$(en)_2Br_2^+$ which takes place with change of configuration.

In all careful studies so far reported where a cis substrate aquates with change of configuration (principally base hydrolysis[19,20] and induced aquation[10,13] studies) the steric course has provided evidence of a genuine five-coordinate intermediate. The spontaneous and induced aquation of *cis*-$Co(en)_2N_3Cl^+$ [6] give the same distribution of isomeric products. However current work in this department[23] indicates that the Hg^{2+}-induced aquation of *cis*-$Co(en)_2Br_2^+$ leads to only 58% of the cis aquobromo isomer at 20°. This contrasts with the 76% obtained by spontaneous aquation. It seems then that *cis*-$Co(en)_2Br_2^+$ is the first example of a nonstereoretentive aquation of a cis complex possibly not proceeding through a true five-coordinate intermediate. Also, *cis*-$Co(en)_2Br_2^+$ and *cis*-$Co(en)_2N_3Cl^+$ are the only cases reported in which the cis isomer displays more steric change than the trans during aquation.

It has been suggested[19] that a comparison of the temperature dependence of steric course for induced and spontaneous aquations would be useful in establishing the occurrence of a five-coordinate intermediate. Table VI shows that in the aquation of *cis*-$Co(en)_2Br_2^+$ there is a decrease from 78 to 65% in the fraction of cis isomer initially produced for a rise of 25° in temperature. This range includes the statistically determined amount (67%) predicted for one of the possible trigonal-bipyramidal intermediates.[3,4] However it should be realized that this simple theory applies strictly only to the symmetrical intermediates and neglects the now well-established effect of the nonparticipating groups[10,13] on the position of water attack. Further, it implies that there would be no variation of the proportion with temperature. Comparison of spontaneous and induced aquations indicates that the lifetime of the intermediate is another factor bearing on the stereochemistry of these reactions.[24]

Acknowledgments.—W. G. J. acknowledges a Commonwealth Postgraduate Research Grant. R. W. B. acknowledges Study Leave from the Footscray Institute of Technology.

[23] W. W. Fee and W. G. Jackson, unpublished work.

[24] R. Niththyananthan and M. L. Tobe, *Inorg. Chem.*, **8**, 1589 (1969).

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A Reactivity Trend Seen in the Reduction of Transition Metal Complexes by Outer-Sphere Reactants Verified for Hydrated Electron Reactions; Pulse Radiolysis Studies of Cobalt(III) Complexes

BY G. D. VENERABLE II[1]

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Hydrated electrons (e_{aq}^-) generated in the pulse radiolysis of aqueous solutions of cobalt(III) cyanide complexes react with the cobalt solute at rate constants in the 10^9–10^{10} M^{-1} sec^{-1} region. Of particular interest is a correlation between the rate constant for $e_{aq}^- + Co(CN)_5X^{3-}$ and the magnitude of the ligand field splitting parameter (Δ) of the heteroligand X^-. Within the standard outer-sphere–inner-sphere terminology, an attempt is made to provide a useful way of looking at the transition state consisting of e_{aq}^- and the metal complex.

Introduction

The reactivity trend relating outer-sphere rates of reduction of transition metal complexes at a dropping-mercury electrode (dme) with the ligand field splitting parameter (Δ) was first recognized by Vlček.[2] Candlin, Halpern, and Trimm[3] subsequently showed the same trend to be operative in the outer-sphere reduction of cobalt(III) complexes[4] by the outer-sphere reductants V^{2+} and $Cr(bipy)_3^{2+}$. An indication of such a trend in the reduction of cobalt(III) cyanide ($Co(CN)_5X^{3-}$) complexes can be seen in some early pulse radiolysis data of Baxendale, Fielden, and Keene.[6] The results of this work on additional complexes do in fact confirm the correlation between Δ and the rate of reduction of $Co(CN)_5X^{3-}$ by e_{aq}^-.

