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Coordination Chemistry of Higher Oxidation States. Part 31*. Platinum(IV) Iodides and Platinum(II) Polyiodides with Phosphorus and Arsenic Ligands

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Abstract

Oxidation of $[Pt(L\text{-}L)_2]I_2$ (L-L = $Me_2PCH_2CH_2PMe_2$ or $o\text{-}C_6H_4(AsMe_2)_2$) with concentrated nitric acid in the presence of HBF_4 produces $[Pt(L\text{-}L)_2I_2]Y_2$ (Y = NO_3 or BF_4). These are shown to contain Pt(IV) by $^{195}Pt\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy, and by an (incomplete) X-ray study of the diarsine, which revealed a *trans* octahedral cation with Pt–As = 2.446(3)–2.454(3) and Pt–I = 2.669(2), 2.672(2) Å. In contrast reaction of diiodine with $[Pt(L\text{-}L)_2]I_2$ in MeCN affords $[Pt(L\text{-}L)_2I_6]$ which are shown to be Pt(II) polyiodides. Diiodine converts a variety of phosphine, arsine, and thioether complexes of platinum(II) iodide to $[Pt(L'\text{-}L')I_4]$, also believed to be Pt(II) materials.

Introduction

The nature of the halogen oxidation products of planar d^8 metal complexes is currently of great interest in connection with the synthesis and properties of mixed-valence anisotropic semi-conductors. Platinum iodocomplexes of nitrogen donor ligands may be classified as follows: (a) platinum(II) iodides e.g. $[Pt(en)I_2]$ [2] (en = ethylenediamine); (b) platinum(II) polyiodides e.g. $[Pt(dimethylimidazole)_4](I_3)_2$ [3]; (c) platinum(IV) iodides e.g. $[Pt(en)_2I_2]I_2$ [4]; (d) platinum(IV) polyiodides e.g. $[Pt(1,10\text{-}phenanthroline)I_6]$ [5]; (e) mixed-valence class II materials e.g. $[Pt(pn)_2(\mu\text{-}I)_2Pt(pn)_2]_nI_{4n}$ [6] (pn = 1,3-diaminopropane). Data on platinum iodocomplexes with phosphorus or arsenic donor ligands is much less extensive [7], and only for type (a) are many examples known. No structurally authenticated examples of the other types have been reported. Previous studies of diphosphine or diarsine palladium(II) or nickel(II) iodocomplexes have shown [8,9]* that attempted iodine or HNO_3 oxidation leads only to polyiodides of the divalent metal. Here we report the investigation of some similar reactions of platinum(II) complexes.

Results

Iodine 'Oxidations'

Treatment of *trans*-$[Pt(L\text{-}L)_2]X_2$ (L-L = $Me_2PCH_2CH_2PMe_2$ (dmpe) or $o\text{-}C_6H_4(AsMe_2)_2$ (das), X = Cl or Br) with the appropriate halogen affords the corresponding Pt(IV) complexes *trans*-$[Pt(L\text{-}L)_2X_2]Y_2$ (Y = X or ClO_4) [11, 12]. In contrast we find that refluxing $[Pt(L\text{-}L)_2I_2]$ with excess I_2 (mol. ratio I_2:Pt 4:1) in MeCN or dichloromethane produces greenish-black powders of composition $Pt(L\text{-}L)_2I_6$. The $Pt(das)_2I_6$ dissolves in MeCN to give a reddish-black solution which has intense UV–Vis absorptions at *c*. 27 800 and 34 500 cm^{-1} (Table 1) characteristic of the I_3^- ion [13], and in a 10^{-3} mol dm^{-3} solution is a 1:2 electrolyte, $\Lambda_m = 259$ ohm^{-1} cm^2 mol^{-1} [14]. This suggests that like the palladium analogue [8] the platinum complex should be formulated as the triiodide(1–) salt of the divalent metal. The ^{195}Pt NMR resonance at $\delta = -5560$ which is only *c*. 30 ppm different from that of $[Pt(das)_2]I_2$ also suggests platinum(II) rather than platinum(IV) [15]. $Pt(dmpe)_2I_6$ is poorly soluble in most organic solvents, dissolving only slightly even in dimethylsulphoxide. This poor solubility prevented a convincing platinum NMR resonance being observed, but a ^{31}P resonance $\delta = 31.9$ ppm with platinum satellites $^1J = 2184$ Hz, is clear evidence for platinum(II) rather than platinum(IV), compare $[Pt(dmpe)_2]X_2$ $^1J = 2227$(Cl) or 2280(Br) Hz and $[Pt(dmpe)_2X_2]X_2$ $^1J = 1383$(Cl) or 1382(Br) Hz [15]. Other data (Table 1) also supports the $[Pt(dmpe)_2](I_3)_2$ formulation.

