crystals was poured into 2 l. of water, and then 10 ml of acetic acid was added and the suspension stirred under air to oxidize traces of $[pyCo(D_2H_2)]_2$. The crystals were then filtered, washed with water, and air dried, yield 117 g (70%). The product was recrystallized from methanol–water.

Methylpyridinatocobaloxime from β-Cyanoethylpyridinatocobaloxime. To a suspension of 12.7 g (0.03 mole) of β-cyanoethylpyridinatocobaloxime in 75 ml of methanol and 5 ml of methyl iodide, there was added with stirring 2.0 g (0.05 mole) of NaOH in 10 ml of water. The solution soon became homogeneous and shortly after crystals of methylpyridinatocobaloxime formed. The yield was 9.2 g (80%).

β-Carboethoxyethylpyridinatocobaloxime. A suspension of 47.6 g (0.2 mole) of $CoCl_2 \cdot 6H,O$ and 46.4 g (0.4 mole) of dimethylglyoxime in 800 ml of ethanol was stirred until the cobalt chloride had dissolved, and then 16 g (0.4 mole) of NaOH in 100 ml of water was added, followed by 16 g (0.2 mole) of pyridine. When complex formation was complete 20 g (0.2 mole) of ethyl acrylate was added, followed by 4.0 g (0.1 mole) of NaOH in 25 ml of water. After 5 min the solution was homogeneous and was added to 2 l. of water containing 10 ml of acetic acid. The solution was filtered and the filtrate extracted with methylene chloride. From the methylene chloride concentrate, on recrystallization from water–methanol, there was obtained 21 g (45%) of orange plates.

Vinylpyridinatocobaloxime. A suspension of 0.1 mole of $[pyCo(D_2H_2)]_2$ in 750 ml of methanol was prepared as described above from cobalt chloride. The suspension was kept saturated with vinyl chloride while 8.0 g (0.2 mole) of NaOH in 50 ml of water was added. The solution was filtered, concentrated to 400 ml, and diluted with 1 l. of water, affording 28.2 g (71%) of yellow crystals.

Chloromethylpyridinatocobaloxime. This product is formed very readily by any of the procedures utilized for preparing alkylcobaloximes. Consequently it is occasionally encountered as an undesirable product during extractions when traces of Co^{II} or Co^{I} are present, *e.g.*, alkaline solutions of β-cyanoethylcobaloxime.

β-Phenylvinylaquocobaloxine. To a stirred suspension of 0.2 mole of $Co(D_2H_2) \cdot 2H_2O$ in 700 ml of methanol there was added 10.2 g of phenylacetylene, and this was then stirred for 5 min with 4.0 g (0.1 mole) of NaOH in 20 ml of water. After filtering the solution and dilution with 1 l. of H_2O there was obtained 24.6 g (63%) of yellow crystals.

Carboxymethylpyridinatocobaloxime. To 70 ml of concentrated sulfuric acid there was added with stirring 20 g of carbomethoxymethylpyridinatocobaloxime in small portions (safety shield). The acid was warmed to about 40° to aid solution and, after 1 hr of standing, poured into 2 l. of water. This solution was made alkaline with KOH, then acidified with acetic acid and cooled, yielding 13.5 g (69%) of orange platelets. The product is purified by dissolving in dilute $NaHCO_3$ and reprecipitating with acetic acid.

2,2-Dimethoxyethylpyridinatocobaloxime. To a suspension of 65.0 g (0.2 mole) of $(Co(D_2H_2) \cdot 2H_2O$ prepared in 700 ml of methanol, there was added, at 0°, 25.4 g (0.15 mole) of bromoacetaldehyde dimethyl acetal, followed by 8.0 g (0.2 mole) of NaOH in 50 ml of water over 10 min. The resulting solution was diluted with water and extracted with methylene chloride containing pyridine. The product was recrystallized from methanol–water, yield 6.4 g (14%) of yellow crystals. If alkaline conditions are not present during all stages, brown crystals of the corresponding aldehyde are isolated.

Conversion of β-Cyanoethylcobaloxime into the α Isomer. A suspension of 3 g of β-cyanoethylpyridinatocobaloxime in 25 ml of methanol–water (1:1) was stirred in an atmosphere of hydrogen while a 1 *N* solution of NaOH was slowly added until the pH of the solution was approximately 11. After 5 hr of continued stirring 1 *N* hydrochloric acid was slowly added up to a pH of about 7. The reaction mixture was subsequently poured into 100 ml of water and filtered. The yellow product was washed with water and dried. Examination of the nmr spectrum revealed that it consisted of a mixture (approximately 1:2.5) of α-cyanoethylcobaloxime and the β isomer. The α derivative is readily recognized by the methyl doublet at 9.43 ppm, $J = 7$ cps, and by the fact that it is stable in 20% KOH solution.

