

with the attendant weaker binding of this condition. Such a similarity of thulium to samarium has been suggested by Selwood.<sup>10</sup> Holleck<sup>11</sup> has reported

- (10) P. W. Selwood, *THIS JOURNAL*, **56**, 2392 (1934).  
 (11) L. Holleck, *Angew. Chem.*, **50**, 819 (1937).

the existence of a divalent thulium ion when trapped in a strontium sulfate lattice. The divalent nature of thulium would appear to be a likely subject for further study.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

## Compounds of Platinum in the Zero Oxidation State<sup>1</sup>

BY GEORGE W. WATT, ROBERT E. MCCARLEY AND JAMES W. DAWES

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The reactions of  $[\text{Pt}(\text{en})_2]\text{I}_2$  with one and two molar equivalents of potassium amide in liquid ammonia at  $-33.5^\circ$  are shown to yield  $[\text{Pt}(\text{en-H})(\text{en})]\text{I}$  and  $[\text{Pt}(\text{en-H})_2]^0$ , respectively. Certain reactions of these species in both liquid ammonia and water are described. The reduction of  $[\text{Pt}(\text{en})_2]\text{I}_2$  with one equivalent of potassium in ammonia is shown to lead to an unstable  $[\text{Pt}(\text{en})_2]\text{I}$  which decomposes at  $-33.5^\circ$  to form  $[\text{Pt}(\text{en-H})(\text{en})]\text{I}$  and hydrogen, and disproportionates at higher temperatures to  $[\text{Pt}(\text{en})_2]\text{I}_2$  and  $[\text{Pt}(\text{en})_2]^0$ . The latter decomposes to form  $[\text{Pt}(\text{en-H})_2]^0$ , hydrogen, platinum and ethylenediamine. The reduction of  $[\text{Pt}(\text{en})_2]\text{I}_2$  with two equivalents of potassium provides  $[\text{Pt}(\text{en})_2]^0$  which decomposes in the manner indicated above.

Earlier work in this Laboratory has shown that the reduction of tetrammineplatinum(II) bromide<sup>2</sup> and bromopentammineiridium(III) bromide<sup>3</sup> with solutions of potassium in liquid ammonia yields amines of the corresponding metals in the zero oxidation state, *i.e.*,  $[\text{Pt}(\text{NH}_3)_4]$  and  $[\text{Ir}(\text{NH}_3)_5]$ . Among compounds of the transitional metals in the zero oxidation state,<sup>4</sup> these species are unusual in the sense that such stability as they exhibit is not attributable to  $\pi$ -bonding. Accordingly, it is of interest to determine the generality of formation of this type of compound and more particularly to determine whether enhanced stability results from substitution of bi- and polydentate ligands for ammonia.

Preliminary studies on the reduction of bisethylenediamineplatinum(II) iodide showed that mixtures of reduction products were formed and that hydrogen was evolved during the course of the reactions. This suggested the formation and possible involvement of potassium amide in concurrent reactions and therefore indicated the desirability of studying the interaction of the iodide and potassium amide. It was shown subsequently, however, that the intermediate formation of potassium amide is not necessary in accounting for the observed products of the reduction reactions.

### Experimental

Unless indicated to the contrary, all experimental materials and methods, including the synthesis of starting materials, procedures for carrying out reactions in ammonia, and the measurement of physical properties of reaction products were the same as those described in earlier publications.<sup>2,3,5</sup>

Bisethylenediamineplatinum(II) iodide was prepared from platinum(IV) iodide<sup>6</sup> by suspending 10.25 g. of  $\text{PtI}_4$  in 100 ml. of water, adding 4 ml. of 90% aqueous ethylenediamine, and heating at  $90^\circ$  until solution was complete.

(1) This work was supported in part by the Atomic Energy Commission, Contract AT-(40-1)-1639.

(2) G. W. Watt, M. T. Walling, Jr., and P. I. Mayfield, *THIS JOURNAL*, **75**, 6175 (1953).

(3) G. W. Watt and P. I. Mayfield, *ibid.*, **75**, 6178 (1953).

(4) J. Kleinberg, *J. Chem. Ed.*, **33**, 73 (1956).

(5) G. W. Watt, *et al.*, *THIS JOURNAL*, **70**, 1197 (1948); **71**, 3833 (1949); **76**, 4742 (1954); **79**, 3315 (1957); *J. Electrochem. Soc.*, **98**, 1 (1951); **102**, 46, 545 (1955).

(6) L. Pigeon, *Ann. chim. phys.*, **2**, 496 (1804).

The solution was evaporated to incipient crystallization, cooled, and the resulting crystals were filtered, washed with water and recrystallized from hot water after boiling with Norite. The yield was 5.82 g. or 69%. *Anal.* Calcd. for  $[\text{Pt}(\text{en})_2]\text{I}_2$ : Pt, 34.3; I, 44.6. Found: Pt, 34.3; I, 44.6. X-Ray diffraction data for this compound are included in Table I.

