

THE DETERMINATION OF THE STABILITIES AND ENTHALPIES
OF DISSOCIATION OF SOME AMMINE COMPLEXES OF PLATINUM(II)

By

Charles P. Knop

A THESIS

Submitted to the School of Advanced Graduate Studies of
Michigan State University of Agriculture and Applied Science
in partial fulfillment of the requirements
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In behalf of each of these, the author humbly offers this and all succeeding work to our Heavenly Father so that they may receive many blessings, as were benignantlly bestowed upon him.

VITA

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ABSTRACT

Dichloro(2,2'-bipyridine)platinum(II), $[\text{Pt}(\text{bipy})\text{Cl}_2]$, suspended in chloroform, was treated with various anhydrous amines and a series of complexes were formed which are represented by the general formula $[\text{Pt}(\text{bipy})(\text{Am})_n]\text{Cl}_2$ where Am is ammonia, methylamine, ethylenediamine and 1,3-diaminopropane and n is 2 for the former two amines and 1 for the latter two. These complexes, upon heating, dissociate into the original components. The pressure of the dissociated ammine vapor over the solid complex was measured as a function of temperature and the thermodynamic quantities ΔF° , ΔH° , and ΔS° for the dissociation were obtained for each complex.

Comparison of these thermodynamic values shows that the four complexes fall into two groups with the complexes containing the monoamine ligands in one group and those of the diamine ligands in the other group. The first group is characterized by large values of ΔH° and ΔS° and the latter group by relatively small values. By a semi-quantitative consideration of lattice energies and entropies it is shown that the large differences in the ΔH° and ΔS° values for the two groups cannot arise from this source

unless the compounds in these groups differ in some way not usually considered. A model is proposed whereby, during the process of heating the complexes, one of the platinum-amine bonds dissociates in the complexes containing the diamine ligands and a chloride ion in the complex becomes coordinated. The thermodynamics for this process are not measured or detected by the experimental methods used in the study and the net result is that the thermodynamic values which are obtained for these two complexes refer to the dissociation of the hypothetical (at 25°) complexes. Difference in lattice energies and entropies between the two groups, under the assumptions of this model, can account for part of the differences in ΔH° and ΔS° but a further comparison cannot be made.

Minor differences in ΔH° and ΔS° within each of the groups are the result of differences in lattice energies and entropies and in the enthalpies and entropies of bonding of the various ligands to the platinum ion. At 25°C the order of decreasing stability for these complexes is given as CH_3NH_2 , NH_3 , en and tn, where these symbols refer to the complexes containing these ligands (en is ethylenediamine and tn is 1,3-diaminopropane). This same order is given for ΔH° and ΔS° .

From the standard free energies and enthalpies of formation of the free amines and their standard entropies and from the thermodynamic values obtained for the dissociation of the complexes, relative values for the standard free energies and enthalpies of formation (from the elements) and the standard entropies of the complexes were obtained. The order of decreasing ΔF°_f for these complexes is given as NH_3 , MeNH_2 , en, tn and for ΔH°_f and S° as CH_3NH_2 , NH_3 , en and tn. These orders refer to the latter two complexes in a hypothetical state.

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BACKGROUND

The Problem

Chelate groups, those which are linked through two atoms to the central atom and so form a ring, give complexes of exceptional stability. Thus, as Werner showed, ethylenediamine has a much greater power of coordination than ammonia ... Again, while phenol is a very weak donor - weaker probably than alcohol - catechol (o-dihydroxybenzene) is a very strong one, and has been shown to be capable of forming complex anions with 27 different metals. Oxalic acid forms far more numerous and stabler complexes than the monocarboxylic acids such as acetic. The list might be continued indefinitely. So general a tendency must be capable of explanation. Now with one important class of chelate compounds, the derivatives of β -diketones, β -keto-esters, salicylic acid and the like, there is a special reason for the stability, since the formation of the ring-complex introduces new possibilities of resonance. But with such groups as ethylenediamine, catechol and the oxalate group, no new resonance possibilities are brought in, and some other explanation must be sought.

... N. Sidgwick (1)

For further development in this field (coordination chemistry) the most urgent need is for more quantitative data. ... the heats of formation of many more series of complexes are required. This information will be particularly valuable if investigations are confined ... to series of complexes in which only one factor is varying from one complex to the next.

... R. Nyholm (2)

Solid dichloro(2,2'-bipyridine)platinum(II) can be treated with various monodentate and bidentate ligands and a series of complexes can be formed, which will evolve the ligand groups on gentle heating, but the 2,2'-bipyridine

will remain bound and the original compound will persist to about 200°C. It was proposed to measure the stability of a series of monodentate and bidentate ammine* complexes by measuring the dissociation pressures of the solid complexes as a function of temperature. This will provide information concerning the stabilities and enthalpies of dissociation of these complexes.

Thermochemistry

Standard free energy, enthalpy, and entropy changes for a chemical reaction are mutually related to the equilibrium constant for the reaction, as shown in the following equations:

$$\Delta F^{\circ} = - RT \cdot \ln K = \Delta H^{\circ} - T \Delta S^{\circ} \quad 1$$

$$\frac{d \ln K}{dT} = \frac{\Delta H^{\circ}}{RT^2} \quad 2$$

The determination of an equilibrium constant is, therefore, of use in obtaining the thermodynamic constants for a

*By the term ammine, it is implied to mean one or more substances containing one or more nitrogen atoms (in the -3 oxidation state) per molecule, including ammonia. By the term amine, the same is implied with the exclusion of ammonia.

reaction. In the reaction for the formation of a complex ion or compound, ML, from the simple ion or compound, M, and some ligand, L,



we define K as

$$K = \frac{a_{ML}}{a_M \cdot a_L} \quad 4$$

where a is the activity of the species involved.

In aqueous solution the activity is a function of the concentration, c,

$$a = \gamma \cdot c \quad 5$$

and K becomes

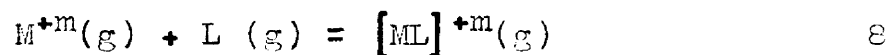
$$K = \frac{c_{ML}}{c_M \cdot c_L} \cdot \frac{\gamma_{ML}}{\gamma_M \cdot \gamma_L} = K_c \cdot \frac{\gamma_{ML}}{\gamma_M \cdot \gamma_L} \quad 6$$

where γ is the activity coefficient. The value of γ is a function of ionic strength and, hence, K_c is also. In practice K_c is determined as a function of the ionic strength and upon extrapolation to infinite dilution the equilibrium constant, K, is obtained (3,4). The " ΔF° , ΔH° and ΔS° " obtained by using K_c in equations 1 and 2 are not thermodynamic values and, as such, they should be used only in comparison with values of other systems obtained under the same condition of ionic strength.

It should be remembered that, in the study of the formation of complex ions in aqueous solution, all of the ions are hydrated to some extent and the actual process being studied is the following (5):



Enthalpy of bonding of the ligand to the metal ion is defined as the enthalpy change for the reaction



Enthalpy of bonding may differ significantly from the enthalpy change for the former process due to possible differences in the hydration energies of the ions involved. Differences may also appear in the formation (equilibrium) constants and in the entropy and free energy changes for the two processes.

There are several factors influencing the bond energy. These are listed in Table I. For their studies of the chelate effect many investigators have chosen the metal-ammine systems. In choosing a given metal-ammine system most of the factors remain constant or nearly so. Factors which may vary are those which involve the ligand molecule. These are (i) the base strength of the ligand and (ii) steric effects of the ligand.

TABLE I

FACTORS WHICH DETERMINE THE MAGNITUDE OF THE BOND ENERGY (5)

1. The bond hybrid of the metal atom;
2. The relative electronegativities of the donor and acceptor atoms;
3. The underlying electronic structure of the metal atom in its bonded state;
4. The electronic structure of the ligand (possible conjugation, etc.);
5. The possibility of double-bonding between the metal atom and the ligand;
6. Steric requirements of the ligand and of the metal ion in a given bonding state;
7. Charge on the complex ion and net charge on the central metal ion;
8. Base strength or proton affinity of the donor atom.

The Chelate Effect

The chelate effect may be described as the increased stability (ΔF°) of complexes that contain polydentate or chelate ligands over complexes containing corresponding monodentate or simple ligands. By corresponding, it is meant that the simple ligands contain the same donor functional groups as the chelate ligand but there are as many simple ligands as there are donor functional groups on the

chelate ligand. This description can be extended to include complexes with tetradentate and corresponding bidentates and the like. Schwarzenbach (6) defined the chelate effect quantitatively as

$$\text{chel} \equiv \log K_{\text{MZ}} - \log K_{\text{MA}_2} \quad 9$$

where K_{MZ} and K_{MA_2} are the formation constants for the chelate complex MZ and simple complex MA_2 respectively.

Sidgwick (1) was one of the first to offer an explanation for the chelate effect.

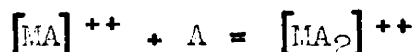
The most probable (explanation) is the very simple one that if one of the two co-ordinate links of a chelate group to the central atom is broken, the other will still keep it in place so that the broken link can be re-formed, where as an atom or group which is attached only through a single link will drift away if that link is broken.

Since this is a question of probability, it should appear in the entropy term for the system.

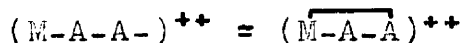
Schwarzenbach (6) and Spike (7) utilized the model suggested by Sidgwick as the basis for a kinetic treatment of the chelate effect. These treatments have been summarized by Parry (8) in the following:

... the formation and dissociation of the nonchelated complex MA_2 and of the chelated complex MAA are considered to be step-wise processes. It is then logical to assume that the chelate molecule AA reacts

with or dissociates from the metal ion in two steps. The intermediate form is a complex in which the chelating ligand is bound by only one donor atom. By application of simple collision theory of reaction rates, by assuming a comparable energy of activation for the reaction of chelate and nonchelate structures, and by using the best available data on sizes of molecules, one can estimate the order of magnitude of the entropy term in the chelate effect. It appears from the above models that the rate of the reaction



can be related to the size of the volume of element containing one free amine molecule and the rate of the comparable reaction



can be related to that volume inside the sphere of radius r' which is available to the second end of the chelating ligand.

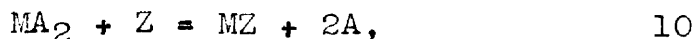
Commenting on this treatment, Parry states:

The above model suggests that the stabilization due to chelation should decrease rapidly as the chain of the ligand is lengthened. Schwarzenbach has shown that the difference in free energy of formation between chelate and nonchelate structures decreases rapidly and even reverses in sign as the chain is lengthened. One also arrives at a justification for the stability of five-membered rings. As a result of steric strain the energy of bond formation is low for small rings but increases as increasing size of the ring relieves strain. On the other hand, the stabilizing influence of chelation, which appears in the entropy term, is greatest for small rings. These two terms, working in opposite directions, produce a stability maximum in a five-membered saturated ring and in a six-membered unsaturated ring, the stereochemistry of which is further restricted by double bond formation.

The model also indicates (i) that further restriction on the mobility of the second ligand should enhance the stability of the complex if the size of the metal ion is such as to fit into the space between the binding atoms. ... (ii) that multiple ring formation should result in enhanced chelate stability, ... (iii) that the chelate effect should be quite independent of the metal except insofar as special steric requirements of the metal are concerned

In criticism of this treatment, Irving et al. (9) showed that it correctly predicts the observed decrease in stability with ring size enlargement but underestimates its magnitude. They state that the decrease in chelate effect of 1-3 diaminopropane compared to ethylenediamine is predicted to be 0.4 log units which is much less than the observed values of 1.0 for copper (II) and 1.3 for nickel (II) complexes. Also, the predicted change in chelate effect on passing from a six to a seven-membered ring is about 0.3 log units but the values found experimentally are larger.

A reaction in which the two simple ligands, A, coordinated to a metal ion, M, are replaced by a corresponding bidentate ligand, Z, may be represented as



Irving et al. pointed out that in this treatment there is the assumption that the enthalpy change for this reaction should be nearly zero. That is, the enthalpy of formation

of MA_2 and MZ are nearly the same. From such an assumption it follows that the magnitude of the chelate effect should be independent of the metal ion involved.

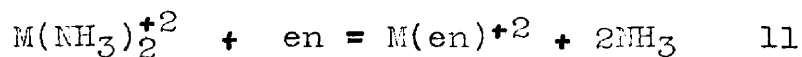
Experimental data do not support this generalization. Among the more stable chelates of the transition metals the magnitude of the chelate effect can be closely related to their individual stabilities. Thus, for $Co(II)$, $Ni(II)$, and $Cu(II)$ we find the linear relations

$$chel(1) = \log \frac{K_1(en)}{K_1K_2(NH_3)} = .20 \log K_1K_2(NH_3) + 1.40$$

$$chel(2) = \log \frac{K_2(en)}{K_3K_4(NH_3)} = .32 \log K_3K_4(NH_3) + 2.43$$

For the three metals $chel(1)$ is materially less than $chel(2)$. For $Co(II)$ and $Ni(II)$ we have $chel(3)$ equal 3.54 and 3.56, respectively, which represents still further increase in stability. ... Such variation can scarcely be coincidental ... (which suggests that the treatment) is over-simplified.

Spike and Parry (7) measured the entropy and enthalpy changes for reactions of the type



where M is Cd , Zn and Cu , and en is ethylenediamine. An examination of the data they obtained (Table II) shows that for the cadmium and zinc systems the chelate effect is due to the entropy term. However, in the copper system, the enthalpy term accounts for a large portion of the chelate

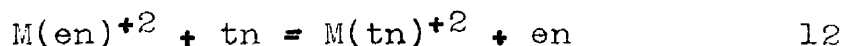
effect indicating a possible increase in bond strength in the chelate complex as compared to the nonchelate complex.

TABLE II

THERMODYNAMIC CONSTANTS FOR THE REACTION
 $M(NH_3)_2^{+2} + en = M(en)^{+2} + 2NH_3$
 IN AQUEOUS SOLUTION AT 25°C, IONIC STRENGTH 2.1

| <u>M</u> | <u>ΔF°(kcal/mole)</u> | <u>ΔH°(kcal/mole)</u> | <u>ΔS°(e.u.)</u> | <u>chel</u> |
|----------|---|---|--|-------------|
| Cd | -1.20 | 0.1 | 4.3 | 0.89 |
| Zn | -1.55 | 0.1 | 5.66 | 1.14 |
| Cu | -4.30 | -2.6 | 5.7 | 3.15 |

Cotton and Harris (10) measured the relative effects of entropy and enthalpy for reactions of the type



where M is Cd, Cu, and Ni and tn is 1,3-diaminopropane. In the complex ion $M(en)^{+2}$ a five-membered ring exists while in the ion $M(tn)^{+2}$ a six-membered ring exists. An examination of the data they obtained (Table III) shows that the five-membered ring is more stable and is favored by the entropy term. The enthalpy term favors the formation of the six-membered ring.

