in the following order: Pt(IV) > Pt(II) > Co(III) > Pd(II) > Cr(III) > Cu(II) > Ni(II) > Co(II). Univalent silver is somewhat out of line, the ammonia ligands in $[Ag(NH_3)_2]^+$ having a rocking frequency slightly greater than that in $[Cu(NH_3)_4]^{++}$. The presence of rocking frequencies in the spectra of the hexammine Ni(II) and Co(II) complex ions indicates that the nitrogen-to-metal bonds have covalent character; the relatively low frequencies along with the paramagnetism of these complexes indicate sp^3d^2 outer orbital type bonds.

The rocking frequencies show a large variation and are thus very sensitive to the nature and oxidation state of the central metal ion. This is understandable from the above discussion of the nature of the rocking vibration.

The symmetrical bending frequencies of coördinated ammonia molecules show a similar variation with the nature of the N–M bond but the percentage difference in frequency in going from the Co(II) to Pt(IV) ammines is not so great as for the rocking frequencies. Moreover, the degenerate frequencies show little variation with the nature of the N–M bond. These observations are also in accord with the foregoing discussions of the natures of the symmetric and degenerate deformation vibrations.

The neutral $Pt(NH_3)_2Cl_2$ molecule (12) has a lower rocking and a lower symmetric deformation frequency than the $[Pt(NH_3)_4]^{++}$ ion (8) and a similar effect is observed in the Pd(II) compounds (13 and 6). The effect of the charge of the complex itself on the ammonia deformation frequencies is seen also in the series of cobalt(III) ammines (compounds 17, 16, 15 and 14). (The position of the rocking band at 790 cm.$^{-1}$ in compound 17 is not accurately known as the NO_2 group also absorbs strongly in this region). Both the rocking and symmetrical deformation frequencies increase, in general, with increasing positive charge on the complex. This increasing positive charge coincides with increasing number of ammonia molecules in these Co(III) complexes.

The replacement of the carbonate group in the $[Co(NH_3)_5CO_3]^+$ ion (compound 24) by a sulfate group (compound 27) has no effect on the rocking frequency, and replacement by an oxalate group (compound 28) has very little effect on either the rocking or the symmetric deformation frequencies. In the $[Co(NH_3)_5X]^{+2}$ ions (compounds 18 to 21 and 26), an appreciable lowering of the rocking and symmetric deformation frequencies occurs only where X is a hydroxyl group. The replacement of an inner chlorine atom by a nitro group in the $[Cr(NH_3)_5Cl]^{++}$ ion (compounds 10 and 11) results in an appreciable increase in the these deformation frequencies.

The spectra of these metal ammine complexes are being determined in the cesium bromide region in these laboratories to study the nature of the lower frequencies, as reported in a previous paper.[25]

[25] D. M. Sweeny, I. Nakagawa, S. Mizushima and J. V. Quagliano, THIS JOURNAL, **78**, 889 (1956).

NOTRE DAME, INDIANA

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

The Synthesis of Certain Ethylenediamineplatinum(II) and (IV) Bromides and Iodides[1]

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Methods for the synthesis of ethylenediamine coördination compounds of certain halides of platinum(II) and (IV) in high yield and high purity are described. It is shown that $[Pt(en)Br_2]$ and its isomer $[Pt(en)_2]PtBr_4$ may be separated quantitatively owing to the solubility of the former in liquid ammonia at −33.5°.

In the course of studies on the lower oxidation states of platinum,[2] we have had occasion to prepare numerous ethylenediamine coördination compounds of platinum halides. Although many of the corresponding chlorides have been synthesized and are well characterized, they are not desirable as starting materials for reactions in liquid ammonia owing to their generally low solubility. Accordingly, the necessary bromides and iodides were prepared. The syntheses described below either correspond to compounds not previously reported or represent new and/or improved procedures.

Experimental

Methods.—Platinum, when present as the only nonvolatile component, was determined by ignition to the metal; otherwise, platinum was reduced to the metal with hydrazine, dissolved in aqua regia, and determined spectrophotometrically.[3] Halogens were determined as silver halide; where halogen was covalently bonded in complexes, it was displaced with ethylenediamine prior to precipitation.

All X-ray diffraction patterns were obtained using a Hayes unit, Cu Kα radiation, an Ni filter, a tube voltage of 35 kv., a filament current of 15 ma. and exposure times that varied with the nature of the sample. All of the X-ray diffraction data reported here are assembled in Table I and include only the six most intense lines for each compound for which such data are not already available; more nearly complete data are tabulated elsewhere.[4]

For potentiometric titrations, the potential was measured with a Leeds and Northrup type K potentiometer, a platinum indicator electrode, and a saturated calomel reference electrode.

