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(36) We consider here only the process in which the CH_2 molecule is pulled off retaining the molecular symmetry plane; there are more general pathways for dissociation, but we believe that there will be a significant activation barrier for getting onto the more favorable dissociation pathways.
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Stereochemistry of Complex Inorganic Compounds, XXXV, A Complex Containing a Ligand That Spans Trans Positions

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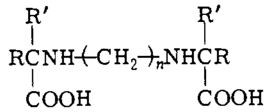
Abstract: By chlorination of *trans*-[$Pt(NH_3)_2Cl_2$] to *trans*-[$Pt(NH_3)_2Cl_4$] and replacement of three of the coordinated chlorine atoms with $RN(CH_2CH_2NH_2)_2$ (R = H or CH_3), a compound, chloro-2,4-diammine-3,5,6-$RN(CH_2CH_2NH_2)_2$platinum(IV), is formed. Reduction of the platinum atom to the platinum(II) state converts the compound to a four-covalent, planar molecule again, with the two ammonia molecules trans to each other and the two primary nitrogen atoms of the $RN(CH_2CH_2NH_2)$ molecule trans to each other. In this compound, the central nitrogen atom of the triamine is not attached to the platinum.

One of the postulates of Werner's coordination theory is that a chelating ligand will attach itself only to cis positions in the coordination complex. Werner used this postulate in much of his stereochemical work, and it has become almost universally accepted by coordination chemists. Werner[2a] assumed it, for example, when he compared the stability of chelate rings of coordination compounds with those of five- and six-membered organic rings and Grinberg[2b] used it in his famous method of distinguishing the cis and trans forms of $[Pt(NH_3)_2Cl_2]$ and similar compounds. Tress[3] argued that the inability of ligands to span trans positions can be deduced from the numbers of isomers in certain types of complexes. Many other coordination chemists have speculated on the possibility of building complexes in which a ligand reaches across a square planar complex. Most investigators admit the possibility that such compounds might be formed and agree that a bidentate ligand of sufficient length might span the trans positions in a planar complex if the proper conditions were found. However, nearly all efforts to build complexes with trans-spanning ligands have met with inconclusive or negative results. Drew and Tress[4] studied the possibility of spanning the trans positions of platinum(II) complexes with the aliphatic diamines, $NH_2(CH_2)_nNH_2$, where n had values from 2 to 5. When $n = 2$ or 3, sparingly soluble complexes of the normal type were formed (e.g., $[Pt(en)Cl_2]$). When $n = 4$ or 5, only ill-defined insoluble substances were formed. These were judged to be polymers. Chugaev[5] reported similar results. Pfeiffer and his coworkers[6] tried similar experiments with the octahedral complexes of chromium, copper, and nickel, but without success. Other investigators[7] attempted to span the trans positions, both in planar and in octahedral complexes, using such bases as decamethylenediamine and octadecamethylenediamine. None of their experiments gave complexes with trans-spanning ligands, and it was generally agreed that such complexes are not to be attained simply by lengthening the chain between the two donor atoms.

Schlesinger[8] reported that by the use of a tetradentate ligand with a long methylene chain between the donor chelating groups, he had been able to span the trans positions in a copper(II) complex. His ligands were bis(α-imino) acids of the type



$$\begin{array}{ccc} R' & & R' \\ RCNH & \!\!\!\text{-(}CH_2\text{)}_n\text{-}\!\!\! & NHCR \\ COOH & & COOH \end{array}$$

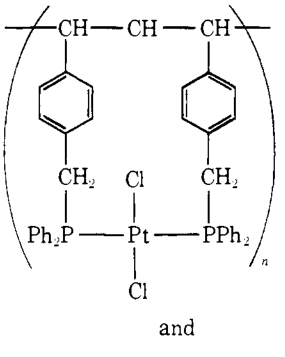
When $n = 2$ or 3, blue, soluble complexes were produced, but when $n = 10$, a violet, much less soluble substance was formed. Values of $n = 5$ or 7 gave rise to both the blue and the violet forms. Both types of compounds were found to be nonelectrolytes and to have normal molecular weights. Schlesinger believed that in the violet form, the nitrogen atoms of the ligand occupied trans positions. Although the evidence supports Schlesinger's hypothesis, the result is hardly conclusive, for it was not shown that the complexes of both types are planar or monomolecular. Also, as Reihlen[9] has pointed out, the asymmetry of the two nitrogen atoms might lead to racemic and meso modifications of the complex.

