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Iridium Complexes of the Type $[\mathrm{Ir}^{n+}(\mathrm{en}\text{-}x\mathrm{H})_y]^{(n-yx)+}$[1,2]

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The interaction of tris-(ethylenediamine)-iridium(III) iodide and potassium amide in liquid ammonia at low temperatures has been shown to provide a sequence of products corresponding to successive removal of protons from the ligand nitrogen atoms. Of these products, $[\mathrm{Ir(en\text{-}H)_2(en)}]\mathrm{I}$ and $\mathrm{K_2[Ir(en\text{-}2H)_2(en\text{-}H)]}$ have been isolated and characterized. The former also has been produced by the reduction of tris-(ethylenediamine)-iridium(III) iodide with solutions of potassium in ammonia. Numerous properties and reactions of these species are described.

Earlier work in this laboratory[3-5] has demonstrated that protons associated with the ligand nitrogen atoms in $[\mathrm{Pt(en)_2}]\mathrm{I_2}$ and $[\mathrm{Pd(en)_2}]\mathrm{I_2}$ are sufficiently acidic to permit their successive removal by reaction with the basic amide ion in liquid ammonia. Thus from the above complexes, $[\mathrm{Pt(en\text{-}H)(en)}]\mathrm{I}$, $[\mathrm{Pt(en\text{-}H)_2}]$, $\mathrm{K[Pt(en\text{-}2H)(en\text{-}H)]}$, $[\mathrm{Pd(en\text{-}H)(en)}]\mathrm{I}$, and $[\mathrm{Pd(en\text{-}H)_2}]$ have been isolated and characterized. Evidence for charge transfer from ligand atom to central metal ion has been found for $[\mathrm{Pd(en\text{-}H)(en)}]^+$ but the others appear to be π-bonded complexes. Evidence for the formation of analogous species has been recorded earlier, *i.e.*, $[\mathrm{Au(en\text{-}H)(en)}]\mathrm{Br_2}$ from aqueous solution[6] and $[\mathrm{Os(en\text{-}H)(en)_2}]\mathrm{Br_3}$, $[\mathrm{Os(en\text{-}H)_2(en)}]\mathrm{I_2}$, $[\mathrm{Os(en\text{-}H)_2(en)_2}]\mathrm{I_2}$, $[\mathrm{Os(en\text{-}H)_3(en)}]\mathrm{I_2}$, and $[\mathrm{Os(en\text{-}H)_4}]\mathrm{I_2}$ from anhydrous ethylenediamine.[7] The properties of the platinum and palladium complexes (as well as of those reported in the present paper) are consistent with the well known acidic properties of ligands (in general[8]) bonded to transitional metals, and ethylenediamine[9] and substituted ethylenediamines[10] in particular.

The present paper is concerned with the synthesis and properties of analogous species derived from tris-(ethylenediamine)-iridium(III) ion.

Experimental

With one exception, all equipment, experimental procedures, and materials were the same as those described elsewhere.[11]

Tris-(ethylenediamine)-iridium(III) iodide was prepared by a modification of the method of Lebedinskii[12] designed to provide higher yields. In a typical case, 5 g. of $\mathrm{Na_3IrCl_6}\cdot x\mathrm{H_2O}$ (where $x \cong 2$), 50 ml. of water, and 10 ml. of 95% ethylenediamine were heated in a sealed tube at 145° for 20 hr. The tube was cooled in the autoclave, opened, and the reaction mixture was filtered. The filtrate was evaporated to dryness under reduced pressure on a steam bath to remove excess ethylenediamine. The residue was dissolved in a minimum of water, filtered, and evaporated to a volume of 25 ml. Addition of 10 g. of KI followed by cooling to 0° resulted in the formation of a finely divided tan precipitate which continued to crystallize for *ca.* 5 hr. This product was filtered, dissolved in 20 ml. of hot water, and recrystallized by the addition of 10 g. of NaI and then cooling at 0° for 5 hr. The resulting tan crystals were filtered, washed several times with ethanol, and dried at 110° for 2 hr. The yield was 3.15 g. or 43% based on iridium used as hydrated $\mathrm{Na_3IrCl_6}$. *Anal.* Calcd. for $[\mathrm{Ir(en)_3}]\mathrm{I_3}$: Ir, 25.6; I, 50.5. Found: Ir, 25.2; I, 50.5. X-Ray diffraction data for this compound are included in Table I. The ultraviolet absorption spectrum of a solution of $[\mathrm{Ir(en)_3}]\mathrm{I_3}$ in water showed no change with time; maxima at 226 mμ (attributable to iodide ion) and 320 mμ [attributable to tris-(ethylenediamine)-iridium(III) ion][13] were observed. The infrared spectrum of solid $[\mathrm{Ir(en)_3}]\mathrm{I_3}$ (in KBr) exhibited bands at 3310, 3090, and 1460 cm.$^{-1}$.[14] As expected, this substance was found to be diamagnetic at 25°.