Some years ago we [12] described the products of the reactions of $[Pt(L\text{-}L)I_2]$ (L-L = $Ph_2PCH_2CH_2PPh_2$,

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*For part 30 see ref. 1.

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*The first Ni(III) iodocomplex *trans*-$[Ni(PMe_3)_2I_3]$ has been made very recently by the serendipitous reaction of I_2 with $[\{Ni(\mu\text{-}^tBu_2As)(PMe_3)_2\}_2]$ [10].

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TABLE 1. Selected spectroscopic data

Compound	δ(Pt) (ppm)[a]	δ(P) (ppm)[b]	^1J (Hz)	Λ_M (ohm^{-1} cm^2 mol^{-1})[c]	E_{max} (10^3 cm^{-1}) (ε mol (dm^3 mol^{-1} cm^{-1}))
$[Pt(das)_2]I_2$	−5593[d]			135[d]	
$[Pt(das)_2](I_3)_2$	−5560[d]			259[d]	27.8(~40000), 34.5(~70000)[d]
$[Pt(das)_2I_2](BF_4)_2$	−5270[d]			270[d]	23.2(2260), 33.9(6200)[d]
$[Pt(dmpe)_2]I_2$	−5246(q)[d]	26.7	2298	39[e]	23.1(sh), 25.8(2620)[e]
$[Pt(dmpe)_2](I_3)_2$		31.9	2184	54[e]	27.8(–)[e]
$[Pt(dmpe)_2I_2](NO_3)_2$	−4883(q)[d]	22.9[d]	1410	55[e]	22.2(1260), 33.0(4200)[e]
$[Pt(Ph_2PCH_2CH_2PPh_2)I_4]$	−5371(t)	47.4	3400		
$[Pt(Ph_2PCHCHPPh_2)I_4]$	−5430(t)	55.4	3410		
$[Pt(Ph_2AsCH_2CH_2AsPh_2)I_4]$	−5632				
$[Pt(MeSCH_2CH_2SMe)I_4]$	−4887, −4907				

[a] In DMSO relative to Na_2PtCl_6 in H_2O. [b] In DMSO relative to H_3PO_4. [c] 10^{-3} mol dm^{-3} solutions. 1:2 electrolytes have Λ_M ~60 ohm^{-1} cm^2 mol^{-1} in DMSO, and 220–300 ohm^{-1} cm^2 mol^{-1} in MeCN. From ref. 14. [d] MeCN solution. [e] DMSO solution.

cis-$Ph_2PCHCHPPh_2$, $Ph_2AsCH_2CH_2AsPh_2$, or $MeSCH_2CH_2SMe$) with excess diiodine, as black–brown powders which lost diiodine on washing with chlorinated solvents or on heating. Subsequently we showed by an X-ray study that [Pd(*cis*-$Ph_2PCHCHPPh_2)I_4$] was a palladium(II) complex with bridging I_4^{2-} ligands. All attempts to produce good crystals of the platinum complexes have failed. The [Pt(L-L)I_4] complexes are poorly soluble in chlorocarbons, but dissolve easily in dimethylsulphoxide, in which they have ^{195}Pt NMR resonances identical with those of the corresponding platinum(II) complexes [Pt(L-L)I_2] [15] (Table 1). Dimethylsulphoxide is a strong donor and it is always possible that decomposition may occur on dissolution in this solvent. However although the solubilities are too low in CH_2Cl_2 for ^{195}Pt NMR studies, ^{31}P NMR spectra of the diphosphine samples were obtained. The δ(P) are identical to those of [Pt(L-L)I_2] and $^1J(^{195}Pt-^{31}P)$ are *c.* 3400 Hz consistent with Pt(II) complexes, compare $^1J(^{195}Pt-^{31}P)$ in [Pt(L-L)Cl_4] *c.* 2000–2200 Hz [15]. In the absence of single crystal X-ray data it is not possible to establish the nature of these materials in the solid state beyond doubt, but it seems probable that like the palladium complexes of similar formulae, they are polyiodides rather than complexes of the higher oxidation state.

