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Compounds of Platinum in Lower Oxidation States. II. Evidence for the Existence of K[Pt(en-H)(en-2H)] and [Pt(en)(en-H)][1]

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The reaction of bisethylenediamineplatinum(II) iodide in liquid ammonia at −33.5° with potassium amide in excess of three molar equivalents has been shown most probably to yield ammonia-soluble $K[Pt^{II}(en\text{-}H)(en\text{-}2H)]$. The reaction of the iodide with successive one molar equivalent quantities of potassium amide and potassium has provided indirect evidence for the formation of unstable $[Pt^{I}(en)(en\text{-}H)]^0$; the role of this species in the spontaneous decomposition of $[Pt(en)_2]^0$ is discussed.

It was reported[2] previously that bisethylenediamineplatinum(II) iodide reacts with one and two equivalents of potassium amide in liquid ammonia to provide basic platinum–ethylenediamine complexes in which one and two protons, respectively, are removed from the amino groups of the coördinated ligands. The reduction of bisethylenediamineplatinum(II) iodide was shown to yield compounds of $Pt^{<2+}$ which decompose spontaneously at −33.5° to form basic complexes of the type referred to above and hydrogen; at 25° the decomposition yields only platinum and ethylenediamine. The demonstrated mode of decomposition of bisethylenediamineplatinum(I) iodide involves an initial disproportionation that regenerates starting material and at the same time forms bisethylenediamineplatinum(0), $[Pt(en)_2]^0$.

Since the low temperature decomposition of the latter product results in the formation of $[Pt(en\text{-}H)_2]^0$, it seemed reasonable to assume that the hitherto undetected species $[Pt^{I}(en)(en\text{-}H)]^0$ might exist at least transitorily as an intermediate in the decomposition process. In view of the results reported previously, it is evident that it should be possible to form this material by the reactions

$$[Pt^{II}(en)_2]I_2 + KNH_2 \longrightarrow [Pt^{II}(en)(en\text{-}H)]I + KI + NH_3 \quad (1)$$

$$[Pt^{II}(en)(en\text{-}H)]I + K^+ + e^- \longrightarrow [Pt^{I}(en)(en\text{-}H)]^0 + KI \quad (2)$$

Detection of this product not only would provide additional evidence bearing upon the mechanism of decomposition of $[Pt(en)_2]^0$ but also would complete the sequence of basic complexes derivable from bisethylenediamineplatinum(II) iodide. Although the experiments described below show that $[Pt^{I}(en)(en\text{-}H)]^0$ is unstable, evidence in support of its formation has been obtained through the study of its decomposition products.

Also in the course of the earlier investigation,[2] we obtained evidence indicating that treatment of bisethylenediamineplatinum(II) iodide with potassium amide considerably in excess of three equivalents results in the formation of an ammonia-soluble species in which platinum was assumed to be in the form of an anionic complex. This product was assumed tentatively to be $K[Pt^{II}(en\text{-}H)(en\text{-}2H)]$; supporting evidence was not then available but is provided by the experiments described below.

Experimental

All materials, experimental methods and procedures employed in this work were essentially the same as those described or referred to previously.[2]

The Conversion of $[Pt(en\text{-}H)_2]$ to $K[Pt(en\text{-}H)(en\text{-}2H)]$.—Since all of the ultimate products of the direct treatment of bisethylenediamineplatinum(II) iodide with excess potassium amide are ammonia-soluble, the complexity of the end product mixture was minimized as follows. A 3.2345-g. sample of $[Pt(en)_2]I_2$ in 75 ml. of anhydrous liquid ammonia at −33.5° was treated dropwise with an ammonia solution of the potassium amide previously formed from 0.6675 g. of potassium (equivalent to three moles[2] of $[Pt(en)_2]I_2$). The resulting precipitate of $[Pt(en\text{-}H)_2]$ was filtered, washed with three 50-ml. portions of ammonia, resuspended in 50 ml. of ammonia and treated dropwise with additional potassium amide solution. The white solid redissolved to form an intensely green-yellow solution; this conversion was complete upon addition of a total of 1.54 equivalents of amide. Upon evaporation of the solvent, a white crystalline solid separated; this was dried *in vacuo* at room temperature, and all subsequent transfers of the solid products were carried out in an anhydrous helium atmosphere.

