Mass Spectrometry of Platinum(II) Complexes. Comparison of Cis and Trans Isomers. Fragmentation and Rearrangement Pathways[1,2]

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Received October 26, 1970

Abstract: The mass spectra of eight pairs of cis and trans isomers of PtL_2X_2 (L = NH_3, pyridine $P(C_2H_5)_3$, or $P(C_2H_5)_3$; X = Cl, Br, or I) are presented and discussed. Two chelates, $Pt(bipy)Cl_2$ and $Pt(dpm)Cl_2$ (dpm = di-α-pyridylmethane), are also included. The most significant results are: (1) parent ions can be observed for almost all these relatively involatile coordination compounds; (2) most ligand fragmentations and rearrangements occur with ligand–metal bonds intact; (3) some rearrangements appear to involve the metal; (4) cis and trans isomers of phosphine complexes give different fragmentation patterns; (5) spectra of chelates differ considerably from the spectra of analogous nonchelates; (6) in $Pt(NH_3)_2Cl_2$ and $Pt(py)_2Cl_2$, little or no difference is observed in the spectra of cis and trans isomers after electron impact. Therefore, excitation to a tetrahedral state may take place.

There have been a limited number of applications of mass spectrometry to relatively involatile coordination compounds[5-8] including a few studies of platinum(II) compounds.[9-11] There are several important questions that have been addressed in the research reported in this paper. Is the excitation imparted to tetragonal planar platinum(II) complexes on electron impact sufficient to cause cis–trans isomerization?[12,13] Can mass spectrometry be used to identify platinum(II) complexes and distinguish cis and trans isomers? Can parent peaks be used to obtain molecular weights and thereby assist in structure proofs? What contrasts are there between chelated and nonchelated compounds?[14] In fragmentation, how readily do coordinate bonds break compared to covalent bonds in the ligands?

Results

Tri-*n*-perfluorobutylamine was used to establish *m/e* values at *m/e* <731;[16] mass measurement accurate to ±0.5 unit was used to establish *m/e* >731. Peak intensities were tabulated as per cent of the base peak and as a per cent contribution to the total ionization using a computer program which also plotted the spectra and calculated possible origins of metastables.[17,18] Generally, peaks above *m/e* 194 with intensities greater than 5.0% of the base peak were included in the tabulations.[19] In some spectra there were many peaks of lower intensity, and intensities down to 0.5% are available.[1] Duplicate spectra at 70 eV indicate ±10% reproducibility in peak intensities.

The isotopic distributions of naturally abundant platinum, chlorine, and bromine cause characteristic patterns of peak intensities (Figure 1). These patterns and *m/e* values have been used to assign elemental compositions to the ions responsible for groups of peaks in the spectra. These groups are referred to in the text and tables by the *m/e* value of the lightest ion of considerable intensity in each group, *e.g.*, *m/e* = 264 (194 + 35 + 35) for $PtCl_2^+$. As an example, the fragmentation pattern for *cis*-$Pt(NH_3)_2Cl_2$ is shown in Figure 2 and the data are in Table I. Intensities of groups of peaks are tabulated for the compounds studied in Tables I–VI. The $\Sigma(>194)$ value is the per cent contribution to the total ionization by *all* peaks in the group. In iodide complexes we observed an I_2^+ peak (*m/e* 254) which has been omitted. Use of lower ionizing voltages in the spectra of triethylphosphine complexes altered the relative intensities of groups of peaks and therefore facilitated identification of ions. These results indicate that there

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[1] S. H. Mastin, Ph.D. Thesis, University of California, Los Angeles, 1968; *Diss. Abstr. B*, **29**, 2800 (1969).

[2] Supported partially by Grant No. GP-13453 from the National Science Foundation, by grants from the Research Committee of the University of California at Los Angeles, by an Alfred P. Sloan Research Fellowship to P. Haake, and by postdoctoral support to S. H. Mastin from the Atomic Energy Commission.

[3] Wesleyan University.

[4] National Science Foundation Summer Research Fellow, 1967.

[5] *Advan. Chem. Ser.*, No. 72 (1968); J. Lewis and B. F. G. Johnson, *Accounts Chem. Res.*, **1**, 245 (1968).

