Synthesis and Properties of Pentachloro(ligand)iridate(IV) Anions $[IrLCl_5]^-$ (L = pyridine, PPh_3, $AsPh_3$, $SbPh_3$, SMe_2, SPh_2, or $SeMe_2$)

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Purple $[NEt_4][Ir(py)Cl_5]$ (py = pyridine) is conveniently obtained by reaction of *trans*-$[Ir(py)_2Cl_4]$ with HCl gas and NEt_4Cl in CH_2Cl_2 solution. Reduction of this anion with ascorbic acid, followed by successive treatment with L (L = SMe_2, $SeMe_2$, PPh_3, $AsPh_3$, or $SbPh_3$), Cl_2, and HCl, afford $[NEt_4][IrLCl_5]$, which have been characterised by analysis, i.r. and u.v.–visible spectroscopy, and conductance measurements. The potentials for the reductions were measured, and the formal potentials for the Ir^{III}–Ir^{IV} couples are compared with those of *trans*-$[IrL_2Cl_4]^{0/-}$ and *cis*-$[Ir(L\text{–}L)Cl_4]^{0/-}$ (L–L = bidentate ligand analogue of L).

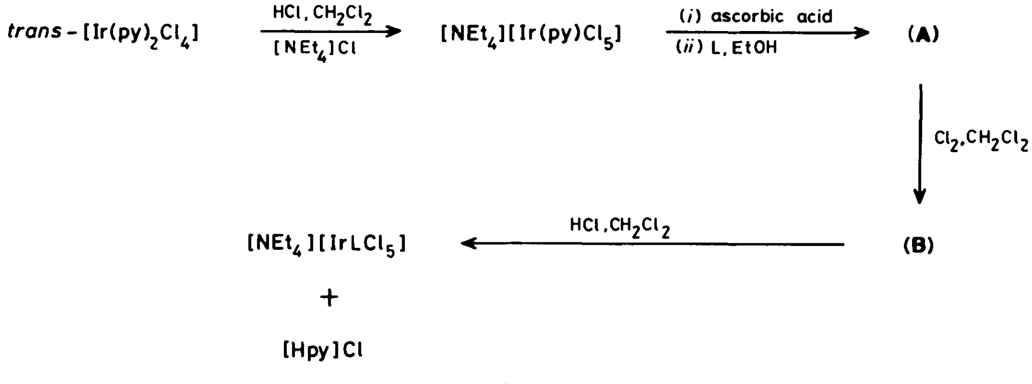
The chemistry of iridium(IV) is the most restricted of any M^{IV} oxidation state of the 5*d* elements Hf–Pt.[1] We have reported investigations of two series of iridium(IV) complexes, *trans*-$[IrL_2X_4]$ [2] and *cis*-$[Ir(L\text{–}L)X_4]$ [3] (L, L–L = respectively mono- and bi-dentate Group 5B or 6B donor ligand, X = Cl or Br). The properties are markedly dependent upon the stereochemistry, and in particular the Ir^{III}–Ir^{IV} redox potentials revealed that the oxidising power is *cis* > *trans* for the same donor set. With a few exceptions {*e.g.* $[Ir(H_2O)_3Cl_3]^4$} complexes of types $[IrL_3Cl_3]$ or $[IrL_4Cl_2]^+$ do not oxidise to isolable Ir^{IV} species, but anions $[IrLX_5]^-$ should be obtainable. In fact only three examples have been reported: $[Ir(H_2O)Cl_5]^-$, $[Ir(H_2O)Br_5]^-$,[4–6] and $[Ir(py)Cl_5]^-$ (py = pyridine).[7]