A representative sample of the solid was transferred to a capillary tube and used in obtaining an X-ray diffraction pattern. Although potassium amide was inescapably present as a minor component, none of the *d*-spacings characteristic of this substance[3] were detected. From the otherwise satisfactory pattern that is attributed to $K[Pt(en\text{-}H)(en\text{-}2H)]$, the six most intense lines gave the following *d*-spacings (Å.); relative intensities are in parentheses: 9.04 (0.7), 8.22 (1.0), 6.32 (0.6), 5.82 (0.6), 5.16 (0.6), 5.00 (0.6).

A 0.9559-g. sample of the solid product was removed and dissolved in 100 ml. of 0.1040 *N* HCl; aliquots of this solution were taken for analysis. Found[4]: KNH_2, 0.0229 g. (0.416 mmole). Since upon dissolution of the solid sample in the standard acid, NH_2^- is converted to NH_4^+ and $K[Pt(en\text{-}H)(en\text{-}2H)]$ is converted to KCl and $[Pt(en)_2]Cl_2$,[2] the residual acidity should be equivalent to 16.2 ml. of 0.0979 *N* sodium hydroxide solution. Found: 16.0 ml.

The Reduction of $[Pt(en)(en\text{-}H)]I$ with Potassium.—In accordance with equation 1,[2] 5.8049 g. of $[Pt(en)_2]I_2$ in 80 ml. of liquid ammonia at −33.5° was converted to $[Pt(en)(en\text{-}H)]I$ by treatment with the potassium amide previously formed from 0.4211 g. of potassium. The white solid was washed four times with 25-ml. portions of ammonia; the combined supernatant solution and washings were found to contain 53.6% of the initial iodine and to be platinum-free.

The white solid was resuspended in 50 ml. of ammonia and treated with 4–5 drop portions of standard potassium solution; after each addition, 1–5 sec. was required for complete discharge of the blue color. After addition of a total of 10.74 mmole of potassium, a faint blue color persisted for 1 hr. Following filtration, the white solid was washed four times with 50-ml. portions of ammonia; the combined filtrate and washings were treated as described below.

The solid product was allowed to stand overnight at −33.5° during which time 1.31 mmoles of hydrogen was evolved without other evidence of change. The solid was then brought to 25° and allowed to stand overnight, where-

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[2] G. W. Watt, R. E. McCarley and J. W. Dawes, THIS JOURNAL, **79**, 5163 (1957).

[3] J. Kelly, Jr., and C. P. Kempter, *Z. anorg. allgem. Chem.*, **288**, 216 (1956).

[4] By the Kjeldahl procedure, but without digestion.

upon 0.276 mmole of hydrogen was liberated and the solid turned black owing to the liberation of elemental platinum. When the decomposition was complete, as evidenced by the cessation of hydrogen evolution, the solid black residue was washed twice with 50-ml. portions of ammonia. These washings were combined with the filtrate and washings from the preceding filtration. *Anal.* Found: elemental Pt, 0.0237 g. (0.121 mmole); water-soluble Pt, 0.0548 g. (0.281 mmole); I, 1.142 g. or 44% of that used in the initial reaction.

A small sample of the black solid residue was sealed in a capillary tube in an anhydrous helium atmosphere and used in obtaining an X-ray diffraction pattern[2] that led to the unequivocal identification of $[\mathrm{Pt(en\text{-}H)_2}]$ as the only water-soluble platinum-containing species present. Subsequently, a 2.3952-g. sample was similarly removed for analysis. Found: elemental Pt, 0.6707 g. (3.32 mmole); water-soluble Pt, 1.033 g. (5.29 mmoles); I, absent. The remainder of the black solid was washed out of the reactor and collected for analysis. Found: elemental Pt, 0.0811 g. (0.415 mmole); water-soluble Pt, 0.110 g. (0.570 mmole); I, absent. In order to provide supporting evidence for the presence of $[\mathrm{Pt(en\text{-}H)_2}]$ as the only water-soluble platinum-containing species present in the solid decomposition product, an aqueous aliquot calculated to require 11.72 mmoles of $\mathrm{H^+}$ for neutralization was titrated with standard hydrochloric acid.[2] Found: 11.75 mmole.