Materials.—Unless otherwise indicated, all chemicals employed in this work were reagent grade materials that were used without further purification.

Hexabromoplatinic acid was obtained by dissolving finely divided platinum in bromine and concentrated hydrobromic acid followed by boiling to remove excess bromine and acid. Massive platinum was dissolved in aqua regia and the re-

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

[2] G. W. Watt and R. E. McCarley, THIS JOURNAL, **79**, in press (1957).

[3] G. H. Ayres and A. S. Meyer, Jr., *Anal. Chem.*, **23**, 299 (1951).

[4] R. E. McCarley, Dissertation, The University of Texas, 1956.

sulting solution was evaporated to dryness several times with concentrated hydrobromic acid to expel hydrogen chloride and oxides of nitrogen.

TABLE I

X-RAY DIFFRACTION DATA

d. Å.	I/I_0	d. Å.	I/I_0	d. Å.	I/I_0
K_2PtBr_6		$(enH_2)PtBr_6$		$[Pt(en)Br_2]$	
5.98	1.0	6.50	0.9	6.99	1.0
5.19	0.8	5.97	1.0	6.46	0.5
3.13	.6	5.49	0.4	4.94	.7
2.99	.6	3.81	.6	3.83	.6
2.59	.9	2.98	.7	3.49	.8
1.93	.7	2.40	.7	3.12	.7
$[Pt(en)_2]PtBr_4$		$[Pt(en)_2]Br_2$		$[Pt(en)Br_4]$	
7.81	0.9	7.88	1.0	6.32	1.0
5.91	1.0	6.56	0.4	5.83	0.5
5.21	0.5	4.92	.6	5.28	.4
4.94	.5	4.03	.9	4.77	.8
3.85	.4	3.76	.7	3.87	.4
3.48	.7	3.53	.9	3.07	.6

$[Pt(en)Cl_2]$		$[Pt(en)I_4]$	
d. Å.	I/I_0	d. Å.	I/I_0
7.43	0.5	6.63	Strong
6.73	1.0	5.82	Strong
6.14	0.5	5.11	Very strong
5.63	.5	4.42	Medium
3.37	.9	3.84	Strong
3.02	.7	3.31	Weak

Potassium hexabromoplatinate(IV) was prepared from solutions of hexabromoplatinic acid by the method of Weber.[5]

Ethylenediammonium hexabromoplatinate(IV) was formed by slow addition of ethylenediamine to a cold solution of hexabromoplatinic acid. This brilliant red salt is only sparingly soluble in water. *Anal.* Calcd. for $(C_2H_{10}N_2)_2PtBr_6$: Pt, 26.5; Br, 65.1. Found: Pt, 26.5; Br, 64.7.

Tetrabromoplatinate(II) ion was, in some instances, prepared by the reduction of potassium hexabromoplatinate(IV) with potassium oxalate by the method of Bülman and Anderson.[6] This reaction however is quite slow, and complete reduction is achieved only by evaporating the reaction mixture to a small volume.

Since, in other cases, it was desirable to form the free acid in the absence of extraneous by-product ions, conditions were devised for the production of this ion by electrolytic reduction. A platinum wire cathode was immersed in 220 ml. of solution containing 3 g. of platinum as hexabromoplatinic acid. A platinum wire anode was immersed in a solution of potassium chloride that was connected to the cathode compartment by a potassium chloride–agar bridge. The catholyte was stirred vigorously, the current was maintained at *ca.* 0.1 amp., and the cathode potential was followed by means of a Leeds and Northrup No. 7664 *p*H meter using a saturated calomel reference electrode. During the course of the electrolysis, the color of the solution changed progressively from maroon-red to the deep red-brown color characteristic of the tetrabromoplatinate(II) ion. Concurrently, the potential gradually became more positive but there was no definite break in the time *vs.* potential curve. Accordingly, the appearance of a deposit of platinum on the cathode that appeared after about 60 hr. was taken as the end-point for the reduction process. As evidenced by the nature of the products obtained upon treatment of the product solutions with ethylenediamine, reduction is incomplete unless time is allowed for deposition of a considerable quantity of platinum on the cathode. The current efficiency is *ca.* 10%.