[6] J. S. Shannon and J. M. Swan, *Chem. Commun.*, 33 (1965); S. H. H. Chaston, J. E. Livingstone, T. N. Lockyer, and J. S. Shannon, *Aust. J. Chem.*, **18**, 1539 (1965).

[7] E. P. Dudek and M. Barber, *Inorg. Chem.*, **5**, 375 (1966).

[8] S. E. Binns, R. H. Cragg, R. D. Gullard, B. T. Heaton, and M. F. Pilbrow, *J. Chem. Soc. A*, 1227 (1969).

[9] S. M. Bloom and G. O. Dudek, *Inorg. Nucl. Chem. Lett.*, **2**, 183 (1966).

[10] S. Sasaki, Y. Itagaki, T. Kurokawa, K. Nakanishi, and A. Kasahara, *Bull. Chem. Soc. Jap.*, **40**, 76 (1967).

[11] J. K. Becconsall, B. E. Job, and S. O'Brien, *J. Chem. Soc. A*, 423 (1967).

[12] Photochemical isomerization through tetrahedral intermediates is observed in the same complexes that have been studied by mass spectrometry in this research.[1,13]

[13] P. Haake and T. A. Hylton, *J. Amer. Chem. Soc.*, **84**, 3774 (1962); P. Haake and S. H. Mastin, *Chem. Commun.*, 202 (1970).

[14] There is a large difference in rate of hydrolysis of $Pt(py)_2Cl_2$ and $Pt(bipy)Cl_2$: P. Haake and P. A. Cronin, *Inorg. Chem.*, **2**, 879 (1963).[15]

[15] Abbreviations: py = pyridine; bipy = 2,2′-bipyridyl; dpm = di-α-pyridylmethane.

[16] Instruction manual for MS-9 mass spectrometer, Associated Electrical Industries, Ltd.

[17] Dr. D. A. Lightner supplied the program which was used with minor modifications.

[18] K. Biemann, "Mass Spectrometry," McGraw-Hill, New York, N. Y., 1962.

[19] Groups of very strong peaks were observed in some spectra, sometimes at very high *m/e* ratios. The *m/e* values are consistent with these peaks being due to $Cu_nX_m^+$. They were observed only with inlet temperatures greater than 220°. The source, therefore, is probably CuX[20] formed on the surface of the copper leads of the inlet system. These peaks are not included in the tabulations. Also, peaks containing Cl were found in the mass spectrum of $Pt(PEt_3)_2I_2$, and $Pt(P(C_6H_5)_3)_2Br_2$ complexes.

[20] H. M. Rosenstock, J. R. Sites, J. R. Walton, and R. Baldock, *J. Chem. Phys.*, **23**, 2442 (1955).

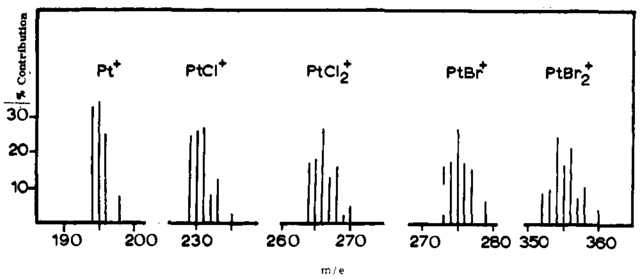

Figure 1. Characteristic isotopic patterns for ions containing platinum and halogens.

