Photo-oxidation of Alcohols by Hexachlorometalate(IV) Ions (M = Pt, Pd, or Ir): Spin Trapping and Matrix Isolation Electron Spin Resonance Studies

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Spin-trapping studies reveal that whereas the mild ($\lambda > 380$ nm) photolysis of ions $[MCl_6]^{2-}$ (M = Pd, Pt, or Ir) in alcohol (RCH_2OH)–water mixtures leads invariably to $R\dot{C}HOH$, in pure alcoholic media many of the oxidations lead to $RCH_2\dot{O}$. Prolonged, wide-band photolysis leads to the production of H atoms. At 77 K, wide-band photolysis leads to the production of platinum(III) and palladium(III) centres, identified by their $g_\perp$ features, in addition to the expected *C*-centred organic radicals.

The recent surge of interest in the long-established problem[1] of the photoactivation of hexachloroplatinate(IV) ion reflects a number of viewpoints. The activation of alkanes by $[PtCl_6]^{2-}$ ion under photoirradiation[2] represented a singular advance, and the same group[3] characterised the photoreduction ($\lambda > 320$ nm) of $[PtCl_6]^{2-}$ by CO to yield $[PtCl_3(CO)]^-$ and the photoreaction with acetone[4] to yield $[PtCl_5(CH_2COCH_3)]^{2-}$. The 488-nm photoreduction of $[PtCl_6]^{2-}$ by alcohols[5] leads to the production of colloidal platinum in a mild and controlled way with obvious potential in the formulation of catalysts. Characterisation of intermediates in these photoprocesses has been by microsecond flash photolysis,[6] enabling determination of the optical spectrum of a platinum(III) species, while picosecond flash photolysis[7] gives rise to a transient ($\tau \approx 210 \pm 10$ ps) attributed to either $[PtCl_5]^{2-}$ or $[PtCl_6{}^{2-}]^*$. Cryogenic e.s.r. studies of the photolysis of $[PtCl_6]^{2-}$ ions in organic glasses reveal the presence of platinum(III) species[4,8] and of solvent-derived organic radicals,[8] and photoreaction of $[PtCl_6]^{2-}$ with $SnMe_4$ in CH_3CO_2H at 77 K also leads to a platinum(III) signal at $g = 2.4$.[9]

In the present study we report (*i*) the spin trapping[10] at room temperature of both *O*- and *C*-centred organic radicals in the photolysis of $[PtCl_6]^{2-}$ and also $[PdCl_6]^{2-}$ and $[IrCl_6]^{2-}$ ions in a range of alcohols, and (*ii*) cryogenic e.s.r. studies at 77 K on these systems enabling observation of the metal(III) species (M = Pt or Pd) in addition to the organic radical. A previous spin-trapping study of photoirradiated $[PtCl_6]^{2-}$ in CH_3CN indicated trapping of $Cl^\bullet$,[11] and the notion of a homolytic cleavage of the Pt^{IV}–Cl bond on excitation, originated by Rich and Taube,[12] has been viewed as a key example of photo-driven production of a catalyst, namely Pt^{III}, in a recent review.[13]

Experimental

E.s.r. measurements were carried out with a Bruker model ER 200tt instrument using 1,1-diphenyl-2-picrylhydrazyl (dpph) as a calibrant. The following materials obtained from Aldrich were used as spin traps: benzylidene(t-butyl)amine *N*-oxide (bbao); sodium 2-sulphonatobenzylidene(t-butyl)amine *N*-oxide (**1**). Solutions of the inorganic salt (1.0×10^{-2}—1.3×10^{-2} mol dm^{-3}) and the spin trap (1.0×10^{-1} mol dm^{-3}) were purged with white spot nitrogen for 10—15 min prior to photolysis at room temperature. 18-Crown-6 (1,4,7,10,13,16-hexaoxacyclo-octadecane) was added to solutions in pure alcohols to solubilise the salt, although this was unnecessary for solutions in alcohol–water mixtures. The lamps used were high-pressure point sources (100 and 200 W), the output of which was filtered through broad-band interference filters as follows: for solutions of $[PtCl_6]^{2-}$ and $[PdCl_6]^{2-}$, 400 ± 10 nm; for $[IrCl_6]^{2-}$, 380—440 nm. (No signals were obtained from photolysis of the spin traps under these conditions in the absence of metal salt.) For cryogenic work, a 1000-W Xe/Hg point source was used, the output of which was filtered through a UG-5 broad-band interference filter immersed in circulating water.