TABLE I  
X-RAY DIFFRACTION DATA

$[\text{Pt}(\text{en})_2]\text{I}_2$		$[\text{Pt}(\text{en})_2]\text{ICl}$		$[\text{Pt}(\text{en})_2]\text{Cl}_2$		$[\text{Pt}(\text{en-H})(\text{en})]\text{I}$		$[\text{Pt}(\text{en-H})_2]^0$	
<i>d</i> , Å.	<i>I</i> / <i>I</i> <sub>0</sub>	<i>d</i> , Å.	<i>I</i> / <i>I</i> <sub>0</sub>	<i>d</i> , Å.	<i>I</i> / <i>I</i> <sub>0</sub>	<i>d</i> , Å.	<i>I</i> / <i>I</i> <sub>0</sub>	<i>d</i> , Å.	<i>I</i> / <i>I</i> <sub>0</sub>
8.10	0.7	7.92	1.0	7.83	1.0	4.98	1.0	8.96	1.0
4.85	.7	4.83	0.4	6.42	0.7	3.78	0.8	6.37	0.5
4.45	.6 <sup>a</sup>	4.41	.4	6.04	.5	3.45	.6	4.91	.7
4.22	1.0	4.20	.7	4.77	.5	3.14	.4	3.62	.6
3.94	0.7	3.91	.4 <sup>a</sup>	4.50	.3 <sup>a</sup>	2.70	.4 <sup>a</sup>	3.33	.4 <sup>a</sup>
3.70	.9	3.66	.5	3.87	.5	2.49	.5		

<sup>a</sup> Less intense lines not included here.

Although preliminary studies showed that bisethylenediamineplatinum(II) bromide is reduced by liquid ammonia solutions of potassium, this salt is substantially insoluble in ammonia at its boiling point.<sup>7</sup> In the study of reaction products corresponding to intermediate steps, the presence of solid unreacted bromide complicated the separation of ammonia-insoluble reduction products; hence the bromide was not used further as a starting material. In order to determine whether the iodide undergoes solvolysis in the presence of liquid ammonia, a sample of the pure iodide was dissolved in liquid ammonia at  $-33.5^\circ$ , the solvent was evaporated, and the residual solid was found to give an X-ray diffraction pattern identical with that of the starting material.<sup>7</sup> *Anal.* Calcd. for  $[\text{Pt}(\text{en})_2]\text{I}_2$ : Pt, 34.3. Found: Pt, 34.3.

Each of the cases described below is a typical example of reactions of demonstrated reproducibility.

**Potentiometric Titration of  $[\text{Pt}(\text{en})_2]\text{I}_2$  with  $\text{KNH}_2$ .**—A solution of 0.0374 g. of  $[\text{Pt}(\text{en})_2]\text{I}_2$  in 30 ml. of liquid ammonia was titrated at  $-39^\circ$  with 0.0092 *M*  $\text{KNH}_2$  solution over a period of 5 hr. After about 5 ml. of the titrant had been added, a white precipitate appeared and continued to form throughout the remainder of the titration. The data are shown in Fig. 1; the change in potential that occurred upon addition of 6.3 ml. of titrant corresponds to the reaction of one mole of the iodide with one mole of potassium amide (calcd., 7.2 ml.).

**The Reaction between  $[\text{Pt}(\text{en})_2]\text{I}_2$  and  $\text{KNH}_2$  (1:1).**—In order to isolate and characterize the product of this reaction, 4.3218 g. of the iodide in 75 ml. of ammonia was treated dropwise at  $-38^\circ$  with the potassium amide equivalent to

(7) G. W. Watt and R. E. McCarley, *THIS JOURNAL*, **79**, 3315 (1957).

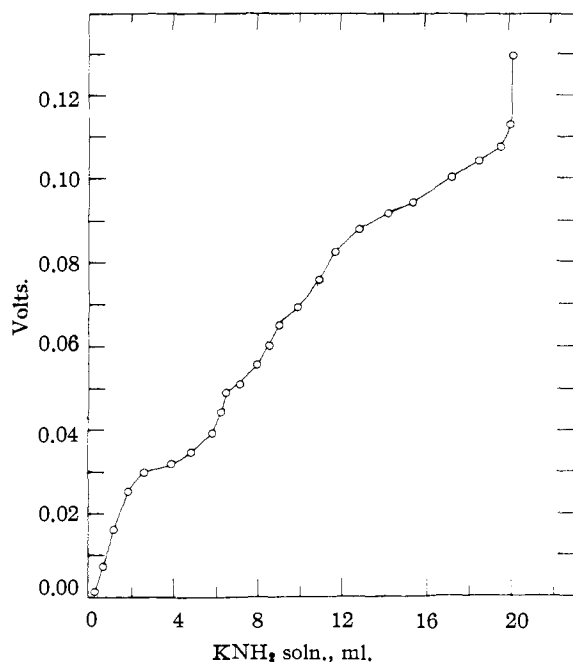


Fig. 1.—Potentiometric titration of bisethylenediamine-platinum(II) iodide with potassium amide in liquid ammonia at  $-33.5^{\circ}$ .