Pulse radiolysis experiments were carried out on aqueous solutions of some cobalt(III) cyanide complexes and rate constants for the reaction of the hydrated electron with the $Co(CN)_5X^{3-}$ solutes measured (X^- = *C*N^-, H^-, OH^-, *N*CS^-, I^-, the italic letter indicating which atom is bonded to cobalt). These studies were originally undertaken to explore the possibility of generating a reaction sequence of the type

$$Co(CN)_6^{3-} + e_{aq}^- \longrightarrow Co(CN)_6^{4-} \longrightarrow Co(CN)_5^{3-} + CN^- \quad (1)$$

While the experimental results[7] reveal pentacyanoco-

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[1] Laboratory of Nuclear Medicine and Radiation Biology, University of California, Los Angeles, Calif. 90024.

[2] A. A. Vlček, *Discuss. Faraday Soc.*, **26**, 164 (1958).

[3] J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Amer. Chem. Soc.*, **86**, 1019 (1964).

[4] In the reduction of $Co(NH_3)_5X^{n+}$ by V^{2+}, the apparent "high" values of rate constants for the X = $CH_3CO_2^-$, F^-, SO_4^{2-}, N_3^- complexes may indicate an inner-sphere bridging mechanism. However, there is evidence[5] that outer-sphere electron transfer occurs between V^{2+} and chloroammineruthenium(III) complexes.

[5] W. G. Movius and R. G. Linck, *J. Amer. Chem. Soc.*, **92**, 2677 (1970).

[6] J. H. Baxendale, E. M. Fielden, and J. P. Keene, *Proc. Roy. Soc., Ser. A*, **286**, 320 (1965).

[7] G. D. Venerable II, E. J. Hart, and J. Halpern, *J. Amer. Chem. Soc.*, **91**, 7538 (1969).

baltate(II) to be the final product, the intermediary stages observed are indicative of reactive pathways of considerably greater complexity than represented by eq 1 and will be discussed in a subsequent paper.

Experimental Section

Hydrated electrons were generated in the aqueous solutions by pulsed electron irradiation with the Argonne National Laboratory ARCO linear accelerator (linac) in accord with the general procedures described elsewhere.[8,9] Electron beam conditions, the experimental details of the spectrophotometric detection of e_{aq}^-, the particulars of the radiation dosimetry, and a description of the radical scavenging systems have been discussed in a previous paper.[10]

Solutions were prepared with triply distilled water which had been deaerated by successive evacuations and saturations with hydrogen and preirradiated with ^{60}Co γ-rays to destroy residual traces of oxygen and carbon dioxide. The final step in preparing a solution called for the injection (using the syringe technique) of *ca.* 10^{-2} *M* stock solution of the $Co(CN)_5X^{3-}$ solute into the syringe of the matrix (which contains all of the other solution components). The syringe technique[11] was also employed in filling and emptying the irradiation cell at the linac.

Sodium hydroxide and methyl alcohol were analytical grade reagents. Hydrogen gas (Matheson 99.95%, prepurified) was passed through a liquid nitrogen trap.

Potassium Hexacyanocobaltate(III).—$K_3Co(CN)_6$, was synthesized and recrystallized according to Bigelow.[12]

Potassium Hydridopentacyanocobaltate(III), $K_3Co(CN)_5H$.—Pure 5 m*M* solutions of $Co(CN)_5^{3-}$ were hydrogenated in 1 atm of $H_2(g)$ in a refrigerated syringe to give a product 90% pure. Pentacyanocobaltate(II) was prepared pure *in vacuo* to 5 m*M* concentration by a modified syringe technique. Mallinckrodt analytical grade $CoCl_2 \cdot 6H_2O$ and Baker Analyzed grade KCN reagents were combined in a 1:5.2 ratio in the preparation.

Potassium Aquopentacyanocobaltate(III).—$K_3Co(CN)_5OH_2$ was prepared 98% pure in aqueous solution by the photolysis of pure $Co(CN)_6^{3-}$ as given by Adamson and Sporer.[13] The excess cyanide ion produced in the photolysis was driven off as hydrogen cyanide upon slightly acidifying and gently heating the product solution. The solution was then neutralized by the addition of sodium hydroxide. In basic solution (pH >10) $Co(CN)_5OH^{3-}$ is the predominant form, the pK_a of the aquo complex being *ca.* 10.[14]

Tetra-*n*-butylammonium Isothiocyanatopentacyanocobaltate(III).—$[(n\text{-}C_4H_9)_4N]_3Co(CN)_5NCS$ was made available through the generosity of Professor H. B. Gray and D. F. Gutterman of the California Institute of Technology.