Synthesis of Platinum(II) and (IV) Halides.—In several of the cases that follow, numerous procedural variables were studied, but only the final procedures that gave optimum results are described.

Ethylenediaminedibromoplatinum(II), $[Pt(en)Br_2]$.—This compound was prepared by a method similar to that used by Basolo, *et al.*,[7] for the synthesis of the corresponding chloride.

A suspension of 10.5 g. (0.0140 mole) of potassium hexabromoplatinate(IV) in 50 ml. of water was reduced to potassium tetrabromoplatinate(II) with 2.57 g. (0.0140 mole) of potassium oxalate 1-hydrate,[6] and treated with 1:10 aqueous ethylenediamine *in 0.1-ml. portions* at room temperature. After each addition, the reaction was allowed to proceed to completion (*i.e.*, until the *p*H of the reaction mixture ≅ 6) before the next portion was added. During the reaction of the first portion of ethylenediamine solution, iridescent green crystals [see ref. 2] separated and continued to form until 0.5 ml. of the base had been added. This product (0.85 g.) was removed by filtration and the reaction was continued in the same manner. Upon addition of the next portion of the diamine, bright yellow crystals formed and after addition of 5 ml. of the diamine, 2.60 g. of this product was separated. Another crop (1.87 g.) of this same product was separated after adding an additional 3 ml. of ethylenediamine solution. A final incremental addition of 2 ml. of ethylenediamine solution provided a mixture of yellow crystals contaminated with a pale green solid. (Subsequent work—see below—has shown that this yellow product $[Pt(en)Br_2]$ is contaminated with a polymerization isomer. Conditions leading to the formation of $[Pt(en)Br_2]$ while minimizing the formation of the isomer are embodied in the procedure given.) The total yield was 4.47 g. or 77% based on potassium hexabromoplatinate(IV). *Anal.* Calcd. for $[Pt(en)Br_2]$: Pt, 47.0; Br, 38.5. Found: Pt, 46.9; Br, 38.7.

Ethylenediaminedibromoplatinum(II) is soluble in liquid ammonia at −33.5° apparently without reaction. Evaporation of the solvent from the yellow solution provided yellow crystals that gave an X-ray diffraction pattern identical with that of the solid originally dissolved. When a mixture of the yellow solid and its green polymerization isomer is treated with liquid ammonia at −33.5°, the former dissolves while the latter remains as a brown insoluble ammoniate. Pure $[Pt(en)Br_2]$ was recovered from the ammonia solution; the ammonia-insoluble brown ammoniate was deammoniated at 10^{-2} mm. at room temperature to provide the original green component of the mixture. Yellow $[Pt(en)Br_2]$ is also readily soluble in N,N-dimethylformamide, from which the bromide may be recrystallized by addition of water. If, however, these solutions are heated to *ca.* 50°, decomposition resulting in deposition of elemental platinum occurs.

Bisethylenediamineplatinum(II) Tetrabromoplatinate(II), $[Pt(en)_2]PtBr_4$.—A solution of tetrabromoplatinic acid was divided into two equal portions, ethylenediamine was added to one portion at 80–90° until all of the solid dissolved whereupon this was added to the other portion of the original solution. The pale green crystals that separated in quantitative yield were washed with water and dried at 110° for 2 hr. *Anal.* Calcd. for $[Pt(en)_2]PtBr_4$: Pt, 47.0; Br, 38.5. Found: Pt, 47.1; Br, 38.5.

As a means of providing evidence (other than that arising from the mode of synthesis) for the identity of the ionic components of this salt, precipitation of $PtBr_4^{2-}$ as the silver salt proved unsuccessful at or below room temperature owing to incomplete reaction; precipitation at elevated temperatures is impractical because of formation of silver bromide. Accordingly, the presence of two distinctly different ionic species containing platinum(II) was demonstrated by the potentiometric titration method of Grinberg and Ryabchikov.[8] Thus, 0.2801 g. of the salt was suspended with efficient stirring in 110 ml. of 1.0 *N* hydrochloric acid solution at 25° and titrated with 0.1384 *N* sodium bromate solution; the results are given in Fig. 1. About 4 hr. was required for the titration to the first end-point, at which stage all of the solid had dissolved and the color of the solution was pale yellow. Titration to the second end-point required only 30 min.; the final solution had an intense yellow color, and should be expected to contain $[Pt(en)_2Br_2]PtCl_6$ and/or its isomers. Evaporation of the solution to a small volume yielded 0.1 g. of orange colored crystals. *Anal.* Calcd. for

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[5] H. C. P. Weber, THIS JOURNAL, **34**, 1300 (1912).