Preliminary Experiments.—In order to establish that $[\mathrm{Ir(en)_3}]\mathrm{I_3}$ is not solvolyzed by ammonia, 0.537 g. of the iodide was treated with 5.5 ml. of liquid ammonia in a

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[2] Where (en-*x*H) denotes the removal of *x* protons from ligand nitrogen atoms.

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sealed tube for 12 hr. at 25°. The solvent was removed completely and the residual solid was shown to be identical with the starting material by analysis and an X-ray diffraction pattern (Table I). *Anal.* Calcd. for $[Ir(en)_3]I_3$: Ir, 25.6; I, 50.5. Found: Ir, 25.5; I, 50.5.

TABLE I

X-RAY DIFFRACTION DATA FOR TRIS-(ETHYLENEDIAMINE)-IRIDIUM(III) IODIDE[a]

Starting material		After exposure to $NH_3(l)$ at 25°	
d, Å.	I/I_0	d, Å.	I/I_0
7.20	0.90	7.16	1.00
5.18	.15	5.13	0.20
4.69	.20	4.65	$.15^b$
4.35	1.00	4.34	1.00
4.19	0.15^b	4.19	0.20
3.67	.30	3.63	.50
3.51	.20	3.47	.20
From $[Ir(en\text{-}H)_2(en)]I$ + 2HI		From $K_2[Ir(en\text{-}2H)_2(en\text{-}H)]$ + 5HI	
d, Å.	I/I_0	d, Å.	I/I_0
7.12	1.00	7.16	1.00
5.19	0.20	5.19	0.20
4.41	1.00	4.34	1.00
4.14	0.20^b	4.19	0.20^b
3.53	0.80	3.58	0.30

[a] All X-ray diffraction data reported in this paper were obtained from patterns made using CuK_α radiation (Ni filter), 35 kv. tube voltage, 15 mamp. filament current, and 6–8 hr. exposure times. Samples were diluted with 1–5 volumes of starch; relative intensities were estimated visually. [b] Less intense lines not included here.

Following equilibration of excess $[Ir(en)_3]I_3$ with anhydrous liquid ammonia at −33.5°, the solubility of this substance was estimated to be of the order of 0.2 g./100 ml. of NH_3 on the basis of the weight of the iodide recovered from a known volume of the solvent.

In order to explore the over-all reaction between $[Ir(en)_3]I_3$ and potassium amide, 0.383 g. of the iodide was dissolved and suspended in 50 ml. of ammonia and titrated potentiometrically with the potassium amide (11.2 molar equivalents) formed from 0.231 g. of potassium. Complete dissolution of the iodide occurred upon addition of 0.72 equivalent of KNH_2, and the appearance of a white voluminous solid was observed after addition of 1.6 equivalents; this solid continued to form until 3 equivalents of amide had been added, whereupon the color of the solid began to change from white to gray and the previously colorless solution assumed a distinct purple color. At 4 equivalents of KNH_2, both the solid phase and the solution were purple; at 5.2, they were tan and red, respectively. The tan solid was digested in the red solution for 2 hr. without change in the appearance of either component or in the observed potential. Accordingly, the remainder of the amide solution was added and the tan precipitate was digested in the presence of excess amide for 12 hr. The solution was removed by filtration and the solid was washed 5 times with 30-ml. portions of ammonia. Following complete removal of the solvent from the very small quantity of solid product, an X-ray diffraction pattern led to the data listed in Table II. During the course of this titration, significant changes in potential that correlated reasonably well with the addition of successive molar equivalents of potassium amide and with the recorded changes in the colors of the solids and solutions were observed. From a differential plot of potential *vs.* volume of amide solution added, the calculated and observed (in parentheses) $KNH_2/[Ir(en)_3]I_3$ ratios were found: 1 (0.92), 2 (1.84), 3 (2.8), 4 (4.0), 5 (5.2). It is important also to record the fact that only the products corresponding to 2 and 5 mole ratios were sufficiently insoluble to permit their isolation and purification (see below). Experiments not reported in detail here but which were designed to permit isolation of the ammonia-soluble iridium-containing species were based upon possible reactions of such species with strong Lewis acids; these experiments did not lead to useful results.