0.3118 g. of potassium. The resulting white precipitate was separated by filtration, washed six times with 25-ml. portions of ammonia, and dried *in vacuo* at room temperature. *Anal.* Calcd. for  $[\text{Pt}(\text{en}-\text{H})(\text{en})]\text{I}$ : Pt, 44.2; I, 28.8; N, 12.7. Found: Pt, 44.0; I, 28.8; N, 13.5. The combined filtrate and washings were analyzed for iodine; found: 0.9500 g. or 49.3% of the iodine used as  $[\text{Pt}(\text{en})_2]\text{I}_2$ . X-Ray diffraction data for this product are included in Table I; the product was found to be diamagnetic.

**The Reaction between  $[\text{Pt}(\text{en})_2]\text{I}_2$  and  $\text{KNH}_2$  (1:2).**—In a manner strictly analogous to the preceding case, 2.0000 g. of the iodide (3.52 mmoles) in 45 ml. of ammonia at  $-38^{\circ}$  was treated with the potassium amide formed from 0.4120 g. of potassium (10.5 mmoles—see Discussion). The white solid product was treated as described above. *Anal.* Calcd. for  $[\text{Pt}(\text{en}-\text{H})_2]^0$ : Pt, 62.4; N, 17.9. Found: Pt, 62.5; N, 17.6. A qualitative test for iodine was negative. X-Ray diffraction data for this product are given in Table I; this product also was diamagnetic.

**Reactions of  $\beta$ -Aminoethylamidoethylenediamineplatinum(II)iodide,  $[\text{Pt}(\text{en}-\text{H})(\text{en})]\text{I}$  and Bis-( $\beta$ -aminoethylamido)-platinum(II),  $[\text{Pt}(\text{en}-\text{H})_2]^0$ .**—In order further to characterize these products that are formed successively by the interaction of  $[\text{Pt}(\text{en})_2]\text{I}_2$  and  $\text{KNH}_2$ , the following reactions were investigated. In each case, the appropriate starting material was prepared as described above.

**Reactions with Aqueous Hydriodic Acid.**—A 0.2058-g. sample of  $[\text{Pt}(\text{en}-\text{H})(\text{en})]\text{I}$  was dissolved in 20 ml. of water at room temperature and titrated with 0.0231 *N* hydriodic acid; 20.1 cc. was required for complete neutralization as determined by potentiometric titration (calcd., 20.2 cc.). The resulting solution was evaporated nearly to dryness, cooled, and the resulting crystals were identified as  $[\text{Pt}(\text{en})_2]\text{I}_2$  by means of an X-ray diffraction pattern substantially identical with that upon which the corresponding data in Table I are based.

Similarly, 0.0887 g. of  $[\text{Pt}(\text{en}-\text{H})_2]^0$  was dissolved in 15 ml. of water and neutralized with 25.00 ml. of 0.0231 *N* hydriodic acid (calcd., 24.50 ml.). The solid product isolated from the resulting solution was also identified as  $[\text{Pt}(\text{en})_2]\text{I}_2$  by means of its characteristic X-ray diffraction pattern.

**Reaction with Aqueous Hydrochloric and Hydriodic Acids.**—In an experiment analogous to that described above, 1.0 g. of  $[\text{Pt}(\text{en}-\text{H})_2]^0$  was dissolved in water and neutralized with an equimolar mixture of 0.1 *N* hydrochloric acid and 0.1 *N* hydriodic acid. The resulting solution was evapo-

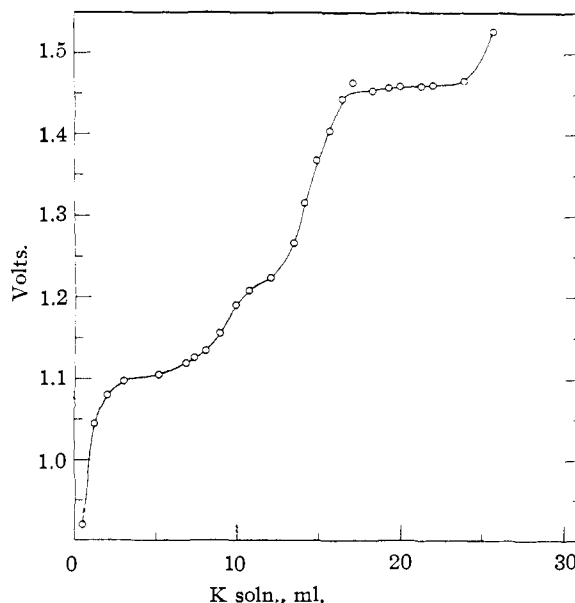


Fig. 2.—Potentiometric titration of bisethylenediamine-platinum(II) iodide with potassium in liquid ammonia at  $-33.5^{\circ}$ .

rated to incipient crystallization, cooled and filtered. The crude solid product (1.32 g.) was crystallized from a minimum quantity of water; the purified product (1.21 g.) was a white crystalline solid. *Anal.* Calcd. for  $[\text{Pt}(\text{en})_2]\text{I}_2$ : Pt, 40.8; I, 26.7; Cl, 7.43. Found: Pt, 39.6; I, 26.2; Cl, 7.44. X-Ray diffraction data for this compound are included in Table I.