Reactions of Substituted Alkylcobaloximes. The reactions of the organocobaloximes were carried out as indicated in the text; the procedures were straightforward in all cases and need not be described in this section. The products of the various cleavage reactions were identified by usual methods (gas–liquid chromatography infrared, nmr, and mass spectroscopy.

The polarographic measurements were carried out by Dr. D. C. Olson on an ORNL controlled potential instrument, Model Q-1988 A, using a Varian F-80 X–Y recorder. The pyrolysis experiments were performed without solvent *in vacuo* at the temperatures given in the text. The volatile products were collected by vacuum condensation and identified as indicated above. Gaseous products were transported into a gas-sample tube and analyzed mass spectrographically.

Attempted Rearrangement Reactions. Samples of the pyridinatocobaloximes, $RCo(D_2H_2)py$ with $R = EtOOC\dot{C}HCH_2COOH$, were decomposed without solvent *in vacuo* at about 200°. The volatile products consisted of a mixture of monoethyl fumarate and monoethyl succinate. Decomposition in the presence of H_2 (10 atm) afforded only monomethyl succinate. The complex (5 g in 50 ml of ethanol) was allowed to stand in the dark in the presence of 5 ml of CH_3SH for 1 week. Glpc analysis of the remaining solution indicated the presence of monoethyl succinate and a trace of monoethyl fumarate. Similar experiments were also carried out with the cobaloximes with $R = NC\dot{C}HCH_2CN$ and $R = CH_3CHCH_2COOCH_3$. Rearrangement products (*e.g.*, methylmalononitrile or isobutyric ester) could not be detected. Similarly, no rearrangement occurred in alkaline (pH 11) solutions of mercaptans.

The Infrared Spectra and Structure of Methylamine Complexes of Platinum(II)

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Abstract: The infrared spectra of the complexes *cis*-$[Pt(CH_3NH_2)_2X_2]$, *trans*-$[Pt(CH_3NH_2)_2X_2]$, $[Pt(CH_3NH_2)_4]X_2$, and $[Pt(CH_3NH_2)_4][PtX_4]$ ($X = Cl^-, Br^-$) have been measured and assignments made in the region 200–4000 cm^{-1}. The structure of each complex has been elucidated through a group theoretical treatment of the observed spectra of the crystalline complexes.

In order to interrelate the vibrational assignments for the ammonia[1] and ethylenediamine[2,3] complexes of platinum(II), the infrared spectra of certain methylamine complexes have been studied; the results are reported here.

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[1] H. Poulet, P. Delorme, and J. P. Mathieu, *Spectrochim. Acta*, **20**, 1855 (1964).

[2] D. B. Powell and N. Sheppard, *ibid.*, **17**, 68 (1961).

[3] G. W. Watt and D. S. Klett, *Inorg. Chem.*, **5**, 1278 (1966).

Experimental Section

The routine materials used in all syntheses were reagent grade and were used without further purification. The methylamine used in synthesis procedures was a 40% aqueous solution in all cases.

The procedure of Klyuchnikov and Savel'eva[4] was used to prepare $K_2[PtCl_4]$ and $K_2[PtBr_4]$. *Anal.* Calcd for $K_2[PtCl_4]$: Pt + 2KCl, 82.7. Found: Pt + 2KCl, 82.9. Calcd for $K_2[PtBr_4]$: Pt + 2KBr, 72.2. Found: Pt + 2KBr, 72.9.

Tetrakis(methylamine)platinum(II) Bromide. Potassium tetrabromoplatinate(II), $K_2[PtBr_4]$ (1.55 g), was dissolved in 40 ml of boiling water, to which was added 10 ml of boiling methylamine solution. The solution immediately cleared to a light yellow color. Boiling was continued for 10 min; then an additional 5 ml of methylamine solution was added and the solution boiled for 10 min. The volume of the solution was reduced at 50° to *ca.* 15 ml and then cooled. The addition of acetone produced a white flocculent precipitate (volume *ca.* 100 ml); 50 ml of acetone was added and the solution was cooled for 1 hr at 0°. The resulting white precipitate was filtered, recrystallized twice by dissolving the crude product in water and precipitating with acetone, and then dried at 50° for 4 hr: yield, 0.7 g or 65% based on $K_2[PtBr_4]$. *Anal.* Calcd for $[Pt(CH_3NH_2)_4]Br_2$: Pt, 40.7; Br, 26.7. Found: Pt, 40.8; Br, 26.4.