E.s.r. spectra were simulated with a program run on a BBC Micro and supplied by Professor B. C. Gilbert of York University.

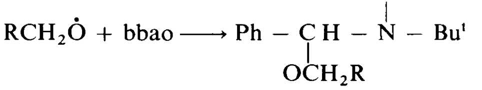
Results and Discussion

Spin-trapping Studies.—The results are illustrated in Figures 1 and 2 and summarised in Tables 1 and 2. There is an apparent dichotomy in the main photochemical pathway as evinced by the character of the trapped radical; thus in alcohol (RCH_2OH)–water mixtures (Table 1) the radical $R\dot{C}HOH$ is formed exclusively whereas in pure alcohols (Table 2) the production of $RCH_2\dot{O}$ occurs either in parallel with or even to the exclusion of $R\dot{C}HOH$.

The production of the alkoxyl radical adduct (**2**) is attributable to direct attack of $([MCl_6]^{2-})^*$ upon the OH group [equations (1)—(3)]; however, an alternative pathway involving

$$[MCl_6]^{2-} \xrightarrow{h\nu} ([MCl_6]^{2-})^* \qquad (1)$$

$$([MCl_6]^{2-})^* + RCH_2OH \longrightarrow [MCl_6]^{3-} + RCH_2\dot{O} + H^+ \qquad (2)$$



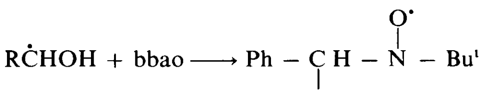
$$RCH_2\dot{O} + bbao \longrightarrow Ph-\underset{OCH_2R}{\underset{|}{C}}H-\overset{O^\bullet}{\overset{|}{N}}-Bu^t$$

(2) (3)

$Cl^\bullet$ as a precursor of $RCH_2\dot{O}$ is a possibility (see below) (**3**).

The adduct of $R\dot{C}HOH$ (**3**) can originate in one of three ways. (*a*) Direct attack of $([MCl_6]^{2-})^*$ upon the C–H bond in

$$([MCl_6]^{2-})^* + RCH_2OH \longrightarrow [MCl_6]^{3-} + R\dot{C}HOH + H^+ \qquad (4)$$



$$R\dot{C}HOH + bbao \longrightarrow Ph-\underset{R\dot{C}HOH}{\underset{|}{C}}H-\overset{O^\bullet}{\overset{|}{N}}-Bu^t$$

(3) (5)

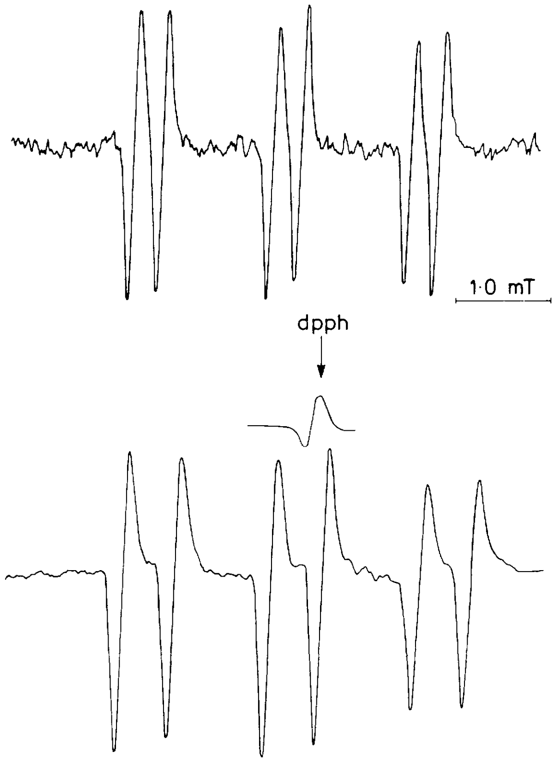


Figure 1. E.s.r. spectra of the spin adduct with $CH_3\dot{O}$ (upper) obtained on photoirradiation of $K_2[PdCl_6]$ (1.0×10^{-2} mol dm^{-3}) in pure methanol in the presence of bbao (0.1 mol dm^{-3}) (for coupling constants see Table 2), and of the spin adduct with $\dot{C}H_2OH$ (lower) obtained on photolysis of $K_2[PtCl_6]$ (1.3×10^{-2} mol dm^{-3}) in methanol–water (1:1, v/v) in the presence of (**1**) (0.1 mol dm^{-3}) (for coupling constants see Table 1)