**Reactions with Liquid Sulfur Dioxide.**—Liquid sulfur dioxide (*ca.* 300 ml.) and 4.06 g. of  $[\text{Pt}(\text{en}-\text{H})(\text{en})]\text{I}$  were agitated at regular intervals in a sealed tube at room temperature over a period of 10 days. During the initial stages of the reaction a yellow solid was formed; this was more slowly converted to a dark green crystalline solid. The sulfur dioxide was evaporated and the residual solid was analyzed for platinum and for sulfur (as  $\text{BaSO}_4$ ). *Anal.* Calcd. for an equimolar mixture of  $[\text{Pt}(\text{en})_2]\text{I}_2$  and  $[\text{Pt}(\text{SO}_2\text{NHCH}_2\text{CH}_2\text{NH}_2)_2]^0$ : Pt, 38.6; S, 6.34. Found: Pt, 38.6; S, 6.15. The X-ray diffraction pattern obtained using a sample of the gross solid product showed clearly the presence of  $[\text{Pt}(\text{en})_2]\text{I}_2$  and additional very faint lines presumably attributable to the other component of the mixture.

In a similar manner, 1.0 g. of  $[\text{Pt}(\text{en}-\text{H})_2]^0$  was treated with 30 ml. of liquid sulfur dioxide in a sealed tube at  $25^{\circ}$ . Owing to poor agitation, the reaction was slow and 2 months was allowed to ensure complete conversion. The product, isolated as described above, consisted of a yellow-tan solid. *Anal.* Calcd. for  $[\text{Pt}(\text{SO}_2\text{NHCH}_2\text{CH}_2\text{NH}_2)_2]^0$ : Pt, 44.2; S, 14.5. Found: Pt, 43.7; S, 16.5. The analytical data for sulfur were consistently high, probably because of difficulty encountered in complete removal of the solvent without decomposition of the solid product.

**Potentiometric Titration of  $[\text{Pt}(\text{en})_2]\text{I}_2$  with K.**—A solution of 0.1983 g. of the iodide and 0.10 g. of potassium iodide (as a supporting electrolyte) in 19 ml. of liquid ammonia at  $-38^{\circ}$  was titrated with 0.0478 *M* potassium solution over a period of 7 hr. Upon addition of the first increment of the potassium solution, its blue color was discharged immediately and the solution assumed a pale tan color. Throughout the addition of 10 ml. of titrant, the intensity of color of the solution progressively increased and a very dark red solid separated. Between 10 and 15 ml., the color intensity decreased and the color of the solid became pink; this color persisted to the end of the titration, but beyond 17 ml. of titrant the rate of reaction became relatively slow and the blue color of the potassium solution finally persisted for more than 1 hr. The data are shown in Fig. 2; a differential plot of these data shows significant changes in potential corresponding to 9.6, 14.2 and 25.0 ml. of potassium solution. The calculated values for 1:1, 2:1 and 3:1 mole ratios of K to  $[\text{Pt}(\text{en})_2]\text{I}_2$  are 7.3, 14.5 and 21.8 ml., respectively.

**Reduction of  $[\text{Pt}(\text{en})_2]\text{I}_2$  with K (1:1).**—In order to characterize the solid product formed during the addition of one equivalent of potassium/mole of the iodide, 2.56 g. of  $[\text{Pt}(\text{en})_2]\text{I}_2$  in 40 ml. of ammonia was treated dropwise with 0.180 g. of potassium in 15 ml. of ammonia at  $-35^\circ$ . During this reaction, 3.4 cc. of hydrogen was evolved. The resulting very dark red solid was filtered, washed eight times with 15-ml. portions of ammonia, and dried *in vacuo* at  $-33.5^\circ$ . The residual solid product was warmed to room temperature, whereupon the solid decomposed with liberation of 12.1 cc. of hydrogen, ethylenediamine condensed on the walls of the reactor, and the solid became black. The reactor was partially immersed in boiling water and the uncombined ethylenediamine was removed by alternately lowering the pressure and flushing with dry nitrogen. Finally, the remaining solid was removed from the reactor in an anhydrous oxygen-free atmosphere. This solid (1.2540 g.) was treated with dilute nitric acid, and thereafter 0.258 g. of elemental platinum was removed by filtration and washed with water. The filtrate and washings were diluted to 50.0 ml. and aliquots were analyzed for iodine (found, 0.327 g.) and water-soluble platinum (found, 0.392 g.). Prior to treatment of the solid product with nitric acid, samples were taken for X-ray diffraction patterns. Although these patterns were complicated by the relatively large quantities of elemental platinum that were present, the patterns nevertheless led to the unequivocal identification of  $[\text{Pt}(\text{en})_2]\text{I}_2$  and  $[\text{Pt}(\text{en-H})(\text{en})]\text{I}$  as components of this product.