Nitric Acid Oxidation

Concentrated nitric acid at *c.* −5 °C rapidly converts $[Pt(dmpe)_2]I_2$ into a brown–black powder, identified by analysis and IR spectroscopy as $[Pt(dmpe)_2I_2](NO_3)_2$. A similar reaction involving $[Pt(das)_2]I_2$, followed by addition of HBF_4 produced orange–brown $[Pt(das)_2I_2](BF_4)_2$. The latter can be obtained as dark red crystals by cooling of a saturated solution in aqueous HBF_4 in a refrigerator. $[Pt(das)_2X_2]Y_2$ complexes (X = Cl or Br, Y = ClO_4 or NO_3) are known [11]. $[Pt(dmpe)_2I_2](NO_3)_2$ is poorly soluble in most solvents, but in 10^{-3} mol dm^{-3} solution in DMSO it is a 2:1 electrolyte (Table 1) and has a $\delta(^{195}Pt)$ NMR resonance at −4883 ppm (quintet) due to coupling to four equivalent phosphorus atoms, with $^1J(^{195}Pt-^{31}P)$ = 1410 Hz, showing it is the *trans* isomer. The presence of Pt(IV) is shown both by the oxidation shift in the platinum NMR spectrum of +363 ppm, and by the much smaller ^1J coupling constant than the starting material. The oxidation shift in the $[Pt(dmpe)_2Cl_2]^{0\backslash 2+}$ (+1151 ppm) and $[Pt(dmpe)_2Br_2]^{0\backslash 2+}$ (+331 ppm) systems reveal similar trends [15]. There is also a low frequency shift in δ(P) along the series $[Pt(dmpe)_2X_2]^{2+}$ 35.1 (Cl), 26.0 (Br) [15], 22.9 (I) ppm. $[Pt(das)_2I_2](BF_4)_2$ has $\delta(^{195}Pt)$ = −5195 ppm in *N,N*-dimethylformamide solution, and −5270 ppm in DMSO; in the former case the oxidation shift is 325 ppm, and in the latter it is 323 ppm. The solution of $[Pt(das)_2]I_2$ in HNO_3 (10 mol dm^{-3}) has a single line at

$\delta(^{195}Pt) = -5406$ ppm in the NMR spectrum, which is probably also due to the Pt(IV) cation, the 130 ppm difference between nitric acid and DMSO solutions being a solvent shift. Solvent shifts are often substantial for heavy nuclei. Addition of iodide ions to the DMSO solution of $[Pt(das)_2I_2]^{2+}$ results in an immediate black precipitate, and the reddish supernatant liquid has a ^{195}Pt NMR shift of –5562 ppm showing reduction to Pt(II) has occurred.

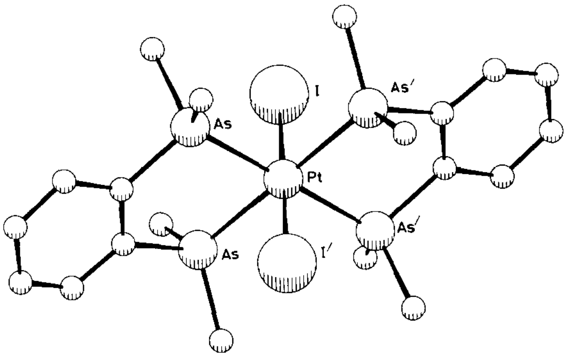

Fig. 1. View showing one of the independent centrosymmetric cations.