TABLE III

THERMODYNAMIC CONSTANTS FOR THE REACTION
 $M(en)^{+2} + tn = M(tn)^{+2} + en$
 IN AQUEOUS SOLUTION AT 25°C, IONIC STRENGTH 0.15

| <u>M</u> | <u>ΔF°(kcal/mole)</u> | <u>ΔH°(kcal/mole)</u> | <u>ΔS°(e.u.)</u> |
|----------|---|---|--|
| Cu | 1.4 | -0.6 | -7 |
| Cd | 1.2 | 0.0 | -4 |
| Ni | 1.3 | -0.9 | -11 |

For the process shown in equation 10 in aqueous solution Adamson (11) has proposed that the standard states of the solutes be changed from the hypothetical one molal state, which is conventional, to a state with mole fraction equal to one. The entropy (ΔS°) and free energy (ΔF°) changes obtained by use of the former standard state can be converted to those ($\Delta S'^{\circ}$ and $\Delta F'^{\circ}$) of the latter standard state using the following equations:

$$\Delta S'^{\circ} = \Delta S^{\circ} - \Delta n R \ln 55.5 = \Delta S^{\circ} - 7.9 \Delta n \quad (25^{\circ}\text{C}) \quad 12$$

$$\Delta F'^{\circ} = \Delta F^{\circ} - \Delta n RT \ln 55.5 = \Delta F^{\circ} - 2360 \Delta n \quad (25^{\circ}\text{C}) \quad 13$$

where Δn denotes the moles of product minus the moles of reactants. For a reaction in which there is no change in ionic charge, the use of the hypothetical mole fraction unity standard state tends to minimize the translational entropy effect due to Δn values.

However, as Schwarzenbach (12) has pointed out, difficulties would be encountered with such a standard state in the case of ionic ligands and, in general, there would be no advantage to such a change. The decrease in the entropy on making the change in standard state does emphasize that the chelate effect is primarily an entropy effect.

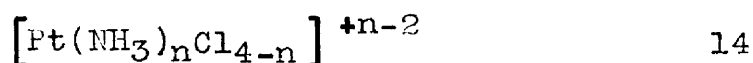
Platinum(II) Ammine Compounds

The stereochemistry of tetravalent platinum(II) compounds has been well established by both chemical and physical studies. In almost all such compounds the square planar configuration is formed (13, 14), i.e., the bonds of the platinum atom to the four groups are directed to the four corners of a square and the ligand atoms of the four groups are coplanar with the platinum atom.

The chemistry of divalent platinum, which is essentially the chemistry of its complex compounds, is well known and is discussed extensively in several inorganic chemistry reference books (15, 16, 17). Especially well known is the chemistry of tetravalent platinum(II) compounds containing chloride ions and amines such as ammonia, ethylenediamine, pyridine, etc. These compounds are also

discussed extensively in review articles by Mellor (13) and Quagliano and Schubert (18).

The general formula for a series of tetravalent platinum(II) complexes containing only chloride ions and ammonia molecules is

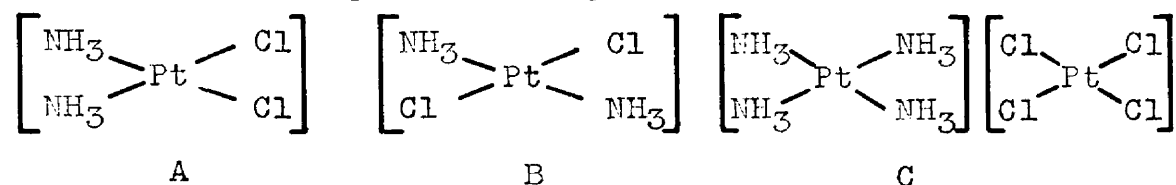


where n is a positive integer less than five. In general, for a given compound, n may be increased by treatment with aqueous ammonia and decreased by treatment with hydrochloric acid or by heating the solid chloride salt.

For n equal to two, several isomeric forms of the compound can be prepared, each dependent upon the mode of preparation. Cis-dichlorodiammineplatinum(II), $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ (A), where the chloro groups occupy adjacent positions in the square plane configuration, can be prepared by the addition of ammonia to tetrachloroplatinate(II) ion in aqueous solution. The trans form (B), where the chloro groups occupy nonadjacent positions, can be prepared by the removal of ammonia from tetraamineplatinum(II) ion, $[\text{Pt}(\text{NH}_3)_4]^{+2}$, by treatment with hydrochloric acid or by heating the dry chloride salt of the ion (19). Tetraamineplatinum(II) tetrachloroplatinate(II) $[\text{Pt}(\text{NH}_3)_4] [\text{PtCl}_4]$ (C),

a polymerization isomer of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, can be prepared by mixing solutions containing the respective ions (20).

It has been shown that cis- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ are converted to trans- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ at about 290°C (21).



Ammonia can be replaced by various amines including methylamine, ethylamine, and pyridine and by diamines such as ethylenediamine, 1,2-diaminopropane, 2,3-diaminobutane, 1,3-diaminopropane, and bipyridine. The amine groups in the diamines occupy adjacent positions in the platinum atom coordination sphere. The 1,4- and 1,5-diaminoalkanes, in which the amine groups are separated by more than three methylene groups, form ill-defined products with platinum(II) (19). The chloro groups can also be replaced in the series by other coordinating anions.

The thermal stabilities of the tetrammineplatinum(II) halides and the sulfate, chromate, nitrite, and thiocyanate have been studied (22). The order of decreasing stability for these tetrammines is given as follows: SO_4^{--} , CrO_4^{--} ,

Cl^- , Br^- , NO_2^- , I^- , SCN^- . The order of stability for the diammines is about the same.

Some thermodynamic data have been obtained for various diammines and tetrammines of platinum(II) by Chernyaev and co-workers. They determined the heat capacities of the cis and trans isomers of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$. The heat capacities follow the equation

$$C_p = 0.00125t + 0.118 \quad 15$$

over the temperature ranges 22-78°C and 22-45°C, respectively(23).

Enthalpies of reaction with aqueous ammonia of various isomers having the empirical formula $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ have been determined and enthalpies of transition of each isomer to the trans isomer have been calculated. These are summarized in Table IV (24).

TABLE IV

ENTHALPY CHANGES FOR THE REACTIONS

| $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]_n + 2n\text{NH}_3 = n[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2 \quad \Delta H_1^\circ$ | | |
|---|-----------------------------------|---------------------------------------|
| $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]_n = n \text{ trans-} [\text{Pt}(\text{NH}_3)_2\text{Cl}_2] \quad \Delta H_2^\circ$ | | |
| Compound | $\Delta H_1^\circ (\text{cal/g})$ | $\Delta H_2^\circ (\text{kcal/mole})$ |
| <u>trans</u> - $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ | 52.2 | --- |
| <u>cis</u> - $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ | 62.4 | 3.0 ± 0.2 |
| $[\text{Pt}(\text{NH}_3)_3\text{Cl}] [\text{PtNH}_3\text{Cl}_3]$ | 61.8 | 5.8 ± 0.3 |
| $[\text{Pt}(\text{NH}_3)_3\text{Cl}]_2 [\text{PtCl}_4]$ | 54.9 | 2.5 ± 0.3 |
| $[\text{Pt}(\text{NH}_3)_4] [\text{PtCl}_4]$ | 59.5 | 6.6 ± 1.2 |

Enthalpies of solution and lattice energies of several platinum complexes have been determined. These are summarized in Table V for the tetrammineplatinum(II) salts (25).

TABLE V
ENTHALPIES OF SOLUTION AND LATTICE ENERGIES
OF SOME TETRAMMINEPLATINUM(II) SALTS

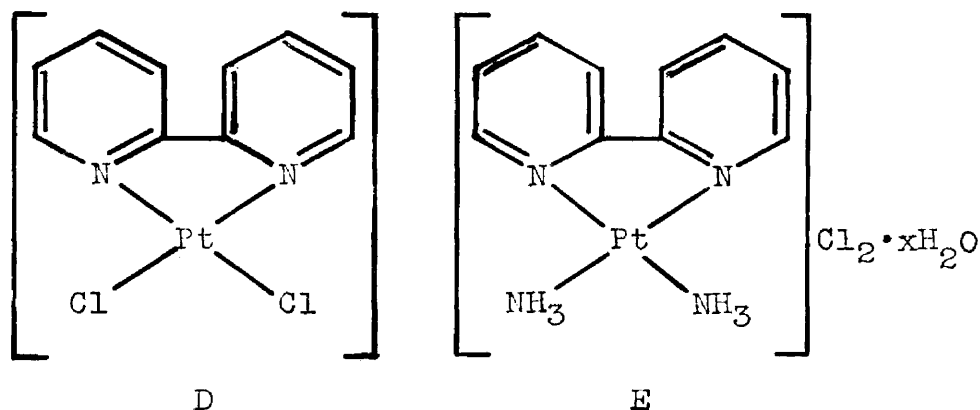
| <u>Salt</u> | <u>Enthalpy of Solution (cal/g)</u> | <u>Crystal Energy (kcal/mole)</u> |
|-------------|---|---------------------------------------|
| Fluoride | --- | 388 |
| Chloride | -20.95 | 351 |
| Iodide | -28.9 | 340 |
| Bromide | --- | 325 |
| Nitrite | -37.1 | 342 |

Dichloro(2,2'-bipyridine)platinum(II)

The preparation of dichloro(2,2'-bipyridine)platinum(II) was first reported by Rosenblatt and Schleede (26) and a short time later by Morgan and Burstall (27). Morgan and Burstall also described many of the reactions of this substance with various amines and anions in aqueous solution.

Dichloro(2,2'-bipyridine)platinum(II) (henceforth referred to by the formula $[\text{Pt}(\text{bipy})\text{Cl}_2]$ where bipy means 2,2'-bipyridine) is a yellow or red fibrous crystalline

compound, insoluble in water but slightly soluble in chloroform and methylene chloride giving only yellow solutions. The color of the solid material is dependent upon the mode of preparation. The yellow form, which is the most common form, is prepared by the addition of 2,2'-bipyridine to a hot, slightly acid solution of potassium tetrachloroplatinate(II). As with almost all tetravalent platinum(II) compounds (14), the structure of $[\text{Pt}(\text{bipy})\text{Cl}_2]$ is square planar, and the ligand atoms of the bipyridine occupy adjacent coordinating positions (D).



Diammine(2,2'-bipyridine)platinum(II) chloride can be prepared by dissolving $[\text{Pt}(\text{bipy})\text{Cl}_2]$ in aqueous ammonia. The hydrated solid $[\text{Pt}(\text{bipy})(\text{NH}_3)_2]\text{Cl}_2 \cdot x\text{H}_2\text{O}$ (E) is obtained by crystallization from a solution containing excess ammonia or by precipitation from a concentrated solution by the

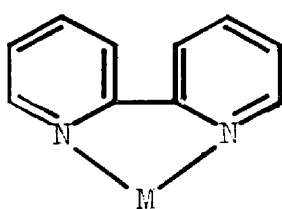
addition of alcohol; a dihydrate and a monohydrate, respectively, are formed. Other complexes with $[\text{Pt}(\text{bipy})\text{Cl}_2]$ can also be formed with ethylenediamine, pyridine, and 2,2'-bipyridine. With the latter two substances the chloride salts were not obtained, but the tetrachloroplatinate(II) salts $[\text{Pt}(\text{bipy})\text{py}_2][\text{PtCl}_4]$ and $[\text{Pt}(\text{bipy})_2][\text{PtCl}_4]$ were. By various treatments the chloro groups, either inside or outside the coordination sphere of the platinum atom, can be replaced by other anions such as bromide, iodide, and nitrate.

The addition of ammonia and other amines to $[\text{Pt}(\text{bipy})\text{Cl}_2]$ is reversible since they can be removed from the complex with hydrochloric acid, reforming the original compound. The color of the $[\text{Pt}(\text{bipy})\text{Cl}_2]$ which is reformed varies from yellow to red and is dependent upon the ammine being removed and the concentration of the acid. A bright red color is obtained if concentrated hydrochloric acid is used on the ethylenediamine complex.

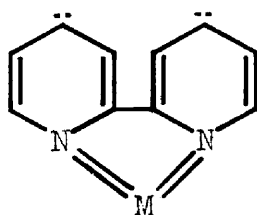
The bonds of the nitrogen atoms of the bipyridine to the platinum atom are very stable as shown by their persistence throughout the various treatments mentioned. The lone exception to this is in the case of the bis(2,2'-bipyridine) platinum(II) ion from which one molecule of the bipyridine is easily removed by treating it with hydrochloric acid.

However, the other molecule remains firmly bonded.

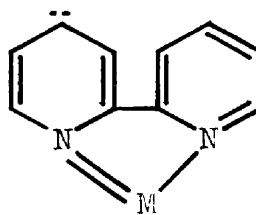
Bipyridine also forms strong complexes with other group VIII metal ions, especially the iron group (iron, ruthenium, and osmium) (28). Burstall and Nyholm (29) suggest that the major factor responsible for the strong bonds found in the iron group is due to the formation of strong double bonds using the outer d electrons of the metal ion and the p orbitals of the nitrogen atoms. This would give rise to resonance structures shown in F and G. Brandt, et al. (28) also add the structures H and J. It is reasonable to assume that some of these resonance structures occur in these Pt-N bonds, giving rise to their great stability.



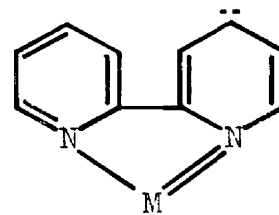
F



G



H



J

EXPERIMENTAL

Reagents

Reagent grade chemicals were used in the preparation of all compounds listed except those whose grade and/or method of purification are indicated. Commercially available anhydrous ammonia and methylamine were condensed on an excess of alkali metal (sodium and lithium, respectively) immediately before being used to remove all trace of water. Ethylenediamine and 1,3-diaminopropane* were purified by the method described by Rollinson and Bailar (30). The 2,2'-bipyridine** and anhydrous sulfur dioxide were used without further purification. U.S.P. grade chloroform was stored over anhydrous calcium chloride and was filtered prior to use.