Results and Discussion

Iridium(III) anions $[IrL'Cl_5]^{2-}$ are known with various *N*-donor heterocycles (L′ = py, pyrimidine, pyrazine, 3-methylpyridine, *etc.*),[7–10] and with SPh_2.[11] Numerous attempts to prepare $[IrLCl_5]^{2-}$ (L = SMe_2, $SePh_2$, or PPh_3) directly from $IrCl_3 \cdot nH_2O$, NR_4Cl, and L under a variety of reaction conditions gave mainly $[IrL_3Cl_3]$ and $[IrL_2Cl_4]^-$.[2,12] Occasionally traces of $[IrLCl_5]^{2-}$ were also identified, but the preparations were not reproducible. The ready production of $[Ir(SPh_2)Cl_5]^{2-}$ [11] was confirmed, but it remains unclear why this ligand behaves anomalously. Nucleophilic attack of N_3^- or NH_2OH on $[Ir(NO)Cl_5]^-$ gives [13] $[Ir(H_2O)Cl_5]^{2-}$, but even in the presence of a ten-fold excess of SMe_2 or PPh_3, the product was still the aqua complex. Attempts to cleave the Cl bridges in $[Cl_3Ir(\mu\text{-}Cl)_3IrCl_3]^{3-}$ [14] by L (which might have been expected to give an equimolar mixture of $[IrL_2Cl_4]^-$ and $[IrLCl_5]^{2-}$) gave complex mixtures.

Good yields of $[NEt_4][Ir(py)Cl_5]$ (>90%) are obtainable from reaction of *trans*-$[Ir(py)_2Cl_4]$ with gaseous HCl, and NEt_4Cl in CH_2Cl_2, and this can be extended into a route to other $[IrLCl_5]^-$ anions (Scheme). Attempts to isolate the telluroether analogue $[Ir(TeMe_2)Cl_5]^-$ failed (*cf.* refs. 2 and 3). *trans*-$[Ir(py)_2Br_4]$ [2] is decomposed to $[IrBr_6]^{2-}$ by HBr–CH_2Cl_2, and $[Ir(py)Br_5]^-$ has not been isolated; this may be as a consequence of the greater *trans* influence of Br over Cl.[15] The intermediates in the Scheme were not isolated, but (**A**) and (**B**) are almost certainly *trans*-$[IrL(py)Cl_4]^{-/0}$ respectively, support for the formulation of (**B**) coming from the characteristic pattern of $\pi_{Cl} \longrightarrow Ir_{t_{2g}}$ charge-transfer bands in the u.v.–visible spectra of the solutions. Overall yields vary with L, but are *ca.* 15—30% based upon $[NEt_4][Ir(py)Cl_5]$.

The compounds $[NEt_4][IrLCl_5]$ are reddish-purple crystalline solids, soluble in CH_2Cl_2 or MeCN and 1:1 electrolytes in the latter (Table). The far-i.r. spectra contain strong broad absorptions at *ca.* 300—330 cm^{-1} assigned as Ir–Cl stretching vibrations (theory C_{4v}; $2A_1 + E$). The complexes are reduced to Ir^{III} only slowly on heating in ethanol, in contrast to the rapid reduction of *cis*-$[Ir(L\text{–}L)Cl_4]$ and most *trans*-$[IrL_2Cl_4]$ complexes,[2,3] but rapid clean reduction is possible with ascorbic acid.



Scheme.

Table. Selected physical data for $[NR_4][IrLCl_5]$

$[NEt_4][IrLCl_5]$	$\nu(Ir–Cl)^{a}/cm^{-1}$	$10^{-3}E_{max.}{}^{b}/cm^{-1}$ ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$)	$\Lambda_M{}^{c}/\Omega^{-1}\ cm^2\ mol^{-1}$	$E_e{}^{\ominus}/V^{d}$
L = py	326, 315 (sh), 305 (sh)	15.9 (sh), 17.18 (580), 20.00 (sh), 20.40 (3 570), 25.77 (1 145)	130	0.65, 0.61^{e}
PPh_3	325, 315, 303 (sh)	17.24 (490), 19.60 (sh), 20.40 (2 400), 26.04 (1 150)		0.65
$AsPh_3$	322, 313, 305 (sh)	17.06 (sh), 19.84 (sh), 20.30 (1 770), 25.91 (770)	124	0.67
$SbPh_3$	325, 310	17.85 (1 050), 19.53 (1 760), 20.16 (1 705), 25.90 (1 160)	133	0.68
SMe_2	328, 314 (sh), 304 (sh)	16.03 (200), 17.78 (420), 20.00 (1 470), 20.32 (1 510), 25.91 (640), 31.05 (930)		0.63^{e}
$SPh_2{}^{f}$	334 (sh), 321, 300 (sh)	14.90 (sh), 18.90 (2 500), 19.60 (sh), 23.15 (sh), 25.5 (sh)		0.71
$SeMe_2$	324, 314 (sh)	16.03 (sh), 17.61 (270), 19.84 (sh), 20.33 (1 280), 25.77 (520), 32.90 (585)	114	0.62^{e}
$[Ir(H_2O)Cl_5]^{-\,g}$		19.46 (1 280), 22.47 (3 250), 28.17 (1 040)		