Potassium Iodopentacyanocobaltate(III).—$K_3Co(CN)_5I$ was kindly provided by Dr. M. Pribanić of the University of Chicago Chemistry Department.

Results

The reaction of e_{aq}^- with the several $Co(CN)_5X^{3-}$ complexes (eq 2) was followed by monitoring the decay

$$Co(CN)_5X^{3-} + e_{aq}^- \longrightarrow Co(CN)_5^{3-} + X^- \qquad (2)$$

in absorbance of e_{aq}^- at 578 nm [$\epsilon(e_{aq}^-)$ 1.06×10^4 M^{-1} cm^{-1}]. The pseudo-first-order disappearance of the hydrated electron was observed in solutions on the average 10–30 μ*M* in cobalti complex, yielding the data presented in Table I. The results demonstrate that the reactions obey the second-order rate law

$$-d[e_{aq}^-]/dt = -d[Co(CN)_5X^{3-}]/dt = k_2[Co(CN)_5X^{3-}][e_{aq}^-] \qquad (3)$$

TABLE I

KINETIC DATA FOR THE REACTION OF $e_{aq}^- + Co(CN)_5X^{3-}$ AT 20°, pH 13, 1 ATM OF $H_2(g)$ AND 10^{-2} *M* CH_3OH

X^-	$[Co(CN)_5X^{3-}]$,[a] μ*M*	$[e_{aq}^-]_{max}$, μ*M*	$10^{-5}k'$,[b] sec^{-1}	$10^{-10}k_2$,[c] M^{-1} sec^{-1}
*C*N⁻	18.3	1.4	0.86	0.47
	20	1.7	1.12[d]	0.56
	20[e]	1.3	0.96	0.48
	30[e]	0.9	1.74	0.58
	300[e]	0.9	6.3	0.21
H^-	17[f]	3.0	1.2	0.70
	20[g,f]	1.8	1.38	0.69
	20[h,f]	1.3	1.12	0.56
	30[g,f]	2.6	2.10[d]	0.70
OH^-	19[g,f]	3.2	2.10	1.10
	19[h]	1.9	2.04	1.07
	38[e]	1.3	4.6[d]	1.2
*N*CS⁻	18.5[e,i]	1.5	2.86[j]	1.55
	20[e,i]	1.9	3.26[j,d]	1.63
I^-	12.8[e,i]	1.5	2.66[j]	2.08
	19[e,i]	2.2	3.92[j,d]	2.06

[a] Initial concentration. [b] Decay of e_{aq}^- monitored at 578 nm unless otherwise specified. [c] Second-order rate constant for e_{aq}^- + Co calculated from k'/[solute]. [d] See Figure 1 for kinetic plots. [e] pH 7. [f] No CH_3OH added. [g] At 1500 psi of $H_2(g)$. [h] D_2O solution, pD 13. [i] 1 m*M* sodium formate in place of methyl alcohol. [j] e_{aq}^- monitored at 478 nm (ε 4470).

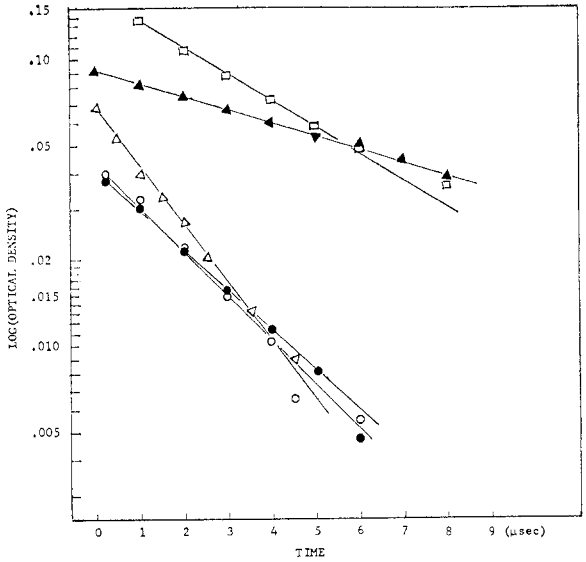

Figure 1.—Kinetic plots for pseudo-first-order decay of e_{aq}^- in 20 μ*M* $Co(CN)_6^{3-}$ (▲), 30 μ*M* $Co(CN)_5H^{3-}$ (□), 38 μ*M* $Co(CN)_5OH^{3-}$ (△), 20 μ*M* $Co(CN)_5NCS^{3-}$ (●), and 19 μ*M* $Co(CN)_5I^{3-}$ (○).