Preparation of Compounds

Potassium tetrachloroplatinate(II), $K_2[PtCl_4]$, was prepared by the reduction of the hexachloroplatinate(IV) salt, $K_2[PtCl_6]$, with sulfur dioxide in aqueous solution as

*Obtained from K and K Laboratories, Long Island, New York.
**Obtained from Matheson, Coleman and Bell Division of The Matheson Co., Inc.

described by Keller (31), although the procedure is tedious and time consuming. A more rapid procedure employs hydrazine sulfate (32) as the reducing agent. Other suitable methods make use of potassium oxalate (33) and hydrazine hydrochloride (34) as reductants.

Dichloro(2,2'-bipyridine)platinum(II), $[\text{Pt}(\text{bipy})\text{Cl}_2]$, was prepared by the method described by Morgan and Burstall (27). A solution containing 0.01 mole of 2,2'-bipyridine, 0.01 mole of potassium tetrachloroplatinate(II), and 0.04 mole of hydrochloric acid was brought to a boil, whereupon the yellow form of the compound precipitated. The precipitate was removed by filtration, washed with acetone and ether, then allowed to dry in air. This compound was recovered from its various ammine complex compounds by precipitation from a hot aqueous solution of the ammine complex with hydrochloric acid. The product so formed varied in color from yellow to red depending upon the ammine in the complex and upon the concentration of the acid. This is in accordance with the observations of Morgan and Burstall.

Diammine(2,2'-bipyridine)platinum(II) chloride, $[\text{Pt}(\text{bipy})(\text{NH}_3)_2]\text{Cl}_2$, and dimethylamine(2,2'-bipyridine)platinum(II) chloride, $[\text{Pt}(\text{bipy})(\text{CH}_3\text{NH}_2)_2]\text{Cl}_2$, were prepared

by condensing the appropriate anhydrous ammine on a chloroform suspension of 1-2 grams of $[\text{Pt}(\text{bipy})\text{Cl}_2]$ in the apparatus shown in Figure I. The ammine was condensed and dried in Tube A and then recondensed in the reaction Tube B containing the chloroform suspension. After 2-3 milliliters had condensed, the dry ice bath used as the refrigerant was removed from B and the mixture in B was allowed to warm to room temperature. During this time any excess ammine distilled from the system through a drying tube while the mixture was stirred with a magnetic stirrer. No apparent reaction occurred until the mixture was near room temperature. After the reaction had occurred (as indicated by a slight, but distinct, color change) the suspended solid was collected on a fritted glass filter, washed successively with chloroform, acetone and ether and then air dried. The compounds obtained by this method contained up to two moles of the ammine in excess of the theoretical quantity required for a diammine complex. This excess ammine was loosely bound in the compound and was readily removed by placing the compound over phosphorous pentoxide in a vacuum. ($[\text{Pt}(\text{bipy})(\text{NH}_3)_2]\text{Cl}_2$ requires Pt, 42.78%; C, 26.32%; H, 3.09%. Found Pt, 42.92%; C, 25.68%; H, 3.08%. $[\text{Pt}(\text{bipy})(\text{CH}_3\text{NH}_2)_2]\text{Cl}_2$ requires Pt, 40.30%; Cl, 14.64%. Found Pt, 40.28%; Cl, 14.66%.)

Ethylenediamine(2,2**b**ipyridine)platinum(II) chloride, $[\text{Pt}(\text{bipy})\text{en}]\text{Cl}_2$, and 1,3-diaminopropane(2,2**b**ipyridine)platinum(II) chloride, $[\text{Pt}(\text{bipy})\text{tn}]\text{Cl}_2$, were prepared by the addition of 1-2 milliliters of the diamine to 1-2 grams of $[\text{Pt}(\text{bipy})\text{Cl}_2]$ suspended in chloroform. The mixture was stirred for 1-2 hours during which time there was a slight color change in the suspended substance. The solid was collected on a fritted glass filter, washed and dried as with the previous ammine complexes. The compounds prepared by this method contained up to one mole of the diamine in excess of the theoretical quantity required for the compounds with the above formulae. This excess diamine was relatively loosely bound and was removed by placing the compound over phosphorous pentoxide in a vacuum. ($[\text{Pt}(\text{bipy})\text{en}]\text{Cl}_2$ requires Pt, 40.47%; Cl, 14.70%. Found Pt, 40.37%; Cl, 14.41%. $[\text{Pt}(\text{bipy})\text{tn}]\text{Cl}_2$ requires Pt, 39.32%; Cl, 14.28%. Found Pt, 39.25%; Cl, 14.30%.)

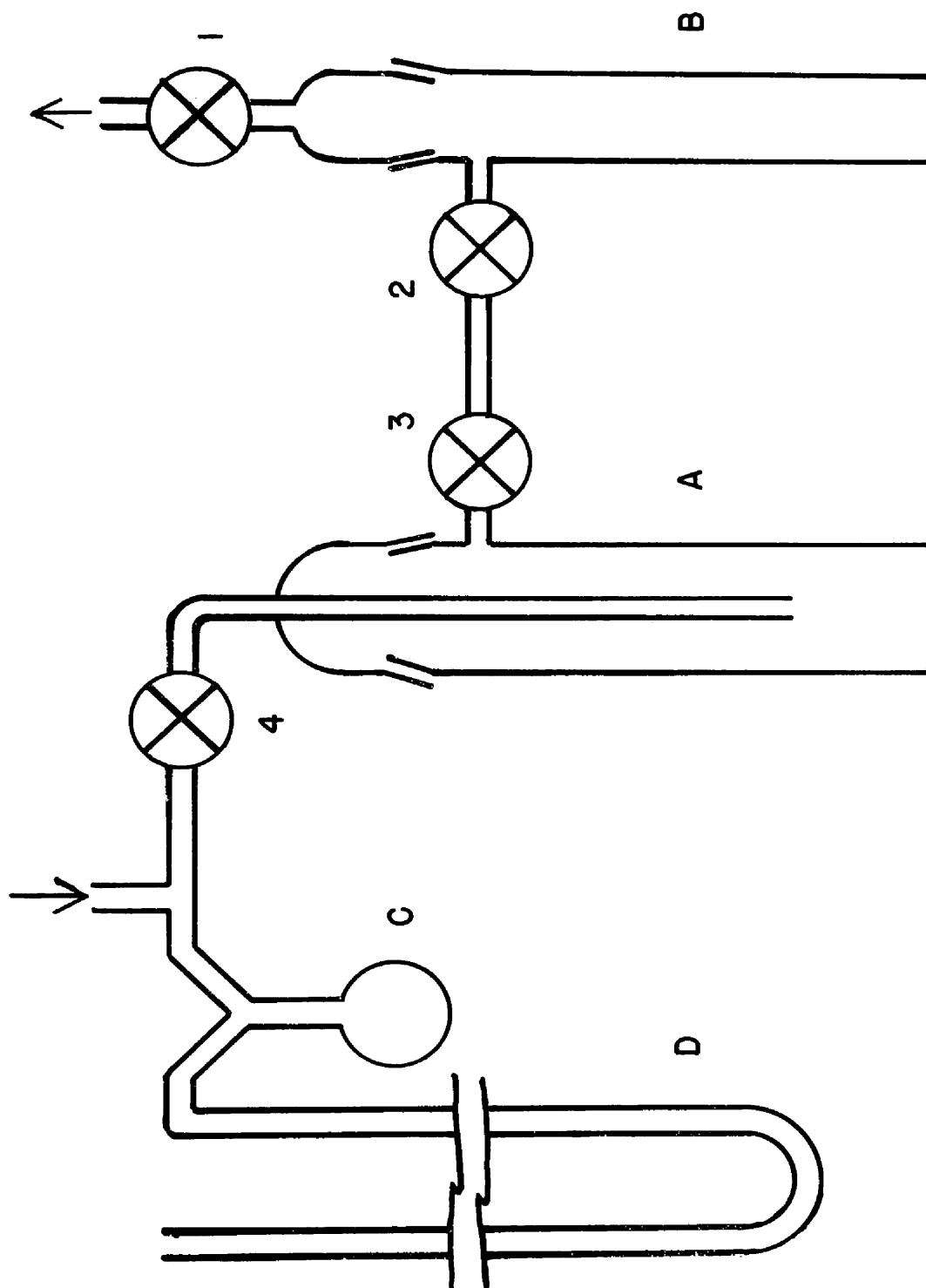
Attempts were made to add phosphine, carbon monoxide, pyridine*, and acetonitrile* to $[\text{Pt}(\text{bipy})\text{Cl}_2]$ but these were unsuccessful. Phosphine, in a stream of nitrogen, was

*These attempts were made by J. A. Sincius.

bubbled through a chloroform suspension of the compound with no apparent reaction. Two containers of the compound were placed in a bomb with relatively pure carbon monoxide at 1.5 atmosphere pressure for several hours with no apparent reaction. In both cases mentioned the lack of reaction was determined by the lack in color change which accompanied the reactions previously described. The procedure for the attempted addition of pyridine and acetonitrile to the compound was identical to that described for the preparation of the diamine complexes. Again, there were no apparent reactions as determined by the lack of color change and weight increase of the starting material.

The apparatus shown in Figure I was used for the preparation of the compounds which required gaseous amines. The system was partially evacuated; then the ammine was condensed in A with a dry ice bath, where it was dried with an alkali metal. The dry ice bath was removed and placed at B which contained the chloroform suspension. After all the ammine was recondensed in B, the dry ice bath was removed and the ammine was allowed to distill from the container through stopcock 1 and, subsequently, through a drying tube or a cold trap. Also included in the apparatus was a U-tube C

FIGURE I



APPARATUS USED IN PREPARATION OF THE
COMPLEXES CONTAINING MONOAMINE LIGANDS

and mercury leveling bulb*, which acted as a "rough" manometer and a pressure safety device, and a bulb D, which acted as a mercury trap in the event of an unexpected pressure decrease. The stopcocks 2, 3, and 4 facilitated the handling of the gas and the evacuation of the system.

Apparatus

The apparatus used for the measurement of the vapor pressure of the various solid ammine complexes of $[\text{Pt}(\text{bipy})\text{Cl}_2]$ is shown in Figure II. It consists of three major sections. These sections will be referred to as the Sample Section A, the Pressure Measurement Section B, and the Manifold Section C.

The sample section consists of a short section of a male $\frac{3}{8}$ 45/50 sealing tube which has been sealed at both ends. Two side arms have been attached to the tube. One side arm is a $\frac{3}{8}$ 24/40 sealing tube fitted with a cap through which the sample is introduced. The other arm is of smaller diameter and is connected to the manifold section for the evacuation of this section. Each side arm is sealed off after serving its purpose and resealed to the apparatus prior to the introduction of the next sample. A double bulb sickle gauge is sealed to the tapered end of the tube and serves as an isotenoscope in the system.

*Not shown.

The sickle gauge bulbs were constructed primarily according to the directions given by Phipps, et al. (35). Two sickle bulbs in series are incorporated in this isotenscope as suggested by the work of Foster (36). The use of more than one bulb permits sturdier construction without sacrificing sensitivity.

The sample section is sealed in a long female 45/50 sealing tube with a high melting vacuum sealing resin. This tube is the pressure measurement section. It is connected to the manifold section through a metal needle valve. A large bore mercury manometer is also connected to this tube. The function of this section is to maintain a pressure identical to that of the sample section as indicated by the position of the tip of a long thin rod attached to the end of the sickle bulb. The pressure in this section is controlled by the use of the needle valve.

A reference point for the sickle indicating pointer was constructed on the outside of the pressure measurement section near the tip of the pointer. This reference consists of two narrow slits in a black band painted around the tube. These two slits are aligned with the tip of the pointer so that the alignment is perpendicular to the travel

of the pointer. A burette telescope mounted in front of the slits aids in the alignment of the pointer during the pressure regulation.

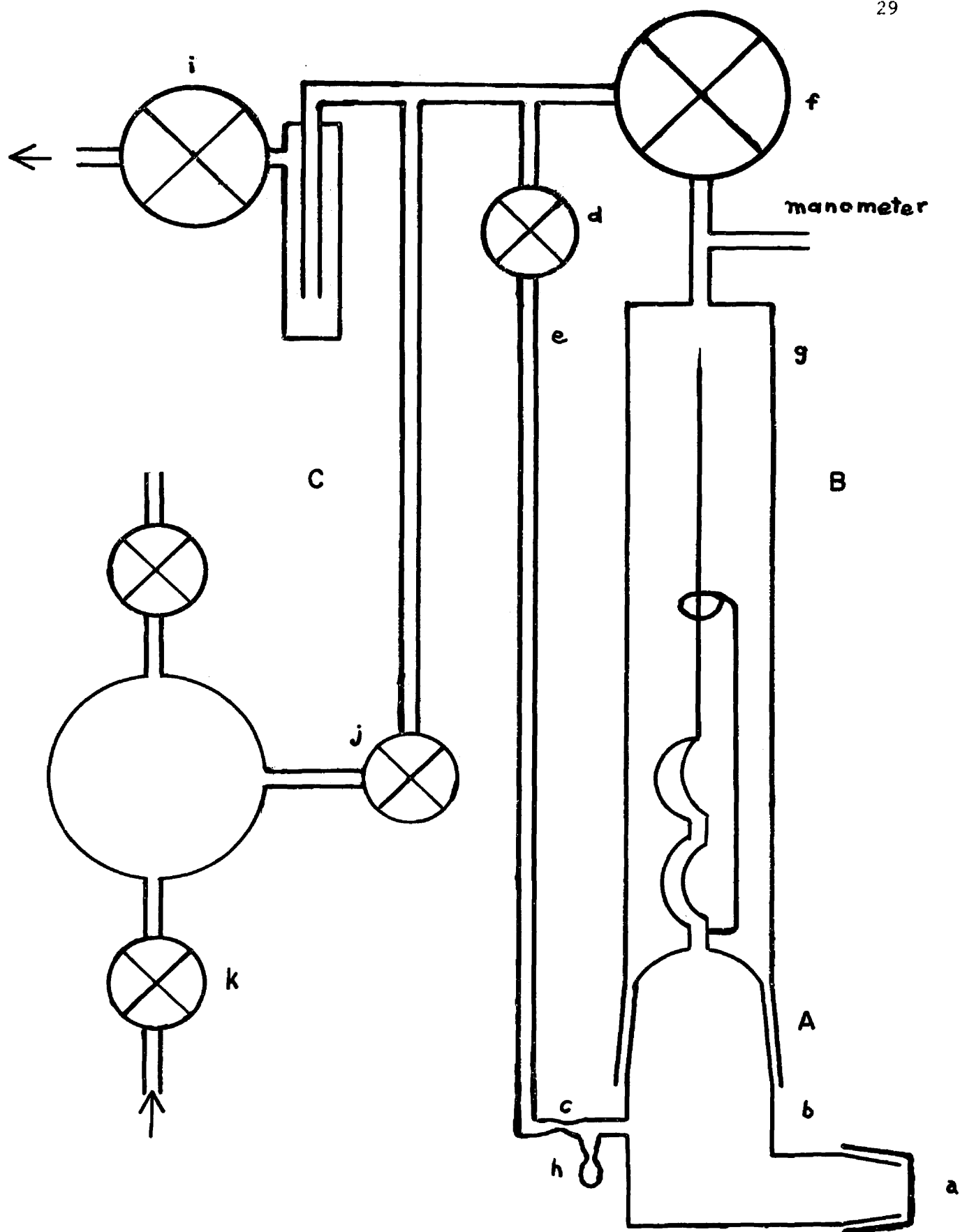
The manifold section is connected to a vacuum pump and to a supply of dry nitrogen gas. It is through this section that the pressure in the other sections is changed, either in their evacuation prior to the vapor pressure determinations, in pressure regulation during the determinations, or in bleeding gas back into them after the determinations are completed.