Table 1. Hyperfine splitting constants for spin adducts of (**1**) in the photolysis (λ > 380 nm) of $[MCl_6]^{2-}$ ions in aqueous alkanol mixtures (1:1)

Metal salt	Alkanol	Radical trapped	$a(^{14}N)$/ mT	$a_\beta(^1H)$/ mT
$[PtCl_6]^{2-}$	Methanol	$\dot{C}H_2OH$	1.526	0.513
$[IrCl_6]^{2-}$	Methanol	$\dot{C}H_2OH$	1.526 (1.516)*	0.500 (0.502)*
$[PtCl_6]^{2-}$	Methanol (deuteriated)	$\dot{C}D_2OH$	1.513 (1.518)*	0.506 (0.509)*
$[PtCl_6]^{2-}$	Ethanol	$CH_3\dot{C}HOH$	1.532	0.370
$[IrCl_6]^{2-}$	Ethanol	$CH_3\dot{C}HOH$	1.552 (1.520)*	0.368 (0.368)*
$[PtCl_6]^{2-}$	1-Propanol	$CH_3CH_2\dot{C}HOH$	1.506	0.360
$[IrCl_6]^{2-}$	1-Propanol	$CH_3CH_2\dot{C}HOH$	1.526	0.401
$[PtCl_6]^{2-}$	2-Propanol	$(CH_3)_2\dot{C}OH$	1.579	0.351
$[IrCl_6]^{2-}$	2-Propanol	$(CH_3)_2\dot{C}OH$	1.500	0.342
$[PtCl_6]^{2-}$	Ethanediol	$CH_2OH\dot{C}HOH$	1.526	0.345
$[IrCl_6]^{2-}$	Ethanediol	$CH_2OH\dot{C}HOH$	1.526	0.385
$[IrCl_6]^{2-}$	Mannitol	$CH_2OH(CHOH)_4$– $\dot{C}HOH$	1.552	0.381

* Ref. 20.

RCH_2OH [equations (4) and (5)]. (*b*) *via* secondary reactions of $RCH_2\dot{O}$ such as the well known H-atom transfer reaction (6), or the isomerisation reaction (7).[14] Equation (6) occurs readily even at temperatures below 77 K,[15] which suggests that

$$RCH_2\dot{O} + RCH_2OH \longrightarrow R\dot{C}HOH + RCH_2OH \quad (6)$$

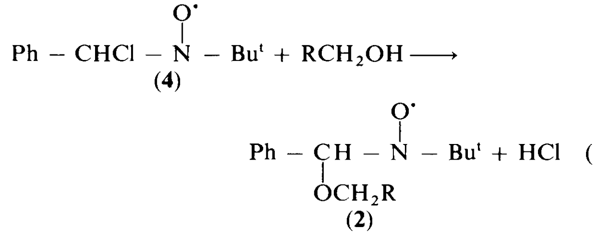
$$RCH_2\dot{O} + H_2O \longrightarrow R\dot{C}HOH + H_2O \quad (7)$$

conclusions based solely on matrix–e.s.r. spectroscopy at 77 K should be treated cautiously. Reaction (6) has also been characterised in fluid solution by pulse radiolysis, with k_6 = 2.6×10^5 dm^3 mol^{-1} s^{-1} for R = H.[16] (*c*) *via* secondary reactions of $Cl^{\bullet}$ through equation (8): the radical $Cl^{\bullet}$ is

$$([MCl_6]^{2-})^* \longrightarrow [MCl_5]^{2-} + Cl^{\bullet} \quad (8)$$

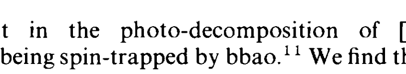
$$Cl^{\bullet} + RCH_2OH \longrightarrow HCl + R\dot{C}HOH \quad (9)$$