Tetrakis(methylamine)platinum(II) Chloride. A sample of $[Pt(CH_3NH_2)_4]Br_2$, 1.2 g, was dissolved in 40 ml of water and 1.5 g of $AgNO_3$ in 30 ml of H_2O added to the solution at 25°. After 5 min of shaking in the absence of light, the solution was allowed to stand for 3 hr in the dark. The AgBr was filtered off and 10 ml of concentrated HCl was added to the filtrate. The filtrate volume was then reduced to *ca.* 15 ml at 50° and cooled; 200 ml of acetone was added and the solution cooled for 1 hr at 0°. The white precipitate was recrystallized once by dissolution in H_2O and precipitation with acetone: yield, 0.78 g or 75% based on $[Pt(CH_3NH_2)_4]Br_2$. *Anal.* Calcd for $[Pt(CH_3NH_2)_4]Cl_2 \cdot H_2O$: Pt, 47.9; Cl, 17.5. Found: Pt, 48.1; Cl, 17.7. The $[Pt(CH_3NH_2)_4]Cl_2 \cdot H_2O$ was dehydrated by heating the sample in an oven for 1 hr at 110°.

***trans*-Dibromobis(methylamine)platinum(II).** The following procedure utilizes a suggestion by Drew and Tress.[5] A 2-g sample of $K_2[PtBr_4]$ was dissolved in 20 ml of boiling H_2O, to which was added 10 ml of warm (50°) CH_3NH_2 solution, and the solution was boiled until very light yellow (10 min). When the volume of the solution was about 20 ml, 5 ml of CH_3NH_2 solution was added and the solution was boiled for another 10 min or until almost clear. Upon addition of 15 ml of concentrated HCl the solution turned yellow. The volume was reduced at 50° to *ca.* 20 ml and then cooled to 0°. From the clear solution, a yellow precipitate was filtered off and recrystallized from boiling H_2O: yield, 0.6 g or 43% based on $K_2[PtBr_4]$. *Anal.* Calcd for $[Pt(CH_3NH_2)_2Br_2]$: Pt, 46.8. Found: Pt, 46.5.

***trans*-Dichlorobis(methylamine)platinum(II).** A sample of *trans*-$[Pt(CH_3NH_2)_2Br_2]$, 1 g, was dissolved in 100 ml of boiling H_2O, and 2 g of $AgNO_3$ in 20 ml of H_2O was added with stirring. After boiling the solution for 10 min, the solution was cooled for 1 hr at 25°. The AgBr was filtered off and 5 ml of concentrated HCl was added to the filtrate which was cooled to 0°. The product was recrystallized from boiling H_2O, filtered, and dried at 100° for 3 hr: yield, 1.15 g or 90% based on $[Pt(CH_3NH_2)_2Br_2]$. *Anal.* Calcd for $[Pt(CH_3NH_2)_2Cl_2]$: Pt, 59.8. Found: Pt, 60.1.

***cis*-Dibromobis(methylamine)platinum(II).** The following procedure is based upon a method suggested by Drew and Tress.[5] A sample of $K_2[PtBr_4]$, 1.5 g, was dissolved in 30 ml of H_2O and cooled to 0°; 1 ml of cool (10°) CH_3NH_2 solution was added and the mixture allowed to stand for 10 hr at 10°. After about 7 hr yellow crystals were observed, and 1 hr later some green crystals were also present. The precipitate was filtered and the filtrate (A) collected. The precipitate was dissolved in 40 ml of boiling H_2O and 0.1 g of $[Pt(NH_3)_4]Cl_2$ was added to precipitate $[Pt(NH_3)_4][PtBr_4]$, which was then filtered off; the yellow filtrate was combined with filtrate A. This solution was reduced in volume to 10 ml at 50° and cooled to 0°. A yellow precipitate was filtered and recrystallized from 30 ml of H_2O, 0.1 ml of concentrated HBr was added, and the mixture was then cooled at 0° for 2 hr. The precipitate was filtered and dried for 4 hr at 65°: yield, 0.4 g or 38% based on $K_2[PtBr_4]$. *Anal.* Calcd for $[Pt(CH_3NH_2)_2Br_2]$: Pt, 46.8. Found: Pt, 46.8.

***cis*-Dichlorobis(methylamine)platinum(II).** One gram of *cis*-$[Pt(CH_3NH_2)_2Br_2]$ was dissolved in 50 ml of boiling H_2O, to which 1.6 g of $AgNO_3$ in 20 ml of H_2O was added, and the solution warmed at 60° with constant stirring for 20 min. The AgBr was filtered off, and 30 ml of concentrated HCl was added to the filtrate. The yellow filtrate was reduced in volume and yellow crystals were obtained. The product was filtered and recrystallized from H_2O at 60°, washed with H_2O and ether, and dried at 55° for 12 hr; yield, 0.71 g or 90% based on $[Pt(CH_3NH_2)_2Br_2]$. *Anal.* Calcd for $[Pt(CH_3NH_2)_2Cl_2]$: Pt, 59.8. Found: Pt, 59.2.

