$BiBr_5^=$ gives an estimate, 180, for the ratio of the formation constants of the two ions. This value at $\mu = 5.00$ is in good qualitative agreement with the value derived from potentiometric measurements on the chloride and bromide series made by Dr. Sten Åhrland at $\mu = 2.00$ and kindly made available to us prior to publication.

Continuous Variations.—It has been shown that when chloride and bromide were added in varying ratios to a bismuth solution containing 1 *M* perchloric acid, three mixed ligand complexes, $BiBr_4Cl^=$, $BiBr_2Cl_3^=$, $BiBrCl_4^=$ with a small amount of $BiBr_3Cl_2^=$ were formed in equilibrium with the parent complexes $BiBr_5^-$ and $BiCl_5^=$. Since the total halide concentration was maintained at 4 *M* and the bismuth concentration at 15 p.p.m., the data plotted in Fig. 1 might be used for a continuous variations plot. The simplifying assumption was made that the parent complexes would react to form a single mixed ligand complex.

As Katzin and Gebert[6] and Woldbye[7] have concluded that the method of continuous variations should not be strictly valid under conditions like these where more than one complex is present and absorbing, it was of interest to see what application of the method would indicate. Application of the method of continuous variations at a number of wave lengths showed several maxima and minima, of which the most definite corresponded to formation of the species $BiBrCl_4^=$. The results as a whole, however, did not tend to inspire confidence and it was concluded that as predicted,[6,7] the method was not properly applicable to such a complicated system.

Acknowledgment.—This work was supported in part by the United States Atomic Energy Commission.

[6] I. I. Katzin and E. Gebert, THIS JOURNAL, **72**, 5455 (1950).

[7] F. Woldbye, *Acta Chem. Scand.*, **9**, 299 (1955).

CAMBRIDGE, MASS.

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

The Ethylenediamineplatinum Trihalides[1]

BY GEORGE W. WATT AND ROBERT E. MCCARLEY

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The mode of formation of $Pt(en)X_3$, where X = Cl, Br or I, together with a variety of chemical and physical properties, are interpreted as indicating that these compounds do not involve the 3^+ oxidation state of platinum. Partly by analogy with other platinum and palladium compounds, it is concluded that these compounds contain alternating Pt^{2+} and Pt^{4+} in polymeric species in which the essential units $[Pt(en)Br_2]$ and $[Pt(en)Br_4]$ are bridged through halogen. Accordingly, the bromide, for example, should be formulated as ethylenediaminedibromoplatinum(II) tetrabromoethylenediamineplatinum (IV), $[Pt(en)Br_2][Pt(en)Br_4]$. Evidence bearing upon some unusual color changes exhibited by these compounds is presented and discussed.

As a part of a program of studies on the lower oxidation states of platinum, we have carried out an extensive investigation of the synthesis and properties of compounds of the type $Pt(en)X_3$, in which platinum exhibits the *apparent* but still controversial 3^+ oxidation state. That platinum should form compounds corresponding to the 3^+ state is reasonable by analogy to complexes of the type represented by bis-(triethylphosphine)-tribromonickel(III)[2–6] and the monomeric[7] palladium(III) fluoride.[8,9] Levy[10] has reported the preparation of $H[Pt(CN)_4]$ and $Pt(CN)_3$, but whether these species involve Pt^{3+} remains in doubt. There are several other cases that involve the apparent 3^+ oxidation state of platinum but in which it seems more likely that halogen bridging between alternating Pt^{2+} and Pt^{4+} is involved,[11–18] and much the same conclusions have been reached with respect to closely related palladium compounds.[19] In addition, Hall and Plowman[20] interpret an inflection in the current–potential curve for the reduction of $[Pt(en)_3]^{4+}$ at the dropping mercury electrode as indicative of the transient intermediation of Pt^{3+}. Finally, Rich and Taube[21] postulate Pt^{3+} as an intermediate involved in the exchange of Cl^- with $(PtCl_6)^{2-}$ and of Cl between $(PtCl_6)^{2-}$ and $(PtCl_4)^{2-}$.

Although originally concerned largely with the question of the oxidation states of platinum, some of the work described in this paper was stimulated by the unusual color characteristics of (particularly) $Pt(en)Br_3$.

Experimental

Unless otherwise indicated, all materials used were reagent grade chemicals. Reactions in liquid ammonia were carried out under strictly anhydrous conditions.[22]

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

[2] K. A. Jensen, *Z. anorg. allgem. Chem.*, **229**, 275 (1936).

[3] K. A. Jensen and B. Nygaard, *Acta Chem. Scand.*, **3**, 474 (1949).

[4] R. Daudel and A. Bucher, *J. chim. phys.*, **42**, 6 (1945).