TABLE II

SUMMARY OF RATE CONSTANTS, $k_2(e_{aq}^- + Co(CN)_5X^{3-})$[a]

	k_2, M^{-1} sec^{-1}	
X^-	This work	Lit. values[c]
*C*N⁻	$(5.4 \pm 1.7) \times 10^9$ [b]	4.1×10^9 (pH 10) 2.7×10^9
H^-	$(6.7 \pm 0.7) \times 10^9$ [b]	...
*N*O₂⁻	...	8.0×10^9
*N*CS⁻	$(1.6 \pm 0.2) \times 10^{10}$	...
OH^-	$(1.2 \pm 0.12) \times 10^{10}$ [b]	1.1×10^{10}
N_3^-	...	1.3×10^{10}
Cl^-	...	1.8×10^{10}
I^-	$(2.1 \pm 0.2) \times 10^{10}$	...

[a] At 20° over pH range 7–13. Rate constants in D_2O found to be 80–90% of those in H_2O. [b] From least-squares fit of data to $k_2 = k_{1st\ order}$/[solute]. [c] See tables of M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotop.*, **18,** 493 (1967).

The final calculated second-order rate constants, k_2, for all of the complexes are listed in Table II. k_2 exhibits

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[8] A. S. Ghosh-Mazumdar and E. J. Hart, *Advan. Chem. Ser.*, **81,** 193 (1968).

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[10] G. D. Venerable II and J. Halpern, *J. Amer. Chem. Soc.*, **93,** 2176 (1971).

[11] E. J. Hart, S. Gordon, and J. K. Thomas, *J. Phys. Chem.*, **68,** 1271 (1964).

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[13] A. W. Adamson and A. H. Sporer, *J. Amer. Chem. Soc.*, **80,** 3865 (1958).

[14] A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1,** 573 (1962).

but a small D_2O isotope effect. That is, $k_{H_2O}/k_{D_2O} \approx 1.2$. Figure 1 displays some typical kinetic plots.

Discussion

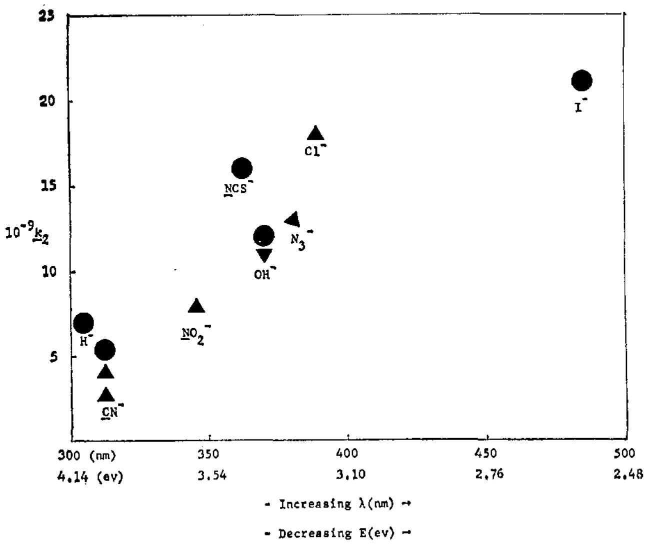

Figure 2.—Plot of the rate constant k_2 *vs.* the energy of the d–d electronic transition of $Co(CN)_5X^{3-}$: ●, this work; ▲, literature values.

The rate constant k_2 increases monotonically with decreasing Δ for the heteroligand. Figure 2 correlates[15,16] the reactivity of e_{aq}^- toward $Co(CN)_5X^{3-}$ with the energy of the d–d electronic transition. The uniformity of the trend points to a simple dependence of e_{aq}^- reactivity on the energy gap between the highest energy filled orbitals (t_{2g}) and the lowest energy vacant orbitals (e_g^*) of the cobalt complexes. The magnitude of this energy gap is, of course, dependent on the magnitude of Δ. It is possible that the upper end of the observed reactivity range, where the heteroligand is a halide, lies in the diffusion-controlled range.