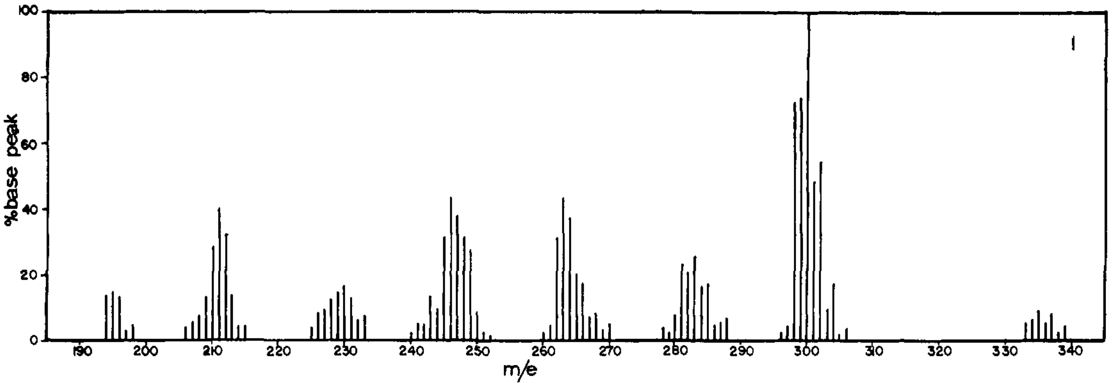

Figure 2. Mass spectrum of $Pt(NH_3)_2Cl_2$ at ionizing voltage (70 eV), source temperature 245°.

is a threshold effect for many fragmentation processes in these complexes.

Table I. Major Fragments in the Mass Spectra of *cis*- and *trans*-$Pt(NH_3)_2Cl_2$[a]

Group	*m/e* range	$\Sigma(>194)$,[b] % From cis	$\Sigma(>194)$,[b] % From trans	Assignment[c]
A	333–339	3.0	0.5	$Pt(NH_2)_2Cl_3^+$
B	296–306	30.0	37.0	$M\cdot^+$
C	278–288	10.0	9.5	$Pt(NH_3)Cl_2^+$, $Pt(NH_2)Cl_2^+$
D	259–270	15.5	13.0	$PtCl_2^+$, $Pt(NH_3)(NH_2)Cl$
E	238–252	16.0	15.0	$Pt(NH_2)Cl^+$
F	224–233	6.5	7.0	$PtCl^+$, $Pt(NH_2)_2^+$
G	204–215	11.5	14.0	$PtNH_2^+$, $PtNH_3^+$, $PtNH^+$

[a] 70 eV, 245–250°. [b] Per cent contribution to total ionization $\geq m/e$ 194. [c] The major fragments are listed in order of abundance.

Table II. Major Fragments in Mass Spectra of $Pt(bipy)Cl_2$[a] and $Pt(dpm)Cl_2$[b,c]

$PtLCl_2$	*m/e* range	$\Sigma(>194)$,[d] %	Assignment
bipy	420–428	13.3	$M\cdot^+$
dpm	434–438	10.7	$M\cdot^+$
bipy	385–391	16.0	$(M - Cl)^+$
dpm	399–403	10.7	$(M - Cl)^+$
bipy	350–354	30.0	$(M - 2Cl)^+$
dpm	364–372	32.0	$(M - 2Cl)^+$

[a] 70 eV, 260°. [b] 70 eV, 210°. [c] See ref 15. [d] Per cent contribution to total ionization $\geq m/e$ 194.

Discussion

Fragmentation Pathways.[21] There is clear evidence for the following order of ease of cleavage of metal–halogen bonds after electron impact: M–I > M–Br > M–Cl. This is demonstrated by *the intensity of:* (1) M^+ and $(M - HX)^+$ fragments from the pyridine complexes (Table III); (2) M^+ and $(M - X)^+$ fragments from the $Pt(Et_3P)_2X_2$ complexes (Tables IV and V); and (3) especially, M^+ and $(M - X)^+$ fragments from the $Pt(Ph_3P)_2X_2$ complexes (Table VI). Vibrational studies[22,23] and thermodynamic data[24] indicate the same order of Pt(II)–X bond strengths: M–I < M–Br < M–Cl.

This effect of bond strength on fragmentation is particularly evident in a comparison of the 10-eV spectra of *trans*-$Pt(Et_3P)_2Cl_2$ and *trans*-$Pt(Et_3P)_2I_2$. The parent ion, M +, carries 96% of the ionization current in the spectrum of the dichloride, but only 67% in the spec-

Table III. Major Fragments in Mass Spectra of $Pt(py)_2X_2$[a]