[6] E. Bülman and A. C. Anderson, *Ber.*, **36**, 1566 (1903).

[7] F. Basolo, J. C. Bailar, Jr., and B. R. Tarr, THIS JOURNAL, **72**, 2433 (1950).

[8] A. A. Grinberg and D. I. Ryabchikov, *Compt. rend. acad. sci. U.R.S.S.*, **14**, 119 (1937).

$[Pt(en)_2Br_2]PtCl_6$: Pt, 45.0. Found: Pt, 44.3. The calculated end-points for oxidation of half and all of the platinum to the 4^+ oxidation state are 4.87 and 9.75 ml. of titrant, respectively. The end-points established by means of a differential plot are 4.68 and 9.75 ml.

Bisethylenediamineplatinum(II) Bromide, $[Pt(en)_2]Br_2$.—Although this compound should be formed readily by the action of ethylenediamine upon either $[Pt(en)Br_2]$ or $[Pt(en)_2]PtBr_4$, the reaction with the latter was found to be impractically slow. Accordingly, 1.87 g. of $[Pt(en)Br_2]$ was suspended in 30 ml. of water, treated with 1 ml. of ethylenediamine and heated at 80–90° for 4 hr. A small quantity of residual solid was removed by filtration, the filtrate was diluted with 500 ml. of ethanol, and cooled to 0°. The fine white crystals that separated were filtered, washed with ethanol, and dried at 110°. The yield was 1.96 g. or 92% based on $[Pt(en)Br_2]$. *Anal.* Calcd. for $[Pt(en)_2]Br_2$: Pt, 41.1; Br, 33.6. Found: Pt, 41.1; Br, 33.4.

***trans*-Bisethylenediaminedibromoplatinum(IV) Bromide,** $[Pt(en)_2Br_2]Br_2$.—This synthesis was effected by a procedure similar to that used by Schleicher, Henkel and Spies[9] for the preparation of $[Pt(en)_2Br_2]Cl_2$. Thus, 0.424 g. of $[Pt(en)_2]Br_2$ was dissolved in 25 ml. of water and treated with 0.2 ml. of bromine at 50°. After 15 min., the temperature was raised to 100° and air was blown over the surface of the solution to remove excess bromine. When the volume of the solution was reduced to 10 ml., it was cooled to room temperature, treated with 1 ml. of concentrated hydrobromic acid solution, and finally diluted with 100 ml. of 2:1 ethanol–acetone mixture. The fine yellow crystals that separated were filtered, washed with ethanol and acetone, and dried in air.[10] *Anal.* Calcd. for $[Pt(en)_2Br_2]Br_2$: Pt, 30.7. Found: Pt, 29.7.

Ethylenediaminetetrabromoplatinum(IV), $[Pt(en)Br_4]$.—Although this compound was formed successfully by the oxidation of $[Pt(en)Br_2]$ with bromine, this procedure[7,9] was found to be much less satisfactory than that which follows. An excess of 50% aqueous ethylenediamine was added to 2.99 g. of K_2PtBr_6 in 100 ml. of water at room temperature. After 3 hr., the solution was acidified with hydrobromic acid, heated to 90°, then cooled to 10°. The orange-colored powder that separated was filtered, washed with water followed by ethanol and ether, and dried in air. The yield was 1.78 g. or 78% based on K_2PtBr_6. *Anal.* Calcd. for $[Pt(en)Br_4]$: Pt, 34.0; Br, 55.6. Found: Pt, 34.0; Br, 55.3. This substance is soluble in both N,N'-dimethylformamide and γ-butyrolactone, and dissolves in liquid ammonia owing to the occurrence of reactions described elsewhere.[2]

Ethylenediaminedichloroplatinum(II), $[Pt(en)Cl_2]$.—Although another method of synthesis has been reported,[7] the following procedure is both simple and efficient. To 1.30 g. (0.00313 mole) of $[Pt(en)Br_2]$ suspended in 75 ml. of water was added to 1.064 g. (0.00626 mole) of silver nitrate and the mixture was acidified with 1 ml. of 6 *N* nitric acid. After heating the reaction mixture at 90° for 2 hr., the precipitated silver bromide was filtered off, and the filtrate was treated with excess potassium chloride solution. Golden yellow needles of the desired chloride separated after about 5 min., whereupon the solution was cooled to 0° and filtered. The product was washed with water, ethanol, and dried for 12 hr. at 110°. The yield was 0.93 g. or 91% based on $[Pt(en)Br_2]$. *Anal.* Calcd. for $[Pt(en)Cl_2]$: Pt, 59.8; Cl, 21.7. Found: Pt, 59.6; Cl, 21.7.