Tetrakis(methylamine)platinum(II) Tetrabromoplatinate(II). A 0.1-g sample of $[Pt(CH_3NH_2)_4]Br_2$ was dissolved in 7.0 ml of water, and 0.1 g of $K_2[PtBr_4]$ in 10.0 ml of water was added with stirring. A green precipitate was formed immediately; it was cooled to 0°, filtered, washed with water, and dried at 110° for 8 hr. The yield was 0.16 g or 98% based on $[Pt(CH_3NH_2)_4]Br_2$. *Anal.* Calcd for $[Pt(CH_3NH_2)_4][PtBr_4]$: Pt, 46.8. Found: Pt, 46.8.

Tetrakis(methylamine)platinum(II) Tetrachloroplatinate(II). Potassium tetrachloroplatinate(II), 0.5 g, was dissolved in 10.0 ml of water and heated to boiling. To the boiling solution 7.0 ml of methylamine solution was added. After 10 min of boiling the very light yellow solution was cooled to 25° and 0.5 g of solid $K_2[PtCl_4]$ was added to the solution with stirring, whereupon the solution became green and a green precipitate separated. The solution was cooled to 10° and filtered under reduced pressure. The green precipitate was recrystallized by dissolving it in 50.0 ml of boiling, dilute HCl (0.1 *M*) and cooling to 10°. The product was filtered and dried at 110° for *ca.* 8 hr. The yield was 0.5 g or 67% based on $K_2[PtCl_4]$. *Anal.* Calcd for $[Pt(CH_3NH_2)_4][PtCl_4]$: Pt, 59.5. Found: Pt, 59.7.

X-Ray diffraction data for $[Pt(CH_3NH_2)_4][PtCl_4]$ and $[Pt(CH_3NH_2)_4][PtBr_4]$ have been reported previously.[6] Data for the other complexes studied are listed in Table I.

Table I. X-Ray Diffraction Data

d, A	I/I_0	*d*, A	I/I_0
trans-$[Pt(CH_3NH_2)_2Cl_2]$		*cis*-$[Pt(CH_3NH_2)_2Cl_2]$	
6.33	0.9	8.04	0.7
5.34	0.5[a]	7.31	1.0
5.04	0.5	5.87	0.6
3.22	0.8	5.19	0.5
2.79	1.0	3.99	0.6
2.12	0.7	2.34	0.4[a]
1.97	0.8	2.04	0.4
$[Pt(CH_3NH_2)_4]Cl_2 \cdot H_2O$		$[Pt(CH_3NH_2)_4]Br_2$	
7.08	0.6	7.14	0.8
5.87	1.0	5.04	0.8
5.04	0.5[a]	4.25	1.0
4.11	0.5	4.13	0.8
3.82	0.5	3.85	0.7
3.56	0.5	3.64	0.7
3.19	0.5	3.26	0.8
3.07	0.5	3.06	0.5[a]
2.91	0.5	2.96	0.6
2.60	0.5	2.42	0.5
2.37	0.5	2.09	0.6
1.93	0.5		
trans-$[Pt(CH_3NH_2)_2Br_2]$		*cis*-$[Pt(CH_3NH_2)_2Br_2]$	
6.33	0.9	9.02	0.6
5.41	1.0	7.13	1.0
4.48	0.7[a]	6.70	0.5[a]
4.29	0.7	4.39	0.9
3.71	0.8	2.91	0.9

[a] Less intense lines not reported.

Infrared spectra were recorded using a Beckman IR-7 spectrophotometer equipped with NaCl and CsI optics. The compounds listed in Tables II–V were studied as Nujol or perfluorokerosene mulls. The instrument was calibrated with a polystyrene strip in the NaCl region and the rotational spectrum of atmospheric water vapor in the CsI region. Specimen spectra are shown in Figure 1.

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(4) N. G. Klyuchnikov and R. N. Savel'eva, *Russ. J. Inorg. Chem.*, **1**, 2764 (1956).

(5) H. D. K. Drew and H. J. Tress, *J. Chem. Soc.*, 1213 (1935).

(6) J. R. Miller, *ibid.*, 4452 (1961).