[5] G. A. Barclay and R. S. Nyholm, *Chem. and Ind.*, 378 (1953).

[6] R. S. Nyholm, *J. Chem. Soc.*, 2016 (1950).

[7] A. G. Sharpe, *ibid.*, 3444 (1950).

[8] O. Ruff and E. Ascher, *Z. anorg. allgem. Chem.*, **183**, 206 (1929).

[9] R. S. Nyholm and A. G. Sharpe, *J. Chem. Soc.*, 3579 (1952).

[10] L. A. Levy, *ibid*, **101**, 1081 (1912).

[11] S. M. Jorgensen, *J. prakt. Chem.*, **33**, 489 (1886).

[12] H. Reihlen and E. Flohr, *Ber.*, **67**, 2010 (1934).

[13] H. D. K. Drew and H. J. Tress, *J. Chem. Soc.*, 1244 (1935).

[14] K. A. Jensen, *Z. anorg. allgem. Chem.*, **229**, 252 (1936).

[15] F. G. Mann and D. Purdie, *J. Chem. Soc.*, 873 (1936).

[16] L. Chugaev and I. Chernyaev, *Z. anorg. allgem. Chem.*, **182**, 159 (1929).

[17] C. Brosset, *Arkiv. Kemi, Min. Geol.*, **25A**, No. 19 (1948).

[18] C. S. Adams, M.S. Thesis, The University of Sydney (Australia); *cf.*, P. E. Fielding and D. P. Mellor, *J. Chem. Phys.*, **22**, 1152 (1954).

[19] A. J. Cohen and N. Davidson, THIS JOURNAL, **73**, 1955 (1951).

[20] J. R. Hall and R. A. Plowman, *Australian J. Chem.*, **8**, 158 (1955).

[21] R. L. Rich and H. Taube, THIS JOURNAL, **76**, 2608 (1954).

[22] G. W. Watt and C. W. Keenan, *ibid.*, **71**, 3833 (1949).

Platinum was determined either by ignition to the metal or spectrophotometrically.[23] X-Ray diffraction patterns were obtained using a Hayes diffraction unit, Cu $K\alpha$ radiation, an Ni filter, a tube voltage of 35 kv., a filament current of 15 ma. and exposure times that depended upon the nature of the sample. Infrared spectra[24] were obtained using a Baird recording spectrophotometer, Model 4-55. Magnetic susceptibility measurements were made with a modified Curie–Cheneveau balance.[25,26]

Synthesis of $Pt(en)Br_3$.—Ethylenediaminedibromoplatinum(II), $[Pt(en)Br_2]$ (0.590 g.), was slurried in 50 ml. of water, 0.540 g. of potassium hexabromoplatinate(IV),[27] K_2PtBr_6, was added, and the reaction mixture was heated at 90° for 30 min. The product was cooled to room temperature, and the iridescent green crystals were separated from the red-brown solution, washed five times with 5 ml. of water, and dried in air. The yield was 0.68 g. or 96.5%. *Anal.*[28] Calcd. for $Pt(en)Br_3$: Pt, 39.4; Br, 48.4; N, 5.66. Found: Pt, 39.5; Br, 48.1; N, 5.65. That the anticipated K_2PtBr_4 was present in the filtrate was verified by adding 50% aqueous ethylenediamine until the solution was distinctly basic, cooling to 0° for 4 hr., and filtering the resulting $[Pt(en)Br_2]$ (*ca.* 200 mg.) and washing with cold water. *Anal.* Calcd. for $[Pt(en)Br_2]$: Pt, 47.0. Found: Pt, 47.0

By a procedure analogous to that used by Drew and Tress[13] for the synthesis of $Pt(en)Cl_3$, the corresponding bromide was prepared by suspending 0.356 g. of $[Pt(en)Br_2]$ and 0.257 g. of $[Pt(en)Br_4]$ each in 25 ml. of water at 90°, mixing the two, heating for 30 min. at 90°, cooling to 0° and filtering the resulting green crystals of $Pt(en)Br_3$. The yield was 0.515 g. or 84%.

By another method, 0.318 g. of $[Pt(en)Br_2]$ and 0.231 g of $[Pt(en)_2Br_2]Br_2$ were heated for 30 min. at 90° in 50 ml. of water. After cooling the reaction mixture to room temperature, the green crystals were filtered, washed with water and acetone, and dried in air. The yield of $Pt(en)Br_3$ was 0.254 g. or 92%.

