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An unusual six-co-ordinate platinum(II) complex containing a neutral I$_2$ ligand

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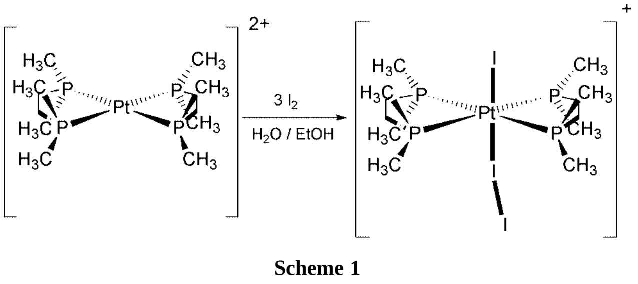
The present paper deals with a rare platinum(II) complex containing the κ-I$_2$ ligand, which is an unusual example of a six-co-ordinated octahedral platinum(II) complex.

Platinum(II) strongly demands a square-planar co-ordination geometry and very few six-co-ordinate complexes have so far been characterized.[1] *Trans*-[PtI$_2$(diars)$_2$] (diars = *o*-phenylenebis(dimethylarsine)) has been the only example of a six-co-ordinate platinum(II) complex determined by X-ray study.[1b] However, Pt–I bonds in this complex seem to be weak because of long Pt–I distances of 3.50 Å. Here, we present a novel octahedral platinum(II) complex, [PtI(dmpe)$_2$(κ-I$_2$)]I$_3$ (dmpe = 1,2-bis(dimethylphosphino)ethane) in which the neutral molecular iodine co-ordinates to the platinum(II) ion. This is a quite rare example of the platinum(II) complex having clearly short Pt–I bond distances.

Treatment of [Pt(dmpe)$_2$](SCN)$_2$ **1**[2] with a 3 molar amount of iodine gave black needle crystals formulated as [PtI(dmpe)$_2$(κ-I$_2$)]I$_3$ **2** (Scheme 1, yield 21%).†

The molecular structure of complex **2** is displayed in Fig. 1, with partial labeling.‡ Complex **2** is a mononuclear complex with Pt1, I1, I2, and I3 atoms located on a crystallographic mirror plane that is coincident with mirror symmetry of the complex. The I4, I5 and I6 atoms of I$_3^-$ anion are located on a crystallographic mirror. The co-ordination geometry around the platinum atom is octahedral with 4P and 2I donor atoms, with two iodine atoms having *trans* geometry. The bond distances between platinum and iodine atoms are 2.811(1) and 2.817(1) Å for Pt1–I1 and Pt1–I2, respectively. These values are considerably shorter than those in the complex *trans*-[PtI$_2$(diars)$_2$] **3** (here the bond length of Pt–I is 3.50 Å).[1b] Compared to **3**, complex **2** can be undoubtedly considered to be a six-co-ordinate octahedral platinum(II) complex. Furthermore, it is worthy of note that the neutral molecular iodine co-ordinates to the platinum(II) ion by end-on type (Pt1–I2–I3 = 171.58(3)°), and the I2–I3 bond distance of 3.061(1) Å is much longer than that of 2.715(6) Å in free diiodine molecules.[3] This means that the electrons on the central platinum(II) flow into the κ-I$_2$ ligand, which is attributable to a d$_{z^2}$ (Pt) to σ^* (I$_2$) donation.[4] Van Koten and coworkers have reported five-co-ordinate platinum(II) complexes containing the κ-I$_2$ ligand, [PtI{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}(κ-I$_2$)] **4a** and [Pt(κ-I$_3$)(κ-I$_2$){C$_6$H$_3$(CH$_2$N(*t*-Bu)Me)$_2$-2,6}] **4b**.[5] The Pt–I$_2$ bond distances of 2.895(1) and 2.906(2) Å in **4a** and **4b**, respectively,[5d] are longer than 2.817(1) Å in **2**, showing that a stronger platinum–molecular iodine bond is realised in **2**. The I–I bond distances in these complexes show a marked difference: the I2–I3 distance of 3.061(1) Å in **2** is much longer than that of 2.822(1) and 2.793(1) Å in **4a** and **4b**, respectively. This elongation is attributable to the existence of the ligand on a *trans* position of the κ-I$_2$ ligand. The bond distances between platinum and co-ordinated phosphorus in **2** are 2.369(2) and 2.374(2) Å for Pt1–P1 and Pt1–P2, respectively. These values are longer than that of starting square-planar complex **1** with a Pt–P of 2.317(1) Å.[6]

The formal oxidation state of the platinum ion in **2** is expected to be +2. To confirm this, X-ray photoelectron spectroscopy (XPS) measurements were performed.§ Binding energies of the Pt 4f region given in Table 1 were determined by a conventional deconvolution procedure. The XPS spectrum of **2** shows a doublet, whose binding energies are coincident with the values of Pt(II) binding energies.[5c,7] From XPS measurements, the platinum ion in complex **2** was found to have the +2 oxidation state.



