both the highest filled benzene orbitals and the lowest empty Tl(I) (p_x,p_y) orbitals belong to the e_1 irreducible representation of C_{6v} symmetry. These same arguments can be used to predict an inverted ferrocene structure of $C_6H_6\cdot 2Tl(I)$, *i.e.*, metals on the sixfold axis on either side of the aromatic ring. However, these theoretical arguments assume a passive role for the $AlCl_4^-$ entity, and we have shown that this is anything but the case for Ag(I)[1] and Cu(I)[2,3] as well as for the ClO_4^- ion in $(C_6H_5C_6H_{11})_2\cdot AgClO_4$[8] and $[m\text{-}(CH_3)_2C_6H_4]_2AgClO_4$.[9] This is particularly true for the $(C_6H_6)_2\cdot TlAlCl_4$ complex since benzene cannot be readily removed from this complex under vacuum at ambient temperature. The most likely structure for the $C_6H_6\cdot 2TlAlCl_4$ complex is one in which each Tl(I) coordinates to the aromatic ring as well as with, at least, one halogen of nearby $AlCl_4^-$ groups.

With the fourth group metals we have prepared $(C_6H_6)_2Sn(AlCl_4)_2$ and $(C_6H_6)_2Pb(AlCl_4)_2$ by the same methods. *Anal.* Calcd for $(C_6H_6)_2\cdot Sn(AlCl_4)_2$: Sn, 19.38; Al, 8.81; Cl, 46.32; C_6H_6, 25.48. Found: Sn, 18.85; Al, 9.19; Cl, 45.78; C_6H_6, 25.81. For this compound we have also been able to obtain single crystals for preliminary X-ray diffraction data and found the crystals to be monoclinic with a = 11.92 Å, b = 17.46 Å, c = 11.32 Å, $\beta \sim 90°$, and space group $P2_1/n$. With four $(C_6H_6)_2Sn(AlCl_4)_2$ units per cell, the calculated density is 1.73 g cm^{-3} compared to the observed value of 1.76 g cm^{-3} found by flotation in a carbon tetrachloride–bromoform mixture. Hence, the molecular weight is that of $(C_6H_6)_2\cdot Sn(AlCl_4)_2$ well within experimental error (1.7%). Mössbauer spectra[10] show a single line with an isomer shift of 1.6 mm/sec relative to Mg_2Sn as zero with no observable quadrupole splitting. The fluorocarbon mull infrared spectra give no indication of any symmetry less than D_{6h}. *Anal.* Calcd for dibenzene·Pb(II) complex, $(C_6H_6)_2Pb(AlCl_4)_2$: Pb, 29.57; Al, 7.70; Cl, 40.47; C_6H_6, 22.27. Found: Pb, 28.81; Al, 7.60; Cl, 40.59; C_6H_6, 22.43. Preliminary X-ray single-crystal diffraction data show the crystals of this compound to be triclinic with a = 14.1 Å, b = 8.76 Å, c = 15.3 Å, $\alpha \sim \beta \sim \gamma \sim 90°$. With four $(C_6H_6)_2\cdot Pb(AlCl_4)_2$ entities per cell, the calculated density is 1.96 g cm^{-3} compared to the observed value of 1.93 g cm^{-3} measured by flotation in a carbon tetrachloride–bromoform mixture. The molecular weight is not as clear cut as in the case of $(C_6H_6)_2\cdot Sn(AlCl_4)_2$ because of the low crystal symmetry but is consistent with $(C_6H_6)_2\cdot Pb(AlCl_4)_2$. As with the Tl(I) complexes no evidence is found in the infrared fluorocarbon mull spectra of an environment about the metal ion of symmetry lower than D_{6h}. Since these two compounds are isoelectronic in the valence shell with Tl(I), the same theoretical formalism is applicable and predicts a C_{6v} ferrocene sandwich-type structure. All the available evidence points to a symmetrical D_{6h} sandwich structure for $(C_6H_6)_2M(AlCl_4)_2$ where M is Sn(II) and Pb(II). However, a quadrupole splitting should be observed in the Mössbauer spectra of $(C_6H_6)_2Sn(AlCl_4)_2$ due to the fact that the sandwich structure has a point group symmetry lower than cubic. Nevertheless, there exist numerous examples where Sn does not show a Mössbauer quadrupole splitting in low-symmetry environments if the atoms bonded directly to Sn have no unpaired electrons.[11] This is to our knowledge the first report of a π complex of Sn(II). In contrast, the structure of bis(cyclopentadienyl)tin(II) is generally accepted as that of a σ-bonded molecule.[12]

With the fifth-group metals we have prepared $C_6H_6\cdot BiCl_2AlCl_4$. *Anal.* Calcd for $C_6H_6\cdot BiCl_2\,AlCl_4$: Bi, 39.68; Al, 5.12; Cl, 40.39; C_6H_6, 14.81. Found: Bi, 38.92; Al, 4.96; Cl, 39.66; C_6H_6, 14.21. This formulation of a BiX_2^+ ion is supported by the fact that the phase diagram of $BiBr_3$–$AlBr_3$ shows the existence of a 1:1 compound.[13]

A reasonable view of the $BiCl_2^+$ ion is that of an ion with an empty 6p orbital that can accept electrons from the e_1 MO's of benzene. This would lead to the prediction that the Bi atom would be located above a carbon–carbon bond of the benzene ring with the empty orbital pointed toward the π orbitals of the ring. Again, the interaction of the anion may well change this over-simplified picture.