Some years after these experiments were performed, Isslieb and Hohlfeld[10] advanced evidence that they had been successful in spanning the trans positions in nickel complexes by the use of the simple bidentate diphosphines $(C_6H_{11})_2P(CH_2)_nP(C_6H_{11})_2$. They showed that their nickel complexes [Ni(diphosphine)X_2] were monomolecular. They were red and diamagnetic, which indicate planar structures. With $n = 3$ (X = Br), the dipole moment of the complex was 11.13 D, but, with $n = 5$ (X = Cl), it was only 2.37 D. Isslieb and Hohlfeld interpreted the difference in the dipole moments to indicate that, in the latter compound, the methylene chain reached across the coordination plane but was close to it, so produced little disymmetry.

Pryde, Shaw, and Weeks[11] have expressed the opinion that if a chain of seven members is to span the trans positions, the plane of the complex must be somewhat distorted. They feel that to be planar, the complex should have a ring of 12 or 13 members.

Fleischer and Wang, as well as Khosropour and Hambright,[12] concluded that metal ions attach themselves to porphyrins and porphyrin-like molecules through two nitrogen atoms which lie at opposite corners of the nitrogen plane. There is little experimental evidence to support this conclusion, though it may be that such a structure exists as an intermediate in the formation of porphyrin complexes.[13]

Infrared spectra[14] indicate that in "heterogenized" homogeneous catalysts of the types



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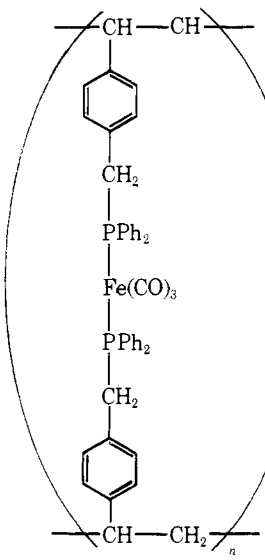
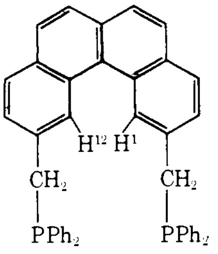


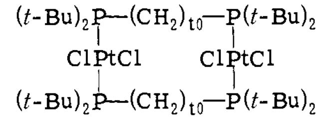
the phosphorus atoms may occupy trans positions on the metal.

Within the last 2 years, there have been two reports of the formation of well-characterized trans-spanning ligands. Venanzi and his students[15] have prepared the ligand 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene



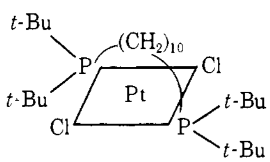
which, because of its size and rigidity, cannot form a cis chelate ring but can attach itself to opposite corners of the coordination plane of palladium(II) or platinum(II). They prepared compounds of the type $[MLX_2]$, and showed that they are monomeric nonelectrolytes. The trans structures were shown by the NMR spectra. When treated with base, these complexes lose protons reversibly, supposedly from the 1 and 12 positions, the carbon atoms of which then form σ bonds with the metal.

Pryde, Shaw, and Weeks[11] have pointed out that there may be less ring strain in large rings, e.g., 12 or 13 members, than in rings of intermediate size, e.g., eight members, as has been shown to be the case with cycloalkanes. When they allowed $t\text{-}Bu_2P(CH_2)_{10}P\text{-}t\text{-}Bu_2$ to react with $[PtCl_2(PhCN)_2]$, they obtained two isomeric complexes. The less soluble of these was shown to be binuclear and to give a well-defined 1:2:1 t-Bu ^{1}H NMR pattern, indicating trans phosphorus nuclei. It also showed a strong infrared absorption band at 334 cm^{-1}, which is characteristic of a linear Cl-Pt-Cl system. They feel that this compound is probably



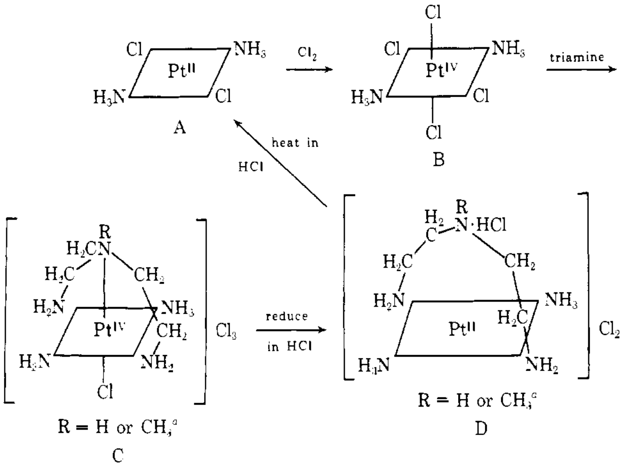
$$\begin{array}{c}(t\text{-Bu})_2\text{P}-(\text{CH}_2)_{10}-\text{P}(t\text{-Bu})_2\\ \text{ClPtCl}\qquad\text{ClPtCl}\\ (t\text{-Bu})_2\text{P}-(\text{CH}_2)_{10}-\text{P}(t\text{-Bu})_2\end{array}$$