The entire apparatus, as shown in Figure II, is mounted on a movable rack for convenience in immersing the sample section into a constant temperature bath.

Several liquid media were tried and used in the constant temperature bath. Technical grade tritolyl phosphate was found to be the most suitable bath media.

A thermistor was used for the measurement of the bath temperature. The resistance of the thermistor was measured with a wheatstone bridge and a sensitive galvanometer. The resistance of a thermistor is related to its absolute temperature by the equation (37)

$$\ln \frac{R}{R_0} = B\left(\frac{1}{T} - \frac{1}{T_0}\right) \quad 16$$



APPARATUS USED FOR THE MEASUREMENT OF THE
VAPOR PRESSURE OF THE SOLID COMPLEXES

where R and R_0 are the resistances at temperatures T and T_0 , and B is a constant characteristic of the particular thermistor. The constant B was evaluated by the calibration of the thermistors at 25° and 100°C . These data are summarized in Table VI.

TABLE VI
THERMISTOR CALIBRATION DATA

| <u>Thermistor Number</u> | <u>1</u> | | <u>2</u> | |
|----------------------------------|--------------------|--------------------|--------------------|--------------------|
| Temperature ($^\circ\text{C}$) | 24.98 ^a | 99.28 ^b | 24.85 ^a | 99.13 ^b |
| Resistance (ohms) | 101300 | 5786 | 102600 | 6002 |
| B (deg)(calculated) | 4278 | | 4240 | |

a Measured by a Beckmann thermometer calibrated against a platinum resistance thermometer.

b Temperature of boiling water corrected for barometric pressure.

Vapor Pressure Measurement

The following is a general description of the procedure which was followed to obtain the vapor pressures of the platinum complex compounds under study. The letters used are in reference to the corresponding letters in Figure II.

A 50-100 milligram sample of the solid compound was placed in A and the entrance port, a, was sealed off at b.

The entire apparatus was then evacuated using high vacuum techniques when possible. The evacuation process was continued for several hours while the bottom portion of A was partially immersed in a dry ice bath to prevent the removal of the ammine ligands from the sample. This precaution, however, prevented proper degassing of the system. After several hours of evacuation the dry ice bath was removed and A was sealed at the constriction at c. The stopcock d was closed and a cap was placed at e. The apparatus was then lowered into a constant temperature bath.

The bath was heated to about 50°C and allowed to remain at 50°C for a short time, after which it was increased 5°. The temperature was increased 15-20° daily, in 5° intervals until a pressure sufficient for measurement was obtained. At this point the temperature was kept constant for several hours before pressure measurements were made. After the pressure measurements were obtained, the temperature was increased 3-5°, maintained constant for several hours and the pressure was again measured. This process was repeated until further readings were either unnecessary or impractical.

The pressure in A was measured at each temperature by adjusting the pressure in B, using the needle valve, f,

until the tip of the reference pointer on the sickle bulb was aligned in the reference slits on the outside of B at g. The pressure in B was then obtained by measuring the difference in the heights of the mercury in the two arms of a mercury manometer. These heights were measured with a high precision cathetometer placed several feet from the manometer. After the pressure in B was obtained, the section was partially evacuated and the process was repeated. Several such independent pressure adjustments in B were obtained and the pressure in B for each adjustment was measured and recorded. Several independent measurements were also made of the resistance of the thermistor in the constant temperature bath, from which the temperature of the bath was calculated.

When the series of measurements were completed for a given sample the apparatus was removed from the oil bath and rinsed with carbon tetrachloride. To open the apparatus one end of a piece of rubber pressure tubing was connected to the system at e while the other end was placed securely over the constriction at h. (This constriction was previously scratched with a file edge.) The manifold section, including the rubber tubing, was then evacuated, after which

the stopcock i to the vacuum pump was closed. The constriction at h was broken, and the valves d and f were immediately opened. With A, B and C open nitrogen was bled into the system through stopcocks j and k until atmospheric pressure was obtained. The side arms were resealed to the apparatus at b and c and a new constricted seal was placed at h in preparation for a new sample.

Apparatus Calibration

The apparatus was calibrated in the following manner. The entire apparatus was completely evacuated after which a small amount of nitrogen was allowed to enter the apparatus until a pressure was obtained which was comparable to the pressures of the samples. With the sections A, B and C open the pressure was measured and recorded. Section A was then isolated from B and C by closing the stopcock d. The pressure in B was then adjusted until the references were aligned. This pressure was measured and recorded. Several independent measurements in A were obtained at a given pressure and such measurements were repeated at different pressures. In all, 30-50 independent measurements were made at 3-5 different pressures for each calibration. The differences in the true pressure in A and the apparent pressure in A, as measured by

the adjusted pressure in B, were calculated. The average difference was added to the pressures obtained in the actual experimental measurements.

Errors

For each series of measurements of pressure or temperature at a given temperature the mean (or average) and standard deviations were calculated. The standard deviation was calculated according to the equation

$$s = \frac{1}{n-1} \sqrt{\sum (X_i - \bar{X})^2} \quad 17$$

where \bar{X} is the average of n measurements. In almost all cases the value of s for the temperature measurements was found to be 0.3° , which was also its maximum value. The value of s for the various pressure measurements varied from 0.10 to 0.30 millimeter. There is no correlation between the absolute pressure measured and the value of s obtained. It is believed that the variability of s is due to visual and mechanical errors in the pressure adjustments.

It was found that if the temperature of the apparatus exceeded 100° by more than a few degrees, the calibration correction value changed by a slight amount. This is believed to be due to a slight shift of the sample section at the

standard taper joint when the sealing resin in the joint was sufficiently soft. The sealing resin was found to begin to soften at about 100°C. The apparatus was calibrated before and after each series of vapor pressure measurements. In practice, if the calibration correction changed, the correction which was used for that series of measurements was dependent upon the temperature at which the measurements were obtained. For example, for measurements at lower temperatures the calibration correction used was that obtained before the series of measurements was begun, while for the measurements at higher temperatures the calibration correction used was the one obtained after the measurements were made.

Corrections due to the difference in the heights of the menisci of the mercury were employed only in the case of the NH_3 complex. A small bore manometer (7.7 millimeters) was used for the pressure measurements of this compound. The corrections used were interpolated from the tables listed by Weissberger (38) and ranged from 0.1 to 0.3 millimeter. For the vapor pressure measurements of the other compounds a wide bore manometer (14 millimeters) was used. It was found that menisci corrections for this manometer ranged from 0.01 to 0.03 millimeter. These were ignored. In all cases, the pressures obtained were corrected to the density of mercury at 0°C.

RESULTS

The vapor pressures of the following four compounds were measured as a function of temperature by the method described: $[\text{Pt}(\text{bipy})(\text{NH}_3)_2]\text{Cl}_2$, $[\text{Pt}(\text{bipy})(\text{CH}_3\text{NH}_2)_2]\text{Cl}_2$, $[\text{Pt}(\text{bipy})(\text{en})]\text{Cl}_2$ and $[\text{Pt}(\text{bipy})(\text{tn})]\text{Cl}_2$, where en is ethylenediamine and tn is 1,3-diaminopropane. These four compounds will generally be indicated by the formula $[\text{Pt}(\text{bipy})(\text{Am})_n]\text{Cl}_2$ and specifically as the NH_3 , CH_3NH_2 , en and tn complex, respectively. The vapor pressure data obtained are listed in Tables XV through XVIII in the Appendix. These data include the individual measurements and their averages, the temperature and the inverse absolute temperatures, the calibration corrections which had been applied to the pressure data, and the standard deviations of the averages which are listed.

For the NH_3 and CH_3NH_2 complexes, the pressures were not measured until a pressure of about 10 millimeters of Hg was obtained. With the en and tn complexes, the pressures obtained were much lower than those of the simple complexes, and it was necessary to obtain all the measurements below 15 millimeters. Attempts to obtain higher pressures with

the en complex at much higher temperatures did not yield satisfactory results.

The average of the pressure measurements obtained at each temperature was plotted on a log scale versus the inverse absolute temperature (Figures III through VI in the Appendix). The data for that part of the curve which approaches a straight line were treated according to standard statistical methods (39). The equations obtained are of the form

$$\log P = A - B \left(\frac{10^3}{T} \right) \quad 18$$

$$\text{letting} \quad X = \frac{10^3}{T} \quad 19$$

$$\text{and} \quad Y = \log P \quad 20$$

$$\text{then} \quad -B = \frac{n \sum X_i Y_i - \sum X_i \sum Y_i}{n \sum X_i^2 - (\sum X_i)^2} \quad 21$$

$$\text{and} \quad A = \bar{Y} + B\bar{X} \quad 22$$

where \bar{X} and \bar{Y} are average values and n is the number of observations. Estimates of the standard deviation of a single measurement (s) and of B (s_b) were obtained using the equations

$$(n-2)s^2 = \sum Y_i^2 - \frac{(\sum Y_i)^2}{n} - \frac{1}{n} \frac{(n \sum X_i Y_i - \sum X_i \sum Y_i)^2}{n \sum X_i^2 - (\sum X_i)^2} \quad 23$$

and

$$s_b^2 = \frac{ns^2}{n \sum X_1^2 - (\sum X_1)^2} \quad 24$$

The coefficients A and B and the standard deviations s and s_b obtained are listed in Table VII.

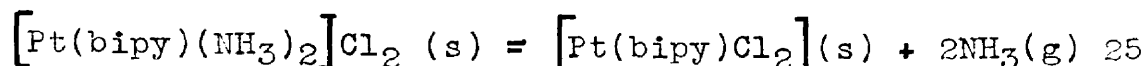
TABLE VII

CONSTANTS FOR THE EQUATION $\log P_{mm} = A - B\left(\frac{10^3}{T}\right)$
FOR COMPOUND $[\text{Pt}(\text{bipy})(\text{Am})_n]\text{Cl}_2$

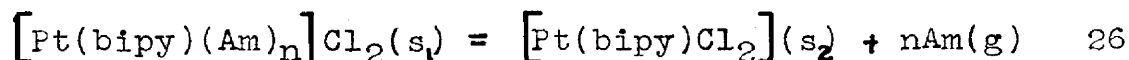
| Compound | A | B \pm s_b | s | Valid Temperature Range |
|---------------------------------|--------|------------------|-------------|-------------------------|
| NH ₃ | 11.659 | 3.878 \pm .059 | \pm 0.022 | 87-110°C |
| CH ₃ NH ₂ | 17.486 | 5.791 \pm .118 | \pm 0.023 | 78-89°C |
| en | 5.675 | 1.951 \pm .114 | \pm 0.017 | 114-125°C |
| tn | 3.247 | .813 \pm .051 | \pm 0.009 | 97-108°C |

It was found that upon heating $[\text{Pt}(\text{bipy})\text{Cl}_2]$, from which the various complexes were prepared, there was no significant loss in weight until the temperature exceeded 200°C. It was also found that upon heating the pale yellow NH₃ complex at 100°C, there was a loss in weight and a deeper shade of yellow, comparable to that of the $[\text{Pt}(\text{bipy})\text{Cl}_2]$, was acquired by the complex. With these observations in mind it is assumed that upon heating the

NH_3 complex dissociates according to the equation



and that the pressure which is measured over this complex is due to the NH_3 vapor liberated. By analogy, it is assumed a similar dissociation occurs with each of the other complexes studied and that the pressure measured over the complex is due to the liberated ammine vapor. This dissociation process can be represented by the general equation



where n is 1 or 2.

If the process represented in equation 26 is reversible and at equilibrium when the pressure is measured, an equilibrium constant can be defined for the process as

$$K = \frac{a(\text{g})^n \cdot a(\text{s}_2)}{a(\text{s}_1)} \quad 27$$

where a is the activity of the species represented. Applying the usual choice of standard states (hypothetical ideal gas at unit fugacity for gases and pure substance at one atmosphere pressure for solids), the equilibrium constant expression reduces to the form

$$K = p^n \quad 28$$

(where p is measured in atmospheres) if the activity of the solids are unity or are equal.

From the equations

$$\Delta F^{\circ} = -RT \ln K \quad 29$$

$$\log K = \frac{-\Delta H^{\circ}}{2.303RT} + \text{const.} \quad 30$$

$$\Delta F^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \quad 31$$

the thermodynamic constants can be obtained for the dissociation process in equation 26. Equation 30 is the integrated form of equation 2, assuming ΔH° is constant, and it is similar in form to equation 18. Comparison of these two equations (30 and 18) shows that

$$\Delta H^{\circ} = 2.303 \cdot (10^3) \cdot nRB \quad 32$$

Using equations 18, 29, 31, 32 and the data in Table VII, the thermodynamic constants were calculated at 100° and 25° and are tabulated in Tables VIII and IX.