Since the interpretation (see Discussion) of the foregoing observations and data involves the assumption that the primary reduction product,  $[\text{Pt}(\text{en})_2]\text{I}$ , decomposes by two paths that are strongly temperature dependent, it was desirable to secure supporting evidence by establishing conditions favorable to the low temperature decomposition step. Thus, 2.37 g. of  $[\text{Pt}(\text{en})_2]\text{I}_2$  in 40 ml. of ammonia at  $-33.5^\circ$  was reduced with one equivalent of potassium (0.17 g.) and the ammonia-insoluble product was washed 5 times with 15-ml. portions of ammonia and resuspended in 40 ml. of fresh ammonia. During these operations, 11.2 cc. of hydrogen was collected. The solid reduction product was allowed to remain suspended in ammonia at  $-33.5^\circ$  for 43 hr., after which a total of 12.3 cc. of hydrogen was collected. Finally, the solvent was evaporated and the decomposition was allowed to go to completion at room temperature, whereupon the solid turned black owing to the liberation of elemental platinum. The end-products were washed 5 times with 15-ml. portions of ammonia to remove  $[\text{Pt}(\text{en})_2]\text{I}_2$  (postulated as arising from the disproportionation of  $[\text{Pt}(\text{en})_2]\text{I}$ ). After removal of ammonia, the product was treated with water, elemental platinum (0.0939 g.) was removed by filtration, washed, and the combined filtrate and washings was analyzed for platinum and iodide ion; found: Pt, 0.3894 g.; I, 0.2450 g.

**Reaction of  $[\text{Pt}(\text{en})_2]\text{I}_2$  with K (1:2).**—In a similar manner, 2.50 g. of the iodide in 35 ml. of liquid ammonia was reduced at  $-35^\circ$  by dropwise addition of 10 ml. of solution containing 0.456 g. of potassium, over a period of 50 min. The sequence of changes observed was essentially the same as those recorded above for the corresponding part of the potentiometric titration; the final insoluble product was a light pink solid. After filtration, the solid was washed eight times with 15-ml. portions of ammonia and dried *in vacuo* at  $-35^\circ$ . Decomposition, as described above, occurred as the solid was warmed to room temperature, but in this case the ethylenediamine was not removed. The products were removed for analysis (also as described above); found: elemental Pt, 0.3494 g.; water-soluble Pt, 0.4800 g.; I, 0.0815 g. Total hydrogen evolved (*i.e.*, during the initial reduction reaction and the subsequent decomposition) amounted to 44.5 cc. Owing to the relatively large quantity of platinum metal present in these products, satisfactory X-ray diffraction patterns useful in the detection of other reaction products could not be obtained.

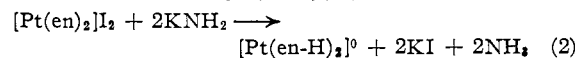
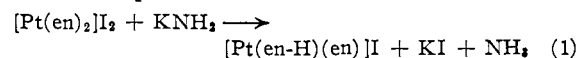
**Reduction of  $[\text{Pt}(\text{en})_2]\text{I}_2$  with K (1:2) at  $-78^\circ$ .**—In an effort to suppress intermediate steps and to reduce  $[\text{Pt}(\text{en})_2]\text{I}_2$  directly to  $[\text{Pt}(\text{en})_2]^0$ , the iodide was reduced at  $-78^\circ$  by addition of a large excess of solid potassium. Thus, 2.1021 g. of the iodide dissolved in 20 ml. of ammonia was treated with 0.5 g. of solid potassium. The pink solid precipitated immediately and the blue solution was stirred for 1 hr., filtered, and the solid product was washed 5 times with 20-ml. portions of ammonia. After drying at  $-33.5^\circ$ , the

pink solid decomposed slowly while warming to and standing at room temperature. The total hydrogen evolved was 39.6 cc. (1.77 mmoles). Since the major objective of this kind of experiment was to establish the en/Pt ratio, the entire residue was treated with water, 0.3194 g. of elemental platinum was recovered by filtration, washed with water, and the combined filtrate and washings (which gave a negative test for iodide ion) were titrated with standard hydriodic acid. A sharp end-point corresponding to complete neutralization was found upon addition of 10.14 mmoles of acid (calcd., 10.06 mmoles). Finally this solution was analyzed for water-soluble platinum; found: 0.3410 g. (1.75 mmoles).

In order to provide more direct proof that  $[\text{Pt}(\text{en-H})_2]^0$  is one of the products of the spontaneous decomposition of  $[\text{Pt}(\text{en})_2]^0$ , experiments of the following type were conducted. A solution of 2.0107 g. of  $[\text{Pt}(\text{en})_2]\text{I}_2$  in 30 ml. of ammonia was reduced with an excess of potassium (*ca.* 0.4 g.) at  $-33.5^\circ$ , and the ammonia-insoluble product was washed 6 times with 15-ml. portions of ammonia. Residual solvent was removed *in vacuo* and the solid was allowed to decompose at room temperature. The gray-black solid was again washed with ammonia to remove ethylenediamine, resuspended in 20 ml. of ammonia and treated with 0.40 g. of solid ammonium chloride. Most of the solid dissolved, leaving a precipitate of elemental platinum. After evaporation of the solvent, the residue was treated with water, filtered to remove elemental platinum, and the aqueous filtrate was evaporated to a volume of 10 ml. Addition of 20 ml. of ethanol followed by cooling yielded a white crystalline solid which was removed by filtration, washed with ethanol-water and air-dried. *Anal.* Calcd. for  $[\text{Pt}(\text{en})_2]\text{Cl}_2$ : Pt, 50.5; Cl, 18.4. Found: Pt, 50.3; Cl, 18.3. X-Ray diffraction data for this substance are included in Table I. Analysis of the combined liquid ammonia filtrates and washings accounted for 0.900 g. of iodine, or 100.1% of that used in the initial reaction as  $[\text{Pt}(\text{en})_2]\text{I}_2$ .