TABLE II

X-RAY DIFFRACTION DATA FOR $[Ir(en\text{-}H)_2(en)]I$ AND $K_2[Ir(en\text{-}2H)_2(en\text{-}H)]$[a]

$[Ir(en\text{-}2H)_2(en)]I$			
From $[Ir(en)_3]I_3$ + $2KNH_2$		From $[Ir(en)_3]I_3$ + 2K	
d, Å.	I/I_0	d, Å.	I/I_0
7.56	1.00	7.56	1.00
5.03	0.05^b	5.03	0.40
4.41	.90	4.39	.80
2.90	.10	2.89	.10
2.55	.25	2.54	.20
2.21	.10	2.20	$.10^b$
$K_2[Ir(en\text{-}2H)_2(en\text{-}H)]$			
From $[Ir(en)_3]I_3$ + $11.2KNH_2$		From $[Ir(en)_3]I_3$ + $5KNH_2$	
7.57	1.00	7.62	1.00
6.09	0.90	6.09	0.90
5.11	.30	5.14	.30
3.30	$.05^b$	3.31	$.05^b$

[a] See footnote (*a*), Table I. [b] Less intense lines not included here.

Isolation of $[Ir(en\text{-}H)_2(en)]I$.—A solution and suspension of 0.690 g. of $[Ir(en)_3]I_3$ in 50 ml. of ammonia was treated with a solution containing exactly two molar equivalents of KNH_2 in 25 ml. of ammonia. The resulting tan precipitate was separated by filtration, and washed 4 times with 15-ml. portions of ammonia. After complete removal of the solvent under reduced pressure, the solid was transferred to the dry box for removal of samples. *Anal.* Calcd. for $[Ir(en\text{-}H)_2(en)]I$: Ir, 38.7; I, 25.5. Found: Ir, 38.1; I, 24.7; X-ray diffraction data are given in Table II.

This same complex also was formed by reducing 0.5347 g. of $[Ir(en)_3]I_3$ with a solution of 0.261 g. of potassium in 18.6 ml. of ammonia. After addition of 9.4 ml. (1 equivalent) of the titrant, all of the iodide had dissolved and the solution was colorless. After addition of 14 ml. (1.67 equivalents), a white precipitate began to form and continued to form until the solution assumed a permanent blue color. Hydrogen was evolved throughout the course of the reaction. Collection of hydrogen was continued while the solvent was evaporated and while the solid reaction products were maintained at 25° for 12 hr.[15] The total water-insoluble gas was found by analysis to consist of 48.0 cc. (2.08 equivalents) of hydrogen. The reaction vessel again was cooled to −33.5°, the solid product was washed 5 times with 30-ml. portions of ammonia, and the solvent was removed under reduced pressure. *Anal.* Calcd. for $[Ir(en\text{-}H)_2(en)]I$: Ir, 38.7; I, 25.5. Found: Ir, 38.5; I, 24.2; X-ray diffraction data are included in Table II.

