occurs with a series of added amines. The quenching rates k_q ($M^{-1}\ s^{-1}$) range from 1.2×10^{10} for *N,N,N′,N′*-tetramethyl-1,4-benzenediamine (TMPD) to 1.5×10^6 for *N,N*-diphenylbenzenamine, a variation corresponding to a change in $E_{1/2}$ from 0.11 to 0.92 V vs SCE.[40] With *N,N*-dimethylaniline (DMA) as a quencher, the oxidized product DMA^+ is observed.[41]

A common problem encountered in the design of chemical processes based on photoredox reactions is the difficulty of preventing back electron transfer reactions. Because the oxidized electron-transfer product Pt_2^+ has available axial coordination sites, it is possible to inhibit back electron transfer by ligand addition. For example, in experiments in which a solution containing (cytochrome c)$^{3+}$/Pt_2[NaSCN (0.1 M)] is irradiated, the decay of photogenerated (cytochrome c)$^{2+}$ to (cytochrome c)$^{3+}$ is strongly inhibited by the presence of thiocyanate ion.[42]

Excited-State Atom Transfer

Triplet Pt_2* is quenched by halogen atom transfer reagents such as alkyl and aryl halides, as well as by hydrogen-atom donors such as $(CH_3)_2CHOH$, $PhCH(OH)CH_3$, Bu_3SnH, Et_3SiH, and H_3PO_3.[43-48] No quenching is observed with alcohols such as *tert*-butyl alcohol or triphenylcarbinol that have no α-hydrogens present. The relative rates for hydrogen-atom abstraction from the s^2p^2-group hydrides follow the sequence $Ph_3SnH > Ph_3GeH > Ph_3SiH$ (Table IV). This sequence qualitatively parallels that for hydrogen abstraction by *tert*-butoxy radicals,[49] and the rate constants decrease as the E–H bond energy increases (Sn < Ge < Si). The kinetic isotope effect for the reaction with Bu_3SnH, $k_2(H)/k_2(D) = 1.7$, accords with H-atom transfer via a linear Pt–H–Sn transition state with negligible charge transfer.[45] The reactivity of Pt_2* toward Bu_3SnH is comparable to that of the $n\pi^*$ excited states of ketones with similar triplet energies. Comparisons of Pt_2* (E_t ~ 57.7 kcal/mol) and triplet benzophenone (Ph_2CO*, E_t ~ 69 kcal/mol) rate constants for hydrogen-atom abstractions are given in Table IV.[49,45]

For alkyl and aryl halides, the quenching rates with Pt_2* follow the sequence aryl iodide > alkyl halide, and PhI > PhBr > PhCl. The latter order parallels the ArX bond strength sequence. By transient difference spectroscopy, the first step in the reaction with alkyl and aryl halides is halogen atom abstraction by the $^3A_{2u}$ state (reaction 7). The initial product is Pt_2X.[43,46] The

$$Pt_2^* + RX \rightarrow Pt_2X + R \tag{7}$$

$$Pt_2X_2 + e^- \rightarrow Pt_2X + X^- \tag{8}$$

identification of this transient has been confirmed independently by its synthesis from the reaction of Pt_2X_2 with hydrated electrons (reaction 8).[32] Pt_2* reacts with RX in a reaction that is first order in Pt_2*, and Pt_2X decays by a pathway that is second order in Pt_2X. Spectroscopic data for these complexes are collected in Table II.

The first example of C–H bond cleavage by Pt_2 is the photochemical conversion of isopropyl alcohol to acetone and hydrogen (reaction 9).[47] The photoinduced

$$(CH_3)_2CHOH \xrightarrow[Pt_2]{h\nu} (CH_3)_2CO + H_2 \tag{9}$$

reaction is catalytic in Pt_2 and involves the $^3A_{2u}$ state as a reactive intermediate. The first step is hydrogen-atom abstraction of the methine hydrogen to give the radical pair Pt_2H and $(CH_3)_2COH$. Supporting evidence for the formation of the isopropyl radical as an intermediate comes from the finding that pinacol, $(CH_3)_2C(OH)C(OH)(CH_3)_2$, is a byproduct in the photoreaction. The transient Pt_2H has been directly observed in the abstraction of hydrogen atoms from cyclohexene, $(CH_3)_2CHOH$, $C_6H_5CH_2OH$, Bu_3SnH, Et_3SiH, and H_3PO_3 by Pt_2*.[43,45] When a conventional radical chain approach was used, it was originally suggested that Pt_2H reacted with $(CH_3)_2CHOH$, but kinetic studies suggest that the reaction primarily involves disproportionation of Pt_2H. Narrow-wavelength irradiation (λ 370 nm) of an acetonitrile solution containing Pt_2 and either