Both small and large scale syntheses of $Pt(en)Br_3$ were effected by still another procedure. A solution (50 ml.) containing 0.959 g. of Pt as H_2PtBr_6 was divided into two equal portions and the H_2PtBr_6 in one portion was reduced to H_2PtBr_4 at 90° by dropwise addition of a solution containing the calculated quantity of sodium sulfide. The two solutions were combined and ethylenediamine was added until the *p*H was adjusted to 5, whereupon red crystals of $(enH_2)PtBr_6$ separated but were converted slowly to $Pt(en)Br_3$. After filtration, the product was washed with a hot dilute solution of ethylenediamine, hot water and ethanol. The yield was 35.3% based on total platinum used.

Synthesis of $Pt(en)Cl_3$.—For comparison studies, $Pt(en)Cl_3$ was prepared in 90% yield by the method of Chugaev and Chernyaev.[16]

Synthesis of $Pt(en)I_3$.—For use in this synthesis, platinum(IV) iodide was prepared as described by Pigeon[29] and ethylenediaminediiodoplatinum(II) was prepared by the method of Henkel.[30] A solution of K_2PtI_6 was produced by adding 0.190 g. of KI to 0.389 g. of PtI_4 in 15 ml. of water; 0.561 g. of $[Pt(en)I_2]$ was added and this mixture was heated for 30 min. on a steam-bath. The resulting crystals were dissolved in 30 ml. of warm dimethylformamide, filtered to removea small quantity of an insoluble black solid, and diluted with water. The bronze colored crystals (*ca.* 0.4 g.) that separated were filtered, washed with water and acetone, and dried at 110°. *Anal.* Calcd. for $Pt(en)I_3$: Pt, 30.7; I, 59.9. Found: Pt, 30.8; I, 59.9.

Synthesis of $Pt(en)BrI_2$.—Solutions containing 0.336 g. of $[Pt(en)Br_2]$ in 20 ml. of dimethylformamide and 0.633 g. of $[Pt(en)I_4]$[31] in 20 ml. of dimethylformamide were mixed and diluted *immediately* with water to minimize halogen exchange and to precipitate the bronze-colored $Pt(en)BrI_2$ in 100% yield (0.952 g.). *Anal.* Calcd. for $Pt(en)BrI_2$: Pt, 33.1. Found: Pt, 33.0. The total silver halide calculated for a 0.1880-g. sample of this product is 0.2097 g.; found, 0.2075 g.

Properties of the Solids, $Pt(en)X_3$.—X-Ray diffraction data for X = Cl, Br and I are listed in Table I. The pattern for $Pt(en)BrI_2$ showed lines of maximum intensity for d = 7.11, 4.86 and 2.96; lines of medium intensity for d = 5.91, 5.34, 4.29 and 3.85; and seven less intense lines.

TABLE I

X-RAY DIFFRACTION DATA FOR $Pt(en)X_3$

$Pt(en)Cl_3$		$Pt(en)Br_3$		$Pt(en)I_3$	
d, Å.	I/I_0	*d*, Å.	I/I_0	*d*, Å.	I/I_0
6.71	0.8	6.99	0.6	7.09	1.0
4.89	0.4	5.85	.3	5.97	0.3
4.54	1.0	4.94	.8	5.44	.4
3.98	0.7	4.70	1.0	4.85	.9
2.78	.7	4.15	0.6	4.35	.9
2.57	.2[a]	2.84	.7	3.02	.7
2.39	.4	2.48	.5	2.95	.7
2.31	.2	2.42	.2[a]	2.62	.5
2.27	.3	2.34	.5	2.57	.3
1.99	.2	2.02	.4	2.46	.4
1.96	.3	1.92	.3	2.20	.4
		1.84	.5	2.12	.7
		1.72	.2	1.95	.2[a]
		1.67	.2		

[a] Less intense lines omitted.

When *green* $Pt(en)Br_3$ is ground in a mortar, the crystals are converted to a solid that is black in bulk but *purple* when viewed in thin cross-section against a white background. No gradation in the color of either form is observed among crystals retained on 100, 150 and 200 mesh sieves, and the colors of −200 mesh crystals of both forms are the same as in bulk. This color change is not effected by heating the green form (*e.g.*, at 200° for 12 hr.) or by subjecting it to pressures up to 5000 p.s.i. Both the green and purple forms decompose at temperatures that depend upon the rate of heating; *e.g.*, at 285° with a heating rate of 2°/min. The composition of the purple form was found to be the same as that of the green crystals (found: Pt, 39.5; N, 5.67), and the X-ray diffraction pattern gave substantially the same data as those listed in Table I for the green form. Both the green and the purple crystals were found to be diamagnetic and to have the same susceptibility, *i.e.*, -0.1×10^{-6} c.g.s.[32] When *bronze* $Pt(en)I_3$ or *bronze* $Pt(en)BrI_2$ crystals are ground, an entirely similar color change to *black* occurs. However, *red* $Pt(en)Cl_3$ crystals become less intensely colored upon grinding and are finally light orange-colored.