### Discussion

The results reported above show that the reactions between bisethylenediamine platinum(II) iodide and potassium amide in liquid ammonia at or near its boiling point occur strictly in accordance with the equations

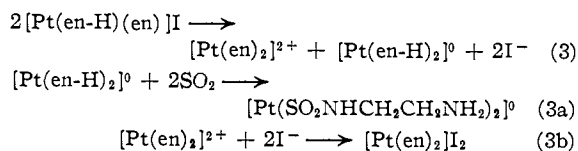


As shown by Fig. 1 and related observations, reaction 1 is essentially instantaneous but 2 is relatively slow and goes to completion only in the presence of one equivalent of excess amide ion. The identification of the above products provides additional evidence of the acidic character of hydrogen in ethylenediamine molecules coordinated with transitional metal ions and these products are apparently analogous to known complexes of osmium<sup>8</sup> and gold.<sup>9</sup> Both  $[\text{Pt}(\text{en-H})(\text{en})]\text{I}$  and  $[\text{Pt}(\text{en-H})_2]^0$  are stable at room temperature in an inert atmosphere; their aqueous solutions are strongly basic and react with one and two moles, respectively, of hydriodic acid and are thereby reconverted to  $[\text{Pt}(\text{en})_2]\text{I}_2$ . Similarly,  $[\text{Pt}(\text{en-H})_2]^0$  reacts with a mixture of hydriodic and hydrochloric acid in aqueous solutions to form  $[\text{Pt}(\text{en})_2]\text{ICl}$ , and with ammonium chloride in liquid ammonia to provide  $[\text{Pt}(\text{en})_2]\text{Cl}_2$ . These reactions therefore suggest a general route to the synthesis of compounds of the  $[\text{Pt}(\text{en})_2]^{2+}$  ion in combination with practically any desired anion. The strongly basic character of these products is also demonstrated by their

(8) F. P. Dwyer and J. W. Hogarth, *THIS JOURNAL*, **77**, 6152 (1955).

(9) B. P. Block and J. C. Bailar, Jr., *ibid.*, **73**, 4722 (1951).

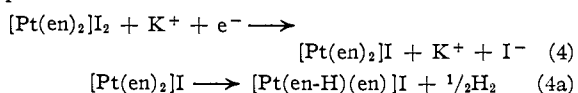
reactions with the weak Lewis acid, sulfur dioxide; for example, the data reported above are entirely in accord with the reactions



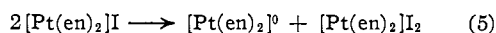
which involve an initial disproportionation that accounts for the presence of  $[\text{Pt}(\text{en})_2]\text{I}_2$  as an end-product and is otherwise compatible with the analytical composition of the gross reaction product.

The reactions of  $[\text{Pt}(\text{en})_2]\text{I}_2$  with liquid ammonia solutions of potassium are more complex, but are subject to interpretations that do not imply any involvement of reactions 1 and 2. Thus, the data of Fig. 2 and the results obtained in reactions designed to permit the isolation and identification of both intermediate and final products are in accord with the following interpretations.

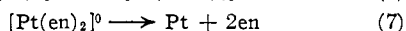
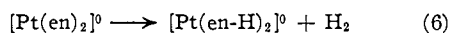
When  $[\text{Pt}(\text{en})_2]\text{I}_2$  is treated with one equivalent of potassium at  $-35^\circ$



Reaction 4 is almost instantaneous whereas reaction 4a is slow, but nevertheless accounts for the hydrogen evolved during the course of the initial reduction reaction. In other experiments (not reported here) it was found that within the time interval required for the necessary manipulations, at least 10% of the  $[\text{Pt}(\text{en})_2]\text{I}$  decomposes as shown by 4a. When the remainder of this product is warmed to room temperature, the monoiodide disproportionates according to



and the bisethylenediamineplatinum(0) decomposes by two paths

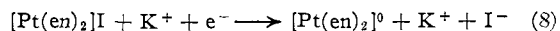


Reaction 5 accounts for the observed regeneration of  $[\text{Pt}(\text{en})_2]\text{I}_2$ , while reactions 6 and 7 account for hydrogen and elemental platinum found and are further consistent with the assumption that free ethylenediamine was completely removed from the system by the procedure described above. This leads to the conclusion that the final reaction product should consist of  $[\text{Pt}(\text{en})_2]\text{I}_2$ ,  $[\text{Pt}(\text{en-H})(\text{en})\text{I}]$ ,  $[\text{Pt}(\text{en-H})_2]^0$  and Pt; X-ray diffraction data provided identification of all these products except  $[\text{Pt}(\text{en-H})_2]^0$ . Finally, if all of the foregoing interpretation is correct, platinum and iodine in the water-soluble fraction should amount to 30.8 and 26.1%, respectively, of the solid sample taken for analysis. Found: Pt, 31.3; I, 25.9.