significant in the photo-decomposition of $[PtCl_6]^{2-}$ in CH_3CN, being spin-trapped by bbao.[11] We find that photolysis of $[AsPh_4]_2[MCl_6]$ (M = Pt, Pd, or Ir) in CH_3CN or CH_2Cl_2 yields the $Cl^{\bullet}$ adduct of bbao with coupling constants in excellent agreement with those in ref. 11. Addition of small quantities (*ca.* 1%) of RCH_2OH to CH_3CN and CH_2Cl_2 solutions (prior to photolysis) resulted in complete loss of the $Cl^{\bullet}$ adduct (**4**) and production of the adduct of $RCH_2\dot{O}$ (**2**). This we attribute to nucleophilic reaction of the $Cl^{\bullet}$ adduct with alcohol, *viz.* equation (10), which parallels the proposed hydrolysis of the same $Cl^{\bullet}$ adduct by water in the photolysis of $[PtCl_6]^{2-}$ in water.[11]



$$\underset{(\mathbf{4})}{Ph - CHCl - \overset{O^{\bullet}}{\overset{|}{N}} - Bu^t} + RCH_2OH \longrightarrow \underset{(\mathbf{2})}{Ph - \underset{OCH_2R}{\underset{|}{C}}H - \overset{O^{\bullet}}{\overset{|}{N}} - Bu^t} + HCl \quad (10)$$

The simplest scheme (see below) would attribute *all* radicals trapped as originating in a $Cl^{\bullet}$ precursor, however the effect of



added water accords more with a mechanism of isomerisation of an intermediate $RCH_2\dot{O}$ into $R\dot{C}HOH$, equation (7).

There is no clear pattern as to which pathway dominates in the pure alcoholic media: all three metal complexes give in at least one instance the alkoxy radical. In the photolysis of $K_2[PdCl_6]$ in 2-propanol first one spin-trapped radical was detected $(CH_3)_2CH\dot{O}$ but, after 30 min of further irradiation this was completely displaced by the other, the adduct of $(CH_3)_2\dot{C}OH$. Evidently very fine tuning is operative in these systems in discriminating between the various pathways. As regards the role of the water present, Ledwith *et al.*[17] found that photo-oxidation of CH_3OH by uranyl nitrate gave the spin trap of $CH_3O^{\bullet}$ in neat CH_3OH but in water–methanol (2:1, v/v) only $\dot{C}H_2OH$ was trapped. This group also found that the uranyl–ethanol photoreaction in aqueous ethanol gave the adduct of $CH_3\dot{C}HOH$; interestingly we found that, in pure ethanol, photo-excited uranyl yields the adduct of $CH_3CH_2\dot{O}$. These observations and also those of Table 1 accord well with those of Gilbert *et al.*[14] who find that the isomerisation of propoxyl radical, equation (7) with R = C_2H_5, takes place only in the presence of water and not in neat solvent. These authors estimate k_7 = 1.4×10^5 dm^3 mol^{-1} s^{-1} for R = C_2H_5 while the rate constant for spin trapping of $CH_3CH_2CH_2O^{\bullet}$ by $CH_2{=}NO_2^-$ exceeds 10^9 dm^3 mol^{-1} s^{-1}. However, since $[H_2O] \approx 55.5$ mol dm^{-3} while [bbao] ≈ 0.1 mol dm^{-3}, it is quite possible for the alkoxyl radicals in alcohol–water mixtures to isomerise before being spin-trapped.

Table 2. Hyperfine splitting constants for spin adducts of bbao in the photolysis ($\lambda > 380$ nm) of $[MCl_6]^{2-}$ ions in pure alkanol media