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Table V
Rate Constants for the Reactions of Pt_2* and Other Metal-Centered Radicals with Halocarbons

radical	halocarbon	solvent	k,ᵃ $M^{-1}\ s^{-1}$	ref
Pt_2*	CCl_4	aqueous MeOH	1.4×10^7	53
$Co(CO)_4$	CCl_4	benzene	$<2.4 \times 10^3$	54
$Mn(CO)_5$	CCl_4	benzene	2.8×10^4	54
$Mn(CO)_5$	CCl_4	hexane	1.4×10^6 (21 °C)	55
$Mn(CO)_5$	CCl_4	EtOH	6.1×10^5 (22 °C)	56
$Re(CO)_5$	CCl_4	EtOH	3.9×10^7 (22 °C)	56
$CpW(CO)_3$	CCl_4	benzene	1.5×10^4	57
$Rh(dmgH)_2(PPh_3)$	CCl_4	EtOH	2.5×10^5	58
Pt_2*	CH_3I	aqueous MeOH	6.7×10^5	43
$Co(CN)_5^{3-}$	CH_3I	aqueous MeOH	9.5×10^{-3}	58
n-Bu_3Sn	CH_3I	cyclohexane	2.5×10^9	60

ᵃ At 25 °C except where noted.

Bu_3SnH, $PhCH(OH)CH_2CH_3$, or $PhCH(OH)CH_3$ has been used to prepare Pt_2H_2 (reaction 10).[48] This complex thermally or photochemically reductively eliminates hydrogen.

$$Pt_2 + PhCH(OH)CH_3 \xrightarrow{h\nu} Pt_2H_2 + Ph(CH_3)CO \quad (10)$$

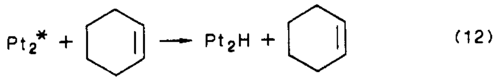
The dihydride Pt_2H_2 reacts with HCl to generate H_2 and rapidly with oxygen to give Pt_2. This reactivity with H^+ supports a $(Pt^{3+})_2(H^-)_2$ formalism, but the oxygen chemistry indicates that the complex can be viewed as $(Pt^{2+})_2(H^\bullet)_2$. The release of $H^\bullet$ from such a complex resembles the chemical reactivity observed for alkyl cobalt(III) complexes. In designing experiments to probe the chemical reactivity of these intermediate platinum hydride complexes, it has been found that Pt_2 is a photochemical catalyst for the conversion of ethyl alcohol to hydrogen and acetaldehyde[50] and for the transfer hydrogenation of cyclohexene and cyclopentene with isopropyl alcohol (reaction 11).[51]

$$C_nH_{2n-2} + (CH_3)_2CHOH \xrightarrow[n\,=\,5,\,6]{Pt_2^*} C_nH_{2n} + (CH_3)_2CO \quad (11)$$

The reaction may be related to the hydrogenation of alkenes by $Co(CN)_5^{3-}$, which involves a coordinatively saturated transition-metal hydride that can effect hydrogen-atom transfer to give a stable one-electron-reduced transition-metal ion.[52]

Triplet Pt_2* with its dσ* electron is electronically similar to the methyl radical or $Mn(CO)_5$. The finding that Pt_2* abstracts halogen atoms from halocarbons and hydrogen atoms from aromatic hydrocarbons supports this analogy.[43,45] Among metal-centered radicals studied (Table V),[43,53–60] Pt_2* is one of the most reactive toward CCl_4 and CH_3I.

Reactions with Alkenes and Alkynes. Both alkenes and alkynes react with triplet Pt_2*. For *cis*- and *trans*-stilbenes, energy transfer leads to photoisomerization.[43,61] For cycloalkenes containing allylic C–H bonds, such as cyclohexene and cyclopentene, reactions with Pt_2* proceed by hydrogen-atom abstraction, as evidenced by the observation of Pt_2H (reaction 12).[43]



(12)

Other alkenes and alkynes also quench the Pt_2* emission; for terminal olefins, the quenching is attributable to diradical formation and energy transfer.[43]

Exciplex Formation and Electrochemiluminescence. Photophysical data show conclusively that triplet Pt_2* has a Pt–Pt bond. It is probable, therefore, that ligation will occur in the axial positions of this triplet state. Aqueous solutions containing Pt_2 and thallium(I) salts show no intermetallic interaction in the ground state. The emission spectrum, however, shows a shift in λ_{max} from 514 nm in Pt_2* to 562 nm in the exciplex Pt_2Tl^{+*}. The triplet lifetime and quantum yield for the Pt_2Tl^{+*} exciplex are unchanged from those of Pt_2*.[62]

When a solution of Pt_2 is subjected to alternating-current electrolysis with variable frequency, the 514-nm luminescence of Pt_2* is observed[63] at one electrode. The chemiluminescence has been explained[63] by the generation of triplet Pt_2* from the electron-transfer reaction between electrochemically generated Pt_2^+ and Pt_2^-. It is interesting that electrochemiluminescence also is observed[64] in Pt_2 solutions containing Bu_4N^+ under reducing conditions alone, thereby indicating that Pt_2* may be generated by the reaction of $Bu^\bullet$ with Pt_2^-.