Scheme 1

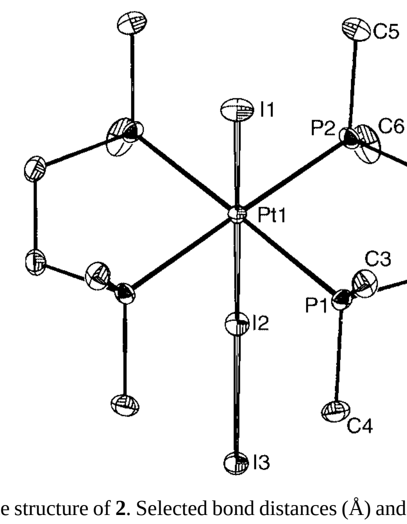


Fig. 1 The structure of **2**. Selected bond distances (Å) and angles (°): Pt1–I1 2.811(1), Pt1–I2 2.817(1), Pt1–P1 2.369(2), Pt1–P2 2.374(2), I2–I3 3.061(1), P1–C1 1.82(1), P1–C3 1.80(1), P1–C4 1.80(1), P2–C2 1.82(1), P2–C5 1.82(1), P2–C6 1.80(1), C1–C2 1.52(1); I1–Pt1–I2 177.75(3), I1–Pt1–P1 89.73(5), I1–Pt1–P2 92.45(5), I2–Pt1–P1 91.78(5), I2–Pt1–P2 86.04(5), P1–Pt1–P2 84.46(6), Pt1–I2–I3 171.58(3).

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Table 1 Binding energies (eV) for the 4f region of platinum

Compound	$4f_{5/2}$	$4f_{7/2}$
1	76.0	72.7
2	76.0	72.6

The ^{31}P MAS NMR spectral data for **1** and **2** in the solid state and in CD_3CN or D_2O solution are given in Table 2. In the ^{31}P MAS NMR spectrum of **2**, a signal appeared at δ 11.9 ppm with satellites due to the coupling with ^{195}Pt (1758 Hz). The smaller coupling constant $^1J_{Pt-P}$ in **2** compared with 2173 Hz in **1**, is explained by the difference in the co-ordination number.[8] $^1J_{Pt-P}$ of 2173 Hz in **1** is a normal value compared with analogous platinum(II) square-planar co-ordinate complexes.[9] On the other hand, in CD_3CN solution, the observed $^1J_{Pt-P}$ of 2172 Hz in **2** was very close to 2162 Hz observed in D_2O solution for **1**. This result indicates that complex **2** has a square-planar geometry caused by the dissociation of iodine in CD_3CN solution.

Table 2 ^{31}P NMR spectroscopic data

Compound	$\delta_{^{31}P}$/ppm	$^1J(^{195}Pt-^{31}P)$/Hz
1	32.75^a	21 273^a
	33.06^b	2162^b
2	11.85^a	1758^a
	28.95^c	2172^c

^{a} MAS NMR spectrum in the solid state with a spinning rate of 4–5 kHz. ^{b} In D_2O. ^{c} In CD_3CN solution.

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Notes and references

† In this reaction, two electrons are gained, but the fully balanced equation was not understood. The authors consider that the reaction is related to the redox systems of Pt(II) with Pt(IV) and of $2I^-$ with I_2.

‡ *Crystal data* for **2**: $C_{12}H_{32}I_6P_4Pt$, M = 1256.8, orthorhombic, *Pnma*, a = 8.6718(4), b = 10.7317(5), c = 30.9849(3) Å, U = 2883.6(3) Å^3, D_c = 2.89 g cm^{-3}, Z = 4, $F(000)$ = 2240, μ(Mo-Kα) = 11.51 mm^{-1}, graphite monochromator, room temperature, 4933 reflections measured, 2734 observed [$I > 3\sigma(I)$], 115 parameters. Empirical absorption corrections (ψ-scan) were applied. Final R factor = 0.033, R_w = 0.040. Hydrogen atoms were included in fixed positions with isotropic thermal parameters, while all other atoms were refined by anisotropic thermal parameters.

CCDC reference number 155325. See http://www.rsc.org/suppdata/cc/b1/b103648n/ for crystallographic data in CIF or other electronic format.

§ XPS spectra were carried out on an Ulvac Phi 5600ci with monochromated Al-Kα X-rays (1487 eV). Binding energies were measured relative to the Au $4f_{7/2}$ peak of the gold fine powder mixed with the sample.

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