The more soluble isomer also shows a 1:2:1 NMR triplet and a strong infrared band at 326 cm^{-1}. It is monomolecular in $CHCl_3$ and shows an intense mass spectral absorption for the parent peak (*m/e* 696). It is believed to have the structure



In the work described in this paper, an entirely different approach was used. It depends upon the fact that platinum(II) normally forms square planar four-coordinate complexes, whereas platinum(IV) forms octahedral six-coordinate ones. It was reasoned that if a tridentate ligand occupied meridional positions in a platinum(IV) complex, and if this complex were reduced to the platinum(II) state, the central donor atom of the ligand might be released from the metal, leaving the end groups attached in trans positions. To ensure that the triamine would occupy meridional positions in the platinum(IV) octahedron, the synthesis was begun with *trans*-dichlorodiammineplatinum(II) (compound A) which was converted to *trans*-tetrachlorodiammineplatinum(IV) (B) and thence to chloro-2,4-diammine-3,5,6-triamineplatinum(IV) chloride (C) (Scheme I).

Scheme I



[a] In those cases in which it is indicated that R represents a methyl group, the experiment was tried *only* with the methylated triamine. In the cases in which both the unmethylated and the methylated triamine were used, the results were strictly parallel.

The formation of compounds A, B, and C is straightforward. There was, however, serious question about what would happen when the metal in C was reduced. It seemed probable that the coordination number of the metal would change from six to four, but, at the outset, there was no certainty that the -NR and the chloro groups would be the ones eliminated from the coordination sphere. The central amine group of the diethylenetriamine is trans to the chloro group, which exerts a moderate trans influence, and it is a secondary amine (or tertiary, when R = CH_3), which gives a weaker bond to the metal than the primary $-NH_2$ groups do. On the other hand, the central nitrogen atom of the chain is a member of two fused chelate rings, which increases the strength of its binding to the metal atom. Happily, as subsequent experiments showed, the secondary amine and the chloro groups were the ones eliminated from coordination to the metal. The central nitrogen atom of the trans-spanning chelate ring is still close to the platinum atom, but a study of scale models shows that the ring can twist enough to expose the unshared pair of electrons on the nitrogen atom and thus to allow it to combine with a proton.

Analysis of compound D (R = H or CH_3) showed it to be slightly low in both chlorine and nitrogen, and recrystallization from water gave a product which gave still lower values for those elements. Repeated recrystallizations (R = H) converted it entirely to E. This is explained by the fact that the eight-membered chelate ring is not stable and tends to revert to the two five-membered rings shown in compound E (Scheme II), which contains one less chloride ion and one less nitrogen atom than does D. When either compound (R = H or CH_3) was boiled in hydrochloric acid, the triamine was eliminated and compound A was formed again. This is strong evidence that, in compound D, the two ammonia molecules occupy their original trans positions, for cis-trans rearrangements are very rare in Pt(II) chemistry. The triamine, then, must be attached to the other two trans positions.

Experimental Section

Apparatus. The infrared spectra were measured on a Perkin-Elmer 457 spectrometer, and the ultraviolet spectrum on a Beckman quartz spectrometer, Model DU, fitted with 1-cm cells, and a hydrogen tube as the light source. The NMR spectra were measured on a Varian A60A instrument. The magnetic susceptibility was measured in a PAR 150A vibrating sample magnetometer.

Preparation of Platinum Compounds. The synthesis of *trans*-$[Pt(NH_3)_2Cl_4]$ was accomplished through the following steps.

$$H_2PtCl_6\cdot 6H_2O \xrightarrow{1} PtCl_2 \xrightarrow{2} [Pt(NH_3)_4]Cl_2 \xrightarrow{3}$$
$$trans\text{-}[Pt(NH_3)_2Cl_2] \xrightarrow{4} trans\text{-}[Pt(NH_3)_2Cl_4]$$

Two different methods were used in the preparation of $PtCl_2$. The method of Kharasch and Ashford[16] consists simply of heating $H_2PtCl_6{\cdot}6H_2O$ in a slow stream of air to 360-380° for 2 hr. The platinum(II) chloride prepared in this way was powdered, heated again for 1 hr, and thoroughly washed. The second method is, on the whole, more convenient. The $H_2PtCl_6{\cdot}6H_2O$, in water solution, is reduced to H_2PtCl_4 with $N_2H_4{\cdot}2HCl$, and the product is heated on the steam bath to convert it to $PtCl_2$.[17]

Step 2 followed the method of Reiset,[18] with some modifications. A mixture of 6.11 g of $PtCl_2$ and 0.5 g of Norite charcoal was allowed to stand in a solution of 30 ml of concentrated NH_4OH and 30 ml of water for 2 hr with occasional stirring. The mixture was heated on the steam bath overnight and filtered, and the precipitate was washed with water. The filtrate and washings were evaporated to a volume of about 20 ml and added dropwise with vigorous stirring to 150 ml of 95% ethanol. After cooling in ice, the pure white tetraammine which precipitated was washed with alcohol and dried, yield 6.59 g (86%). Anal. Calcd for $[Pt(NH_3)_4]Cl_2$: Pt, 58.40. Found: Pt, 58.2.