In view of the preceding results, it was of interest to determine whether the same iridium complex could be produced by the tandem addition of molar equivalents of amide and metal solution. Accordingly, 1.044 g. of $[Ir(en)_3]I_3$ in 50 ml. of ammonia was titrated with the KNH_2 formed from 0.0543 g. (one equivalent) of potassium to provide a clear solution which then was titrated with a solution of 0.0175 g. of potassium in 25 ml. of ammonia. A permanent blue color persisted after addition of 1.04 equivalents of the potassium solution. The ammonia-insoluble product was treated as described above; during the addition of potassium, 3.5 cc. (0.19 equivalent) of hydrogen was collected. *Anal.* Calcd. for $[Ir(en\text{-}H)_2(en)]I$: Ir, 38.7. Found: Ir, 38.4. This product gave an X-ray diffraction pattern substantially identical with those which led to the data recorded in Table II.

In all experiments of the types described above, analysis of the combined filtrates and washings failed to provide a measure of the removal of iodide ion from $[Ir(en)_3]I_3$ because $[Ir(en\text{-}H)_2(en)]I$ is appreciably soluble in liquid ammonia. The presence of KI in the residues remaining upon evaporation of the solvent, however, was confirmed by X-ray diffraction patterns.

Properties and Reactions of $[Ir(en\text{-}H)_2(en)]I$.—This substance was found to be diamagnetic at 25°. The ultraviolet absorption spectrum of an aqueous solution of the monoiodide exhibitied maxima at 220 and 320 mμ; these are attributable to I^- and $[Ir(en)_3]^{3+}$, respectively. Anticipated measurements of dipole moment and conductance were precluded by the fact that $[Ir(en\text{-}H)_2(en)]I$ does not retain its identity upon dissolution in any polar solvent.

Titration of an aqueous solution of 0.196 g. of $[Ir(en\text{-}H)_2(en)]I$ required 4.15 ml. of 0.185 *N* hydriodic acid solution (1.92 equivalents). The solid product isolated from the resulting solution gave an X-ray diffraction pattern identical with that for pure $[Ir(en)_3]I_3$ (Table I). Similarly, 0.19 g. of the monoiodide in 25 ml. of ammonia was titrated potentiometrically with a solution of 0.249 g. of ethylenediammonium iodide in 26 ml. of ammonia. The maximum rate of change of potential occurred upon addition of 12.5 ml. (1.92 equivalents) of the acid. The reaction mixture was filtered, and the solid product was washed 4 times with 10-ml. portions of ammonia and dried *in vacuo* at room temperature. *Anal.* Calcd. for $[Ir(en)_3]I_3$: Ir, 25.6; I, 50.6. Found: Ir, 25.0; I, 49.9. The X-ray pattern confirmed the identity of the product. In an analogous experiment, 0.467 g. of $[Ir(en)_3]I_3$ was converted (as described above) to $[Ir(en\text{-}H)_2(en)]I$ by treatment with 2.03 equivalents of potassium amide in ammonia solution; this was back-titrated (potentiometrically) with a solution of 0.175 g. of NH_4I in 24.8 ml. of liquid ammonia. The end-point corresponded to 24.7 ml. of the acid solution, or 1.98 equivalents.

In order to distinguish between $[Ir(en\text{-}H)_2(en)]I$ and the less probable $[Ir(en\text{-}2H)(en)_2]I$, 0.1797 g. of the product in question was thermally decomposed at *ca.* 10^{-3} mm. under conditions such that volatile products could be collected in a trap cooled with Dry Ice–2-propanol. At 123 ± 5°, the color of the solid changed from white to purple without loss in weight; at 135 ± 5°, small droplets of colorless liquid began to condense in the trap; at 160 ±5°, the color of the solid sample began to change from purple to red-brown. The solid attained constant weight at 170 ± 5°, and there was no further change upon heating to 415°. The liquid that condensed in the trap was identified as ethylenediamine by both mass spectrographic analysis and by the fact that the melting point of its picrate was not depressed by admixture with an authentic specimen. The total measured loss of weight from the sample was 22 mg.; that calculated for loss of one ethylenediamine ligand was 23 mg.