Photochemistry of Diplatinum(III) Complexes

The complexes Pt_2X_2 (X = Cl, Br, SCN) and $Pt_2py_2^{2+}$ exhibit a strong red luminescence at 77 K.[65] The vibronic fine structure of the emission bands shows that the excited state is very strongly distorted along the Pt–Pt coordinate, and the emissive excited state has dσ* character. These photophysical experiments correlate with the photochemistry of Pt_2X_2. The substitution of X^- in Pt_2X_2 by Y^- is markedly accelerated by light, and

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the conversion to Pt_2 and X_2 is photoinduced.[12] In methanol, Pt_2X_2 is efficiently photoreduced to Pt_2. As this chemistry develops, it will be useful to compare the excited state reactivities with $17e^-$ monomers and other trapped diradical species.

Methylenebis(phosphito) Complexes

An analogue complex $Pt_2(pcp)_4^{4-}$ having a methylenic bridge between coordinated phosphorus atoms has been prepared from $CH_2(PH(O)OH)_2$ ($pcpH_2$).[66] This complex shows many structural and spectroscopic features that are similar to Pt_2. The Pt–Pt distance in $Pt_2(pcp)_4^{4-}$ is 2.980 (1) Å, as compared to 2.925 (1) Å in Pt_2. Absorption bands are observed at 382 (ϵ 2.9×10^4) and 470 nm (ϵ 142 M^{-1} cm^{-1}), and the singlet and triplet emissions are observed at 420 and 510 nm, respectively. Triplet $Pt_2(pcp)_4^{4-*}$ also undergoes electron-transfer and atom-transfer reactions. The major difference between $Pt_2(pcp)_4^{4-}$ and Pt_2 is in the triplet lifetimes. In the solid state, the ambient-temperature lifetimes are closely similar, being 7.3 μs for $Pt_2(pcp)_4^{4-*}$ and 9.5 μs for Pt_2^*. In aqueous solution, the Pt_2^* lifetime is unchanged, but the $Pt_2(pcp)_4^{4-*}$ lifetime is reduced to 0.055 μs. The decay of $Pt_2(pcp)_4^{4-*}$ has a thermal activation barrier ($\sim$1100 cm^{-1}) that likely is associated with torsional motions in the binucleating ligand framework.[67]

Concluding Remarks

The chemistry of Pt_2^* shows both similarities to and differences from that[68] of $Ru(bpy)_3^{2+*}$. In $Ru(bpy)_3^{2+}$, MLCT absorption results in an electron being transferred from Ru(II) to one of the bpy ligands,[69] but in Pt_2 the excited state is formed by a transition between *metal-centered* molecular orbitals ($d\sigma^* \rightarrow p\sigma$). As a result, both electrons of triplet (diradical) Pt_2^* are localized on the platinum atoms. Both $Ru(bpy)_3^{2+*}$ and Pt_2^* are oxidants and reductants in reactions with organic or inorganic reagents. For Pt_2^*, however, in contrast to $Ru(bpy)_3^{2+*}$, reactions can occur by an *inner*-sphere pathway at the vacant axial-ligand Pt site. It is becoming clear that Pt_2^* also can react as a free radical, because it possesses an unpaired electron in a frontier orbital ($d\sigma^*$) that is localized at an axial coordination site. This free-radical reactivity of Pt_2^* is shown in atom-transfer reactions that occur with no prior electron-transfer step.

The free-radical reactivity of Pt_2^* strongly resembles that found for ketone $n\pi^*$ triplets and metal carbonyl and alkoxy radicals.[49] However, unlike most organic radicals, $^3Pt_2^*$, because of its μ-pyrophosphito ligands, presents a fairly bulky, hydrophilic axial-site interaction surface to an incoming substrate. Accordingly, $^3Pt_2^*$ has the potential to be more selective than alkoxy radicals in atom abstractions. Work to date suggests that allylic C–H bonds of substituted olefins and benzylic C–H bonds of aromatic hydrocarbons are homolytically cleaved quite rapidly by $^3Pt_2^*$. Additional research could conceivably expand the range of this reaction to the point where it will be possible to achieve photochemical activation of secondary/primary C–H bonds in preference to tertiary C–H in saturated hydrocarbons.

The work that has been done on platinum pop has established some guidelines for the occurrence of excited-state atom-transfer reactions of metal complexes. It seems highly likely that this type of reaction will soon be an important part of the armamentarium of inorganic photochemistry and photocatalysis.

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Registry No. $K_4[Pt_2(\mu\text{-}P_2O_5H_2)_4]$, 80011-26-3; K_2PtCl_4, 10025-99-7; Pt, 7440-06-4; H_2, 1333-74-0.

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