The view that the hydrated electron may react with transition metal complexes by way of an outer-sphere mechanism receives support from the observed narrow limits[17] of the reactivity region for the reduction of $Co(CN)_5X^{3-}$ by e_{aq}^-. The azide–thiocyanate criterion,[18] where the reactivity ratio is

$$k(e_{aq}^- + Co(CN)_5N_3^{3-})/k(e_{aq}^- + Co(CN)_5NCS^{3-}) \approx 1$$

is suggestive of an outer-sphere mechanism.

In view of the evidence cited ascribing outer-sphere behavior to the hydrated electron, the question has to be raised as to the meaning of the outer-sphere–inner-sphere terminology with respect to reactions between e_{aq}^- and transition metal complexes.

By definition,[19] the inner coordination shells of oxidant and reductant remain intact in an outer-sphere transition state, while the two reactants share a common, bridging ligand in an inner-sphere transition state. In other words, no reduction in coordination number of the inner coordination shell is necessary in the two reactants prior to outer-sphere electron transfer, whereas an inner-sphere process requires the splitting off of a ligand (usually water in aqueous systems) from one reactant in order to enter into a bridged transition state with the other reactant.

The structure of the hydrated electron is not yet settled, but perhaps a reasonable physical picture converges on a model where the electron density resides principally inside of a three-dimensional hydrogen-bonded cage of four water molecules, whose oxygen atoms occupy the apices of a tetrahedron.[20] Such a picture would harmonize with some of the latest thinking on the molecular architecture of water[21] which claims a remarkably open structure for liquid water, where icelike, four-coordinate (probably tetrahedral) molecular clusters account for most of the solvent species. These clusters exist in a state of equilibration with the free (non-hydrogen-bonded) water molecules present in the void spaces. The average lifetime ($<10^{-11}$ sec for breaking and re-forming) of a tetrahedral cluster would explain the constant, rapid motion[22,23] attributed to the hydrated electron, as the electron tunnels from cluster to cluster.

If hydrated electron reactions hold any meaning within the outer-sphere–inner-sphere framework, such meaning would have to be inferred from the structure of e_{aq}^-. It would seem reasonable to define the "inner coordination shell" of the hydrated electron as including the four water molecules tetrahedrally disposed about the electron-trapping region and that this "inner coordination shell" remains intact in the case of an *outer-sphere* transition state with the metal complex. The actual electron transfer from e_{aq}^- to the metal complex probably occurs *via* a tunneling mechanism.

The substantial (1.7 eV) binding energy of e_{aq}^- would tend to exclude an *inner-sphere* electron-transfer mechanism for hydrated electron reactions, which presumably would involve the splitting off of an apical H_2O from the "inner shell" tetrahedron of e_{aq}^-. The time required for the splitting-off step and the subsequent closing in of the metal complex should find the electron escaped from its trap and tunneling to a new tetrahedral site.

Inspection of the rate constants of e_{aq}^- with the corresponding lower field cobalt(III)–ammine complexes (Table III) reveals no obvious trends. If a heteroligand field effect occurs in the $Co(NH_3)_5X^{n+}$ system, it is likely obscured by the diffusion-controlled nature of the hydrated electron encounter with these complexes.

TABLE III

SOME RATE CONSTANTS FOR THE REACTION $e_{aq}^- + Co(NH_3)_5X^{n+}$ [a]

X	$10^{-10}k_e$	X	$10^{-10}k_e$	X	$10^{-10}k_e$
NH_3	8.1	N_3^-	6.3	Cl^-	6.1
CN^-	6.3	F^-	7.6	Br^-	6.2
H_2O	6.0				

[a] M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotop.*, **18**, 493 (1967).