X	*m/e* range	$\Sigma(>194)$,[b] % From cis	$\Sigma(>194)$,[b] % From trans	Assignment
I	422–430	43.5	42.0	$M\cdot^+$
I	606–611	33.0	33.5	$M\cdot^+$
Cl	385–390	1.5	2.0	$(M - HCl)^+$, $(M - HCl - H)^+$
I	478–482	14.0	17.0	$(M - HI)^+$
Cl	349–355	16.5	16.0	$(M - 2HCl)^+$, $(M - 2HCl - H)^+$
I	350–355	10.5	11.5	$(M - 2HI)^+$
Cl	343–349	8.0	7.5	$(M - py)^+$
I	527–529	0.5	0.5	$(M - py)^+$
Cl	307–311	6.0	6.0	$(M - HCl - py^+)$
I	397–401	8.5	9.0	$(M - HI\text{-}py\text{-}2H)^+$
Cl	271–276	11.5	11.5	$(Ptpy - H)^+$
I	271–277	16.5	14.5	

[a] $Pt(pt)_2Cl_2$, 70 eV, 250°; $Pt(py)_2I_2$, 70 eV, 220–225°. [b] Per cent contribution to total ionization $\geq m/e$ 194.

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(21) The multiplicity of Pt isotopes causes more difficulties in interpretation of fragmentation pathways than in many other mass spectral studies. Some hypotheses have been omitted from the discussion because of ambiguities in interpretations.[1]

(22) P. J. Hendra, *Nature (London)*, **212**, 179 (1966).

(23) R. J. H. Clark in "Halogen Chemistry," Vol. 3, V. Gutmann, Ed., Academic Press, New York, N. Y., 1967, pp 94–99.

(24) R. G. Pearson and R. J. Mawby in ref 23, pp 55–84.

Table IV. Major Fragments in Mass Spectra of *cis*- and *trans*-$Pt(PEt_3)_2Cl_2$[a]

m/e range	IV, eV	Σ(>194), % From cis	Σ(>194), % From trans[b]	Assignment
500–508	70	31	42	M^+
500–508	20	37	58	M^+
500–508	12	78	89	M^+
500–508	10	88	96	M^+
465–471	70	2	5	$(M - Cl)^+$
465–471	12	6	6	$(M - Cl)^+$
424–435	70	7	6	$(M - 2HCl)^+$
423–432	20	16	12	$(M - 2HCl)^+$
425–431	12	10	3	$(M - 2HCl)^+$
395–406	70	6	8	$(M - 2HCl - C_2H_4)^+$
395–406	20	16	10	$(M - 2HCl - C_2H_4)^+$
365–384	70	12	8	$(M - PEt_3)^+$, $(M - 2HCl - 2C_2H_4)^+$
339–354	70	8	7	$(M - 2HCl - 3C_2H_4)^+$
309–320	70	8	6	$(PtPEt_3)^+$
279–292	70	9	6	$(PtPHEt_2)^+$
251–259	70	7	5	$(PtPH_2Et)^+$

[a] Spectra with IV = 70 eV, 175–180°; spectra with IV = 20 eV, 130–135°. [b] Trans, metastable at *m/e* 432.5 with IV = 12 eV; $[Pt(PEt_3)_2Cl_2]\cdot^+$ (*m/e* 500) → $[Pt(PEt_3)_2Cl]^+$ (*m/e* 465).

Table V. Major Fragments in Mass Spectra of *cis*- and *trans*-$Pt(PEt_3)_2I_2$[a,b]

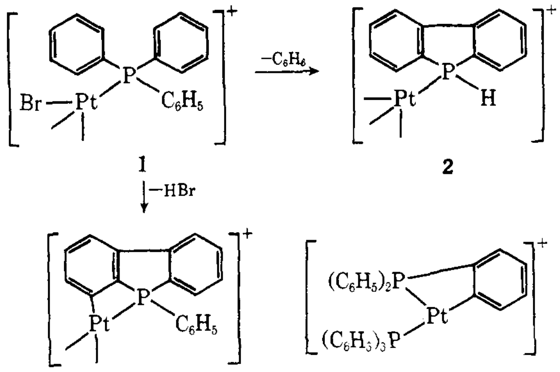
m/e range	IV, eV	Σ(>194), % From cis[c]	Σ(>194), % From trans[d]	Assignment
684–689	70	4	10	$M\cdot^+$
684–689	20	3	13	$M\cdot^+$
684–689	10	14	67	$M\cdot^+$
557–562	70	12	25	$(M - I)^+$
557–562	20	8	40	$(M - I)^+$
557–562	10	13	33	$(M - I)^+$
499–507	70	3	1	$(M - I - 2C_2H_4)^+$
499–507	20	18	0.2	$(M - I - 2C_2H_4)^+$
421–434	70	17	16	$(M - 2HI)^+$
421–434	20	20	22	$(M - 2HI)^+$
392–405	70	18	16	$(M - 2HI - C_2H_4)^+$
392–405	20	12	20	$(M - 2HI - C_2H_4)^+$
364–377	70	7	7	$(M - 2HI - 2C_2H_4)^+$