Petrographic Examination.[33]—Examination of green $Pt(en)Br_3$ under the petrographic microscope showed that the thin platelets consist of parallelogram-shaped crystals having an acute angle of 58–59°, and of regular hexagon-shaped crystals. When the former is oriented with its long axis parallel to the vibration plane of polarized light, a yellow-green color is observed, but the crystal becomes opaque when the short axis is parallel to the vibration plane. Similarly, the hexagonal form exhibits a yellow-green color when the plane of polarization is perpendicular to parallel sides of the crystal and becomes opaque when turned through a 90° arc. Between crossed Nicol prisms, the crystals are opaque in both of the orientations indicated. With purple $Pt(en)Br_3$, no characteristic crystal form was evident; the particles appeared to consist of aggregates that were opaque to polarized light in all positions. The red $Pt(en)Cl_3$ consisted of either hexagonal plates or slender needles that exhibited a red color when the needle axis was

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

(24) We are indebted to Drs. W. H. Reas and M. C. Lambert, General Electric Co., Richland, Washington, for data on certain samples of $Pt(en)Br_3$.

(25) F. W. Gray and J. Farquharson, *J. Sci. Instr.*, **9**, 1 (1932).

(26) W. K. Witherspoon, M.S. Thesis, Tulane University, New Orleans, La., 1949.

(27) Use of ethylenediammoniumhexabromoplatinate(IV), enH_2PtBr_6, gives equally satisfactory results.

(28) The composition of all samples of this compound synthesized by other methods was confirmed by analysis for Pt and/or Br.

(29) L. Pigeon, *Ann. chim. phys.*, **2**, 496 (1894).

(30) H. Henkel, *J. prakt. Chem.*, **105**, 31 (1922).

(31) Prepared by a method to be described elsewhere.

(32) We are indebted to Prof. P. W. Selwood for independent confirmation of these results.

(33) The assistance of Prof. S. E. Clabaugh of the Department of Geology is gratefully acknowledged.

parallel to the plane of polarization and a yellow color when perpendicular. Under crossed Nicols, the crystals showed extinction in both of these positions. The triiodide consisted of slightly elongated six-sided platelets that were brown-opaque when the long axis was oriented parallel to the electric vector of the polarized light and yellow-green when perpendicular. In both positions, the crystals showed extinction when observed through crossed Nicols. The latter was also true of Pt(en)BrI$_2$, the characteristic crystals of which were rectangular platelets that were dichroic; they exhibited a copper color when the short axis was parallel to the electric vector and were opaque when turned through 90°.

Electron photomicrographs failed to provide any conclusive evidence bearing upon the reasons for the color changes exhibited by Pt(en)X$_3$ as a function of particle size.

Infrared Spectra.—The infrared spectra of the green and purple forms of solid Pt(en)Br$_3$ (3–15 μ) and the infrared spectra of the solid compounds [Pt(en)Br$_2$], Pt(en)Br$_3$ and [Pt(en)Br$_4$] (2–16 μ) were studied. The detailed data are available elsewhere[34] and their significance is discussed below.

Properties of Solutions of Pt(en)X$_3$.—Compounds of this type were found to be substantially insoluble in all common solvents and appreciably soluble only in liquid ammonia, dimethylformamide and γ-butyrolactone. From the yellow-orange solutions of either the green or purple form of Pt(en)Br$_3$ in the latter two solvents, only the green form could be crystallized. (Also, when suspended in water and heated, the purple form is converted slowly to the green.)

Conductance.—The conductance of Pt(en)X$_3$ in dimethylformamide at 25.5° was determined using a dipping type cell with platinized platinum electrodes and a cell constant of 0.88 cm.$^{-1}$. The specific conductance of the solvent was 2.26×10^{-6} ohm^{-1} cm.$^{-1}$; Dawson, *et al.*,[35] reported 1.83×10^{-6} at 25.0°. The molar conductances of 0.921 m*M* Pt(en)Br$_3$, 1.07 m*M* Pt(en)Cl$_3$ and 1.48 m*M* Pt(en)I$_3$ were found to be 19.6, 12.7 and 6.9 ohm^{-1} cm.^{2}, respectively. Attempts to measure the conductivity of solid Pt(en)Br$_3$ were unsuccessful owing to its high resistance (>10^6 ohms).

Absorption Spectra.—The absorption spectra of solutions of [Pt(en)Br$_2$], Pt(en)Br$_3$ and [Pt(en)Br$_4$] in dimethylformamide are shown in Fig. 1; the spectrum of Pt(en)Br$_3$ in γ-butyrolactone is included for comparison. Solutions of Pt(en)I$_3$ in dimethylformamide are unstable in that the intensity of the color gradually decreases over several days. Solutions (0.360 m*M*) in γ-butyrolactone however are more stable and show a single intense absorption band at 365 mμ; another strong band in the ultraviolet is indicated but could not be measured owing to strong absorption by the solvent.