[a] Nujol mull. [b] CH_2Cl_2. [c] *ca.* 10^{-3} mol dm^{-3} in MeCN. 1:1 electrolytes have Λ_M in the range *ca.* 120—160 Ω^{-1} cm^2 mol^{-1}. [d] In CH_2Cl_2 *versus* s.c.e. [e] In MeCN *versus* s.c.e. [f] $NMe_4{}^+$ salt. [g] Data calculated from Figure 2 in ref. 5. Spectrum obtained from 2.5 mol dm^{-3} $HClO_4$ solution.

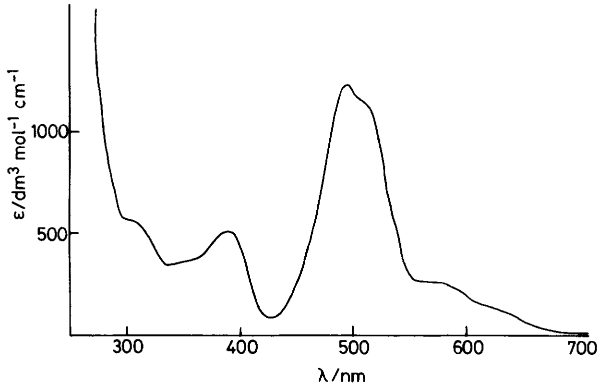


Figure. U.v.-visible spectrum of $[NEt_4][Ir(SeMe_2)Cl_5]$ in CH_2Cl_2

In addition to weak bands at *ca.* 4 000—6 000 cm^{-1} which are intraconfigurational, the electronic spectra (Table) are generally similar, and a typical example is shown in the Figure. By comparison with the spectra of $[IrCl_6]^{2-}$ and *trans*-$[IrL_2Cl_4]$[2,16] the intense absorptions at *ca.* 18 000—21 000 cm^{-1} can be assigned as $\pi_{Cl} \longrightarrow Ir_{t_{2g}}$ ligand-to-metal charge-transfer (l.m.c.t.) bands. Similarly the absorptions > *ca.* 25 000 cm^{-1} are mainly $\sigma_{Cl} \longrightarrow Ir_{t_{2g}}$ l.m.c.t. We tentatively propose that the rather ill-defined weaker absorptions at *ca.* 15 000—18 000 cm^{-1} are charge transfer from the strongly mixed σ_L and σ_{Cl} (*trans*-L) orbitals. {*cf.* McCaffery and Rowe's assignments of the spectra of d^5 *mer*-$[Os(PR_3)_3Cl_3]$.[17]}

Cyclic voltammograms were recorded at a vitreous carbon disc electrode for solutions of $[IrLCl_5]^-$, *ca.* 1 mmol dm^{-3} in CH_2Cl_2 or MeCN containing $[NBu^n{}_4][BF_4]$ (0.1 mol dm^{-3}). All the Ir^{IV} anions show well-formed reduction peaks and the cyclic voltammetric responses had the properties of a one-electron reversible process. The formal potentials of the Ir^{III}–Ir^{IV} couples estimated from the voltammograms are reported in the Table. As expected from earlier studies[3] on *cis*-$[Ir(L–L)Cl_4]$ where L–L is *trans* Cl, the formal potentials are not very sensitive to the choice of L. Much more marked variations were observed when L is *trans* L, *i.e.* in *trans*-$[IrL_2Cl_4]$.[2] The $E_e{}^{\ominus}$ values are intermediate between those for $[IrCl_6]^{3-}$–$[IrCl_6]^{2-}$ and *cis*-$[Ir(L–L)Cl_4]^-$–*cis*-$[Ir(L–L)Cl_4]$.