Structure of $[Pt(das)_2I_2](BF_4)_2$

Dark red crystals were obtained by cooling a concentrated solution of $[Pt(das)_2I_2]$ in conc. HNO_3/40% HBF_4 (*c*. 1:2 vol./vol.) at 0 °C for several days. The analytical composition of the crystals indicated a dihydrate. The crystals are triclinic ($P\bar{1}, Z = 2$)* and show monoclinic pseudosymmetry. The triclinic data set was collected (4295 independent reflections [$I > 3\sigma I$] and solved by conventional means to show two independent centrosymmetric cations, the oxygens of two water molecules and disordered BF_4 groups. The structure failed to refine below $R = 0.09, R_w = 0.101$, possibly due to the pseudosymmetry and disorder, the discrepancy between the measured and calculated density suggests a disorder or twinning problem. The cation (Fig. 1) consists of a *trans* six-coordinate arrangement of two iodines and two chelated diarsines about the platinum, with average *d*(Pt–As) = 2.446(3)–2.454(3) and *d*(Pt–I) = 2.669(2), 2.672(2) Å. The six-coordination provides strong support for the Pt(IV) formulation proposed above on the basis of spectroscopic data. X-ray data on $[Pt(das)_2X_2]^{2+}$ (X = Cl, Br) are not available, although the chloride is isomorphous with $[Pd(das)_2Cl_2](ClO_4)_2$ [16]. In the latter the Pd–As bond lengths are 2.452(1), 2.455(1) Å which are in good agreement with the *d*(Pt–As) in the present cation. The increase in *d*(Pt–As) from the Pt(II) complex $[Pt(das)_2]I_2$ [17] where it is 2.38 Å, parallels that between $[Pd(das)_2]I_2$ and $[Pd(das)_2Cl_2]^{2+}$ [16] and is mainly attributable to the increase in coordination number from four to six. The *d*(Pt–I) of 2.67 Å may be compared with the values of 2.667(1) in *trans*-$[Pt(acac)_2I_2]$ [18] (acac = acetylacetonate(–)) and 2.68(1) in *trans*-$[Pt(en)_2I_2]I_2\cdot 2H_2O$ [19]. The X-ray data thus provides strong support for the Pt(IV) formulation, but in view of the refinement problems full description of the structure is omitted.

Experimental

Physical measurements were made as described in previous parts of the series. NMR spectra are reported using the high frequency positive convention, with chemical shifts referenced to 85% H_3PO_4 (^{31}P) and 1 mol dm^{-3} Na_2PtCl_6 in water (^{195}Pt).

The preparations of the $[Pt(L\text{-}L)I_4]$ complexes have been described elsewhere [12], and $[Pt(das)_2I_2]$ was made as described by Harris *et al.* [11]. $[Pt(dmpe)_2I_2]$ was made by combination of $[PtCl_4]^{2-}$, XS KI, and dmpe in ethanol. *Anal.* Found: C, 19.3; H, 4.3. Calc. for $C_{12}H_{32}I_2P_4Pt$: C, 19.2; H, 4.3%.

$[Pt(L\text{-}L)_2(I_3)_2]$ (L-L = dmpe, das)

Finely powdered $[Pt(L\text{-}L)_2I_2]$ (1 mmol) was suspended in MeCN (20 cm^3), diiodine (4 mmol) added, and the mixture refluxed for 30 min. After cooling the black solid was filtered off, washed with dichloromethane (5 × 10 cm^3), and vacuum dried. Yields >90%. *Anal.* L-L = das, Found: C, 15.5; H, 2.0. Calc. for $C_{20}H_{32}As_4I_6Pt$: C, 15.7; H, 2.1%. L-L = dmpe, Found: C, 11.2; H, 2.6. Calc. for $C_{12}H_{32}I_6P_4Pt$: C, 11.5; H, 2.6%.