Ethylenediaminediiodoplatinum(II), $[Pt(en)I_2]$.—This substance was prepared by a method analogous to that used by Schleicher, *et al.*[9] Thus, 1.4445 g. (0.0035 mole) of $[Pt(en)Br_2]$ slurried in 150 ml. of water was treated with 1.1913 g. (0.0070 mole) of silver nitrate for 1 hr. at 90°. The precipitated silver bromide was removed by filtration and excess potassium iodide was added to the filtrate. The fluffy yellow solid that separated immediately was filtered, washed with water and with ethanol and dried in air. The yield was 1.73 g. or 96.7% based on $[Pt(en)Br_2]$. *Anal.* Calcd. for $[Pt(en)I_2]$: Pt, 38.3; I, 49.8. Found: Pt, 38.4; I, 49.5.

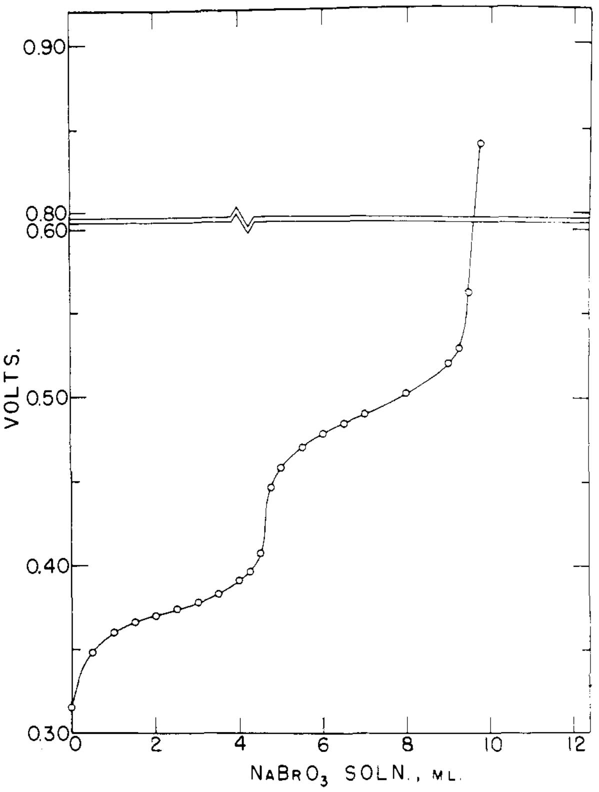

Fig. 1.—Potentiometric titration of $[Pt(en)_2]PtBr_4$ with sodium bromate.

Platinum(IV) Iodide, PtI_4.—In accordance with the procedure described by Pigeon,[11] PtI_4 was prepared in quantitative yield by heating 5.54 g. of platinum as H_2PtCl_6 with 19 g. of KI at 80°. *Anal.* Calcd. for PtI_4: Pt, 27.8. Found: Pt, 27.8.

Ethylenediaminetetraiodoplatinum(IV), $[Pt(en)I_4]$.—Approximately 1 g. of PtI_4 was dissolved in a slight excess of aqueous potassium iodide solution to provide a solution of K_2PtI_6 which was treated dropwise with 50% aqueous ethylenediamine. A very fine maroon-red precipitate separated at once and continued to form until the solution was colorless. Since analysis showed that this product was impure, it was treated with 100 ml. of γ-butyrolactone at room temperature; this resulted in a deep red solution and a bronze colored solid that was removed and discarded. The filtrate was diluted fivefold with water and fine glistening black crystals separated. This product was filtered, washed with water and with ethanol and dried in air; the yield was *ca.* 1 g. *Anal.* Calcd. for $[Pt(en)I_4]$: Pt, 25.6; I, 66.5. Found: Pt, 25.5; I, 66.5.

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[9] A. Schleicher, H. Henkel and L. Spies, *J. prakt. Chem.*, **105**, 31 (1922).

[10] It is assumed that this product is the *trans* isomer since it seems well established that complexes of the type $[Pt(en)_2]Br_2$ retain their configuration upon oxidation [see F. Basolo, *Chem. Revs.*, **52**, 459 (1953)].

[11] L. Pigeon, *Ann. chim. Phys.*, **2**, 496 (1894).