The data presented in Tables VIII and IX are valid only if each of the following are true:

- I - the dissociation process is reversible;
- II - the activity of the two solid substances involved in the dissociation process are equal or nearly equal, and the fugacity of the gas is equal to its pressure;

TABLE VIII

THERMODYNAMIC CONSTANTS FOR THE THERMAL DISSOCIATION
OF THE AMMINE COMPLEXES OF $[\text{Pt}(\text{bipy})\text{Cl}_2]$ at 100°C

| <u>Complex</u> | <u>Log P_{mm}^*</u> | <u>ΔF° (kcal/mole)</u> | <u>ΔH° (kcal/mole)</u> | <u>ΔS°(e.u.)</u> |
|--------------------------|---|--|--|--|
| NH_3 | 1.266 \pm .022 | 5.52 \pm .08 | 35.49 \pm .54 | 80.31 \pm 1.47 |
| CH_3NH_2 | 1.966 \pm .027 | 3.13 \pm .09 | 53.00 \pm 1.08 | 133.6 \pm 2.9 |
| en | 0.446 \pm .023 | 4.16 \pm .04 | 8.93 \pm .52 | 12.8 \pm 1.4 |
| tn | 1.068 \pm .009 | 3.10 \pm .02 | 3.72 \pm .23 | 1.66 \pm .62 |

TABLE IX

THERMODYNAMIC CONSTANTS FOR THE THERMAL DISSOCIATION
OF THE AMMINE COMPLEXES OF $[\text{Pt}(\text{bipy})\text{Cl}_2]$ at 25°C

| <u>Complex</u> | <u>Log P_{mm}^*</u> | <u>ΔF° (kcal/mole)</u> | <u>ΔH° (kcal/mole)</u> | <u>ΔS°(e.u.)</u> |
|--------------------------|---|--|--|--|
| NH_3 | -1.348 \pm .045 | 11.54 \pm .12 | 35.49 \pm .54 | 80.32 \pm 1.85 |
| CH_3NH_2 | -1.938 \pm .069 | 13.16 \pm .19 | 53.00 \pm 1.10 | 133.6 \pm 3.7 |
| en | -0.867 \pm .093 | 5.12 \pm .13 | 8.93 \pm .52 | 12.8 \pm 1.8 |
| tn | 0.520 \pm .036 | 3.22 \pm .05 | 3.72 \pm .23 | 1.68 \pm .81 |

*The estimate of the standard deviation s_p is given as

$$s_p = s \sqrt{\frac{n+1}{n} + \frac{(X_0 - \bar{X})^2}{n \sum X_i^2 - (\sum X_i)^2}}$$

where X_0 is defined by equation 19 using the corresponding value of T_0 .

- III - the extrapolations of the data for the CH_3NH_2 and en complexes to 100°C are valid (Table VIII only); and
- IV - the extrapolation of the data for all compounds to 25°C are valid (Table IX only).

It was not unequivocally demonstrated that the dissociation processes are reversible. Several times during the vapor pressure determinations, at least once for each different compound, the temperature of the system was lowered. The pressure in the system decreased but not to the extent to show the process to be reversible. However, the decrease in pressure was greater than the amount predicted by the ideal gas law, indicating that some of the gas molecules were either adsorbed or absorbed by the solid present. This adsorption or absorption can occur by either of two different methods. It may be due (1) to the adsorption of the ammine on the surface of the $[\text{Pt}(\text{bipy})\text{Cl}_2]$ crystals by reaction with them to form the original complex, with slow diffusion of the ammine molecules through the crystal to react with the inner molecules; or (2) to the absorption of the ammine by the undissociated crystals to form solvates, which are readily formed in the preparation of these materials. If the first occurs, then the dissociation is reversible

but not rapidly so, shown by the slow attainment of equilibrium on temperature decrease. If the second occurs, then it is necessary that the process is reversible; otherwise, the ammine complex would dissociate completely leaving no ammine complex with which to form the solvated complex. Solvates of $[\text{Pt}(\text{bipy})\text{Cl}_2]$ are not known to exist.

The change in free energy of a pure substance with a change in pressure at constant temperature is given by the equation

$$\left(\frac{dF}{dP}\right)_T = V \quad 33$$

where V is the molar volume. Integration of this equation, assuming V to be constant, gives

$$\Delta F = V\Delta P \quad 34$$

for a given pressure change. The error in ΔF^0 for the dissociation process, under the assumption that the activities of the solids are equal, is given by the expression

$$\Delta F_e = (V_1 - V_2)\Delta P \quad 35$$

where V_1 and V_2 are the molar volumes of the two solid substances involved in the process. With ΔP of approximately one atmosphere and an assumed value of 0.1 liter for $V_1 - V_2$ (corresponding to a difference in density of 2-3 grams per cubic centimeter at an average density of 5 grams per cubic

centimeter) the error in ΔF° is 2.4 calories per mole. This is insignificant in this system. The fugacity approaches the pressure as the pressure decreases so that at low pressures they may be assumed to be equal.

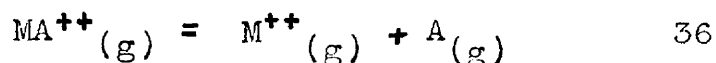
The short extrapolation of the data to 100°C for the CH_3NH_2 and en complexes is not unreasonable and implies the assumption that ΔH° is constant in this temperature range.

The extended extrapolation of the data to 25°C for all the complexes also implies that ΔH° is constant over this temperature range. The validity of this assumption will be discussed later.

DISCUSSION

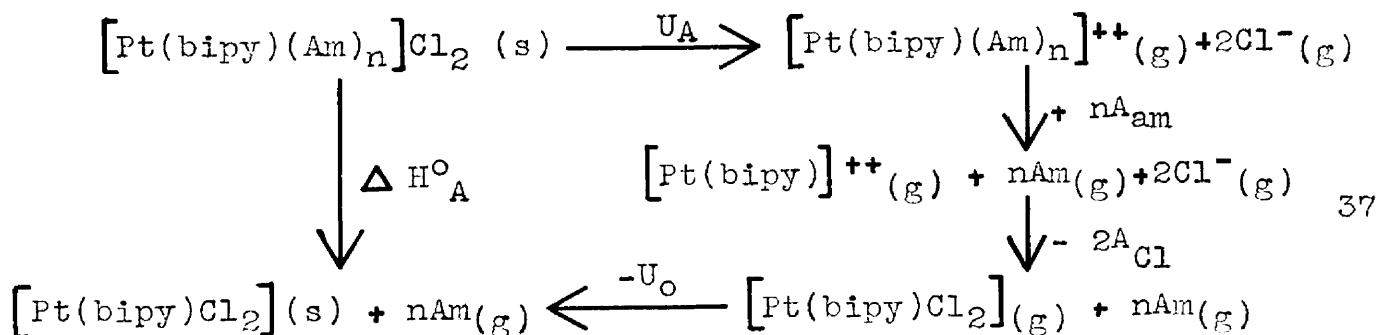
In aqueous solution, it has been shown (7) that ethylenediamine forms more stable complex ions with various metal ions than does ammonia and methylamine. Comparison of available data for 1,3-diaminopropane complexes with corresponding ammonia complexes (7, 10) shows that 1,3-diaminopropane complexes are of equal or greater stability than the ammonia complexes but they are not as stable as the ethylenediamine complexes. On the basis of these observations and on the basis that methylamine is a stronger base than ammonia and should form stronger bonds to the metal ion, the following order of increasing stability would be expected in the series of complexes in this study: $\text{NH}_3 < \text{CH}_3\text{NH}_2 < \text{tn} < \text{en}$. From an examination of the data in Tables VIII and IX, the following orders were found experimentally: at 100°C , $\text{tn} < \text{CH}_3\text{NH}_2 < \text{en} < \text{NH}_3$; at 25°C , $\text{tn} < \text{en} < \text{NH}_3 < \text{CH}_3\text{NH}_2$. These orders differ significantly from that expected. It should be noted from the data that while there is relatively little difference in ΔF° for these complexes, there is a much larger difference in ΔH° and ΔS° . These differences are especially noteworthy in comparing the values of the NH_3 and CH_3NH_2 complexes with those of the en and tn complexes. An explanation for these large differences should also explain the anomalous stability order.

In studying the stabilities and thermodynamic constants of complex ions or compounds, it is desirable to compare the thermodynamic constants for the process



in which the gaseous complex metal ion dissociates into the gaseous metal ion and gaseous ligand. This process is hypothetical but the thermodynamic constants can be obtained with the use of a thermochemical cycle (40) if the other values in the cycle are known or can be estimated. All statements concerning enthalpies, entropies and free energies of bonding are in reference to this process. This reaction is, in general, endothermic.

The thermodynamic constants for the process represented by equation 26 can be treated by a thermodynamic cycle and subsequently shown to be the sum of several component steps. Such a cycle is given below for the enthalpy of dissociation.



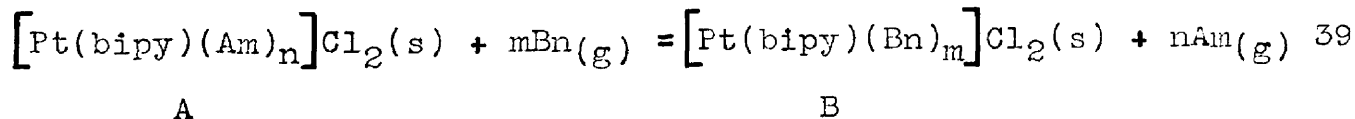
From this cycle

$$\Delta H_A^\circ = U_A - U_O + nA_{am} - 2A_{Cl} \quad 38$$

where U_A and U_O are the lattice energies of the solid compounds, and A_{am} and A_{Cl} are the enthalpies of bonding per ligand molecule or ion. The component steps of this cycle are endothermic unless indicated by a negative sign preceding the term.

From equation 38 we may note that the enthalpy of dissociation is the sum of the differences in lattice energies and in the enthalpies of bonding of the ligands to the platinum ion. Qualitatively in this series, the enthalpy of bonding of the chloride ligand is probably greater than that of the ammine due to electrostatic considerations, but a positive value in ΔH° is obtained because the lattice energy of the ammine complex is greater than that of the $[Pt(bipy)Cl_2]$ compound.

If we consider differences in the dissociation thermodynamic constants for the various complexes in this series, we obtain the thermodynamic constants for the following type of reaction.



where Am and Bn are two different amines and m or n is 1 or 2. The enthalpy change for this reaction is given as

$$\Delta H^\circ_T = \Delta H^\circ_A - \Delta H^\circ_B \quad 40$$

$$= U_A - U_B + nA_{am} - mA_{bn} \quad 41$$

By analogy, similar equations can be obtained for free energy, ΔF°_T , and entropy, ΔS°_T , changes. The experimental values of ΔF°_T , ΔH°_T and ΔS°_T are listed in Tables X and XI.

Kapustinskii (41) has given the following empirical equation for lattice energies, independent of crystal structure

$$U = 287.2 \left(\frac{n\nu_1\nu_2}{r_1+r_2} \right) \left(1 - \frac{.34}{r_1+r_2} \right) \quad 42$$

where n is the number of ions per molecule, ν_1 and ν_2 are ionic valences and r_1 and r_2 are ionic radii. From this relation one would expect U_A and U_B to be nearly equal if their cationic radii are nearly equal.

From lattice energy data for the tetrammineplatinum(II) salts in Table IV and the Goldschmidt values for the halide ionic radii (42) (1.33, 1.81, 1.91, 2.20 Å for F^- , Cl^- , Br^- and I^- , respectively) a value of 2.73 Å was calculated for the ionic radius of the tetrammineplatinum(II) ion. Using the Kapustinskii equation with $n = 3$, $\nu_1 \nu_2 = 2$, $r_2 = 1.81$ Å and a minimum value of 2.70 Å for r_1 , lattice energies were calculated for increasing values of r_1 . These values are listed in Table XII.

TABLE X

THERMODYNAMIC CONSTANTS FOR THE REACTION
 $[\text{Pt}(\text{bipy})\text{Am}_n]\text{Cl}_2(\text{s}) + m\text{Bn}(\text{g}) = [\text{Pt}(\text{bipy})\text{Bn}_m]\text{Cl}_2(\text{s}) + n\text{Am}(\text{g})$
 AT 100°C

| <u>nAm - mBn</u> | <u>ΔF°_T</u> | <u>ΔH°_T</u> | <u>ΔS°_T</u> |
|---|--------------------------------------|--------------------------------------|--------------------------------------|
| 2NH ₃ - 2CH ₃ NH ₂ | 2.39 | -17.51 | -53.3 |
| 2NH ₃ - en | 1.36 | 26.56 | 67.5 |
| 2NH ₃ - tn | 2.42 | 31.77 | 78.6 |
| 2CH ₃ NH ₂ - en | -1.03 | 44.07 | 120.8 |
| 2CH ₃ NH ₂ - tn | 0.03 | 49.28 | 131.9 |
| en - tn | 1.06 | 5.21 | 11.1 |

TABLE XI

THERMODYNAMIC CONSTANTS FOR THE REACTION
 $[\text{Pt}(\text{bipy})\text{Am}_n]\text{Cl}_2(\text{s}) + m\text{Bn}(\text{g}) = [\text{Pt}(\text{bipy})\text{Bn}_m]\text{Cl}_2(\text{s}) + n\text{Am}(\text{g})$
 AT 25°C

| <u>nAm - mBn</u> | <u>ΔF°_T</u> | <u>ΔH°_T</u> | <u>ΔS°_T</u> |
|---|--------------------------------------|--------------------------------------|--------------------------------------|
| 2NH ₃ - 2CH ₃ NH ₂ | -1.62 | -17.51 | -53.3 |
| 2NH ₃ - en | 6.42 | 26.56 | 67.5 |
| 2NH ₃ - tn | 8.32 | 31.77 | 78.6 |
| 2CH ₃ NH ₂ - en | 8.04 | 44.07 | 120.8 |
| 2CH ₃ NH ₂ - tn | 9.94 | 49.28 | 131.9 |
| en - tn | 1.90 | 5.21 | 11.1 |

TABLE XII

LATTICE ENERGIES CALCULATED FROM THE KAPUSTINSKII EQUATION USING $n = 3$, $\nu_1\nu_2 = 2$, $r_2 = 1.81$ AND VARIOUS VALUES OF r_1

| <u>r_1</u> | <u>U(kcal/mole)</u> | <u>r_1</u> | <u>U(kcal/mole)</u> |
|-------------------------|---------------------|-------------------------|---------------------|
| 2.70 | 353 | 3.10 | 327 |
| 2.80 | 346 | 3.20 | 321 |
| 2.90 | 340 | 3.30 | 315 |
| 3.00 | 333 | 3.40 | 309 |
| | | 3.50 | 304 |

These calculations show that where cationic radii differ by 0.10\AA , the lattice energies will differ by only 5-7 kilocalories per mole while a difference in radii of $0.7\text{-}0.8\text{\AA}$ is necessary to give a lattice energy difference of 40-50 kilocalories per mole.

Altshuller (43) has calculated lattice entropies for several simple salts. He has shown that lattice entropies vary from 40 entropy units per mole for the alkali halides to 85 entropy units per mole for salts containing oxyanions. He has also shown, however, that for a given series of salts the lattice entropies vary by 5 entropy units or less.