Discussion

The data presented above support the conclusion that the reaction between bisethylenediamineplatinum(II) iodide in liquid ammonia at −33.5° and potassium amide in excess of three molar equivalents occurs in accordance with the equation

$$[\mathrm{Pt(en)_2}]\mathrm{I_2} + 3\mathrm{KNH_2} \longrightarrow \mathrm{K}[\mathrm{Pt(en\text{-}H)(en\text{-}2H)}] + 2\mathrm{KI} + 3\mathrm{NH_3} \quad (3)$$

Since all of the products represented are soluble in liquid ammonia, including the excess potassium amide, the complexity of the mixture of reaction products was minimized as follows. The iodide was first converted successively[2] to $[\mathrm{Pt(en)(en\text{-}H)}]\mathrm{I}$ and the white ammonia-insoluble $[\mathrm{Pt(en\text{-}H)_2}]$; the latter was washed with liquid ammonia to provide an iodide-free product which was subsequently resuspended in ammonia and converted to the anionic platinum species represented above by the reaction with excess potassium amide. Upon complete removal of the solvent, a weighed sample of the mixture of $\mathrm{KNH_2}$ and $\mathrm{K}[\mathrm{Pt(en\text{-}H)(en\text{-}2H)}]$ was neutralized with an excess of standard hydrochloric acid and the residual acidity was back-titrated with standard base. The potassium amide present in the sample was determined by direct analysis and the extent of acid consumption by this constituent was thereby established. It was then assumed that the remaining acid neutralized was consumed in the reaction

$$\mathrm{K}[\mathrm{Pt(en\text{-}H)(en\text{-}2H)}] + 3\mathrm{HCl} \longrightarrow \mathrm{KCl} + [\mathrm{Pt(en)_2}]\mathrm{Cl_2} \quad (4)$$

As shown above, the experimental data are rigorously compatible with this interpretation. Although the solid mixture of $\mathrm{KNH_2}$ and $\mathrm{K}[\mathrm{Pt(en\text{-}H)(en\text{-}2H)}]$ gave a reproducible X-ray diffraction pattern, the absence of diffraction attributable to $\mathrm{KNH_2}$ is probably due to the fact that it is a minor component together with the fact that in order to obtain a satisfactory pattern in a reasonable exposure time, an eightfold dilution of the sample with starch was necessary. Furthermore, the known lines for $\mathrm{KNH_2}$ are all relatively weak.[3]

With reference to the species $[\mathrm{Pt(en)(en\text{-}H)}]^0$, it is apparent that synthesis from $[\mathrm{Pt(en)_2}]\mathrm{I_2}$ by successive reactions with potassium amide and potassium in liquid ammonia proceeded in accordance with expectations *via* reactions 1 and 2. However, as soon as $[\mathrm{Pt(en)(en\text{-}H)}]^0$ is formed, it begins to decompose slowly at −33.5° as

$$[\mathrm{Pt(en)(en\text{-}H)}] \longrightarrow [\mathrm{Pt(en\text{-}H)_2}]^0 + {}^1/_2\mathrm{H_2} \quad (5)$$

and hydrogen evolution provides a measure of the extent of occurrence of this reaction. Also, as soon as $[\mathrm{Pt(en)(en\text{-}H)}]^0$ is formed in reaction 2, a concurrent reaction with potassium ensues

$$[\mathrm{Pt(en)(en\text{-}H)}] + \mathrm{K^+} + e^- \longrightarrow \mathrm{K(Pt(en)(en\text{-}H)]} \quad (6)$$

When the reduction reaction was complete, as evidenced by the persistence of the blue color characteristic of the alkali metal solution, the platinum-containing products were found to consist of ammonia-insoluble iodine-free crystalline white solids that apparently were stable at −33.5°. At room temperature, however, the solid became gray-black and more hydrogen was evolved; these reactions are interpreted by (1) and (2).