In order to secure evidence in support of the above interpretation, reactions were carried out under conditions favorable to the occurrence of reaction 4a relative to reaction 5 and the subsequent reactions 6 and 7. As described above, reaction 4 was carried out and the ammonia-insoluble products of reactions 4 and 4a, *i.e.*,  $[\text{Pt}(\text{en})_2]\text{I}$  and  $[\text{Pt}(\text{en-H})(\text{en})\text{I}]$ , were washed with ammonia to ensure

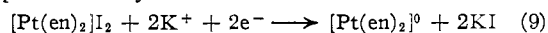
the purity of these products and more particularly to eliminate all other potential sources of hydrogen. Over the time interval involved in these manipulations, 0.50 mmole of hydrogen was evolved in accordance with 4a. Thereafter, part of the remaining  $[\text{Pt}(\text{en})_2]\text{I}$  was allowed to decompose over a period of 43 hr. to provide an additional 0.55 mmole of hydrogen. The decomposition was then completed at room temperature in accordance with 5, 6 and 7, and the resulting mixture was washed with liquid ammonia to remove  $[\text{Pt}(\text{en})_2]\text{I}_2$  and ethylenediamine prior to sampling for analysis. The analytical data reported above are interpreted as follows. Elemental platinum found (0.481 mmole) provides a measure of the extent of occurrence of reaction 7. Water-soluble platinum corresponds to both  $[\text{Pt}(\text{en-H})(\text{en})\text{I}]$  and  $[\text{Pt}(\text{en-H})_2]^0$  formed in reactions 4a and 6, respectively, but since 1.940 mmoles of iodine was found in the water-soluble product, the mixture of the two water-soluble platinum-containing species must have consisted of 1.940 mmoles of  $[\text{Pt}(\text{en-H})(\text{en})\text{I}]$  and 0.056 mmole of  $[\text{Pt}(\text{en-H})_2]^0$ . On this basis, we calculate that a total of 1.04 mmoles of hydrogen should have been liberated as the result of reaction 4a at  $-33.5^\circ$ ; found: 1.05 mmoles.

The reduction of  $[\text{Pt}(\text{en})_2]\text{I}_2$  with two molar equivalents of potassium is similar in that reaction 4 occurs initially, but 4a is suppressed owing to



and when the resulting ammonia-insoluble product is warmed to room temperature,  $[\text{Pt}(\text{en})_2]^0$  decomposes in accordance with 6 and 7. On this basis, the ratio of water-soluble platinum to elemental platinum found by analysis of the final ammonia-insoluble product should be  $<1.00$  since reaction 4a is not entirely suppressed by concurrent reaction 8. The ratio actually found was 1.38 and it is at once apparent that the deviation of this ratio from unity should correlate with both the volume of hydrogen liberated in 4a and the iodine retained in the ammonia-insoluble product (found: I, 0.643 mmole). Unfortunately, the corresponding volume of hydrogen is too small for separate collection and analysis with sufficient accuracy to provide reliable results. However, the total hydrogen evolution implied by the foregoing reaction scheme is 2.1 mmoles (found: 2.0 mmoles). Furthermore, this interpretation requires that the nitrogen content of the ammonia-insoluble product should be 13.0% (found: N, 12.7).

The reduction of  $[\text{Pt}(\text{en})_2]\text{I}_2$  with a large excess of potassium at  $-78^\circ$  was carried out with a view to suppressing entirely the formation of either  $[\text{Pt}(\text{en})_2]\text{I}$  or the resulting  $[\text{Pt}(\text{en-H})(\text{en})\text{I}]$  to provide an iodine-free insoluble product having an en/Pt ratio of 2. The results were entirely in accord with expectations. The formation of the dark red intermediate  $[\text{Pt}(\text{en})_2]\text{I}$  was not observed, the only ammonia-insoluble product was the pink  $[\text{Pt}(\text{en})_2]^0$  and the washed product did not give a test for iodine. The over-all reaction is therefore represented by



and the only subsequent reactions that occurred

were those involved in the decomposition of  $[\text{Pt}(\text{en})_2]^0$ , *i.e.*, 6 and 7. That this interpretation is correct is shown by the data given in Table II.

TABLE II  
EQUIVALENCE RATIOS AMONG AMMONIA-INSOLUBLE PRODUCTS

Ratio	Calcd.	Found
en/Pt	2.00	2.02
$\text{H}_2/[\text{Pt}(\text{en-H})_2]^0$	1.00	1.01
Water-soluble Pt/elemental Pt	1.00 <sup>a</sup>	1.07

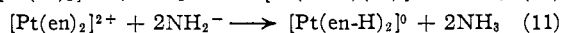
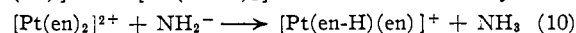
<sup>a</sup> Based on the assumption that the rates of reactions 6 and 7 are substantially equal.

In arriving at these calculated ratios,  $[\text{Pt}(\text{en-H})_2]^0$  was determined separately as soluble platinum, and  $[\text{Pt}(\text{en-H})_2]^0$  and ethylenediamine were determined together by titration with standard hydriodic acid solution as described in the Experimental section.