Metal salt	Alkanol	Radical trapped	$a(^{14}N)$/ mT	$a_\beta(^1H)$/ mT
$[PtCl_6]^{2-}$	Methanol	$\dot{C}H_2OH$	1.526 (1.516)*	0.368 (0.373)*
$[PdCl_6]^{2-}$	Methanol	$CH_3\dot{O}$	1.447 (1.442)*	0.289 (0.287)*
$[PtCl_6]^{2-}$	Ethanol	$CH_3\dot{C}HOH$	1.539 (1.531)*	0.356 (0.356)*
$[PdCl_6]^{2-}$	Ethanol	$CH_3CH_2\dot{O}$	1.434 (1.447)*	0.263 (0.262)*
$[PdCl_6]^{2-}$	1-Propanol	$CH_3CH_2\dot{C}HOH$	1.526	0.342
$[PdCl_6]^{2-}$	2-Propanol	$(CH_3)_2CH\dot{O}$	1.447 (1.449)*	0.210 (0.214)*
		$(CH_3)_2\dot{C}OH$	1.543 (1.542)*	0.355 (0.355)*
$[PtCl_6]^{2-}$	1-Butanol	$CH_3(CH_2)_2CH_2\dot{O}$	1.473	0.269
$[PdCl_6]^{2-}$	1-Butanol	$CH_3(CH_2)_2CH_2\dot{O}$	(1.440)*	(0.242)*
$[IrCl_6]^{2-}$	1-Butanol	$CH_3(CH_2)_2\dot{C}HOH$	1.526 (1.541)*	0.355 (0.355)*
$[PtCl_6]^{2-}$	2-Butanol	$CH_3CH_2\dot{C}(OH)CH_3$	1.553	0.342
$[PdCl_6]^{2-}$	2-Butanol	$CH_3CH_2\dot{C}(OH)CH_3$	1.553	0.344
$[IrCl_6]^{2-}$	2-Butanol	$CH_3CH_2\dot{C}(OH)CH_3$	1.556	0.345
$[PtCl_6]^{2-}$	2-Methyl-1-propanol	$(CH_3)_2CH\dot{C}HOH$	1.500	0.342
$[PdCl_6]^{2-}$	2-Methyl-1-propanol	$(CH_3)_2CH\dot{C}HOH$	1.526	0.342
$[IrCl_6]^{2-}$	2-Methyl-1-propanol	$(CH_3)_2CHCH_2\dot{O}$	1.447	0.289
$[PtCl_6]^{2-}$	Allyl alcohol	$CH_2{=}CH\dot{C}HOH$	1.526	0.325
$[PdCl_6]^{2-}$	Allyl alcohol	$CH_2{=}CH\dot{C}HOH$	1.526	0.362
$[IrCl_6]^{2-}$	Allyl alcohol	$CH_2{=}CH\dot{C}HOH$	1.528	0.336
$[PtCl_6]^{2-}$	Benzyl alcohol	$C_6H_5\dot{C}HOH$	1.526	0.368
$[PdCl_6]^{2-}$	Benzyl alcohol	$C_6H_5CH_2\dot{O}$	1.421	0.263
$[IrCl_6]^{2-}$	Benzyl alcohol	$C_6H_5CH_2\dot{O}$	1.447	0.289

* Ref. 17.

Table 3. Hyperfine splitting constants for the organic radicals produced in the photolysis of $[MCl_6]^{2-}$ ions in organic matrices at 77 K

Metal salt	Substrate	Radical trapped	a(H)/mT
$[PtCl_6]^{2-}$	Methanol	$\dot{C}H_2OH$	2.00
	Ethanediol	$\dot{C}HOHCH_2OH$	2.03
	Acetonitrile	$\dot{C}H_2CN$	2.00
$[IrCl_6]^{2-}$	Methanol	$\dot{C}H_2OH$	2.03
	Ethanol (70%)*	$CH_3\dot{C}HOH$	1.80
	Ethanediol	$\dot{C}HOHCH_2OH$	1.95
	Acetonitrile	$\dot{C}H_2CN$	2.01
	Propan-1-ol (70%)*	$CH_3CH_2\dot{C}HOH$	2.00
	Acetone (70%)*	$\dot{C}H_2COCH_3$	1.87
$[PdCl_6]^{2-}$	Methanol	$\dot{C}H_2OH$	2.03
	Ethanol	$CH_3\dot{C}HOH$	1.97
	Ethanediol	$\dot{C}HOHCH_2OH$	2.03
	Acetonitrile	$\dot{C}H_2CN$	2.04
	Acetone	$\dot{C}H_2COCH_3$	1.82

* Co-solvent is water (v/v).