[a] 120°. [b] Ions from the mixed halide complexes *cis*- or *trans*-$Pt(PEt_3)_2ClI$ were found in the mass spectra of both diiodide complexes. [c] Cis, metastables at *m/e* 467, 453.5, 426, 397.5, 378, 330.5. [d] Trans, metastables at *m/e* 454, 426, 398, 378, 330.

trum of the diiodide, the remaining ion density (33%) occurring as $(M–I)^+$ in the latter case. However, there is a large difference in the abundance of the $M\cdot^+$ ion at 70 eV as well (42% *vs.* 10%).

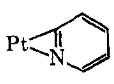
Rearrangements. The loss of HX after electron impact on the triphenylphosphine complexes (Table VI) probably indicates that these complexes are undergoing rearrangements similar to those found in the mass spectra of triphenylphosphine[25] and diphenylphosphinates;[26] in these cases cyclization occurs to form 2,2′-biphenylphosphorus ions. In these Ph_3P-Pt complexes, the loss of both HX and C_6H_6 indicates cyclizations with formation of both C–C and C–Pt bonds to give **2** and **3**, respectively. The formation of **3** is supported by known solution chemistry of d^8 complexes of Rh(I)[27] and Ir(I).[28]

Formation of cyclized fragments, which have structures of the kind depicted in **2** and **3**, is apparently a common theme of fragmentation of these triphenylphosphine complexes. In particular, there are metastables in the spectrum of *cis*-$Pt(Ph_3P)_2Br_2$ for *m/e* 718 $-H\cdot$ → *m/e* 717 (probably **4**), for 797 −HX → 717, and for loss of H_2 and $H\cdot$ from other ions. As is clear from our previous paper,[26] such processes are good evidence for these rearrangements.



1 **2** **3** **4**

Rearrangements also appear in the spectra of the pyridine complexes. Whereas in fragmentation the amine complexes (Table I) lose Cl·, the pyridine complexes (Table III) lose HX. This may be due to the acidity of the α-H's of the coordinated pyridine rings.[29] The resulting ion, *m/e* 478, is particularly intense in the spectra of the iodides. The structure of this ion (M − HX) may involve bridging to give **5**,[30] rearrangement to give **6**, or rearrangement to give **7**.



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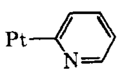

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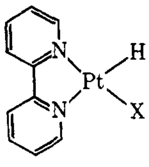

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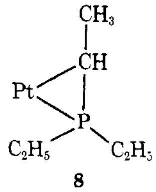

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(25) D. H. Williams, R. S. Ward, and R. G. Cooks, *J. Amer. Chem. Soc.*, **90**, 966 (1968).

(26) P. Haake, M. J. Frearson, and C. E. Diebert, *J. Org. Chem.*, **34**, 788 (1969).

(27) G. W. Parshall, W. H. Knoth, and R. A. Schunn, *J. Amer. Chem. Soc.*, **91**, 4990 (1969).

(28) M. A. Bennett and D. L. Milner, *Chem. Commun.*, 581 (1967); A. F. Reid, J. S. Shannon, J. M. Swan, and P. C. Wailes, *Aust. J. Chem.*, **18**, 173 (1965).

(29) K. W. Ratts, R. K. Howe, and W. G. Phillips, *J. Amer. Chem. Soc.*, **91**, 6115 (1969).

(30) This kind of bonding has been found in $Pt(P(C_6H_5)_3)_2(CF_3CN)$: W. J. Bland, R. D. W. Kemmitt, L. W. Nowell, and D. R. Russell, *Chem. Commun.*, 1065 (1968).