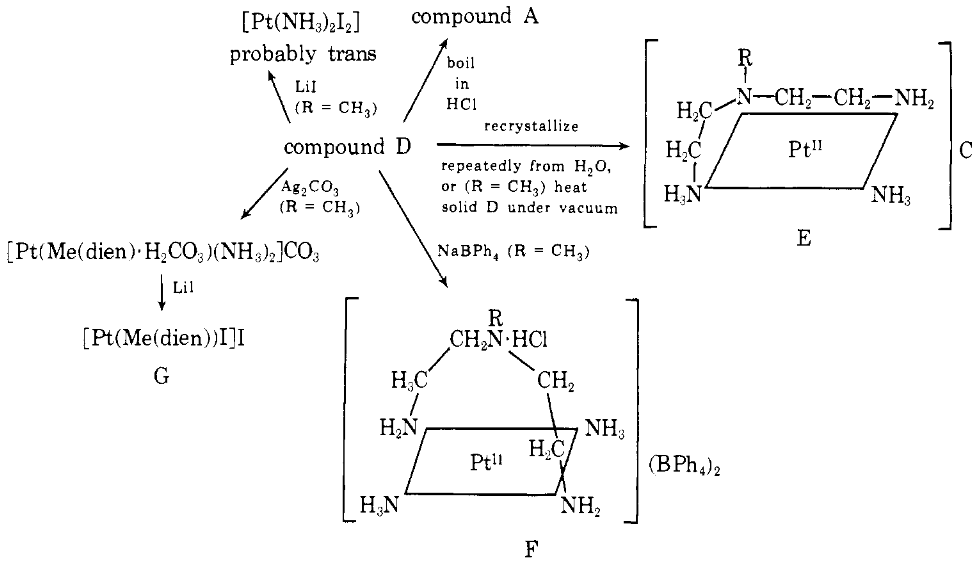
***trans*-Dichlorodiammineplatinum(II)** can be prepared from $[Pt(NH_3)_4]Cl_2$ by heating the dry salt under vacuum to 230-240°[19] or by heating it in 6 *N* hydrochloric acid.[20] The latter method is to be preferred, as it gives a better yield of product.

Oxidation of the planar platinum(II) complex to the octahedral *trans*-tetrachlorodiammineplatinum(IV) was carried out by the method of Kauffman and Cowan.[21] Anal. Calcd: Pt, 52.6; N, 7.55; H, 1.63; Cl, 38.2. Found: Pt, 52.84; N, 7.57; H, 1.74; Cl, 37.96.

***sym*-*N*-Methyldiethylenetriamine** was prepared, as the trihydrochloride, by Mann's method.[22] It was converted to the free base by grinding 2.28 g of it with 3.48 g of Ag_2O in 10 ml of water. The silver chloride was removed by filtration; the washings were added to the filtrate.

For the preparation of the two complexes, C (R = H or CH_3), the solution of the free triamine was added dropwise and with constant stirring (over a period of 6 hr) to a suspension of 3.71 g of *trans*-

Scheme II



$[Pt(NH_3)_2Cl_4]$ and 0.5 g of charcoal in 50 ml of water. After 2 hr of additional stirring, the solution was filtered and the residue was washed with water. The filtrate (with the washings) was evaporated to dryness in a stream of air at room temperature. The residue was purified by dissolving it in water and reprecipitating it by addition of a mixture of equal volumes of methanol and acetone. A second crop was obtained by addition of more methanol and acetone. The total yield, after drying over P_4O_{10}, was 50%. Both compounds were light powders, pale yellow in color, and very hygroscopic. Anal. Calcd for $[Pt(NH_3)_2(C_4H_{13}N_3)Cl]Cl_3$: Pt, 41.16; C, 10.13; H, 4.04; N, 14.77. Found: Pt, 41.19; C, 10.87; H, 4.46; N, 13.97. Anal. Calcd for $[Pt(NH_3)_2(C_5H_{15}N_3)Cl]Cl_3\cdot\frac{1}{2}H_2O\cdot\frac{1}{2}CH_3OH$: Pt, 38.10; C, 12.90; N, 13.70; H, 4.71; Cl, 27.60. Found: Pt, 38.28; C, 12.89; N, 13.37; H, 4.66; Cl, 27.24.