It would be expected that the infrared spectra of this compound would show significant lowering of the symmetry of the local environment of the benzene ring. No indications of lower symmetry have been found. However, infrared investigations of complexes that have been shown by X-ray crystallography to have lower symmetry about the aromatic ring have been equally uninformative, *e.g.*, $C_6H_6\cdot AgClO_4$.[14]

Antimony and arsenic do not form similar complexes and the only benzene complexes we have been able to isolate up to this time are $C_6H_6\cdot 2SbCl_3$ and an analogous arsenic compound which were reported earlier by other workers.[14]

In general, the aromatic complexes of metal ions are less stable than the olefin complexes, and we predict that stable olefin complexes are possible for these ions. Experiments are under way in this direction.

We believe these are the first aromatic complexes reported of the above elements. The crystal structures of these compounds are under investigation in our laboratory at this time.

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[8] E. A. Hall and E. L. Amma, *Chem. Commun.*, 622 (1968).

[9] I. F. Taylor and E. L. Amma, to be submitted for publication.

[10] L. Cathey, University of Southern California, 1968, private communication.

[11] R. H. Herber, *Progr. Inorg. Chem.*, 8, 33 (1967).

[12] E. O. Fischer and H. Grubert, *Z. Naturforsch.*, **11b**, 423 (1956).

[13] J. Kendall, E. D. Crittenden, and H. K. Miller, *J. Am. Chem. Soc.*, **45**, 963 (1923).

[14] L. W. Daasch, *Spectrochim. Acta*, **9**, 726 (1959).

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The Oxidation of Platinum(II) Complexes by Hexachloroiridate(IV). *Evidence for the Intermediate Formation of Platinum(III)*

Sir:

The intermediate formation of platinum(III) in solution has been postulated in various reactions involving the platinum(II)–platinum(IV) redox couple, notably in certain photochemical and catalyzed substitution reactions of platinum(IV) complexes.[1-3] The inhibition of such reactions by hexachloroiridate(IV) has been attributed to rapid oxidation of platinum(III), but the evidence favoring the interpretations in question, while reasonable, has been for the most part indirect and qualitative. We now wish to report quantitative evidence for the intermediate formation of platinum(III) in the chemical oxidation of certain platinum(II) complexes and to describe some features of the chemistry of the intermediate platinum(III) species as revealed by observation of their competitive reactions including oxidation by hexachloroiridate(IV).

Our principal observations relate to the oxidation of tetrachloroplatinate(II) by hexachloroiridate(IV), according to eq 1, in aqueous sodium chloride–hydrochloric acid solution.

$$PtCl_4^{2-} + 2IrCl_6^{2-} + 2Cl^- \longrightarrow PtCl_6^{2-} + 2IrCl_6^{3-} \qquad (1)$$

The stoichiometry of the reaction was established spectrophotometrically and the kinetics were determined, also spectrophotometrically, over the following initial concentration ranges of reactants and products: 4.0 × 10^{-5} to 2.5 × 10^{-3} M $PtCl_4^{2-}$, 1.3 × 10^{-4} to 8.0 × 10^{-4} M $IrCl_6^{2-}$, 0 to 8.0 × 10^{-2} M $IrCl_6^{3-}$, 0.05 to 1.0 M Cl^-, 10^{-5} to 1.0 M H^+. Throughout this combination of concentration ranges the kinetics of the reaction were accurately represented by the rate law, expressed by eq 2, which is derived,

$$\frac{-d[IrCl_6^{2-}]}{dt} = \frac{-2d[PtCl_4^{2-}]}{dt} = \frac{2k_1k_2[PtCl_4^{2-}][IrCl_6^{2-}]^2[Cl^-]}{k_{-1}[IrCl_6^{3-}] + k_2[IrCl_6^{2-}][Cl^-]} \qquad (2)$$

employing the steady-state approximation for $PtCl_4^-$, on the basis of the mechanism depicted by eq 3–5.

$$PtCl_4^{2-} + IrCl_6^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PtCl_4^- + IrCl_6^{3-} \qquad (3)$$

$$PtCl_4^- + IrCl_6^{2-} + Cl^- \xrightarrow{k_2} PtCl_5^- + IrCl_6^{3-} \qquad (4)$$

$$PtCl_5^- + Cl^- \longrightarrow PtCl_6^{2-} \qquad (5)$$

Our kinetic measurements at 25°, and an ionic strength of 1.0 M, maintained with $NaClO_4$, yield the values $k_1 = 0.62 \pm 0.03$ M^{-1} sec^{-1} and $k_{-1}/k_2 = 9.0 \times 10^{-3}$ M. The rate was unaffected by variation of the concentration of H^+ between 10^{-5} and 1 M and by the addition of up to 10^{-3} M $PtCl_6^{2-}$.