Table VI. Major Fragments in Mass Spectra of *cis*- and *trans*-$Pt(Ph_3P)_2X_2$[a–c]

X	*m/e* range	Σ(>194), Pt,[d] %		Assignment
		From cis	From trans	
Cl	788–796	0.8	19	$M\cdot^+$
Br	876–884	0.1	1.1	$M\cdot^+$
Cl	752–760	1	7	$(M - X)^+ (M - HX)^+$
Br	797–805	1	26	$(M - X)^+ (M - HX)^+$
I	845–851	26	35	$(M - X)^+ (M - HX)^+$
Cl	715–724	1	7	$(M - 2X - nH)^+$
Br	715–724	5	24	$(M - 2X - nH)^+$
I	715–724	29	30	$(M - 2X - nH)^+$
Cl	671–684	6	2	$(M - X - C_6H_6 - nH)^+$
Br	534–540	1	5	$(M - HBr - PPh_3)^+$
Cl	459–471	13	12	$(M - 2X - PPh_3 - nH)^+$
Br	459–471	17	10	$(M - 2X - PPh_3 - nH)^+$
I	465–470	7	6	$(M - 2X - PPh_3 - nH)^+$
Cl	375–382	27	16	$(PtPPh_2 - nH)^+$
Br	375–382	30	10	$(PtPPh_2 - nH)^+$
I	377–382	5	8	$(PtPPh_2 - nH)^+$
Cl	300–307	26	19	$(PtPPh - nH)^+$
Br	300–307	14	5	$(PtPPh - nH)^+$
I	300–307	5	6	$(PtPPh - nH)^+$

[a] Ionizing voltage for all spectra 70 eV; source temperatures 210 and 260° for *cis*- and *trans*-$Pt(Ph_3P)_2Cl_2$, respectively, 215 and 270° for *cis*- and *trans*-$Pt(Ph_3P)_2Br_2$, and 160 and 280° for *cis*- and *trans*-$Pt(Ph_3P)_2I_2$. [b] Metastables occur in the spectra of *cis*- and *trans*-$Pt(Ph_3P)_2Br_2$; cis *m/e* 716, 645, 570, 451, 376, 338, 313, 201; trans *m/e* 717, 646, 450. [c] Ions from the mixed dihalide complexes *cis*- and *trans*-$Pt(Ph_3P)_2ClX$ were found in the mass spectra of both the dibromide and diiodide complexes. See ref 19. [d] Peaks due to ions *not* containing platinum occur in the spectra of these compounds; spectra were normalized excluding them.

The loss of hydrogens in the fragmentation of the triethylphosphine complexes, particularly as HX (Tables IV and V), is remarkable. The driving force for this may come from the acidity of the α-H's in coordinated phosphines[31] or from the formation of C–Pt bonds after loss of H· at the α or β positions (*e.g.*, **8** from α-H loss). The details of these processes await study of other phosphine complexes and experiments with labeled phosphines.

Coordinate and Covalent Bonds. Examination of the data in the tables clearly demonstrates that, although coordinate bonds do frequently cleave, many covalent bonds cleave competitively during fragmentation in mass spectra of Pt(II) complexes. Cleavage of coordinate bonds appears favored but is not the only fragmentation process. In addition to data in the tables, peaks were observed in the spectra of PEt_3 complexes for loss of C_2H_4 and for loss of C_2H_4 + halogen although the intensities of these fragments were below 5%.

Comparison of Cis and Trans Isomers. Do the mass spectra of cis and trans isomers differ? If the energy transmitted to the complex on electron impact were sufficient to cause excitation to a tetrahedral state, a phenomenon observed in the photochemistry of these complexes,[13] no cis–trans differences would be noted.

There are few differences in the mass spectra of *cis*- and *trans*-$Pt(NH_3)_2Cl_2$ (Table I). The major difference is in the abundance of $[Pt(NH_3)_2Cl_3]^+$ ions (Table I). These ions may be due to pyrolytic reactions resulting from the high source temperatures. This cis–trans difference may, therefore, be due to differences in crystal structures or vaporization processes[32]—not to any difference after electron impact. Yet, it is possible to distinguish cis and trans isomers.

The results therefore indicate that for the NH_3 complexes and for the pyridine complexes (in the spectra of which there are no differences exceeding experimental error) electron impact may be sufficient to cause excitation to the tetrahedral state. Alternatively, fragmentation pathways may simply not differ significantly even though the cis and trans configurations are retained after electron impact.