Reduction of the Platinum(IV) Complexes to the Pt(II) State. The procedure for the reduction was essentially the same for both compounds. It was carried out electrolytically to allow for close control of the reduction potential and to avoid the addition of chemical reagents. The electrolytic cell was a square U made of 1-in. tubing and was about 5 in. across and 5 in. high. The anode and cathode compartments were separated by a sintered glass frit, filled with an agar layer containing KCl. The electrodes were of bright platinum. The solution in the cathode compartment was stirred by a small magnetically driven stirrer. The anode compartment contained 0.25 *M* HCl and the cathode compartment, 2 g of the Pt(IV) complex in 30 ml of water. A current of 40 mA flowed through the cell at 5 V. Under these conditions, hydrogen and chloride were evolved at the electrodes. As the electrolysis continued, the current slowly decreased. When no further decrease was noted, electrolysis was stopped. A slight coating of black platinum had formed on the cathode. The catholyte was filtered and evaporated to dryness in a stream of air at room temperature. The resulting residue was redissolved in a minimum amount of water.

In the case of the diethylenetriamine complex, the complex was precipitated by pouring the solution dropwise into 75 ml of methanol containing 2 ml of alcoholic HCl. The stirring was continued while the mixture was cooled in ice. The precipitate was removed, washed with alcohol, and dried. It was purified by repetition of this process, yield 50%. Anal. Calcd for $[Pt(NH_3)_2(C_4H_{13}N_3)\cdot HCl]Cl_2$: Pt, 44.39; C, 10.92; H, 4.58; N, 15.92; Cl, 24.19. Found: Pt, 44.70; C, 11.67; H, 4.52; N, 14.65; Cl, 21.1. After four such recrystallizations, the precipitate showed the following composition: Pt, 46.10; C, 11.32; H, 4.39; N, 13.41; Cl, 18.19. $[Pt(NH_3)(C_4H_{13}N_3)]Cl_2\cdot 2H_2O$ requires the following: Pt, 46.22; C, 11.37; H, 4.77; N, 13.27; Cl, 16.79.

In the case of the complex containing the methylated amine $CH_3N(CH_2CH_2NH_2)_2$, the residue left upon evaporation to dryness was dissolved in water and reprecipitated by addition of a mixture of equal volumes of isopropyl alcohol and methanol, yield 50%. Anal. Calcd for $[Pt(NH_3)_2(C_5H_{15}N_3\cdot HCl)]Cl_2\cdot 0.2(H_2O)\cdot 0.2(C_3H_7OH)$: Pt, 41.60; C, 14.38; N, 15.00; H, 5.05; Cl, 22.75. Found: Pt, 40.44; C, 14.75; N, 14.70; H, 4.78; Cl, 23.62. In order to obtain a nonhygroscopic substance (R = CH_3), this compound was converted to the tetraphenylborate by dissolving 0.2 g of it in 10 ml of water and adding a large excess of $NaBPh_4$ to the solution. A pale yellow precipitate immediately formed. This was dissolved in acetone, precipitated by addition of water, and dried. Anal. Calcd for $[Pt(NH_3)_2(triamine)\cdot HCl](BPh_4)_2$: C, 62.48; N, 6.86; H, 6.14; Cl, 3.48. Found: C, 63.00; N, 6.72; H, 6.39; Cl, 3.55. The close agreement between the calculated and found values suggests that the tetraphenylborate of D is precipitated in great preference to that of E.

A mixture of 0.2 g of *trans*-$[Pt(NH_3)_2((triamine)\cdot HCl)]Cl_2$ (R = CH_3) and 10 ml of 6 *N* HCl was warmed on a steam bath for 3 hr, during which time the volume decreased to about one-half. When this solution was cooled in an ice bath, yellow crystals precipitated. These were dried in an oven. Anal. Calcd for $[Pt(NH_3)_2Cl_2]$: Pt, 65.03; N, 9.33; H, 2.01; Cl, 23.62. Found: Pt, 65.20; N, 9.64; H, 2.60; Cl, 23.23. The trans structure was demonstrated by the method of Grinberg[2b] and by comparison of the ultraviolet spectra of the compounds with those of authentic samples of *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$. Following Grinberg's directions, a solution of 0.09 g of the material and 0.09 g of $AgNO_3$ was allowed to stand on the steam bath overnight. After filtering, the filtrate was treated with 1 g of oxalic acid dihydrate and was heated on the steam bath for 2 hr. Upon cooling in ice, white crystals formed. These were washed with methanol, dried, and analyzed. Anal. Calcd for $[Pt(NH_3)_2(HC_2O_4)_2]$: Pt, 47.93; C, 11.79; H, 1.98. Found: Pt, 48.06; C, 11.98; H, 2.16. Treated in this way, *cis*-$[Pt(NH_3)_2Cl_2]$ gives the monooxalato chelate $[Pt(NH_3)_2C_2O_4]$. The ultraviolet spectrum of the $[Pt(NH_3)_2Cl_2]$ prepared from $[Pt((dien)\cdot HCl)(NH_3)_2]Cl_2$ corresponded almost exactly with that of an authentic sample of *trans*-$[Pt(NH_3)_2Cl_2]$, but differed markedly from that of a sample of *cis*-$[Pt(NH_3)_2Cl_2]$.