Table II. The Vibrational Assignments for Absorption Bands (cm^{-1}) in the Infrared Spectra of *trans*-[Pt(CH$_3$NH$_2$)$_2$X$_2$] (X = Cl$^-$, Br$^-$)

trans-[Pt(CH$_3$NH$_2$)$_2$X$_2$]		
Cl$^-$	Br$^-$	Assignment[a]
3272 vs	3268 vs	
3240 vs	3240 vs	(νNH)
3172 vs	3152 vs	
3012 w	3005 w	
2996 w	2990 w	(νCH)
2948 w	2940 w	
2896 w	2885 w	
1594 vs	1590 vs	(δNH$_2$)
1460 s	1460 s	
1449 s	1449 s	(δCH$_3$)
1412 m	1412 m	
1276 m	1274 m	(ωNH$_2$)
1090 vs	1090 vs	(γNH$_2$)
1049 w	1045 w	(νCN)
1000 s	997 s	(ρCH$_3$)
(?)	(?)	(ρNH$_2$)
518 s	514 s	(νPtN)
334 vs	. . .	(νPtCl)
. . .	240 vs	(νPtBr)
293 m	295 m	(πPtN$_2$) (?)

[a] The notation is that approved by the Joint Commission on Spectroscopy; see R. S. Mulliken, *J. Chem. Phys.*, **23**, 1997 (1955).

Table III. The Vibrational Assignments for Absorption Bands (cm^{-1}) in the Infrared Spectra of *cis*-[Pt(CH$_3$NH$_2$)$_2$X$_2$] (X = Cl$^-$, Br$^-$)

cis-[Pt(CH$_3$NH$_2$)$_2$X$_2$]		
Cl$^-$	Br$^-$	Assignment
3270 vs	3268 vs	
3240 vs	3228 vs	(νNH)
3140 s	3132 s	
3016 w	3019 w	
3000 w	3000 w	(νCH)
2952 w	2944 w	
2928 w	(?)	
2896 w	2886 w	
1596 s	1592 s	
1581 m	(?)	(δNH$_2$)
1575 m	1569 m	
1465 m	1460 m	
1453 m	(?)	
1429 m	(?)	(δCH$_3$)
1417 m	1415 m	
1405 w	1405 w	
1275 s	1265 s	
1255 s	1250 s	(ωNH$_2$)
1085 s	1084 s	
1080 s	1076 s	(γNH$_2$)
1037 w	1030 w	(νCN)
1017 w	1010 w	
990 m	990 w	(ρ CH$_3$)
740 m	730 m	(ρNH$_2$)
517 m	509 m	
506 m	496 m	(νPtN)
318 s	. . .	(νPtCl)
. . .	228 s	(νPtBr)

Deuteration of the amino groups was accomplished by either refluxing the complex with 99.7% D$_2$O in a nitrogen atmosphere or allowing the complex to remain in 99.7% D$_2$O for several days, protected by a nitrogen atmosphere. Excess D$_2$O was then removed under reduced pressure.

Discussion

For the calculation of possible selection rules, there are four possible structures to consider for the *trans*-dihalobis(methylamine)platinum(II) complex, *trans*-[Pt(CH$_3$NH$_2$)$_2$X$_2$]. These four conformations occur in symmetrical pairs; *i.e.*, each member of the pair structurally depicts the same point group symmetry. The two complex pairs possess the symmetry elements contained in the groups C_{2h} and C_{2v}. The only pair of structures discussed here belong to the C_{2h} group because subsequent analysis proves this to be the most acceptable choice based on the experimental evidence.

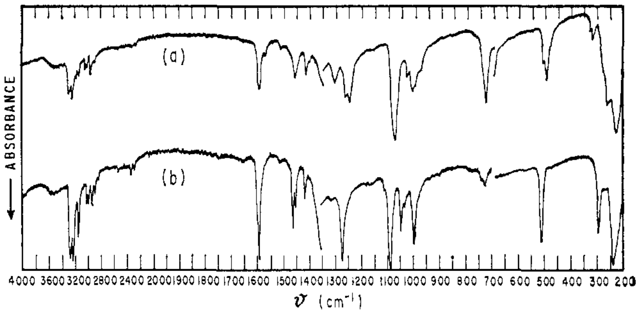

Figure 1. The infrared spectra of (a) *cis*- and (b) *trans*-[Pt(CH$_3$NH$_2$)$_2$Br$_2$].