In all other nonchelated complexes, there are clear differences in the mass spectra of cis and trans isomers: (1) M^+ is more abundant in the spectrum of *trans*-$Pt(PEt_3)_2X_2$ than in the spectrum of the cis isomer, especially when X = I (Tables IV and V). This is probably a manifestation of the trans effect[33] after electron impact. (2) In the rearrangements of $Pt(PPh_3)_2Br_2$ complexes, the *m/e* 717 fragment (probably **4**) is even more abundant in the spectrum of *trans*-$Pt(PPh_3)_2Br_2$ than in the spectrum of the cis isomer. An attractive explanation is that there is an increased amount of concerted loss of HBr from *m/e* 797 due to the statistically larger number of neighboring Br's and ortho H's in the trans isomer compared to the cis isomer. The metastable at *m/e* 338 is present in the spectrum of the cis isomer, but absent in the spectrum of the trans isomer. It appears to correspond to loss of Br_2 in the process *m/e* 614 → *m/e* 456. Its absence in the spectrum of the trans isomer may be due to the lack of adjacent bromines. Both these differences between cis and trans isomers indicate *retention of configuration after electron impact.*

The question of tetrahedral states after electron impact on tetragonal planar compounds may be complex. Since $M\cdot^+$ is different electronically from the parent molecules, it could have a different configuration with lowest energy. It appears that the state of lowest energy of the radical ions generated from phosphine complexes is not tetrahedral because of the differences we observe in the spectra of cis–trans pairs. But the energy

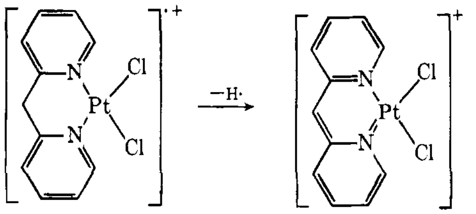
[31] Similar to phosphonium ions: W. von E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, 77, 521 (1955).

[32] An attractive hypothesis for the greater intensity of ion A from the cis isomer would involve the greater intermolecular forces in the cis isomer due to its large dipole moments *vs.* zero dipole moment of the trans isomer.

[33] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Chapter 5.

required to achieve a tetrahedral configuration may be imparted to some but not all radical ions after electron impact. A closer study will be necessary to elucidate completely these possibilities.

Chelates Compared to Nonchelates. We have studied the nonchelated $Pt(py)_2X_2$ complexes and the chelates, $Pt(bipy)Cl_2$ and $Pt(dpm)Cl_2$.[15] The chelates appear to fragment by consecutive loss of Cl· from the parent ion. In contrast, when halogen is lost from a pyridine complex, it is lost as HX (see above). This contrast may indicate that **7** is the preferred structure of the rearranged ion from the pyridine complexes. The abundances of the parent ions, M^+, in these complexes indicate that there is more cleavage of the Pt–Cl bond in the chelates. This may be associated with initial formation of a delocalized structure (**10**)[34] from the dpm chelate (**9**) in which case the cyclic delocalized system in the chelates may be responsible for the ready cleavage of Pt–Cl bonds. Although substitution of Cl^- in solution is facilitated by the delocalized ring in bipy–Pt(II) complexes,[15,33] displacement at platinum(II) is associative[33,35] rather than dissociative as in Pt–X cleavage after electron impact. The similarity of dpm and bipy chelates in these mass spectral studies suggests that the ready Pt–Cl cleavage after electron impact is due to delocalization rather than angle strain[36] since the dpm ring should be unstrained. In both substitutions and cleavage after electron impact, the labilizing effect of the delocalized chelate system may be due to weakening of Pt–Cl bonds. Although infrared[1,37] and Raman[1] studies demonstrate higher ν(Pt–Cl) in $Pt(bipy)Cl_2$ then in $Pt(py)_2Cl_2$, this is not necessarily inconsistent with the mass spectral data since the stretching frequency is a measure of the width at the bottom of the vibronic potential well but the bond dissociation energy is a measure of the energy difference between the zero-point energy and the dissociated fragments. Therefore, if the dissociated Pt fragment can be stabilized by delocalization, the bond will dissociate more readily.