To a solution of 0.2 g of $[Pt(NH_3)_2((triamine)\cdot HCl)]Cl_2$ (R = CH_3) in 10 ml of water was added 1 g of solid LiI, whereupon reddish brown crystals precipitated at once. These were filtered, washed, and dried. Anal. Calcd for $[Pt(NH_3)_2I_2]$: Pt, 40.4; N, 5.80; H, 1.40; I, 52.4. Found: Pt, 39.17; N, 6.24; H, 1.49; I, 51.8.

An aqueous solution of $[Pt(NH_3)_2((triamine)\cdot HCl)]Cl_2$ (R = CH_3) was ground with an excess of Ag_2CO_3. After removal of the excess Ag_2CO_3 and the AgCl which had been formed, the solution was warmed and treated with an excess of solid LiI. Upon cooling in an ice-salt bath and addition of ethanol, crystals of [Pt(triamine)I]I formed. This compound shows the same ir spectrum as an authentic sample of [PtMe(dien)I]I (G) prepared by the method of Watt and Cude.[23] The elimination of ammonia from the complex is doubtless due to the stronger nucleophilicity of iodide as compared with ammonia.[24] Anal. Calcd for $Pt(C_5H_{15}N_3)I_2$: Pt, 34.50; C, 10.70; N, 7.47; H, 2.66; I, 44.60. Found: Pt, 35.00; C, 11.05; N, 7.07; H, 2.76; I, 43.88.

NMR Spectra. The NMR spectrum of the trans-bridged complex is similar to that of $[Pt^{IV}(C_5H_{15}N_3)Cl]Cl_3$. The former shows a broad peak centered at about 3.5 ppm downfield from TMS, whereas the latter shows a similar peak centered at about 3.3 ppm. Both spectra were measured in D_2O. Attempts to decouple the platinum were unsuccessful.

Discussion

The chelate ring which spans trans positions and which is described in this paper is noteworthy in that it contains only eight members. However, this should not be considered at all impossible, for in compound C, which would not be considered unusual, the same atoms occupy similar (but probably not identical) positions in space. The change in radius of the platinum upon reduction from the +4 state to the +2 state is so small that it will not cause any great change in ring strain (radius of Pt(II) = 0.60 Å; radius of Pt(IV) = 0.63 Å). The formation of this ring depends upon the opening of the bond which was part of two five-membered rings in compound C. Whether a ring of only eight members could be formed without the intermediate step is hard to say. Without an X-ray study, it is impossible to say how far the "liberated" nitrogen is from the platinum atom.

Cases are known in which platinum(II) shows a coordination number of 6, at least in the solid state[25] and, at first glance, it might be supposed that such is the case here. This cannot be so, for analysis shows the presence of only three chloride ions, one of which is the counterion for the quaternary nitrogen. Also, the near-diamagnetism of the complex, D, shows that the platinum is not in the +3 state nor can the substance be a dimer, with the platinum atoms bound together through amine linkages, for if an amine nitrogen were released from the platinum in the strongly acid reduction solution, it would form a hydrochloride in preference to combining with another platinum atom. The regeneration of A and the formation of E and of [PtMe(dien)I]I from D also strengthen our belief in our interpretation of the structure of D.

Another possibility is that the platinum has not been reduced at all but that the coordinated chlorine atom in compound C has been replaced by hydridic hydrogen. However, neither the infrared nor the NMR spectrum shows a metal-hydrogen stretching absorption.

Since cis-trans isomerization of platinum(II) complexes under the conditions of these experiments does not occur, it is clear that the two ammonia molecules in the complex retain their positions trans to each other during the reduction. This is confirmed by the fact that boiling the final product with hydrochloric acid yielded the well-known trans dichlorodiammine platinum(II) (A).

It seems certain that D is a four-covalent complex and the very low magnetic moment which it possesses indicates that the complex is essentially planar.