Reactions of Pt(en)X$_3$.—Ten milliliters of anhydrous liquid ammonia was condensed on 0.3318 g. of green Pt(en)Br$_3$ at −70°; the color of the solid changed from green to yellow and the solid dissolved as the temperature was raised to −33.5°. After complete removal of the solvent by evaporation under reduced pressure, the residue was treated with water to provide a yellow water-insoluble solid and a yellow solution. The insoluble product gave an X-ray diffraction pattern substantially identical with that for [Pt(en)Br$_2$][36]; the yield was 0.1287 g., or 92.5% assuming that one-half of the Pt(en)Br$_3$ was converted to [Pt(en)Br$_2$]. The aqueous solution was evaporated to *ca.* 10 ml., a very small quantity of unchanged green Pt(en)Br$_3$ was removed by filtration, and the filtrate was diluted tenfold with acetone. The resulting yellow precipitate could be obtained only in very small quantities owing to its great solubility; this product, however, was isolated in quantity sufficient to establish that (total Br)/Pt = 3, (ionic Br)/Pt = 2, and (by means of X-ray diffraction patterns) that this product is the same as that which results when the initial product of the reaction between [Pt(en)Br$_4$] and liquid ammonia loses HBr in accordance with equation (4); see below. For example, 0.502 g. of [Pt(en)Br$_4$] was treated with liquid ammonia as described above and the yellow crystalline product was dried for 12 hr. at 115°. *Anal.* Calcd. for [Pt(en)(NH$_3$)$_3$Br]Br$_3$·NH$_3$: Pt, 30.4; ionic Br, 37.3; ionic Br/Pt, 3.00. Found: Pt, 31.0; ionic Br, 37.1; ionic Br/Pt, 2.93. This product was also identified on the basis of its X-ray diffraction pattern.[36]

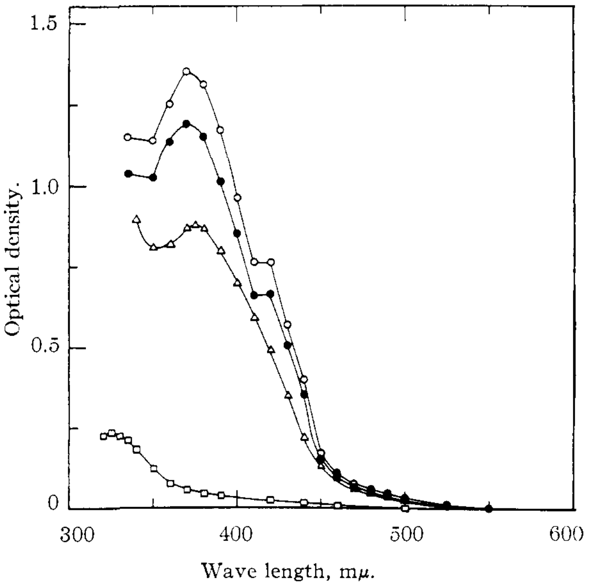

Fig. 1.—The absorption spectra of: ○, [Pt(en)Br$_3$ (1.100 m*M*); ● [Pt(en)Br$_4$] (0.550 m*M*); □, Pt(en)Br$_2$] (0.550 m*M*) in N,N-dimethylformamide; △, Pt(en)Br$_3$ (0.755 m*M*) in γ-butyrolactone.

In order to determine whether Pt(en)BrI$_2$ yields [Pt(en)Br$_2$] upon reaction with liquid ammonia (see Discussion), 0.6260 g. of Pt(en)BrI$_2$ was treated with 5 ml. of liquid ammonia as described above. The resulting product (0.6658 g.) was leached with water and the red insoluble solid was found to contain 28.6% Pt; by means of X-ray diffraction patterns,[36] this product was shown to consist of a mixture of Pt(en)I$_3$ and Pt(en)I$_4$. No evidence whatever could be found for the presence of [Pt(en)Br$_2$] as a product of this reaction.

Discussion

The foregoing evidences lead to the conclusion that compounds of the type Pt(en)X$_3$ do not involve the 3$^+$ oxidation state of platinum, but rather the 2$^+$ and 4$^+$ states in polymers of alternating [Pt(en)Br$_2$] and [Pt(en)Br$_4$] units with halogen bridging between the platinum atoms. The arguments in support of this conclusion are as follows.