It also should be noted that, of the products proposed to explain the reduction of  $[\text{Pt}(\text{en})_2]\text{I}_2$  with ammonia solutions of potassium,  $[\text{Pt}(\text{en-H})_2]^0$  is the only one not identified by direct analysis and/or X-ray diffraction data. However, the presence of this product was established indirectly by reducing  $[\text{Pt}(\text{en})_2]\text{I}_2$  to an iodine-free ammonia-insoluble product, *i.e.*,  $[\text{Pt}(\text{en})_2]^0$  by reaction 8, and allowing this product to decompose at room temperature *via* reactions 6 and 7. Removal of ethylenediamine by washing with liquid ammonia left only a mixture of

elemental platinum and  $[\text{Pt}(\text{en-H})_2]^0$ . Treatment of this mixture with a solution of ammonium chloride in liquid ammonia was shown to lead to the formation of  $[\text{Pt}(\text{en})_2]\text{Cl}_2$  by a reaction strictly analogous to the previously demonstrated reactions of  $[\text{Pt}(\text{en-H})_2]^0$  with hydrochloric and/or hydriodic acids in aqueous solution.

It is further of interest to note that  $[\text{Pt}(\text{en-H})\text{I}(\text{en})]$  and  $[\text{Pt}(\text{en-H})_2]^0$  are formed either by



or by the spontaneous decomposition of  $[\text{Pt}(\text{en})_2]\text{I}$  and  $[\text{Pt}(\text{en})_2]^0$ , respectively. These species, as shown above, may be either ionic or neutral. The reactions of these complexes with aqueous or ammonia solutions of acids and with sulfur dioxide suggests that each nitrogen atom in an (en-H) group bears an unshared pair of electrons that is not utilized by the available orbitals of the central platinum ion. On the other hand,  $[\text{Pt}(\text{en})_2]^0$  is of a low order of stability entirely comparable with the unstable  $[\text{Pt}(\text{NH}_3)_4]^0$  whereas both  $[\text{Pt}(\text{en-H})(\text{en})]\text{I}$  and  $[\text{Pt}(\text{en-H})_2]\text{I}$  exhibit so much greater stability that some strong interaction with the platinum ion must be responsible for the observed difference in stability. Further studies bearing upon this particular aspect of the problem as well as upon the mechanism of the reduction reactions are in progress.

AUSTIN, TEXAS

[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DIVISION, ARGONNE NATIONAL LABORATORY]

## The Preparation and Properties of Vanadium Pentafluoride<sup>1</sup>

BY L. E. TREVORROW, J. FISCHER AND R. K. STEUNENBERG

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Vanadium pentafluoride was prepared by the reaction of fluorine with vanadium metal at 300°. Measurements of the vapor pressure of the liquid from 24.1 to 85.5° resulted in a normal boiling point of 47.9°. The melting point was 19.0 ± 0.9°. Vapor density measurements indicated that the molecular species present in the vapor phase is VF<sub>5</sub>.

Distillation experiments in this Laboratory have suggested that vanadium pentafluoride must be a much more volatile compound than the data of Ruff and Lickfett<sup>2</sup> had indicated. They had erroneously described vanadium pentafluoride as a white solid at room temperature which sublimes at 111.2° (758 mm.), and which melts above 200°.

Pure vanadium pentafluoride was prepared from the elements, and the vapor pressure of the liquid was measured as a function of temperature. Melting point and vapor density determinations were also made.

### Experimental

**Materials.**—Vanadium metal with a purity analysis of 99.5% was obtained from the Vanadium Corporation of America. Commercial fluorine of high purity was used. It was analyzed by the method of Aoyana and Kanda,<sup>3</sup> employing the quantitative reaction of mercury with fluorine, and found to be at least 99% fluorine by volume. It

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) O. Ruff and H. Lickfett, *Ber.*, **44**, 2539 (1911).

(3) A. Aoyana and E. Kanda, *Bull. Chem. Soc. Japan*, **12**, 409 (1937).

was also shown to contain less than 0.5% impurities by its quantitative reaction with bromine<sup>4</sup> and by various physical measurements.

**Apparatus.**—The equipment used in this work was constructed of nickel and Monel. The components were joined by welding or by flare connectors with Teflon gaskets. Preliminary work had shown that vanadium pentafluoride reacts with silver solder, and to a lesser degree with Fluorothene (poly-chlorotrifluoroethylene). These materials were avoided in the apparatus used for the final purification of the vanadium pentafluoride and for the determinations of its physical properties. The various portions of the apparatus were joined to a manifold which was provided with liquid nitrogen-cooled traps and sources of vacuum, helium and fluorine. Monel diaphragm and Teflon-seated bellows valves were employed.

That portion of the apparatus in which the vapor pressure and vapor density measurements were made was housed in a constant-temperature air bath. Care was taken to ensure that no portion of the apparatus was at a lower temperature than the liquid when the vapor pressure measurements were made.

The temperature was measured to the nearest 0.1° with a copper-constantan thermocouple which had been calibrated previously against a standard platinum resistance thermometer using a Leeds and Northrup G-2 Mueller

(4) J. Fischer, J. Bingle and R. C. Vogel, *THIS JOURNAL*, **78**, 902 (1956).