It is noteworthy that the addition of tetraphenylborate ion to the trans-spanned complex precipitated the salt $[M(L{\cdot}HCl)(NH_3)_2](BPh_4)_2$(F), for it might be argued that this indicates a covalent, rather than an ionic, attachment of the third chloride to the complex. That this is not the case is indicated by the ease of removal of the third chloride in other experiments (as, for example, in the precipitation by silver ion). Evidently, the bis(tetraphenylborate) chloride is less soluble than tris(tetraphenylborate), or it precipitates so rapidly that there is no opportunity for the tris compound to form. The nature of the salts containing the tertiary amine in the trans-spanning ligand illustrates this point. The hydrochloride is reasonably stable, and, when the compound is in solution, the nitrogen does not abandon the proton to combine with the platinum unless the solution is allowed to stand for some time or is heated. On the other hand, the less acidic hydrocarbonate ion is liberated spontaneously and very readily, the tertiary nitrogen then replacing an ammonia molecule and attaching itself to the metal.

The presence of three chloride ions in compound D cannot be taken to indicate the formation of platinum(III), for it has been shown by magnetic measurements that the compound does not contain unpaired electrons. Instead, it must be concluded that one nitrogen atom is not coordinated to the platinum and is free to form "ammonium" salts. This must surely be the central nitrogen atom of the chelating chain, for two adjacent nitrogen atoms are much too close together to attach themselves in trans positions. It was hoped that the NMR spectra of compound D ($R = CH_3$) would further demonstrate that this is so. Unfortunately, while the NMR gives evidence consistent with this, that evidence is not conclusive. However, all of the facts that have been collected lead almost indisputably to the conclusion that the triamine ligand spans the trans-positions. A study of solid compound D by X-rays has not now been feasible because the crystals are too small and recrystallization introduces compound E as an impurity.

We hope to be able to report another example of this type of reaction and structure, using, perhaps, $HSCH_2CH_2OCH_2CH_2SH$ or $HSCH_2CH_2N(CH_3)CH_2CH_2SH$ as the trans-spanning ligand. Sulfur forms very strong bonds with platinum(II), whereas oxygen and tertiary nitrogen form much weaker ones. Other platinum(IV) compounds, such as *trans,trans,trans*-$[Pt(NH_3)_2(CN)_2Cl_2]$ and *trans*-$[Pt\{(n\text{-butyl})_3P\}_2Cl_4]$, also offer possibilities.

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References and Notes

(1) The material concerning complexes of diethylenetriamine which is presented in this paper is taken from the doctorate thesis of John Arthur Mattern at the University of Illinois (1946). It was not published at that time because the authors felt that the argument was not as complete as they wished. Additional work, using *sym-N*-methyldiethylenetriamine, by Isao Mochida, has now added the necessary evidence.

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Optical Spectra and the Free-Volume Model for the Transport Behavior of Glass-Forming Melts

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Abstract: The optical spectra of MX_2 (M = Mn, Co, and Ni; X = Cl and Br) -rich mixtures of $R_4B^+X^-$ (R = propyl, butyl, pentyl, hexyl, heptyl, and octyl, and is either the same or different; B = N and P; and X = Cl, Br, and I) have been identified as due to the presence of tetrahedral, T_d tetrahalometalate(II) ions, MX_4^{2-}. The band assignments of NiX_4^{2-} have been made by constructing the energy level diagrams for the d^8 configuration in a cubic T_d field based on the four ligand-field (LF) parameters. These parameters for $NiCl_2X_2^{2-}$ have been taken as approximately averages of those of $NiCl_4^{2-}$ and NiX_4^{2-}. The optical electronegativity of nickel(II), $OE_{[Ni(II)]}$, has been computed from the corresponding LF parameters and the low-energy charge-transfer (CT) spectrum and is found to be 2.1. The CT spectra of X^- in MX_2-rich mixtures of $R_4N^+X^-$ have been found to be unaffected by the low conducting and highly viscous medium containing the species, $\{(R_4N^+)_2MX_4^{2-}\}_x$ and may be due to the transitions to $np^5\gamma_i$ configuration. The free volume model has been found suitable in explaining the transport behavior of glass-forming melts as supported by almost identical secondary glass transition temperatures, $T_{0,\Lambda}$ and $T_{0,\phi}$ for $MnCl_4^{2-}$, $CoCl_4^{2-}$, and $NiCl_4^{2-}$ as 277.23 ± 1.27, 276.60 ± 0.40, and 269.43 ± 2.17°K, respectively, and also by several linear plots.