(1) The unchanged $[\mathrm{Pt(en)(en\text{-}H)}]^0$ disproportionates[2]

$$2[\mathrm{Pt(en)(en\text{-}H)}]^0 \longrightarrow [\mathrm{Pt(en)(en\text{-}H)}]^+ + [\mathrm{Pt(en)(en\text{-}H)}]^- \quad (7)$$

and the disproportionation products interact according to

$$[\mathrm{Pt(en)(en\text{-}H)}]^+ + [\mathrm{Pt(en)(en\text{-}H)}]^- \longrightarrow [\mathrm{Pt(en\text{-}H)_2}]^0 + \mathrm{Pt} + 2\mathrm{en} \quad (8)$$

(2) The other product, $\mathrm{K}[\mathrm{Pt(en)(en\text{-}H)}]$, decomposes by two paths

$$\mathrm{K}[\mathrm{Pt(en)(en\text{-}H)}] \longrightarrow \mathrm{Pt} + \mathrm{en} + \mathrm{K(en\text{-}H)} \quad (9)$$

$$\mathrm{K}[\mathrm{Pt(en)(en\text{-}H)}] \longrightarrow \mathrm{K}[\mathrm{Pt(en\text{-}H)(en\text{-}2H)}] + \mathrm{H_2} \quad (10)$$

The evidence in support of this mechanism may be summarized.

Support for reaction 10 is found not only in the measured hydrogen evolution but also in the fact that extraction of the gray-black residue with liquid ammonia results in a solution that has the intense greenish-yellow color typical of $\mathrm{K}[\mathrm{Pt(en\text{-}H)(en\text{-}2H)}]$ solutions produced *via* reaction 3. Furthermore, if it is assumed that the rates of reactions 9 and 10 are substantially equal, it becomes possible to calculate the extent to which reaction 6 occurs, and the result should correspond to the amount of potassium added over and above the one equivalent required by reaction 2. In a typical case, the excess potassium added amounted to 0.53 mmole; that calculated on the basis of hydrogen evolved in the decomposition reaction at room temperature was 0.56 mmole. Further support is provided by the X-ray diffraction data and potentiometric titrations of the aqueous extract. Both lines of evidence show that the ammonia-washed residue left in the reactor consisted only of $[\mathrm{Pt(en\text{-}H)_2}]^0$, Pt and traces of presumably adsorbed ethylenediamine. Finally, if the foregoing interpretations are correct, twice the total hydrogen evolved at −33.5° should be equivalent to the water-soluble platinum remaining in the reactor less the elemental platinum liberated in reaction 8. In one set of experiments these values were 2.62 and 2.40

mmoles; in an entirely independent case, the corresponding values were 2.02 and 2.05 mmoles, respectively.

With respect to the role of $[Pt(en)(en\text{-}H)]^0$, the experiments involving this intermediate show that the decomposition of $[Pt(en)_2]^0$ is more complex than originally expected. The added complexity, however, arises from the unavoidable presence of excess potassium in the reaction mixture; this results in concurrent reactions that are not involved in the over-all reaction of $[Pt(en)_2]I_2$ with one equivalent of potassium since in this case the potassium is removed prior to the appearance of $[Pt(en)_2]^0$. Although $[Pt(en)(en\text{-}H)]$ undoubtedly appears in the reduction of $[Pt(en)_2]I_2$ with two equivalents of potassium before the excess potassium is removed by washing, the intermediate must react only slightly since after 3 to 4 hr. the final decomposition product, $[Pt(en\text{-}H)_2]^0$, is present to the extent of only about 10% of the Pt used originally as $[Pt(en)_2]I_2$. This interpretation is supported also by the persistence of the blue color at the end of the addition of potassium solution.