Isolation of $K_2[Ir(en\text{-}2H)_2(en\text{-}H)]$.—Treatment of 0.965 g. of $[Ir(en)_3]I_3$ in 75 ml. of ammonia with 0.365 g. (5.25 equivalents) of potassium amide in 25 ml. of ammonia resulted in the formation of a tan precipitate and a deep red solution. The solid product was separated, washed, and dried as described above. Analysis of the combined filtrate and washings accounted for 98.0% of the iodine used as $[Ir(en)_3]I_3$. *Anal.* Calcd. for $K_2[Ir(en\text{-}2H)_2(en\text{-}H)]$: Ir, 43.2; N, 18.1. Found: Ir, 42.7; N, 18.1; X-ray diffraction data are given in Table II.

A 0.1530-g. sample of this product was dissolved in water and titrated potentiometrically with 0.0824 *N* hydriodic acid solution; complete neutralization required 4.9 equivalents of acid. The solid recovered from the resulting solution gave an X-ray diffraction pattern identical with that for $[Ir(en)_3]I_3$.

Discussion

The data presented above indicate that the ethylenediamine ligands in $[Ir(en)_3]I_3$ are sufficiently acidic to permit the successive abstraction of a maximum of five protons by reaction with the rather strongly basic amide ion in liquid ammonia at −33.5°; *i.e.*

$$[Ir(en)_3]^{3+} + NH_2^- \longrightarrow [Ir(en\text{-}H)(en)_2]^{2+} + NH_3 \quad (1)$$

$$[Ir(en\text{-}H)(en)_2]^{2+} + NH_2^- \longrightarrow [Ir(en\text{-}H)_2(en)]^+ + NH_3 \quad (2)$$

$$[Ir(en\text{-}H)_2(en)]^+ + NH_2^- \longrightarrow [Ir(en\text{-}H)_3]^0 + NH_3 \quad (3)$$

$$[Ir(en\text{-}H)_3]^0 + NH_2^- \longrightarrow [Ir(en\text{-}2H)(en\text{-}H)_2]^- + NH_3 \quad (4)$$

$$[Ir(en\text{-}2H)(en\text{-}H)_2]^- + NH_2^- \longrightarrow [Ir(en\text{-}2H)_2(en\text{-}H)]^{2-} + NH_3 \quad (5)$$

The formation of all of the postulated iridium species is strongly indicated by the potentiometric titration data; in addition, the products of reactions 2 and 5 have been isolated as the iodide and potassium salt, respectively, and characterized. That reaction 5 represents the maximum extent of reaction at −33.5° was demonstrated

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[15] Only a fraction of the total hydrogen was evolved at −33.5°; hence it was found necessary to raise the temperature prior to separation and purification of the ammonia-insoluble product.

by the fact that $[Ir(en\text{-}2H)_2(en\text{-}H)]^{2-}$ is unreactive toward a large excess of amide ion over many hours; this, however, does not preclude the possibility of more extensive reaction at higher temperatures.[7] The identity of $[Ir(en\text{-}H)_2(en)]^+$ as opposed to $[Ir(en\text{-}2H)(en)_2]^+$ has been supported by the fact that pyrolysis of the iodide yields one rather than two moles of ethylenediamine per mole of iodide. The present and earlier work[3-5] have shown that ethylenediamine is not recovered from (en-H) and (en-2H) ligands by pyrolysis *in vacuo*.

Although it might appear attractive to suggest that the formation of $[Ir(en\text{-}H)_2(en)]^+$ by the reduction of $[Ir(en)_3]^{3+}$ with potassium in ammonia results from catalytic conversion of K to KNH_2 followed by reactions 1 and 2, this view is untenable for the reasons that are given: The rate of utilization of potassium is vastly greater than the rate of hydrogen evolution; in fact, hydrogen evolution continues for several hours following disappearance of the blue color characteristic of potassium solutions in ammonia and during which time the reaction mixture is warmed to and maintained at room temperature. Furthermore, the maximum quantity of hydrogen collected at −33.5° in any of these experiments is sufficient to account for only a fraction of the total potassium consumed.