$[Pt(dmpe)_2I_2](NO_3)_2$

Concentrated nitric acid (10 cm^3) was cooled to –10 °C and finely powdered $[Pt(dmpe)_2I_2]$ sifted in with vigorous stirring. The yellow solid rapidly darkened and after 10 min, the mixture was allowed to warm to 0 °C, when HBF_4 (20 cm^3, 40% aq.) was added. The dark brown solid was filtered off, rinsed with ice-cold water (5 cm^3), and vacuum dried. Analysis and IR spectroscopy showed it to be the nitrate salt rather than the expected fluoroborate. *Anal.* Found: C, 16.4; H, 3.5; N, 2.9. Calc. for $C_{12}H_{32}I_2N_2O_6P_4Pt$: C, 16.5; H, 3.7; N, 3.1%.

$[Pt(das)_2I_2](BF_4)_2$

$[Pt(das)_2I_2]$ (1 mmol) was added to vigorously stirred concentrated nitric acid (15 cm^3) at 0 °C. After 30 min, HBF_4 (30 cm^3, 40% aq.) was added, and the product stored at 0 °C overnight. The deep orange–brown microcrystalline solid was filtered off and dried in vacuum. *Anal.* Found: C, 19.8; H, 2.8. Calc. for $C_{20}H_{32}As_4B_2F_8I_2Pt$: C, 20.1; H, 2.7%.

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*$a = 11.649(2)$, $b = 11.669(7)$, $c = 15.854(6)$ Å, $\alpha = 102.36(4)$, $\beta = 105.22(3)$, $\gamma = 109.50(4)°$. $V = 1849$ Å^3, $\rho_{calc} = 2.21$, $\rho_{meas} = 2.40$ g cm^{-3}.

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References

1 W. Levason, J. S. Ogden and M. D. Spicer, *Inorg. Chim.*, in press.
2 G. W. Watt and R. E. McCarley, *J. Am. Chem. Soc., 79* (1957) 3315.
3 H.-J. Korte, B. Krebs, C. G. Van Kralingen, A. T. M. Marcelis and J. Reedijk, *Inorg. Chim. Acta, 52* (1981) 61.
4 B. Freckmann and K. F. Tebbe, *Acta Crystallogr., Sect. B, 37* (1981) 1520.
5 K. D. Buse, H. J. Keller and H. Pritzkow, *Inorg. Chem., 16* (1977) 1072.
6 H. Endres, H. J. Keller, R. Martin, U. Traeger and M. Novotney, *Acta Crystallogr., Sect. B, 36* (1980) 35.
7 C. A. McAuliffe and W. Levason, *Phosphine, Arsine, and Stibine Complexes of the Transition Elements*, Elsevier, Amsterdam, 1978.
8 L. R. Gray, D. J. Gulliver, W. Levason and M. Webster, *Inorg. Chem., 22* (1983) 2362.
9 L. R. Gray, S. J. Higgins, W. Levason and M. Webster, *J. Chem. Soc., Dalton Trans.*, (1984) 1433.
10 D. J. Chandler, R. A. Jones and B. R. Whittlesey, *J. Coord. Chem., 16* (1987) 19.
11 C. M. Harris, R. S. Nyholm and D. J. Phillips, *J. Chem. Soc.*, (1960) 4379.
12 D. J. Gulliver, W. Levason and K. G. Smith, *J. Chem. Soc., Dalton Trans.*, (1981) 2153.
13 W. Gabes and D. J. Stufkens, *Spectrochim. Acta, Part A, 30* (1974) 1835.
14 W. J. Geary, *Coord. Chem. Rev., 7* (1971) 81.
15 E. G. Hope, W. Levason and N. A. Powell, *Inorg. Chim. Acta, 115* (1986) 187.
16 L. R. Gray, D. J. Gulliver, W. Levason and M. Webster, *J. Chem. Soc., Dalton Trans.*, (1983) 133.
17 N. C. Stephenson, *J. Inorg. Nucl. Chem., 24* (1962) 791.
18 P. M. Cook. L. F. Dahl, D. Hopgood and R. A. Jenkins, *J. Chem. Soc., Dalton Trans.*, (1973) 294.
19 B. Freckmann and K. Tebbe, *Acta Crystallogr., Sect. B, 35* (1979) 1887.