An obvious variant of this mechanism, which is kinetically indistinguishable from that depicted above, is one in which the termolecular step 4 is replaced by a sequence of bimolecular steps (eq 6 and 7). This

$$PtCl_4^- + Cl^- \overset{K}{\rightleftharpoons} PtCl_5^{2-} \text{ (rapid equilibrium)} \qquad (6)$$

$$PtCl_5^{2-} + IrCl_6^{2-} \xrightarrow{k_2'} PtCl_5^- + IrCl_6^{3-} \qquad (7)$$

variant leads to a rate law identical in form with eq 2, in which k_2 is replaced by $k_2'K$. The observed value of 9.0 × 10^{-3} M then refers to $k_{-1}/k_2'K$, instead of to k_{-1}/k_2. Favoring this formulation is the recent direct observation[4] of the formation of $PtCl_5^{2-}$ in aqueous solution by dissociation of $PtCl_6^{3-}$ following electron capture by $PtCl_6^{2-}$.[4]

Using the stopped-flow method, we have also investigated the kinetics of the oxidation of $Pt(en)_2^{2+}$ (en = ethylenediamine) by $IrCl_6^{2-}$ (eq 8) and, in this case also,

$$Pt(en)_2^{2+} + 2IrCl_6^{2-} + 2Cl^- \longrightarrow \textit{trans}\text{-}Pt(en)_2Cl_2^{2+} + 2IrCl_6^{3-} \qquad (8)$$

found evidence for a stepwise mechanism involving an intermediate platinum(III) species, $Pt(en)_2^{3+}$ (or, alternatively, $Pt(en)_2Cl^{2+}$ or $Pt(en)_2Cl_2^+$). Over the initial concentration ranges, 6.2 × 10^{-5} to 2.5 × 10^{-4} M $Pt(en)_2^{2+}$, 1.3 × 10^{-5} to 2.5 × 10^{-5} M $IrCl_6^{2-}$, 0 to 1.0 × 10^{-3} M $IrCl_6^{3-}$, 10^{-5} to 0.5 M H^+, and 0.1 to 1.0 M Cl^-, the kinetics of this reaction accurately obeyed the rate law described by eq 9, which is derived,

$$\frac{-d[IrCl_6^{2-}]}{dt} = \frac{-2d[Pt(en)_2^{2+}]}{dt} = \frac{2k_1'k_2''[Pt(en)_2^{2+}][IrCl_6^{2-}]^2[Cl^-]^2}{k_{-1}'[IrCl_6^{3-}] + k_2''[IrCl_6^{2-}][Cl^-]^2} \qquad (9)$$

employing the steady-state approximation for $Pt(en)_2^{3+}$, for the mechanism depicted by eq 10 and 11. Our kinetic

$$Pt(en)_2^{2+} + IrCl_6^{2-} \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}} Pt(en)_2^{3+} + IrCl_6^{3-} \qquad (10)$$

$$Pt(en)_2^{3+} + IrCl_6^{2-} + 2Cl^- \xrightarrow{k_2''} Pt(en)_2Cl_2^{2+} + IrCl_6^{3-} \qquad (11)$$

measurements (also at 25° and 1.0 M ionic strength, maintained with $NaClO_4$) yield the values $k_1' = (1.40 \pm 0.05) \times 10^5$ M^{-1} sec^{-1} and $k_{-1}'/k_2'' = 2.0 \times 10^{-2}$ M^2. The $\sim 10^5$-fold difference between the value of k_1 for $PtCl_4^{2-}$ and k_1' for $Pt(en)_2^{2+}$ is in the direction expected from the difference between the charges of the two reactants.

Preliminary kinetic observations also point to similar mechanisms for the oxidations of $PtCl_3(C_2H_4)^-$ and $PtCl_2(OH_2)(C_2H_4)$ by $IrCl_6^{2-}$. The reactivities of these complexes are lower than those of $PtCl_4^{2-}$ and $Pt(en)_2^{2+}$, presumably reflecting stabilization of the +2 oxidation state of platinum by the coordinated ethylene. The oxidation of these complexes is accompanied by release of the ethylene which does not itself undergo oxidation.[5]

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(1) R. L. Rich and H. Taube, *J. Am. Chem. Soc.*, **76**, 2608 (1954).
(2) A. W. Adamson and A. H. Sporer, *ibid.*, **80**, 3865 (1958).
(3) A. J. Pöe and M. S. Vaidya, *J. Chem. Soc.*, 2981 (1961).
(4) G. E. Adams, R. B. Broszkiewicz, and B. D. Michael, *Trans. Faraday Soc.*, **64**, 1256 (1968).
(5) P. B. Chock and J. Halpern, unpublished results.

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Photosensitized Decomposition of Some Cobalt Ammines

Sir:

We wish to report the finding that the redox decomposition of $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5(H_2O)^{3+}$ in various aqueous and organic solvents is photosensitized by organic compounds known to have relatively stable triplet excited states. This effect, while forshadowed