Table IV. The Vibrational Assignments for Absorption Bands (cm^{-1}) in the Infrared Spectra of [Pt(CH$_3$NH$_2$)$_4$][PtX$_4$] (X = Cl$^-$, Br$^-$)

[Pt(CH$_3$NH$_2$)$_4$][PtX$_4$]		
Cl$^-$	Br$^-$	Assignment
3268 vs	3267 vs	
3236 vs	3236 vs	(νNH)
3160 s	3120 s	
2992 w	2998 w	
2928 w	2948 w	(νCH)
(?)	2936 w	
2904 w	2908 w	
1580 s	1589 s	(δNH$_2$)
. . .	1575 s	
1468 m	1465 m	
1458 m	1457 m	(δCH$_3$)
(?)	1449 m	
1415 m	1415 m	
1273 s	1270 s	(ωNH$_2$)
1098 vs	1094 vs	(γNH$_2$)
1050 vw	1045 w	(νCN)
1020 m	1015 w	(ρCH$_3$)
. . .	997 w	
705 s	701 s	(ρNH$_2$)
500 m	514 m	(νPtN)
. . .	498 m	
(?)	306 m	(δPtN$_2$)
313 s	. . .	(νPtCl)
. . .	230 s	(νPtBr)

The vibrational representations[7] for the two C_{2h} configurations (Figure 2) are: $\Gamma_v = 12A_g + 9B_g + 10A_u + 14B_u$ (the methylamine carbons lie above and below the PtN$_2$X$_2$ plane for this structure), and $\Gamma_v = 13A_g + 8B_g + 10A_u + 14B_u$ (the methylamine carbons lie in the PtN$_2$X$_2$ plane for this structure). A molecular symmetry of C_{2h} restricts the possible site symmetries[8-10] in the crystal to C_{2h}, C_i, C_2, C_s, and C_1. If the C_{2h} or C_i selection rules are operative, then 24

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(7) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, Chapters 5, 6.

(8) R. S. Halford, *J. Chem. Phys.*, **14**, 8 (1946).

(9) D. F. Hornig, *ibid.*, **16**, 1063 (1948).

(10) H. Winston and R. S. Halford, *ibid.*, **17**, 607 (1949).

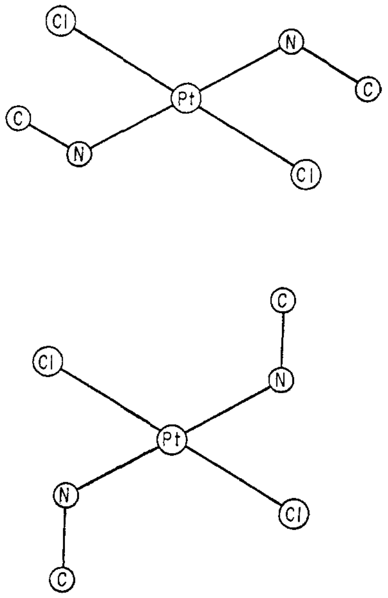

Figure 2. Possible C_{2h} structures for *trans*-[Pt(CH_3NH_2)$_2$$Cl_2$].

infrared active modes are predicted ($10A_u + 14B_u$). Otherwise, the remainder of the subgroups require all motions to be active in the infrared.

Table V. The Vibrational Assignments for Absorption Bands (cm^{-1}) in the Infrared Spectra of [Pt(CH_3NH_2)$_4$]X_2 (X = Cl^-, Br^-)

[Pt(CH_3NH_2)$_4$]X_2		
Cl^-	Br^-	Assignment
3160 s	3156 s	(νNH)
3100 s	3100 s	
2993 w	2993 w	
2952 w	2950 w	(νCH)
2904 w	2860 w	
. . .	1625 w	(δNH_2)
1590 m	1582 m	
1472 m	1469 m	
1458 m	1453 m	
1448 m	1448 m	(δCH_3)
1433 m	1427 m	
1423 m	1420 m	
1226 s	1274 s	(ωNH_2)
1091 s	1098 s	(γNH_2)
1050 vw	1060 vw	(νCN)
1000 w	1008 m	
987 w	990 w	(ρCH_3)
. . .	980 w	
723 w	704 w	(ρNH_2)
535 w	532 w	(νPtN)
527 w	524 w	
503 m	498 m	
325 m	305 m	(δPtN_2)

The *cis* compounds, *cis*-[Pt(CH_3NH_2)$_2$$X_2$], offer fewer structural choices that are symmetrical and sterically reasonable. Probably the two most acceptable structures are those wherein the methylamine carbons either both lie in the PtN_2X_2 plane or above and below the PtN_2X_2 plane. The first structure could conform to the C_{2v} point group while the second configuration would be represented by the C_2 point group.

The vibrational representations for the C_{2v} and C_2 models are, respectively, $\Gamma_v = 14A_1 + 9A_2 + 13B_1 + 9B_2$ and $\Gamma_v = 23A + 22B$. The possible site symmetries for the C_{2v} structure are C_{2v}, C_2, C_s, and C_1, and for the C_2 structure, C_2 or C_1. The only case where infrared absorption is forbidden is the C_{2v} case where the A_2 modes are inactive. For the other site groups the infrared spectrum alone cannot distinguish between the two conformations.