The compound Pt(en)Br$_3$, for example, has been synthesized from a neutral compound of Pt^{2+}, [Pt(en)Br$_2$] and either an anionic Pt^{4+} species, (PtBr$_6$)$^{2-}$, a neutral compound of Pt^{4+}, [Pt(en)Br$_4$], or cationic Pt^{4+} in [Pt(en)$_2$Br$_2$]Br$_2$. Synthesis from (PtBr$_4$)$^{2-}$ and (PtBr$_6$)$^{2-}$ in the presence of ethylenediamine probably differs only in that the reactants [Pt(en)Br$_2$] and [Pt(en)Br$_4$] are generated *in situ* with probably intermediation of (enH$_2$)PtBr$_6$. The mechanism of formation of Pt(en)Br$_3$ from [Pt(en)Br$_2$] and K$_2$PtBr$_6$ may be represented in terms of two steps

$$[\mathrm{Pt(en)Br_2}] + (\mathrm{PtBr_6})^{2-} \rightleftarrows [\mathrm{Pt(en)Br_4}] + (\mathrm{PtBr_4})^{2-} \quad (1)$$

$$[\mathrm{Pt(en)Br_2}] + [\mathrm{Pt(en)Br_4}] \rightleftarrows 2\mathrm{Pt(en)Br_3} \quad (2)$$

where (1) may proceed *via* an electron transfer process with subsequent migration of bromine or by ligand exchange involving both ethylenediamine and bromine. The latter is improbable since these

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

[35] L. R. Dawson, M. Golben, G. R. Leader and H. K. Zimmerman, *J. Electrochem. Soc.*, **99**, 28 (1952).

[36] The data for the corresponding pure compound, upon which this identification was based, are to be included in a forthcoming publication.

reactions are fast and ethylenediamine exchange should be a relatively slow process. On the other hand, conditions are optimum for the formation of a halogen bridge between $[Pt(en)Br_2]$ and $(PtBr_6)^{2-}$ through which the electron transfer may take place[21,37,38] since Pt in $[Pt(en)Br_2]$ has a vacant 4p orbital for the formation of the bridging bond. The synthesis from $[Pt(en)Br_2]$ and $[Pt(en)_2Br_2]Br_2$ is strictly analogous; in this case the necessary $[Pt(en)Br_4]$ could arise from the reaction

$$[Pt(en)Br_2] + [Pt(en)_2Br_2]Br_2 \rightleftharpoons [Pt(en)Br_4] + [Pt(en)_2]Br_2 \quad (3)$$

These methods of synthesis have one feature in common in that they provide either directly or indirectly for the availability of $[Pt(en)Br_2]$ and $[Pt(en)Br_4]$ as the structural units necessary for the formation of the solid product obtained. The yields of product obtained from the various starting materials support this conclusion.

That bridging through halogen is involved is also indicated by analogy with $Pt(NH_3)_2Br_3$ which has been shown to contain bromine bridges between alternating Pt^{2+} and Pt^{4+}.[17] The intense colors exhibited by $Pt(en)X_3$ suggest a high degree of interaction between the two oxidation states of platinum and yet an interaction insufficient to render the two equivalent. The latter is indicated by the diamagnetism of $Pt(en)X_3$, but at the same time the absence of the paramagnetic susceptibility required by monomeric $Pt(en)X_3$ is not entirely conclusive owing to the possibility of magnetic coupling through a metal-to-metal bond or a bridge through the halogen atom.[39] More convincing evidence of the non-equivalence of the platinum atoms is provided by the solid state infrared spectra of $[Pt(en)Br_2]$, $[Pt(en)Br_4]$ and $Pt(en)Br_3$. The spectrum of $Pt(en)Br_3$ is largely a composite of the spectra of $[Pt(en)Br_2]$ and $[Pt(en)Br_4]$. The over-all similarity of these spectra is to be expected since the spectra observed in this region are attributable solely to absorption by the ethylenediamine bound in these complexes; minor shifts in frequencies and alternations in intensities however assure the individuality of the green $Pt(en)Br_3$. The extra bands for $Pt(en)Br_3$ that appear as shoulders on the major absorption bands are suggestive of a change in symmetry of the absorbing group. The behavior of $Pt(en)Br_3$ toward polarized light also supports the bridged structure, since this compound exhibits properties remarkably similar to $Pd(NH_3)_2Cl_3$ which has been shown to contain alternating Pd^{4+} octahedra and Pd^{2+} square planes bridged through chlorine to form infinite chains.[19] The high absorption of light along the one axis of the crystal is due presumably to the chain structure which runs parallel to the axis.