Tetrahedral tetrahalometalates have been reported[1-9] in the low-melting organic halides of large [cation]/[anion] ratio. The metal halide-rich mixtures containing $(R_4B^+)_2MX_4^{2-}$ have been found to supercool to glassy states.[5]

The present work deals with the optical spectra of MX_2-rich mixtures of $R_4B^+X^-$ [$(C_4H_9)_4N^+Cl^-$, $(C_4H_9)_4P^+Br^-$, $(C_4H_9)_4N^+Br^-$, $(C_8H_{17})_3C_3H_7N^+Br^-$, $(C_4H_9)_4N^+I^-$, $(C_5H_{11})_4N^+I^-$, $(C_6H_{13})_4N^+I^-$, $(C_7H_{15})_4N^+I^-$, and $(C_4H_9)_3C_3H_7N^+I^-0$ and their comparison with those in the corresponding dilute solutions. The CT and the LF bands of CoX_4^{2-} and NiX_4^{2-} are recorded. The band assignments of the latter have been made by constructing the energy level diagrams[10] based on the four LF parameters and comparing them with those recorded for NiX_4^{2-} and $NiCl_2X_2^{2-}$, i.e., $NiCl_4^{2-}$, $NiBr_4^{2-}$, $NiCl_2Br_2^{2-}$ and $NiCl_2I_2^{2-}$. The CT spectra of X^- in MX_2-rich mixtures of $R_4N^+X^-$ have also been recorded.

The electrical conductances, densities, and viscosities of MCl_2 in molten $(C_4H_9)_4N^+Cl^-$ have been measured at several temperatures and those of $CoCl_2$ in $(C_4H_9)_4N^+I^-$ as functions of composition and temperature. The applicability of the free-volume model[11-17] in explaining the transport behavior of the glass-forming melts has been examined.

Experimental Section

Tetra-*n*-alkylammonium (Fluka and Eastman) and phosphonium (Alfa Inorganics) halides, $R_4B^+X^-$, were used as solvents in the molten state. Anhydrous metal chlorides, MCl_2, were prepared[18,19] from their recrystallized hydrated salts (E. Merck) while $NiBr_2$ was obtained commercially. The spectra of MX_2 in molten $R_4B^+X^-$ were recorded on digitalized Cary Model 14 and Beckman Model DK-2A spectrophotometers.

Electrical conductances were measured with a Philips-PR9500 conductivity bridge at 50 Hz using calibrated capillary type conductivity cells. The dielectric constant was measured with a Sargent Chemical Oscillometer Model V. The capacitive effect of electrolyte-electrode double layer being of the order of 10^{-4} pF has been neglected. Density measurements were made in a dilatometer calibrated for 0.005 ml at several temperatures with ±0.3% accuracy. The viscosities were measured in a calibrated Ubbelohde capillary viscometer with an accuracy of ±0.1 to 2.5%. Preparation of the samples and the above measurements were carried out in an inert atmosphere in a relay controlled thermostated oil bath of ±0.1 and ±0.2° thermal stabilities over 0 to 100 and 100 to 200°, respectively.

The energy level diagrams for NiX_4^{2-} were constructed[1,10] by computing the energy levels on an IBM-1130 computer.

Results and Discussion

I. **Optical Spectra. Ligand-Field Transitions.** The optical spectra of $NiX_2 + R_4B^+X^-$ have been identified as due to the presence of T_d NiX_4^{2-} on the basis of their comparison with those reported earlier.[1] The LF spectra of $NiCl_4^{2-}$, $NiBr_4^{2-}$, $NiCl_2Br_2^{2-}$, and $NiCl_2I_2^{2-}$ have been fitted to their respective energy level diagrams and the assignments of the bands have been made.

A. **$NiCl_2 + R_4N^+Cl^-$.** The d–d spectra of $NiCl_2$ in molten $(C_4H_9)_4N^+Cl^-$ consist of an intense band with peaks at 14,280 and 15,380 cm^{-1} and a shoulder at ~16,660 cm^{-1}, and a broad band with a peak at ~7500 cm^{-1}. It is apparent from the energy level diagram (Figure 1) that three transitions are spin allowed, two of which are orbital transitions, $\Gamma_{2-5}{:}^3T_2(F) \leftarrow \Gamma_1{:}^3T_1(F)$, and $\Gamma_5{:}^3A_2(F) \leftarrow \Gamma_1{:}^3T_1(F)$, and the third one is due to $\Gamma_5{:}^3T_1(P) \leftarrow \Gamma_1{:}^3T_1(F)$ transitions. The first transition reported[1] at ~4000 cm^{-1} has not been recorded due to the overlapping region of the solvent. The remaining two transitions have been reported by several authors[1,20-24] and agree with those found in the present case at ~7500 and 14,280 cm^{-1}.

In spite of its inherent limitations[25] the LF theory rationalizes the spectrum satisfactorily. However, it does not seem to account for the little details of the band, $^3T_1(P) \leftarrow {}^3T_1(F)$, as predicted by the theory for $\Gamma_3{:}^3T_1(P) \leftarrow \Gamma_1{:}^3T_1(F)$, $\Gamma_4{:}^3T_1(P) \leftarrow \Gamma_1{:}^3T_1(F)$, and $\Gamma_1{:}^3T_1(P) \leftarrow \Gamma_1{:}^3T_1(F)$ transitions at 14,340, 14,650, and 14,840 cm^{-1},