Lattice entropy is the change in entropy upon evaporation of an ionic crystal to gaseous ions. The entropy of a

gaseous substance can be partitioned into translational, rotational and vibrational entropies. Differences in lattice entropies will be reflected by differences in these entropies, assuming the entropies of the solid to be equal. Differences in translation entropies under the same conditions of temperature and pressure are proportional to the difference in $\ln M$ where M is the molecular (or ionic) weight. Differences in rotational entropies of substances with the same symmetry and at the same temperature are proportional to the difference in $\ln I_1 I_2 I_3$ where I_1 , I_2 and I_3 are the moments of inertia about the three axes of rotation. Differences in vibrational entropies depend in some way on the difference in vibrational frequencies and on the number of degrees of freedom within the molecule. For the series $[\text{Pt}(\text{bipy})(\text{Am})_n]^{++}(\text{g})$, translational entropies differ by a maximum of 0.3 entropy units and rotational by less than 5 entropy units assuming a difference in radii of 1 \AA and a spherical ball model for the ion in calculating moments of inertia. Vibrational frequencies are unknown for this series; however, vibrational entropies are relatively small and the difference in them will be smaller. On the basis of these observations and upon the calculations of

Altshuller, it is reasonable to assume that lattice entropies of the series under study will agree within 5 entropy units.

Because of the relative constancy which one would expect to find in the lattice entropies of the series $[\text{Pt}(\text{bipy})(\text{Am})_n]\text{Cl}_2$, the difference in lattice free energies should be similar to the difference in lattice energies.

On the basis of these observations, the large differences in ΔH° values listed in Tables VIII and IX cannot be accounted for alone in terms of lattice energy differences since correspondingly large differences would also occur in ΔF° . Some other explanation must be sought for the apparent abnormal stability order found in this series.

To explain the large differences in ΔH° and ΔS° between these two groups of complexes (the NH_3 and CH_3NH_2 complexes in one group and the en and tn complexes in the other group), it is necessary to propose that the two groups are two different types of compounds or modifications of the same type, so that the process which occurs on heating differs in some way. It is possible to consider one of these groups as normal complex compounds, as previously assumed, and the other group as ammine solvates of the parent

[Pt(bipy)Cl₂], in which the ammine ligands are more loosely bound. However, in this model the vapor pressure of the solvate compound should be higher at a given temperature while the ΔH° should be lower than those of the complex compounds, a combination which is not found in this series.

It is possible that the four complexes in this series have formulas as previously assumed with the exception that the diamine ligands are bonded to the platinum ion through only one amine group. In this model the diamine would be functioning as a monodentate ligand and, as such, these complexes should exhibit higher vapor pressures in the temperature range where the NH₃ and CH₃NH₂ complexes were studied. This model may be modified slightly by assuming that the diamine ligands function as bidentate ligands at lower temperatures but at a higher temperature, near but lower than the temperature range in which these complexes were studied, one of the amine bonds is broken. Above the temperature at which this occurs, the diamine ligand functions as a monodentate. At this temperature the heat capacity and entropy of the solid complex should increase. This would account for the much lower ΔH° and ΔS° for these compounds since these increases are not detectable by the

experimental methods used in this study. This latter model is proposed as the most likely to explain the data obtained in this study.

In this model it can be further assumed that when the one bond of the diamine to the platinum is broken, one of the chloride ions in the compound becomes coordinated to the platinum. Under this assumption a thermochemical cycle treatment would modify equation 41 to the form

$$\Delta H^{\circ}_T = U_A - U_B + 2A_{am} - A'_{bn} - A_{Cl} \quad 43$$

when comparing the NH_3 or CH_3NH_2 (A) complex to the en or tn (B) complex. However, the coordination of the chloride ion occurs before the experimental measurements are made so that these measurements do not include A_{Cl} in this process. The term, A'_{bn} , refers to the breaking of only one amine bond and, in this consideration, equation 41 should be modified by substituting A' for A for the terms representing the diamine ligands. Lattice energy and entropy considerations discussed previously are not valid for all four complexes but only within either of the two separate groups. Hence, lattice energies and entropies for the NH_3 and CH_3NH_2 complexes are similar and also those en and tn complexes are similar but a simple relation cannot be made between the two groups.

By use of Hess' law, the standard thermodynamic constants for the formation of the free amines in the gas phase and their entropies and the thermodynamic constants for the process in equation 39 (ΔF°_T , ΔH°_T and ΔS°_T), the difference in the standard thermodynamic constants of formation for the various pairs of complexes can be calculated along with the difference in standard entropies. The equation to be followed for the standard enthalpies of formation is given as example

$$\Delta H^\circ_{fB} - \Delta H^\circ_{fA} = \Delta H^\circ_T - n \Delta H^\circ_{fAm} + m \Delta H^\circ_{fBn}. \quad 44$$

Some thermodynamic data are available for the pure amines in the literature (44). Data not available were calculated by empirical methods of estimating standard enthalpies of formation and entropies, and heat capacities (45). These data, listed in Table XIII, were used in the calculations appearing in Table XIV from the above equation and the analogous equations for the standard free energies and entropy differences. For the free amines, the estimated data at 100° are less reliable than those at 25°C and the ΔF°_f estimates are relatively poor since they contain an accumulation of the errors found in the estimates of ΔH°_f and ΔS°_f .

TABLE XIII

STANDARD FREE ENERGIES, ENTHALPIES AND ENTROPIES OF
FORMATION FOR GASEOUS AMMINES AT 25°C AND 100°C

| <u>Ammine</u> | ΔF_f° (kcal/ mole) | ΔH_f° (kcal/ mole) | ΔS_f° (e.u.) | S° (e.u.) | $T^\circ\text{C}$ |
|-------------------|---------------------------------------|---------------------------------------|------------------------------|---------------------|-------------------|
| Ammonia | -3.98 | -11.04 | -23.69 | 46.01 | 25 |
| Ammonia | -2.16** | -11.42** | -24.82** | 47.98** | 100 |
| Methylamine | 6.6 | -6.7 | -44.54** | 57.73 | 25 |
| Methylamine | 10.0* | -7.3* | -46.27* | 60.71* | 100 |
| Ethylenediamine | 26.8* | -5.7* | -109.0* | 64.3* | 25 |
| Ethylenediamine | 35.1* | -6.8* | -112.4* | 69.7* | 100 |
| 1-3Diaminopropane | 28.3* | -10.9* | -131.4* | 74.5* | 25 |
| 1-3Diaminopropane | 39.2* | -11.3* | -135.4* | 81.3* | 100 |

*Estimated by empirical methods (45)

**Calculated from available data (44)

TABLE XIV

DIFFERENCES IN ΔF°_f , ΔH°_f , ΔS°_f AND S° FOR THE PAIRS
 $[\text{Pt}(\text{bipy})(\text{Bn})_m]\text{Cl}_2$ AND $[\text{Pt}(\text{bipy})(\text{Am})_n]\text{Cl}_2$ AT 25° AND 100°C

| Complex Pair Bm - An | $\Delta F^\circ_{fB} - \Delta F^\circ_{fA}$ (kcal) | | $\Delta H^\circ_{fB} - \Delta H^\circ_{fA}$ (kcal) | | $\Delta S^\circ_{fB} - \Delta S^\circ_{fA}$ (e.u.) | | $S^\circ_B - S^\circ_A$ (e.u.) | |
|---|---|-------------|---|-------------|---|-------------|-----------------------------------|-------------|
| | <u>25°</u> | <u>100°</u> | <u>25°</u> | <u>100°</u> | <u>25°</u> | <u>100°</u> | <u>25°</u> | <u>100°</u> |
| CH ₃ NH ₂ - NH ₃ | 19.6 | 16.7 | -8.8 | -9.3 | -95.0 | -96.2 | -29.8 | -27.9 |
| en - NH ₃ | 41.1 | 40.8 | 43.1 | 42.6 | 5.9 | 4.7 | 39.8 | 41.2 |
| tn - NH ₃ | 44.6 | 45.9 | 43.0 | 43.3 | -5.4 | -7.2 | 61.1 | 63.9 |
| en - CH ₃ NH ₂ | 21.6 | 14.2 | 51.8 | 51.9 | 100.9 | 100.9 | 69.6 | 69.1 |
| tn - CH ₃ NH ₂ | 25.0 | 19.2 | 51.0 | 52.6 | 89.6 | 89.0 | 90.9 | 91.8 |
| tn - en | 3.4 | 5.2 | 0.0 | 0.7 | -11.3 | -11.9 | 21.1 | 22.7 |

Of the various factors affecting the enthalpy of bonding of a ligand in a complex (Table I) all are constant in the series of complexes in this study, with the exception of the basicity and steric requirements of the four ammine ligands. As the base strength of the ligand increases the enthalpy of bonding increases and the bond tends to be more stable. In aqueous solution the order of increasing basicity of the free amines is given as (46) $\text{NH}_3 < \text{en} < \text{tn} < \text{CH}_3\text{NH}_2$. Consideration of steric factors should be included in a

consideration of lattice energies since these ligands should have no special steric hinderances in forming bonds in the gaseous platinum complex.

A comparison of the enthalpies of bonding in this series can be obtained from equation 41 if the lattice energies involved in the relation are known or can otherwise be treated in a semi-quantitative way. This comparison can, at best, only lead to relative values of the enthalpies of bonding. For the NH_3 and CH_3NH_2 complexes, assuming the lattice energies are equal, the enthalpy of bonding of the CH_3NH_2 ligand is 8.75 kilocalories ($\frac{1}{2}\Delta H^\circ_T$) greater than that of the NH_3 ligand. This is predicted qualitatively by the relative basicities of these ammine ligands. Using the Kapustinskii equation as a good estimate for lattice energies, the assumption that the lattice energies of these two complexes are equal implies that their cationic radii are also equal. Since the CH_3NH_2 ligand is slightly larger than the NH_3 ligand, it can be assumed that the cation in which it is bound is also larger than corresponding ion in the NH_3 complex and the lattice energy of the CH_3NH_2 complex should, therefore, be slightly less than that of the NH_3 complex. The 8.75 kilocalories difference in the

enthalpy of bonding is a lower limit and the actual limit may be several units larger. (The lower lattice energy of the CH_3NH_2 complex may be considered as a consequence of some steric hindrance of the CH_3NH_2 ligand in the solid complex.)

For the en and tn complexes, again assuming equal lattice energies, the enthalpy of bonding of the en ligand is 5.21 kilocalories (ΔH°_T) greater than that of the tn ligand. This is in disagreement with the relative enthalpies of bonding predicted by basicity considerations. However, the lattice energy of the tn complex should be less than that of the en complex. The 5.21 kilocalories difference is an upper limit and may be completely compensated by a larger difference in the lattice energies.

Under the assumptions of the proposed model of this system it is not possible to compare the enthalpies of bonding of the simple ammine ligands to those of the diamine ligands. Assuming equal cationic radii in the two types of complex, the resulting lattice energies would be in a ratio of 3 to 1, with that of the simple ammine complexes being greater, showing that lattice energy differences are a major contribution to ΔH°_T . Further, if the lattice energy

differences could be accounted for quite accurately the resulting value would represent the difference in the enthalpies of bonding of two simple ammine ligands and one bond of the diamine ligand.

From Table XIV the following order of increasing standard enthalpies of formation is found for the complexes in this series: $\text{CH}_3\text{NH}_2 < \text{NH}_3 < \text{en} < \text{tn}$ at both 25° and 100°C .

In the dissociation process for these complexes, a major contribution to ΔS° should be due to the entropy of the liberated ammine. From Table XIII the entropies for the number of moles of ammine liberated per mole of solid complex are 115.5, 92.0, 64.3 and 74.5 for CH_3NH_2 , NH_3 , en and tn, respectively. Comparison of these values with ΔS° for the dissociation of the corresponding complex shows that for the CH_3NH_2 and NH_3 complexes the major contribution to ΔS° is, indeed, due to the entropy of the liberated ammine. With the other two complexes, the entropy of the liberated amines are offset by a large increase in the entropies of the solid substances involved in the process. The order of increasing entropy of the solid complexes, obtainable from Table XIV, is $\text{CH}_3\text{NH}_2 < \text{NH}_3 < \text{en} < \text{tn}$. The larger entropies of the latter two complexes are a result of entropy increase

which accompanied the breaking of one of the amine bonds before the dissociation process occurs.

The relative entropy of bonding (analogous to the enthalpy of bonding) can be obtained from Tables X and XI (ΔS°_T) if the lattice entropies are assumed to be equal. The lattice entropies should be approximately equal only when comparing the NH_3 complex to the CH_3NH_2 complex and the en complex to the tn complex. In the latter comparison ΔS°_T is relatively small and may be compensated by the difference in lattice entropies of the solid complexes. However, as a first approximation, we can assume that $\frac{1}{2}\Delta S^\circ_T$ is the difference in the entropy of bonding of NH_3 and CH_3NH_2 ligands in the complex and ΔS°_T the corresponding difference for the en and tn ligands.

The relative free energy of bonding, applying the same assumptions, can also be obtained from Tables X and XI. As a first approximation, $\frac{1}{2}\Delta F^\circ_T$ can be taken as the difference in the free energy of bonding for the NH_3 and CH_3NH_2 ligands while ΔF°_T is the corresponding difference for the en and tn ligands. Note that the difference in the free energy of bonding indicates that at 100°C the NH_3 complex is more stable than the CH_3NH_2 complex while at 25°C the reverse is

true. From Table XIV the order of increasing standard free energy of formation for the complexes is given as $\text{NH}_3 < \text{CH}_3\text{NH}_2 < \text{en} < \text{tn}$ at both 25°C and 100°C .

It must be emphasized that in these discussions concerning the en and tn complexes, the amine ligands are bound by only one amine group to the platinum ion. At 25°C this model is hypothetical and the discussions have no relation to the compounds as they actually exist at this temperature. However, at, or near, 100°C these complex forms and the processes concerning them are real. It is for this reason that all data have been reported at both 25° and 100°C . Since the various enthalpy and entropy values have little or no temperature dependence all discussions concerning them are valid at both temperatures under the expressed assumptions.

Under the assumptions of the proposed model for the en and tn complexes, it is obvious that comparisons concerning the chelate effect and the effect of ring size in the chelate effect cannot be made.

SUMMARY

Dichloro(2,2'-bipyridine)platinum(II), $[\text{Pt}(\text{bipy})\text{Cl}_2]$, suspended in chloroform, was treated with various anhydrous amines and a series of complexes were formed which are represented by the general formula $[\text{Pt}(\text{bipy})(\text{Am})_n]\text{Cl}_2$ where Am is ammonia, methylamine, ethylenediamine and 1,3-diaminopropane and n is 2 for the former two amines and 1 for the latter two. These complexes, upon heating, dissociate into the original components. The pressure of the dissociated amine vapor over the solid complex was measured as a function of temperature and the thermodynamic quantities ΔF° , ΔH° , and ΔS° for the dissociation were obtained for each complex.