Both the X-ray diffraction data and the petrographic examination show that the compounds $Pt(en)X_3$ where X = Cl, Br and I, have the same structure; they are isomorphous and probably belong to either the rhombic or orthorhombic system. Although the very complex X-ray patterns were not analyzed in detail, they indicate the same basic unit cell, the dimensions of which increase in the order $Cl < Br < I$. The synthesis work reported above shows that the ease of formation increases in the order $Cl < Br < I$ which is the same as the order of polarizability of the halogens. Thus, the iodides should be expected to form the most stable bridged structure, and this is supported by earlier work on the relative stabilities of other binuclear complexes of platinum halides.[40]

The properties of $Pt(en)Br_3$ and $Pt(en)I_3$ in solution in dimethylformamide and in γ-butyrolactone as well as their reactions with liquid ammonia show that the compounds $Pt(en)X_3$ are unstable in solution, and the conductance data given above show that the products formed are predominantly covalent species. As shown by Fig. 1, the sum of the optical densities of solutions of $[Pt(en)Br_2]$ and $[Pt(en)Br_4]$ in dimethylformamide is essentially equal to that for the corresponding concentration of $Pt(en)Br_3$. Similarly, the spectra of $Pt(en)I_3$ and $[Pt(en)I_4]$ in γ-butyrolactone show that the former decomposes to $[Pt(en)I_2]$ and $[Pt(en)I_4]$ in solution. The latter is a highly absorbing species having a molecular extinction coefficient of 6200 at 365 mμ. At the low concentration of 0.380 m*M* $Pt(en)I_3$, the observed spectrum is almost entirely attributable to $[Pt(en)I_4]$ since $[Pt(en)I_2]$ at an equivalent concentration shows only slight absorption in this region of the spectrum. Upon reaction with liquid ammonia at −33.5°, $Pt(en)Br_3$ yields $[Pt(en)Br_2]$ and $[Pt(en)Br_4]$. The former was isolated directly in the anticipated quantity and was thereby shown to be stable toward ligand substitution in the presence of liquid ammonia. The latter was shown by independent experiments to react with ammonia to form $[Pt(en)(NH_3)_3Br]Br_3 \cdot NH_3$ which loses one mole of ammonia when dried. X-Ray diffraction patterns for the gross product of the reaction with ammonia provide a positive identification of both $[Pt(en)Br_2]$ and $[Pt(en)(NH_3)_3Br]Br_3$. Upon treatment with water the latter reacts as

$$[Pt(en)(NH_3)_3Br]Br_3 + H_2O \rightleftharpoons [Pt(en)(NH_3)_2(NH_2)Br]Br_2 + H_3OBr \quad (4)$$

and precedent for this interpretation is found in Tschugaev's work on the interaction of $[Pt(NH_3)_5Br]Br_3$ and aqueous ammonia.[41] Thus, in the present work we find total Br/Pt = 3 and ionic Br/Pt = 2, as required by equation 4.

The primary reason for synthesizing $Pt(en)BrI_2$ was to test further for electron exchange between Pt^{2+} and Pt^{4+} in the solid. By virtue of the method of synthesis employed, this compound should be $[Pt(en)Br_2][Pt(en)I_4]$ and, by analogy with the bromide, treatment with liquid ammonia at −33.5° should yield $[Pt(en)Br_2]$ as a water-insoluble product. However, $Pt(en)I_3$ and $[Pt(en)I_4]$ were the only products that could be identified; $[Pt(en)Br_2]$ was not found in either the water-insoluble or water-soluble fractions. Although these experiments were inconclusive with respect to electron exchange, the reactions observed merit further study.

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(37) H. Taube, H. Myers and T. L. Rich, THIS JOURNAL, **75**, 4118 (1953).

(38) H. Taube and H. Myers, *ibid.*, **76**, 2103 (1954).

(39) R. S. Nyholm, *Quart. Revs.*, **7**, 377 (1954).

(40) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 3858 (1955).

(41) L. Tschugaev, *Z. anorg. allgem. Chem.*, **137**, 1, 401 (1924).

With reference to the unprecedented color changes exhibited by $Pt(en)X_3$ when ground, the data given above rule out both isomerization and crystalline polymorphism. The color change from green to purple $Pt(en)Br_3$ is neither temperature nor pressure dependent. It therefore appears that this change is related to either particle size or a selective cleavage along a specific plane which then appears purple by reflected light. Both electron photomicrographs and the petrographic examination showed that the particle size of the green and purple forms is not significantly different but that the individual particles of the purple form consist of aggregates of very small particles. Thus a random orientation of small particles would render the purple particles opaque to polarized light in all positions. The reason for the difference in color by ordinary white light is less readily understood. If selective cleavage occurs and if the actual crystal size of the purple form is much smaller than that of the green, it is reasonable that color should be more dependent on reflected light owing to the increased surface area.