The speed of reactions (6) and (7) is such that one would expect a dependence of the adduct identified upon the concentration of the trapping agent, low concentrations of the latter tending to produce *C*-centred radical adducts at the expense of *O*-centred adducts, a pattern noted in the γ-radiolysis of various alcohols.[18] This might have been expected to account for the turnover in the example of $[PdCl_6]^{2-}$-2-propanol given above. Variation of the concentration of bbao over a wide range did not, however, result in any change in the relative spin-adduct concentrations. A very detailed account of the production of *C*- and *O*-centred radicals from uranyl–alcohol systems is given by Rehorek.[19]

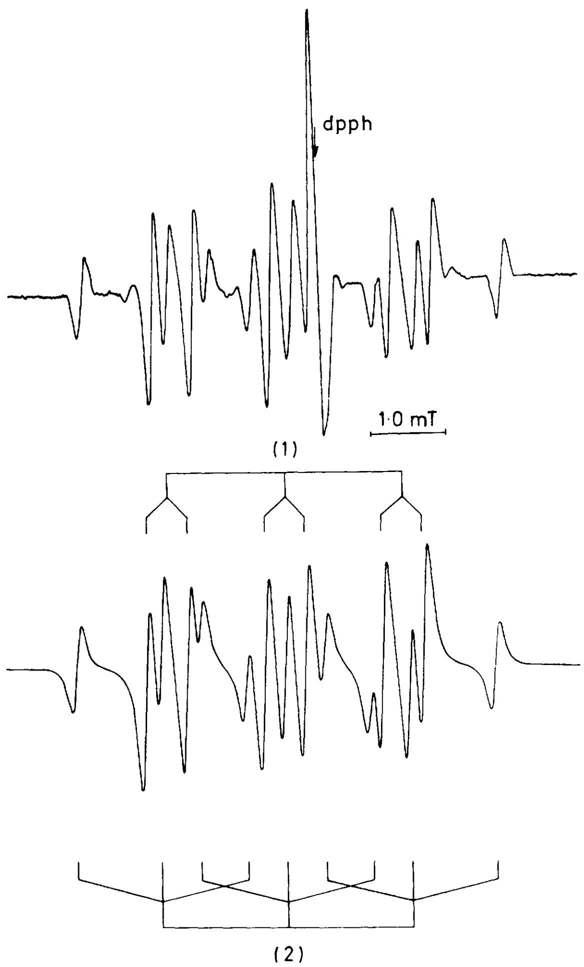


Figure 2. E.s.r. spectrum (upper) of a radical mixture obtained on prolonged photoirradiation (Pyrex filter) of $K_2[PtCl_6]$ (1.3×10^{-2} mol dm^{-3}) in methanol–water (7.2:1, v/v) in the presence of (**1**) (0.1 mol dm^{-3}). Computer simulation (lower) based on coupling constants given for spin adducts of $\dot{C}H_2OH$ (1) (Table 1) and H atoms (2) (see text)

A further trapping process was revealed as follows: prolonged irradiation ($\lambda > 300$ nm) of $[PtCl_6]^{2-}$ solutions in aqueous–MeOH and -EtOH using (**1**) as trapping agent gave rise to a radical mixture consisting of the adducts of $\dot{C}H_2OH$ (and, for ethanol, $CH_3\dot{C}HOH$) and H atoms (Figure 2): the coupling constants for the H-atom adduct are $a(^{14}N) = 1.605$ and $a(2H) = 1.1$ mT which compare with those of Janzen and Shetty[20] of 1.509 and 0.919 mT respectively. We suspect that the origin of the H atoms lies in the colloidal Pt evident at the later stages of photolysis.

The possibility of the spin traps themselves being involved in photo redox reactions with $[MCl_6]^{2-}$ was ruled out by experiments in aqueous solution (*i.e.* in the absence of alcohols): only very weak, broad spectra were apparent after prolonged photolysis.

Cryogenic Photolyses.—Photolysis ($\lambda > 300$ nm) of $[MCl_6]^{2-}$ (M = Pt or Pd) ions in alcohols and CH_3CN gave rise to two principal sets of species, namely matrix-derived