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Iridium(III) and Rhodium(III) Mono- and Bis(1,10-phenanthroline) Complexes and the Optical Isomers of Iridium(III), Rhodium(III), Chromium(III), and Cobalt(III) Dihalogenobis(1,10-phenanthroline) Complex Cations

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phenH[$IrCl_4$phen] (phen = 1,10-phenanthroline) has been prepared, characterized, and used to synthesize new mono and bis complexes of Ir(III) and the tetrachloro-1,10-phenanthrolineiridium(IV) species. Similar reactions have led to greatly improved syntheses of the corresponding Rh(III) complexes. Separate thermal and photochemical aquation reactions of $IrCl_4$phen$^-$ have given tentative "*fac*"- and "*mer*"-$IrX_3(H_2O)$phen (X = Cl or Br), respectively. Chromatographic resolution on cellulose has enabled the assignment of cis configurations to iridium(III), rhodium(III), chromium(III), and cobalt(III) dihalogenobis(1,10-phenanthroline) complex cations. Infrared, nmr, and X-ray diffractometric measurements are also in agreement with a cis geometry. Infrared, ultraviolet, and visible spectra and X-ray diffraction data are reported for the new compounds.

Introduction

Failure of the reported method[1] to give the *trans*-dichlorobis(1,10-phenanthroline)iridium (III) cation has led us to investigate further the chemistry of this metal–ligand system.

In a preliminary note[2] the reaction of 1,10-phenanthroline with ammonium hexachloroiridate(III) in dilute hydrochloric acid was shown to give 1,10-phenanthrolinium tetrachloro(1,10-phenanthroline)iridate(III) instead of *trans*-dichlorobis(1,10-phenanthroline)iridium(III) chloride. We now report the results of these reactions in detail together with a wider study of the synthesis, characterization, and isomerism of other new iridium(III)- and -(IV)–1,10-phenanthroline complexes. For comparative purposes some related reactions of Rh(III), Co(III), and Cr(III) compounds with this ligand have been investigated.

Although iridium(III) complexes are characteristically inert, the presence of strong sunlight is known to accelerate reactions.[3] Delepine[4] reported photochemical effects in his studies of iridium–pyridine complexes and subsequent workers[5-7] have made use of this to synthesize new compounds. In the present work the different reactions of $IrCl_4$phen$^-$ in the dark and in the light enable the isolation of both facial and meridional isomers of $IrCl_3H_2O$phen. Further, the photochemical aquation of *cis*-$IrCl_2(phen)_2^+$ provides an opportunity to attempt an asymmetric synthesis by utilizing circularly polarized light as the radiation. This type of experiment has been tried unsuccessfully by Jaeger and Berger[8] using $Co(C_2O_4)_3^{3-}$ and by Garvan[9] using the rhodium(III)–ethylenediamine- and -propylenediaminetetraacetic acid complexes.

The total resolution of a complex cation using ion-exchange chromatography was first described by Brubaker, Legg, and Douglas.[10] Our previously reported resolution[1] of *cis*-dichlorobis(1,10-phenanthroline)iridium(III) was not in fact produced by the sodium arsenyl (+)-tartrate employed but rather was a consequence of the cellulose ion exchangers used to remove the resolving agent. We now find that the use of cation-exchange cellulose provides a general method of resolution for Ir(III), Rh(III), Co(III), and Cr(III) bis(1,10-phenanthroline)metal complexes.

Experimental Section

Materials.—Ammonium and sodium hexachloroiridate(III) were obtained from Johnson Matthey and Co. and rhodium(III) chloride trihydrate was from Fluka, Buchs, Switzerland. The compounds formulated as $IrO_2 \cdot 2H_2O$ and $Rh_2O_3 \cdot 3H_2O$ were prepared by published methods.[11,12] Purple *cis*-$[CoCl_2(phen)_2]Cl \cdot 3H_2O$ and brown-green $[CrCl_2(phen)_2]Cl$ were prepared by the methods of Ablov[13] and Burstall and Nyholm,[14] respectively.

1,10-Phenanthrolinium Tetrachloro(1,10-phenanthroline)-iridate(III), $(C_{12}H_9N_2)[IrCl_4(C_{12}H_8N_2)]$.—Ammonium hexachloroiridate(III) dihydrate (0.5 g) in water (20 ml) was added to a solution of 1,10-phenanthroline hydrate (0.6 g) in hot water (40 ml) containing hydrochloric acid (0.04 ml, 10 *M*). The solution was stirred magnetically and heated at the boil for a period of 2 hr. The product began to precipitate after the first 10 min as shiny red-orange crystals. The product was filtered off

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