AUSTIN, TEXAS

[CONTRIBUTION FROM THE NORSK HYDRO'S INSTITUTE FOR CANCER RESEARCH, THE NORWEGIAN RADIUM HOSPITAL]

The Equilibrium Constants and Oxidation–Reduction Potentials of Some Thiol–Disulfide Systems[1]

BY LORENTZ ELDJARN AND ALEXANDER PIHL

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A new procedure for the determination of equilibrium constants of thiol–disulfide systems is described. The procedure has been used in the study of the equilibria of five X-ray protective thiols with cystine and glutathione, respectively. The approximate, practical reaction rates, and the appropriate equilibrium constants were measured at *p*H 7.4 and 37°. In all instances *K*-values were found which imply that high concentrations of mixed disulfides were present in the equilibrium mixtures. On the basis of the equilibrium constants, which were obtained at the desired *p*H and temperature under truly reversible conditions, the standard oxidation–reduction potentials relative to that of glutathione were calculated. The data have enabled us to calculate the oxidation–reduction potential of cystine/cysteine relative to that of glutathione.

In the present report a new procedure for the determination of the equilibrium constants of thiol–disulfide systems is described.

When a thiol is allowed to interact with a disulfide several reactions take place[2]

$$\mathrm{XSH + YSSY \rightleftarrows XSSY + YSH} \tag{1}$$

$$\mathrm{XSSY + XSH \rightleftarrows XSSX + YSH} \tag{2}$$

The equilibrium constants of such systems are defined as

$$K_2 = \frac{[\mathrm{XSSY}][\mathrm{YSH}]}{[\mathrm{XSH}][\mathrm{YSSY}]};\ K_3 = \frac{[\mathrm{XSSX}][\mathrm{YSH}]}{[\mathrm{XSH}][\mathrm{XSSY}]};$$

$$K_1 = K_2K_3 = \frac{[\mathrm{XSSX}][\mathrm{YSH}]^2}{[\mathrm{YSSY}][\mathrm{XSH}]^2};$$

$$K_4 = \frac{K_2}{K_3} = \frac{[\mathrm{XSSY}]^2}{[\mathrm{XSSX}][\mathrm{YSSY}]}$$

Our previous determinations of *K*-values were based on measurements of the mixed disulfide content in equilibrium mixtures, in the presence and in the absence of oxygen.[2b] This method was successfully applied to the glutathione + N,N′-diacetylcystamine system. However, attempts to use this method in the study of other systems were uniformly unsuccessful.

The procedure here to be described for the determination of equilibrium constants of thiol–disulfide systems is based on the direct measurement of the equilibrium concentrations of three of the five participating molecular species. After incubation of a thiol with a disulfide, one of which is labeled with S^{35}, the three labeled molecular species (equations 1 and 2) are separated by electrophoresis at *p*H 2 in mercuric acetate treated paper. Paper electrophoresis in the absence of mercuric acetate, as previously used,[2b] permits the separation of mixed disulfides from the labeled thiol and symmetrical disulfides, which migrate together. The pretreatment of the electrophoresis paper with mercuric acetate retards the migration of the thiols so that the three labeled compounds appear as distinct peaks. When the concentrations of the three labeled components have thus been determined, the concentrations of the unlabeled constituents are obtained easily by difference.

In the present paper the procedure is used for the determination of the equilibrium constants, at *p*H 7.4 and 37°, of systems containing cystine or oxidized glutathione and various sulfur containing X-ray protective thiols. Our approach seems to offer a solution to the controversial question of the relative oxidation–reduction potentials of thiol–disulfide systems under physiological conditions.

Experimental

Chemicals.[3]—**Cystamine-S^{35}** and **N,N′-diacetylcystamine-S^{35}** were synthesized as previously described.[4,2b] The corresponding thiols were prepared by electrolytic reduction of the disulfides.[5] **Cystine-S^{35}** and **glutathione-S^{35}** were purchased from The Radiochemical Centre, Amersham, England, and from Schwarz Laboratories, Inc., Mount Vernon, N. Y., U. S. A.

Tetramethylcystamine, tetraethylcystamine and N-pi-

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[2] (a) T. Bersin and J. Steudel, *Ber.*, **71B**, 1015 (1938); (b) L. Eldjarn and A. Pihl, *J. Biol. Chem.*, **225**, 499 (1957).

[3] The following abbreviations are used in this paper: CSH = cysteine, GSH = reduced glutathione, AcRSH = acetylcysteamine, RSH = cysteamine, Me_2RSH = N-dimethylcysteamine, Et_2RSH = N-diethylcysteamine, and PRSH = N-piperidylcysteamine. E_0' = standard oxidation-reduction potential, at *p*H 7.4 and 37°, relative to that of GSSG/GSH, with sign opposite to that used by Latimer (W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952).

[4] L. Eldjarn, *Scand. J. Clin. & Labor. Invest.*, suppl. 13 (1954).

[5] L. Eldjarn and A. Pihl, *J. Biol. Chem.*, **223**, 341 (1956).