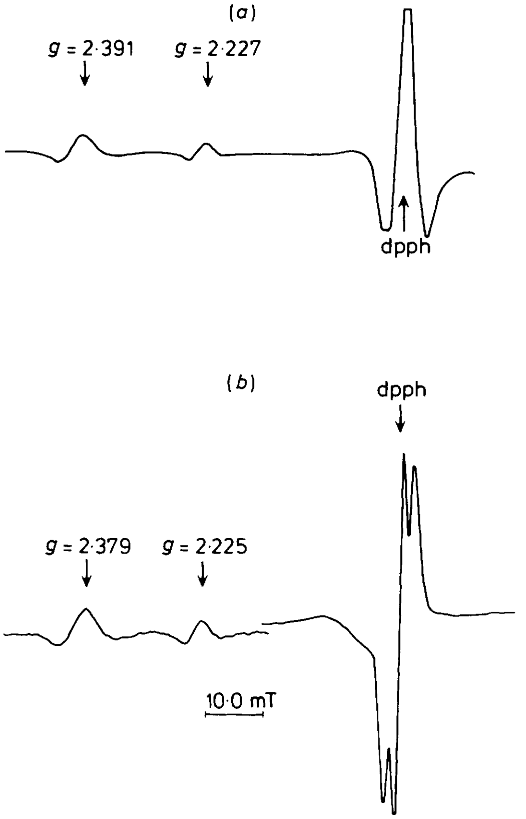


Figure 3. Second-derivative e.s.r. spectra obtained on photolysis at 77 K of solutions of $K_2[PtCl_6]$ in (*a*) CD_3OD and (*b*) CH_3CN

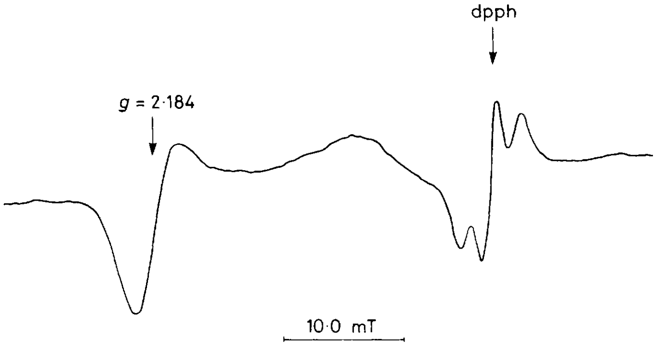


Figure 4. First-derivative e.s.r. spectrum obtained on photolysis at 77 K of a solution of $K_2[PdCl_6]$ in CH_3CN

radicals as summarised in Table 3 and paramagnetic metal centres as illustrated in Figures 3 and 4. The salt $K_2[IrCl_6]$ gave the organic radical but no low-field absorption attributable[21] to Ir^{II} (Ir^{III} is diamagnetic). The alcohols gave the broad, poorly resolved solid state spectra generally attributable to $\dot{R}CHOH$, and only in the case of CD_3OD was a metal(III) species observed, *i.e.* Pt^{III}, in addition to the organic radical [Figure 3(*a*)]. The features at $g = 2.391$ in CD_3OD and at 2.379 in CH_3CN [Figure 3(*b*)] are assigned to the perpendicular component of the platinum(III) species, *cf.* $g_\perp = 2.4$ for Pt^{III} in frozen acetone[4] and $g_\perp = 2.403$ for $[PtCl_5]^{2-}$ in a γ-irradiated single crystal of $K_2[PtCl_4]$.[22] The feature at $g_\perp = 2.225$ is due to the high-field satellite of ^{195}Pt ($I = \frac{1}{2}$, natural abundance 33.8%): its separation from the main peak (from ^{196}Pt) of 19.7 mT compares with figures of 21.5,[4] 22.5,[8] and 21.6 mT.[21] The value of $g_\perp$ is known to be sensitive to solvent[8] but our figure differs somewhat from that of ref. 8 which gives $g_\perp = 2.436 \pm 0.003$ for a CH_3OH glass.

The analogous experiment with $K_2[PdCl_6]$ in CH_3CN gave a feature at $g = 2.184$. The $g_\perp$ component of Pd^{III} in single-crystal MgO[23] and CaO[24] hosts is situated at 2.17 ± 0.01 and 2.22 respectively at 4 K and it appears therefore that we have matrix-isolated the palladium(III) analogue of the better known platinum(III) species. (No attempt to search for Ir^{III} was made in $[IrCl_6]^{2-}$-photosensitised oxidations at 77 K insofar as this species is diamagnetic.)

Conclusions

The photoreduction of $[PtCl_6]^{2-}$ by alcohols,[5] both at room temperature and 77 K, involves a photoredox process yielding Pt^{III} and an alcohol-derived radical. In pure alcohol solvents this radical is often $RCH_2\dot{O}$ but in the presence of water only $\dot{R}CHOH$ is trapped, possibly as a result of a water-promoted isomerisation or *via* attack on RCH_2OH by a photo-produced Cl atom. The photoreductions of $[IrCl_6]^{2-}$ and $[PdCl_6]^{2-}$ follow generally similar patterns both at 77 K and room temperature.

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