There are, however, two alternatives. The first involves a fast and complete two-electron reduction of Ir^{3+} to Ir^+ followed by a relatively slow elimination of hydrogen

$$[Ir^{3+}(en)_3]^{3+} + 2e^- \longrightarrow [Ir^+(en)_3]^+ \tag{6}$$

$$[Ir^+(en)_3]^+ \longrightarrow [Ir^{3+}(en\text{-}H)_2(en)]^+ + H_2 \tag{7}$$

The second is predicated upon reduction of Ir^{3+} only to Ir^{2+} *via* the reactions

$$[Ir^{3+}(en)_3]^{3+} + e^- \longrightarrow [Ir^{2+}(en)_3]^{2+} \tag{8}$$

$$[Ir^{2+}(en)_3]^{2+} \longrightarrow [Ir^{3+}(en\text{-}H)(en)_2]^{2+} + {}^1/_2H_2 \tag{9}$$

$$[Ir^{3+}(en\text{-}H)(en)_2]^{2+} + e^- \longrightarrow [Ir^{2+}(en\text{-}H)(en)_2]^+ \tag{10}$$

$$[Ir^{2+}(en\text{-}H)(en)_2]^+ \longrightarrow [Ir^{3+}(en\text{-}H)_2(en)]^+ + {}^1/_2H_2 \tag{11}$$

where the rate of (9) is significantly greater than that of (11). Thus the formation of $[Ir^{3+}(en\text{-}H)_2(en)]^+$ by the reduction of $[Ir^{3+}(en)_3]^{3+}$ with potassium solution may be accounted for by assuming reduction to either Ir^+ or Ir^{2+}. Support for reactions 8–11 inclusive in preference to reactions 6 and 7, however, is provided by the data given above, *i.e.*, the experiment in which the product in question was formed under conditions that provide only for reduction of Ir^{3+} to Ir^{2+}. Thus, treatment of $[Ir^{3+}(en)_3]^{3+}$ with one molar equivalent of potassium amide followed by one equivalent of potassium should provide $[Ir^{3+}(en\text{-}H)_2(en)]^+$ *via* the reactions

$$[Ir^{3+}(en)_3]^{3+} + NH_2^- \longrightarrow [Ir^{3+}(en\text{-}H)(en)_2]^{2+} + NH_3 \tag{12}$$

$$[Ir^{3+}(en\text{-}H)(en)_2]^{2+} + e^- \longrightarrow [Ir^{2+}(en\text{-}H)(en)_2]^+ \tag{13}$$

$$[Ir^{2+}(en\text{-}H)(en)_2]^+ \longrightarrow [Ir^{3+}(en\text{-}H)_2(en)]^+ + {}^1/_2H_2 \tag{14}$$

The implied instability of these presumably σ-bonded species is consistent with the fact that coördination compounds of iridium in its lower oxidation states exhibit stability only in combination with π-bonding ligands.[16,17]

The strong base properties of $[Ir(en\text{-}H)_2(en)]I$ have been demonstrated by (a) the fact that the ultraviolet absorption spectrum of an aqueous solution of this substance is identical with that of $[Ir(en)_3]I_3$, and (b) regeneration of $[Ir(en)_3]I_3$ by treatment with two equivalents of aqueous hydriodic acid or with two equivalents of either ammonium iodide or ethylenediammonium iodide in liquid ammonia. Similarly, conversion of $K_2[Ir(en\text{-}2H)_2(en\text{-}H)]$ to $[Ir(en)_3]I_3$ was shown to require almost exactly the anticipated five equivalents of aqueous hydriodic acid.

The present results together with those from earlier experiments[3-7] indicate that, in a medium of any given basicity, the acid properties of the ethylenediamine ligands are enhanced by high charge and small size of the central metal ion. Thus, $[Pt(en)_2]^{2+}$ and $[Pd(en)_2]^{2+}$ are stable in the presence of aqueous ethylenediamine, but $[Au(en)_2]^{3+}$ is converted to $[Au(en\text{-}H)(en)]^{2+}$. Similarly, the ethylenediamine complexes of Os^{4+} and Os^{5+} appear to be strongly acidic toward anhydrous ethylenediamine,[7] while the corresponding Os^{3+} species are considerably less so toward amide ion in liquid ammonia.[18] These same trends are evident upon comparison of the reactions of the ethylenediamine complexes of Pt^{2+}, Pd^{2+}, Ir^{3+}, and Os^{3+} with solutions of amide ion in ammonia.

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