The tetracoordinate methylamine complex, [Pt(CH_3NH_2)$_4$]$^{2+}$, was studied with two types of anions: the simple halides and the $(PtX_4)^{2-}$ anions. The complex cation can assume several configurations. Since a completely planar ion would tend to pack into a crystal lattice more efficiently than a nonplanar one, the most reasonable structure is that in which the methylamine carbons all lie in the PtN_4 plane and all are oriented in the same relative direction. This structure contains the symmetry elements describing the C_{4h} point group.

The vibrational representation for the C_{4h} structure is as follows: $\Gamma_v = 11A_g + 12B_g + 8E_g + 9A_u + 9B_u + 12E_u$. For C_{4h} molecular symmetry, the possible site symmetries are C_4, S_4, C_{2h}, C_2, C_s, C_i, and the principal group itself, C_{4h}. Since the [Pt(CH_3NH_2)$_4$]$^{2+}$ species was studied with two different types of anions, which would have a definite effect on the possible crystal structures and thus the site symmetry, the determination of the applicable selection rules is deferred pending discussion of the observed spectra, as follows.

The *trans* compound, *trans*-[Pt(CH_3NH_2)$_2$$X_2$], is interpreted in terms of the C_{2h} structure, which can be shown to fit best the observed data. The two possible C_{2h} structures differ in their vibrational representations for the A_g and B_g modes, which are infrared inactive if the site group is C_{2h} or C_i. Thus on the basis of infrared data alone, a choice between the two configurations cannot be made.

Calculation of the symmetry coordinates[7] for the *trans* complex shows that there should be seven types of antisymmetric stretching modes: (νPtN)B_u, (νPtX)B_u, (νCN)B_u, (νNH)A_u, (νNH)B_u, (νCH)A_u, and (νCH)B_u.

As indicated above, two metal–ligand stretching motions are predictable, assuming a structural symmetry of C_{2h}, and a site symmetry of C_{2h} or C_i. There are sufficient data in the literature[3,11–13] to support the assignment that a PtN stretching vibration should be found between 500 and 600 cm^{-1}. The Cl^- and Br^- spectra both reveal a symmetrically shaped band in this region (518 cm^{-1} for the Cl^- and 514 cm^{-1} for the Br^-) which shifts to somewhat lower frequencies on deuteration. The PtCl and PtBr stretching modes have been substantiated[11,12,14] as occurring at about 330 and 240 cm^{-1}, respectively. Again the Cl^- and Br^- spectra show fairly symmetrically shaped bands in these regions (334 cm^{-1} for the Cl^- and 240 cm^{-1} for the Br^-). Thus these two pieces of data indicate that the assumption of C_{2h} or C_i site symmetry is justified.

The infrared spectrum[15] of uncoordinated methylamine and a normal coordinate analysis[16] have been

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reported. These results can be utilized in the assignments proposed for the coordinated methylamine.

The NH stretching vibrations in uncoordinated methylamine occur above 3000 cm^{-1}. A symmetry coordinate calculation for the C_{2h} structure predicts two active antisymmetric stretching modes. Experimentally three bands are observed, two of which are of nearly equal intensity. This splitting could be due to a Fermi resonance interaction with the (δNH_2) occurring at 1590 cm^{-1}. The NH stretching modes shift to lower frequencies upon deuteration. This interpretation then would agree with the proposed structure.

The (δNH_2), (ωNH_2), and (γNH_2) are all single symmetrically shaped bands as predicted by the C_2' symmetry coordinate calculation. Each band shifts to lower frequencies upon deuteration. The only NH_2 band not observed was the (ρNH_2) which apparently is very weak in intensity.

The C_{2h} symmetry coordinate calculation predicts one active (νCN). In uncoordinated methylamine[15] this band occurs at 1044 cm^{-1}, which would support the assignment of the 1045–1049-cm^{-1} band to (νCN).

The CH vibrations conform to the symmetry coordinate calculation. The only point of interest is that, under the C_{2h} structure, the three CH bonds in each CH_3 group do not form a symmetrically equivalent set; instead, there is a CH_2 set and a CH set, so that a linear combination of CH symmetry coordinates must be calculated in order to discuss the CH_3 vibrations. The CH_3 assignments are easily proposed using the uncoordinated methylamine data[15] as a guide.

The observed data and assignments are listed in Table II. For the *trans* complex, the above discussion supports the conclusion that the C_{2h} structure is correct and that the site group is C_{2h} or C_i.