Comparison of these thermodynamic values shows that the four complexes fall into two groups with the complexes containing the monoamine ligands in one group and those of the diamine ligands in the other group. The first group is characterized by large values of ΔH° and ΔS° and the latter group by relatively small values. By a semi-quantitative consideration of lattice energies and entropies it is shown that the large differences in the ΔH° and ΔS° values for the two groups cannot arise from this source

unless the compounds in these groups differ in some way not usually considered. A model is proposed whereby, during the process of heating the complexes, one of the platinum-amine bonds dissociates in the complexes containing the diamine ligands and a chloride ion in the complex becomes coordinated. The thermodynamics for this process are not measured or detected by the experimental methods used in the study and the net result is that the thermodynamic values which are obtained for these two complexes refer to the dissociation of the hypothetical (at 25°) complexes. Difference in lattice energies and entropies between the two groups, under the assumptions of this model, can account for part of the differences in ΔH° and ΔS° but a further comparison cannot be made.

Minor differences in ΔH° and ΔS° within each of the groups are the result of differences in lattice energies and entropies and in the enthalpies and entropies of bonding of the various ligands to the platinum ion. At 25°C the order of decreasing stability for these complexes is given as CH_3NH_2 , NH_3 , en and tn. This same order is given for ΔH° and ΔS° .

From the standard free energies and enthalpies of formation of the free amines and their standard entropies

and from the thermodynamic values obtained for the dissociation of the complexes, relative values for the standard free energies and enthalpies of formation (from the elements) and the standard entropies of the complexes were obtained. The order of decreasing ΔF_f° for these complexes is given as NH_3 , MeNH_2 , en, tn and for ΔH_f° and S° as CH_3NH_2 , NH_3 , en and tn. These orders refer to the latter two complexes in a hypothetical state.

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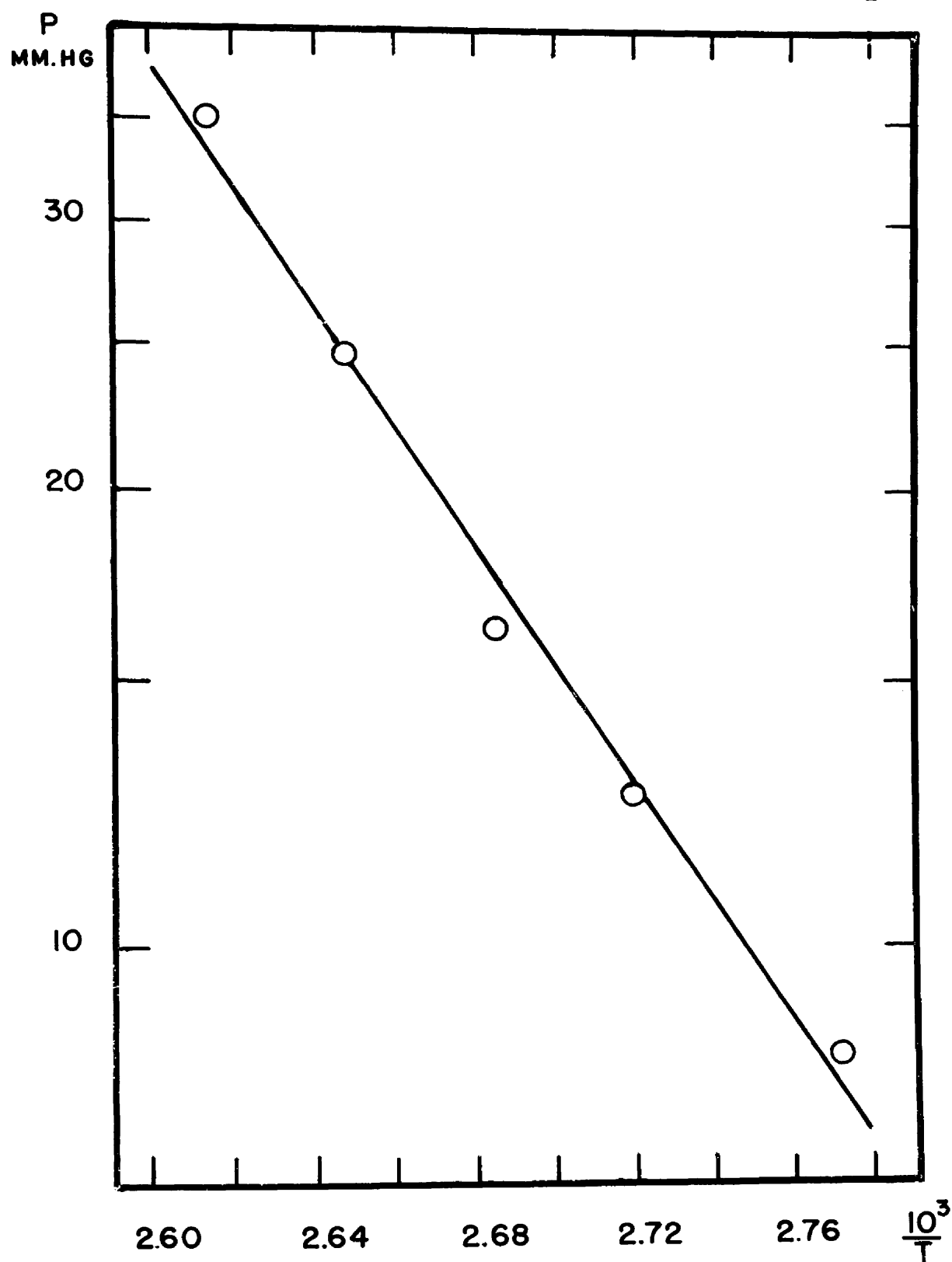
APPENDIX

TABLE XV

70

OBSERVED VAPOR PRESSURES OF DIAMMINE (2,2'-BIPYRIDINE)-
PLATINUM(II) CHLORIDE AT VARIOUS TEMPERATURES

| t°C | 87.4 ± .1 | 94.3 ± .1 | 99.1 ± .1 | 104.4 ± .1 | 109.4 ± .1 |
|----------------------------|-------------|-------------|-------------|-------------|-------------|
| $\frac{10^3}{T}$ | 2.773 | 2.721 | 2.686 | 2.648 | 2.614 |
| P(mm) | 8.36 | 12.30 | 15.94 | 24.51 | 35.27 |
| corrected | 8.49 | 12.65 | 16.37 | 24.93 | 34.94 |
| | 8.37 | 12.69 | 16.49 | 24.59 | 34.99 |
| | 8.72 | 12.66 | 16.12 | 24.38 | 35.04 |
| | 8.49 | 12.37 | 16.23 | 24.48 | 35.15 |
| | 8.48 | 12.73 | 16.06 | 24.90 | 35.23 |
| | 8.72 | 12.48 | 16.32 | 24.61 | 34.94 |
| | 8.46 | 12.85 | 16.20 | 24.76 | 35.10 |
| | 8.52 | 12.70 | 16.44 | 24.53 | 35.01 |
| | | 12.87 | 16.24 | | 35.08 |
| P(ave.) | 8.51 ± .17 | 12.63 ± .19 | 16.24 ± .17 | 24.63 ± .19 | 35.08 ± .11 |
| Applied Correc- tion | -1.11 ± .13 | -1.11 ± .13 | -1.11 ± .13 | -1.11 ± .13 | -1.11 ± .13 |

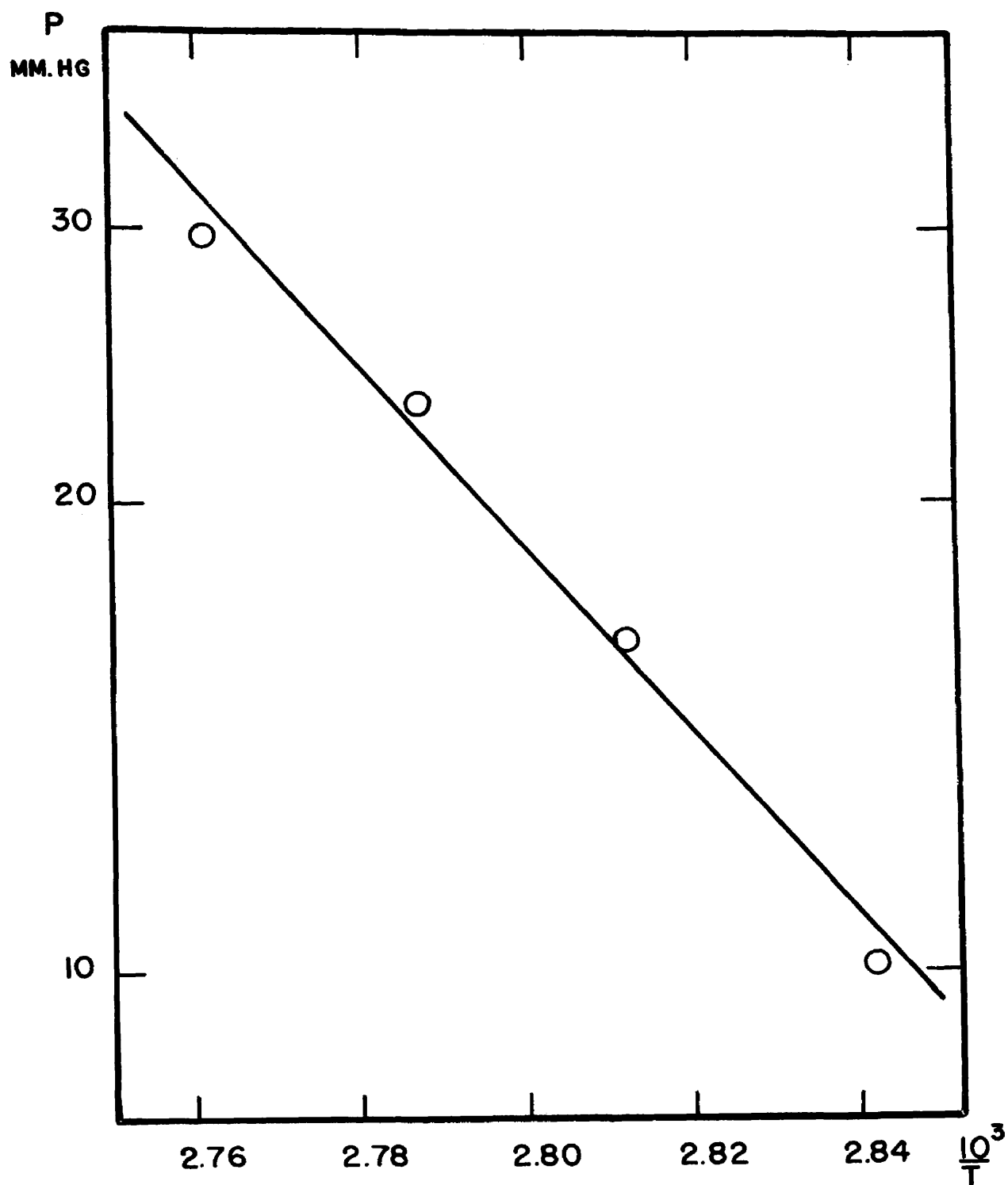


LOG P VERSUS $\frac{1}{T}$ FOR $[\text{Pt}(\text{bipy})(\text{NH}_3)_2]\text{Cl}_2$

TABLE XVI

OBSERVED VAPOR PRESSURES OF DIMETHYLAMINE(2,2-BIPYRIDINE)-
PLATINUM(II) CHLORIDE AT VARIOUS TEMPERATURES

| | | | | |
|----------------------------|-------------|-------------|-------------|-------------|
| t°C | 78.7 ± .3 | 82.2 ± .3 | 85.6 ± .3 | 89.0 ± .3 |
| $\frac{10^3}{T}$ | 2.842 | 2.814 | 2.787 | 2.761 |
| P(mm) Corrected | 10.33 | 16.26 | 22.90 | 29.45 |
| | 10.14 | 16.26 | 23.01 | 29.51 |
| | 10.40 | 16.18 | 23.05 | 29.90 |
| | 9.87 | 16.58 | 23.24 | 29.93 |
| | 10.26 | 16.11 | 23.28 | 29.68 |
| | 9.98 | 16.12 | 23.20 | 29.57 |
| | 9.94 | 16.30 | 23.20 | 29.83 |
| | 10.16 | 16.17 | 23.19 | 29.70 |
| | 10.03 | 16.24 | 23.17 | 29.80 |
| | 10.12 | 16.54 | 23.30 | 29.74 |
| P(ave.) | 10.12 ± .17 | 16.27 ± .16 | 23.16 ± .13 | 29.71 ± .16 |
| Applied Correc- tion | 1.91 ± .19 | 1.91 ± .19 | 1.91 ± .19 | 1.91 ± .19 |



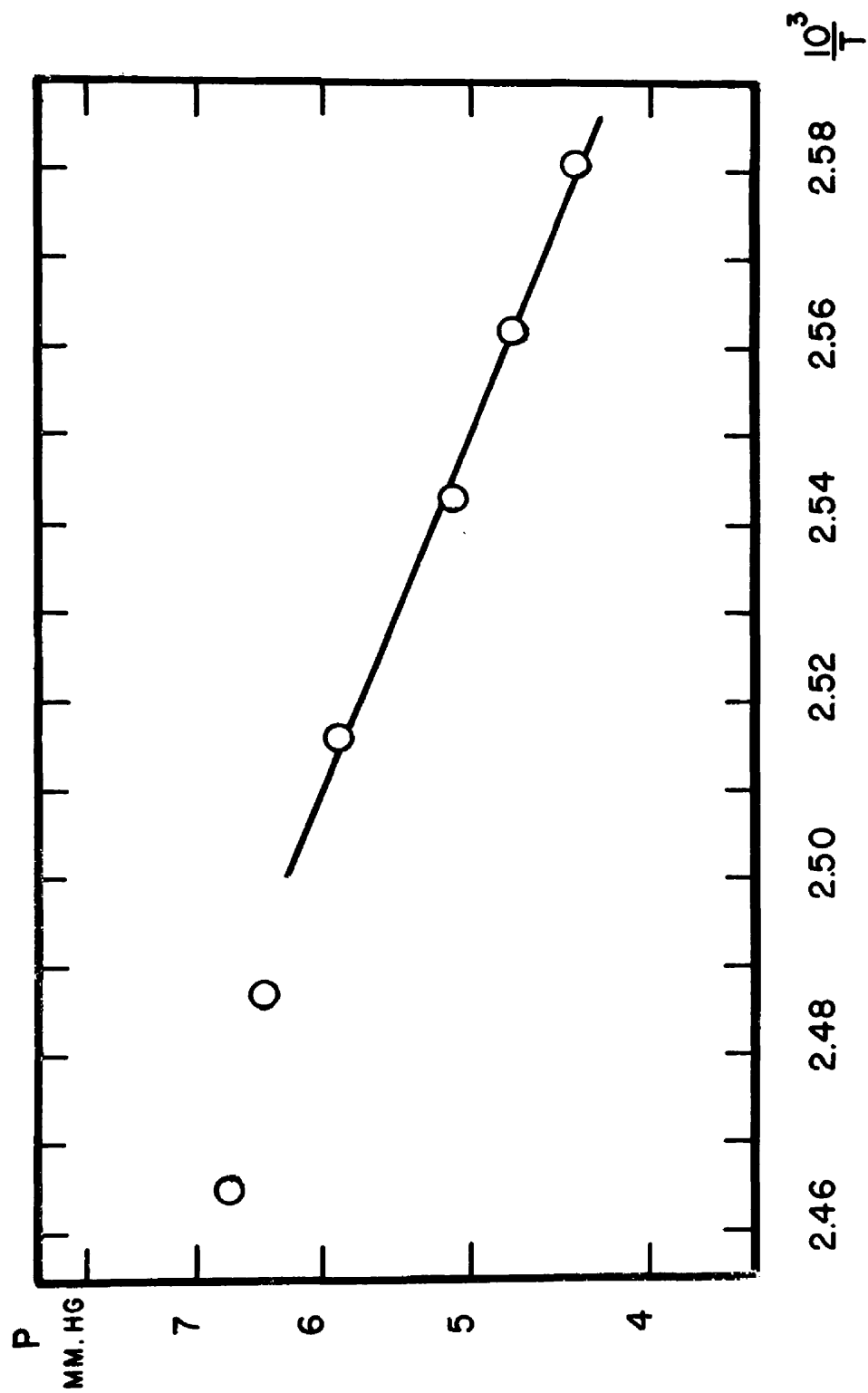
LOG P VERSUS $\frac{1}{T}$ FOR $[\text{Pt}(\text{bipy})(\text{CH}_3\text{NH}_2)_2]\text{Cl}_2$