The unusual species derived from $[Pt(en)_2]I_2$ and reported in this and the preceding communication[2] may be summarized as

(1a) $[Pt(en)_2]I$ (2a) $[Pt(en)(en\text{-}H)]^0$
(1b) $[Pt(en)_2]^0$ (2b) $K[Pt(en)(en\text{-}H)]$

(3a) $[Pt(en)(en\text{-}H)]I$
(3b) $[Pt(en\text{-}H)_2]^0$
(3c) $K[Pt(en\text{-}H)(en\text{-}2H)]$

The complexes 1a and 1b contain platinum in the apparent 1+ and zero oxidation states. These products are unstable with respect to decomposition to elemental platinum and ethylenediamine at room temperature; at −33.5° they decompose with evolution of hydrogen and the formation of one or more of the basic complexes (3a, b, c). Although the dark red $[Pt(en)_2]I$ and the light pink $[Pt(en)_2]^0$ are both insoluble in liquid ammonia, their stabilities are of such a low order that evidence for their existence could be obtained only by analysis of their decomposition products.

The compounds 2a and 2b also contain platinum in their *apparent* 1+ and zero oxidation states, respectively, and their formation involves also the removal of a proton from a nitrogen atom in ethylenediamine coördinated with platinum. These are white ammonia-insoluble solids and evidence for their formation also was obtained through the study of their decomposition products.

The complexes 3a, 3b and 3c appear not only as decomposition products of (1a) and (1b) but also are formed by the interaction of $[Pt(en)_2]I_2$ with one, two and three equivalents of potassium amide. All three of these substances contain platinum in the 2+ oxidation state and although very hygroscopic, they are stable at room temperature in a dry inert atmosphere. Accordingly, these products were isolated, purified and subjected to direct analysis. Aqueous solutions of these products are strongly basic; this of course indicates the displacement of a proton from water. Both $[Pt(en)(en\text{-}H)]I$ and $[Pt(en\text{-}H)_2]^0$ are insoluble in liquid ammonia as well as in more than 20 common organic solvents.

Further studies on the structure of these unusual species are either in progress or are anticipated. Certain evidences suggest that at least some of these substances are polymeric; if so, the presence of platinum in 1+ and zero oxidation states may prove to be more apparent than real.

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Trichloroammineplatinate(II) Ion. Hydrolysis, Isotopic Exchange of Chloride and the *trans*-Effect

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Rates of isotopic exchange between the chloride ligands in $[Pt(NH_3)Cl_3]^-$ and in the acid hydrolysis product, $[Pt(NH_3)Cl_2(H_2O)]$, with Cl^- have been determined in aqueous solutions in the temperature range 0–30°. For each complex the exchange occurs by the observable acid hydrolysis and by additional chloride-independent processes. It is proposed that the non-equivalent chlorides in each complex undergo separate acid hydrolyses. Although all such hydrolysis reactions have roughly the same rate constant and ΔH^*, there is considerable variation in ΔF^0. In support of this proposal, the substitution of chloride by hydroxide in $[Pt(NH_3)Cl_2(H_2O)]$ has been found by a tracer technique to be unsymmetric, indicating the presence of the *cis*-isomer. The mechanism of the acid hydrolysis reactions is discussed.

Introduction

The reaction of trichloroammineplatinate(II) ion with ammonia yields predominantly the *cis*-$[Pt(NH_3)_2Cl_2]$. This procedure for the preparation of the *cis*-isomer is one of the most frequently cited examples of the *trans*-effect which illustrates that a chloride ligand has a greater *trans*-directing influence than ammonia. By this means the isomer is formed which is less stable in a thermodynamic sense since it is converted upon heating into the *trans*-isomer.[1]

The authors have reported in an earlier publication[2] studies of the kinetics of the reversible acid hydrolysis of $[Pt(NH_3)Cl_3]^-$ and $[Pt(NH_3)Cl_2(H_2O)]$ in dilute solutions. The system was described by the reactions

$$[Pt(NH_3)Cl_3]^- + H_2O \underset{k_1}{\overset{k_{-1}}{\leftrightarrows}} [Pt(NH_3)Cl_2(H_2O)] + Cl^- \qquad (1)$$

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[1] A. V. Nikolaev, *Compt. rend. acad. sci. U.R.S.S.*, **20**, 571 (1938).

[2] T. S. Elleman, J. W. Reishus and D. S. Martin, Jr., THIS JOURNAL, **80**, 536 (1958).