For *cis*-$[Pt(CH_3NH_2)_2X_2]$, the distinction between the C_{2v} or C_s structure can be made only by the absence of the A_2 modes, which are represented by NH and CH motions only. Thus, for the C_{2v} configuration, four NH stretching bands are predicted, with the A_2 mode being infrared inactive. The spectra for the Cl^- and Br^- complexes both show four bands in the NH stretching region which would indicate that, if the molecular structure is C_{2v}, then the site group is a subgroup of C_{2v} which allows all bands to be infrared active.

The assignments for the observed *cis* spectra follow from a consideration of the *trans* spectra and the data for methylamine.[15] These data are in Table III.

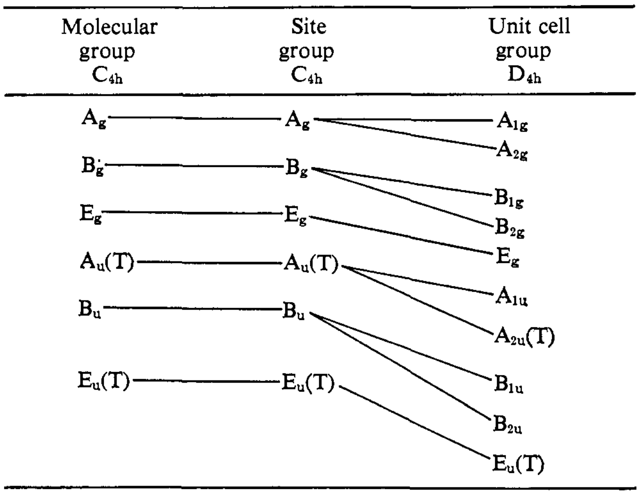
As mentioned above, the tetracoordinate methylamine complex cation, $[Pt(CH_3NH_2)_4]^{2+}$, could assume a C_{4h} molecular symmetry. This assumption was advanced in a study[6] of planar complexes of the type $[Pt(CH_3NH_2)_4][PtX_4]$.

Based on the single crystal X-ray diffraction data[17] of Atoji, *et al.*, on $[Pt(NH_3)_4][PtCl_4]$, X-ray powder diffraction studies[6] have indicated that $[Pt(CH_3NH_2)_4][PtCl_4]$ and $[Pt(CH_3NH_2)_4][PtBr_4]$ are isomorphorous with $[Pt(NH_3)_4][PtCl_4]$, and thus the crystals are described by the space group $D_{4h}{}^6$-P4/mnc and the site group C_{4h} for the cation and anion.

The observed spectrum for $[Pt(CH_3NH_2)_4][PtCl_4]$ can be interpreted in terms of C_{4h} site symmetry and $D_{4h}{}^6$ as the space group. As shown in Table VI, no correlation field splittings[9] are predicted between the C_{4h} site group and the D_{4h} unit cell group. This is supported by the fact that the E_u modes are single symmetrically shaped bands. These modes are represented by (νPtN), ($\nu PtCl$), (δNH_2), and (νCN), none of which is split. Thus, the infrared data reinforce the C_{4h} structure and the probable crystal structure.

The infrared spectrum for $[Pt(CH_3NH_2)_4][PtBr_4]$ indicates that each of the E_u modes for the C_{4h} structure is split. This fact can be explained in two ways: the crystal structure is different from $D_{4h}{}^6$ and the site symmetry is lowered, thus removing the degeneracies of the E_u modes; or, a change in crystal structure maintains the C_{4h} site symmetry, and interaction with a unit cell group of lower symmetry than C_{4h} produces correlation field splittings. A single crystal structure analysis would be required to resolve the question. The infrared data do indicate that the crystal structures of $[Pt(CH_3NH_2)_4][PtCl_4]$ and $[Pt(CH_3NH_2)_4][PtBr_4]$ are different.

Table VI. Group Correlation for $[Pt(CH_3NH_2)_4][PtCl_4]$



The assignment of the spectra were made using the methylamine data and deuteration data; the results are tabulated in Table IV.

The spectra for $[Pt(CH_3NH_2)_4]Cl_2$ and $[Pt(CH_3NH_2)_4]Br_2$ each indicates that the site symmetry is lower than C_{4h}, the latter being assumed as the correct molecular group. Again, the E_u modes are split and the resulting bands are not of equal intensity, indicating that the site symmetry is lower than the molecular symmetry of C_{4h}. There are no crystal data in the literature to support these conclusions, but the data do indicate that the site symmetry is a subgroup of C_{4h}.

The infrared spectra of the Cl^- and Br^- salts were interpreted by comparison with the spectra of the structures discussed above, the deuteration data, and the methylamine data. These results are given in Table V.

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