Experimental

Physical measurements were made as described in ref. 2.

Tetraethylammonium Pentachloro(pyridine)iridate(IV), $[NEt_4][Ir(py)Cl_5]$.—*trans*-$[Ir(py)_2Cl_4]$[2] (0.05 g, 0.1 mmol) was suspended in a solution of excess NEt_4Cl (*ca.* 0.5 mmol) in CH_2Cl_2 (20 cm^3) and hydrogen chloride bubbled into the solution, causing the solid to dissolve. After 1 h the HCl was removed by purging the solution with N_2, and the solution evaporated to dryness. The purple product was thoroughly washed with water to remove [Hpy]Cl and excess NEt_4Cl, and dried *in vacuo* (yield >90%) (Found: C, 27.6; H, 4.4; N, 4.6. $C_{13}H_{25}Cl_5IrN_2$ requires C, 27.0; H, 4.3; N, 4.8%).

Tetramethylammonium Pentachloro(diphenyl sulphide)iridate(IV), $[NMe_4][Ir(SPh_2)Cl_5]$.—$[NMe_4]_2[Ir(SPh_2)Cl_5]$[11] (0.05 g, 0.07 mmol) was dissolved in CH_2Cl_2 (10 cm^3) and chlorine bubbled in, causing an immediate maroon colouration. The product was precipitated by adding cyclohexane (5 cm^3) and cooling to −5 °C (0.031 g, 70%) (Found: C, 30.3; H, 3.4; N, 2.1. $C_{16}H_{22}Cl_5IrNS$ requires C, 30.5; H, 3.5; N, 2.2%).

Tetraethylammonium Pentachloro(ligand)iridate(IV), *General Method.*—$[NEt_4][Ir(py)Cl_5]$ (0.12 g, 0.21 mmol) was dissolved in warm ethanol. Ascorbic acid in ethanol was added dropwise until decolourisation occurred when an equimolar solution of the ligand in CH_2Cl_2 was added and the mixture was refluxed for 1 h. The ethanol was evaporated *in vacuo* and the residue was dissolved in CH_2Cl_2, oxidised with chlorine and the solution saturated with HCl. After 1 h the solution was purged with nitrogen, partitioned with water, the organic phase separated and dried over anhydrous Na_2SO_4. The dried solution was reduced *in vacuo* to a small volume and diethyl ether was added dropwise until turbidity was observed. The product was left at *ca.* −10 °C to crystallise, the liquid decanted off, and the solid dried *in vacuo* {yields *ca.* 20% on $[NEt_4][Ir(py)Cl_5]$} (Found for L = PPh_3: C, 40.9; H, 4.6; N, 1.9. $C_{26}H_{35}Cl_5IrNP$ requires C, 41.0; H, 4.6; N, 1.8%. Found for L = $AsPh_3$: C, 38.9; H, 4.5; N, 1.8. $C_{26}H_{35}AsCl_5IrN$ requires C, 38.7; H, 4.3; N, 1.7%. Found for L = $SbPh_3$: C, 36.9; H, 4.0; N, 1.7. $C_{26}H_{35}IrNSb$ requires C, 36.6; H, 4.1; N, 1.6%. Found for L = SMe_2: C, 21.7; H, 4.5; N, 2.4. $C_{10}H_{26}Cl_5IrNS$ requires C, 21.4; H, 4.6; N, 2.5%. Found for L = $SeMe_2$: C, 19.8; H, 4.3; N, 2.3. $C_{10}H_{26}Cl_5IrNSe$ requires C, 19.7; H, 4.3; N, 2.3%).

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