TABLE XVII

OBSERVED VAPOR PRESSURES OF ETHYLENEDIAMINE (2,2-BIPYRIDINE)-
PLATINUM(II) CHLORIDE AT VARIOUS TEMPERATURES

| t°C | 114.2 ^{±.3} | 117.1 ^{±.3} | 120.0 ^{±.3} | 124.2 ^{±.3} | 129.0 ^{±.3} | 132.5 ^{±.3} |
|----------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| $\frac{10^3}{T}$ | 2.581 | 2.562 | 2.543 | 2.516 | 2.487 | 2.465 |
| P(mm) Corrected | 4.37 | 4.82 | 5.23 | 5.86 | 6.45 | 6.89 |
| | 4.31 | 4.87 | 5.06 | 5.93 | 6.45 | 6.79 |
| | 4.82 | 4.85 | 5.09 | 5.89 | 6.87 | 6.85 |
| | 4.51 | 4.91 | 5.15 | 6.22 | 5.94 | 6.70 |
| | 4.05 | 4.62 | 5.23 | 5.76 | 6.69 | 6.62 |
| | 4.68 | 4.87 | 4.91 | 5.97 | 6.16 | 6.79 |
| | 4.16 | 4.59 | 5.12 | 6.00 | 6.70 | 6.52 |
| | 4.61 | 4.81 | 5.01 | 5.70 | 6.05 | 6.49 |
| | 4.02 | 4.63 | 5.15 | 5.69 | 6.66 | 6.75 |
| | 4.30 | | | | 6.32 | |
| | | | | | 6.34 | |
| | | | | | 6.51 | |
| P(ave.) | 4.39 ^{±.27} | 4.75 ^{±.13} | 5.11 ^{±.10} | 5.89 ^{±.17} | 6.44 ^{±.29} | 6.71 ^{±.14} |
| Applied Correc- tion | 1.91 ^{±.19} | 1.91 ^{±.19} | 1.91 ^{±.19} | 1.91 ^{±.19} | 2.10 ^{±.13} | 2.10 ^{±.13} |

FIGURE V



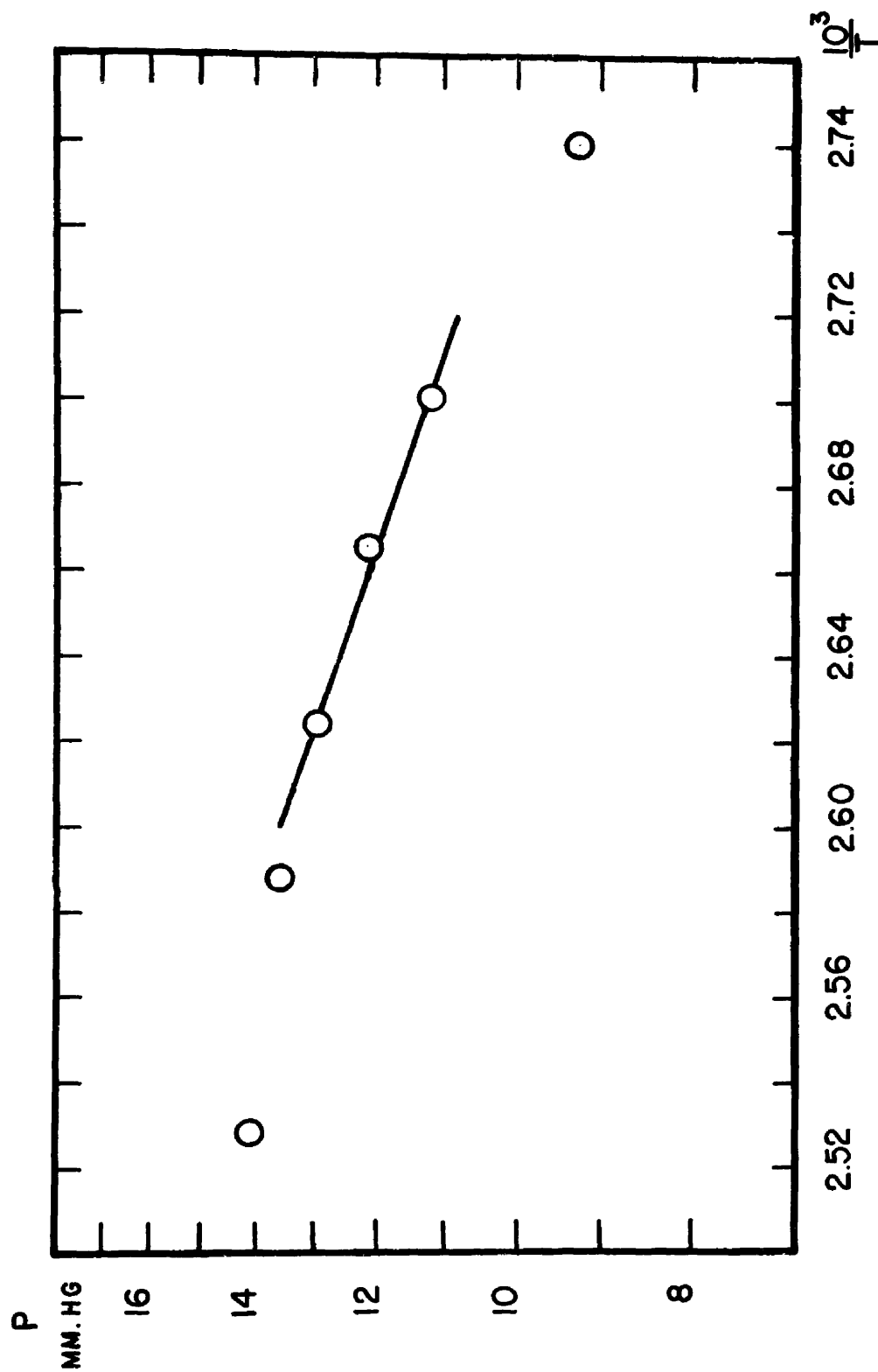
$\log p$ VERSUS $\frac{1}{T}$ FOR $[\text{Pt}(\text{bipy})\text{en}]\text{Cl}_2$

TABLE XVIII

OBSERVED VAPOR PRESSURES OF 1,3-DIAMINOPROPANE (2,2-BIPYRIDINE)-
PLATINUM(II) CHLORIDE AT VARIOUS TEMPERATURES

| | | | | | | |
|------------------|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| t°C | 89.1 \pm .2 | 97.0 \pm .2 | 102.3 \pm .2 | 107.9 \pm .1 | 113.0 \pm .2 | 122.2 \pm .1 |
| $\frac{10^3}{T}$ | 2.760 | 2.701 | 2.663 | 2.624 | 2.589 | 2.529 |
| P(mm) | 9.45 | 11.17 | 11.73 | 13.20 | 13.82 | 14.31 |
| Correct- | 9.12 | 11.38 | 11.99 | 12.75 | 13.96 | 13.92 |
| ed | 9.37 | 11.11 | 11.80 | 13.14 | 13.43 | 13.64 |
| | 9.26 | 11.05 | 12.20 | 12.76 | 13.72 | 14.32 |
| | 9.09 | 11.49 | 12.69 | 13.03 | 13.38 | 14.28 |
| | 9.23 | 11.21 | 12.34 | 13.00 | | 13.96 |
| | 9.21 | 11.40 | 12.00 | 12.68 | | 14.02 |
| | | 11.13 | 12.13 | 12.90 | | 14.15 |
| | | 11.11 | 12.64 | 13.20 | | 13.72 |
| | | 10.87 | 11.68 | 12.86 | | 14.07 |
| | | 11.53 | 12.40 | | | |
| | | | 12.13 | | | |
| P(ave.) | 9.25 \pm .13 | 11.22 \pm .20 | 12.14 \pm .25 | 12.95 \pm .19 | 13.66 \pm .25 | 14.04 \pm .24 |
| Applied | | | | | | |
| Correc- | | | | | | |
| tion | 1.39 \pm .16 | 1.39 \pm .16 | 1.39 \pm .16 | 1.39 \pm .16 | 1.91 \pm .19 | 1.91 \pm .19 |

FIGURE VI



LOG P VERSUS $\frac{1}{T}$ FOR $[\text{Pt}(\text{bipy})\text{en}]\text{Cl}_2$

X-RAY PATTERNS

In an effort to be more specific concerning lattice energies, X-ray powder patterns were obtained for the four ammine complexes and the parent compound $[\text{Pt}(\text{bipy})\text{Cl}_2]$. The d values for the more intense lines of each pattern are listed in Table XIX. The values for the lines of weaker intensity are omitted. For each compound the d values were plotted on a log scale versus relative intensity. The resulting graph was then compared with Hull-Davey charts for the tetragonal and hexagonal structures and a similar type chart for the cubic structure. The d values for the NH_3 complex, as listed in Table XIX, were found to compare with those for a tetragonal structure with $\frac{c}{a} = .90$, $a = 21.7\text{\AA}$ and $c = 19.5\text{\AA}$. Similarly, those for the en complex compared with the tetragonal structure with $\frac{c}{a} = 1.10$, $a = 24.0\text{\AA}$ and $c = 26.4\text{\AA}$. No comparisons could be found for the d values of the remaining three compounds.

Since the structures for all four complexes were not obtained no attempt is made to discuss these data in the lattice energy considerations. Also structures obtained by this method are for the real complexes at 25°C and are not valid for any hypothetical forms which may be assumed.

TABLE XIX

X-RAY POWDER PATTERN DATA

| $[\text{Pt}(\text{bipy})(\text{NH}_3)_2]\text{Cl}_2$ | | $[\text{Pt}(\text{bipy})(\text{CH}_3\text{NH}_2)_2]\text{Cl}_2$ | | $[\text{Pt}(\text{bipy})\text{tn}]\text{Cl}_2$ | |
|--|----------------------|---|----------------------|--|----------|
| <u>d</u> | <u>I^a</u> | <u>d</u> | <u>I^a</u> | <u>d</u> | <u>I</u> |
| 9.47 | VS | 9.92 | S | 10.59 | VS |
| 8.24 | VS | 8.74 | S | 8.28 | VS |
| 6.51 | S | 8.27 | VS | 6.06 | VS |
| 6.23 | VS | 6.04 | VS | 5.36 | S |
| 5.14 | S | 4.17 | VS | 5.02 | S |
| 4.88 | S | 3.78 | S | 4.37 | S |
| 3.76 | S | 3.55 | S | 4.21 | S |
| 3.56 | S | 3.43 | S | 3.55 | VS |
| 3.44 | S | 3.32 | S | 3.36 | S |
| 3.16 | VS | 3.12 | S | 3.19 | S |
| 3.00 | S | 3.00 | S | 3.12 | S |
| | | | | 3.01 | S |
| | | | | 2.92 | S |
| $[\text{Pt}(\text{bipy})\text{Cl}_2]$ | | $[\text{Pt}(\text{bipy})\text{en}]\text{Cl}_2$ | | | |
| <u>d</u> | <u>I^a</u> | <u>d</u> | <u>I^a</u> | | |
| 10.63 | VS | 10.41 | VS | | |
| 8.12 | VS | 8.05 | VS | | |
| 7.17 | S | 6.46 | VS | | |
| 6.68 | S | 5.03 | VS | | |
| 6.04 | VS | 4.81 | VS | | |
| 5.14 | S | 3.54 | S | | |
| 3.57 | S | 3.41 | S | | |
| 3.18 | S | 3.30 | S | | |
| | | 2.46 | S | | |

a Relative intensity; VS Very strong; S Strong
Weaker intensity lines have been omitted.

NOTE ADDED IN PROOF

In the model proposed to explain the anomalous nature of the data obtained in this investigation the assumption was made that one of the platinum amine bonds is broken prior to the dissociation of the diamine ligand (page 53 ff.). An attempt has been made to verify this assumption experimentally by differential thermal analysis (D.T.A.). With D.T.A. a sample is heated at a fairly rapid rate (several degrees per minute) and the temperature of the sample is compared to that of a reference material placed near the sample in the furnace. The difference in the rate of heating of the sample and the reference material is approximately constant until a phase change or decomposition occurs in the sample. (The reference material is chosen so that this does not occur within it in the temperature range under investigation.) At this point the rate of change in the temperature of the sample rapidly increases or decreases depending upon whether the accompanying enthalpy change is exothermic or endothermic. The difference in temperature of the sample and reference material is recorded as a function of time.

In this investigation, a sample of the $\text{PtCl}_2(\text{NH}_3)_2$ complex was heated with aluminum oxide as the reference material.* The

*Experimental D.T.A. by Goro Uehara of the Soil Science Department.

resulting D.T.A. curve indicates two endothermic enthalpy changes occur, one beginning at 80-90°C and the other at 130-140°C. The latter change is attributed to the dissociation of the diamine ligands from the complex and the former to the breaking of the first platinum amine bond, in support of the assumption of the proposed model.