9 **10**

Summary. The many interesting phenomena observed in these mass spectral studies may need further investigation in order to define them and fully clarify them. However, it is clear that mass spectrometry can be a useful tool in the identification of platinum(II) complexes. In these studies it has been demonstrated that parent peaks and, therefore, molecular weight of complexes can be detected, that cis and trans isomers of complexes give different spectra, and that chelates give different spectra from nonchelates. It appears that mass spectrometry will be a useful technique in the chemistry of tetragonal planar complexes.

Experimental Section

Mass spectral data were obtained with a Model MS9 Associated Electrical Industries, Ltd. double-focusing, high-resolution mass spectrometer. Samples were introduced directly into the inlet line of the mass spectrometer.

Preparation of *cis*- and *trans*-$Pt(py)_2X_2$. Kauffman's method[38] was used to prepare the dichloride complexes; the isomers were recrystallized from chloroform. *Anal.* Calcd for $C_{10}H_{10}Cl_2N_2Pt$: Pt, 46.01; C, 28.30; H, 2.38. Found, cis: Pt, 46.26; C, 28.45; H, 2.37. Found, trans: Pt, 46.30; C, 28.50; H, 2.59.

The diiodide complexes were prepared from the corresponding dichlorides by metathesis with excess KI (1:30, mol) in an acetone–chloroform–water mixture. The isomers were recrystallized from acetone. No Pt–Cl stretching bands were observed in the infrared or Raman spectra of the complexes.[1]

Preparation of *cis*- and *trans*-$Pt(PEt_3)_2Cl_2$. A mixture of K_2PtCl_4 (10.4 g, 0.025 mol) dissolved in 50 ml of water and triethylphosphine[39] (5.8 g, 0.050 mol) was stirred under nitrogen at 100° for several hours. The resulting yellow solid was filtered off and extracted with 20–40° petroleum ether. The grayish residue was recrystallized from hot ethanol and filtered through charcoal on Celite to give large white needles, mp 191° (lit.,[40] 192°) after drying at 56° under reduced pressure. *Anal.* Calcd for $C_{12}H_{30}Cl_2P_2Pt$: C, 28.69; H, 6.02. Found: C, 28.75; H, 6.28.

Two Pt–P stretching bands at 425 and 442 cm^{-1} were found in the far-infrared and Raman spectra, as well as Pt–Cl stretching bands at 307 and 283 cm^{-1}, indicative of the cis isomer of $Pt(PEt_3)_2Cl_2$.[1,40]

The yellow petroleum ether solution yielded bright yellow prisms (trans isomer) on evaporation, mp 141° (lit.,[40] 142°) after drying at 56° under reduced pressure. *Anal.* Found: C, 28.84; H, 6.08.

A single Pt–P stretching band at 416 cm^{-1} and a single Pt–Cl stretching band at 341 cm^{-1} were found in the far-infrared, indicative of the trans isomer of $Pt(PEt_3)_2Cl_2$.[1,40]

Preparation of *cis*- and *trans*-$Pt(PEt_3)_2I_2$. Metathesis of an ethanol–water (1:1, v/v) solution of *cis*-$Pt(PEt_3)_2Cl_2$ with an excess of KI (1:30, mol) at room temperature for 1 hr gave an isomeric mixture of the diiodide complex. The mixture was first recrystallized from hot ethanol, then extracted with hot diethyl ether. The yellow residue was recrystallized from ethanol–water (1:1, v/v) to give pale yellow needles of the cis isomer, mp 138–140° (lit.,[41] 137°). Two Pt–P stretching bands at 444 and 428 cm^{-1} were observed; no Pt–Cl stretching band was observed.

The ether extract was recrystallized from hot ethanol to give dark yellow-orange prisms of the trans isomer, mp 136–137° (lit.,[41] 136–137°). A single Pt–P band at 413 cm^{-1} was found in the far-infrared; no Pt–Cl stretching band was observed.

Preparation of *cis*-$Pt(Ph_3P)_2X_2$. Grinberg and Razumova's method[42] was used to prepare *cis*-$Pt(Ph_3P)_2Cl_2$; white needles, mp 304–306° (lit.,[43] 310° dec), were obtained by recrystallization from hot chloroform–acetone (3:1, v/v). Two Pt–Cl stretching bands were found at 316 and 293 cm^{-1} in the infrared, 323 and 299 cm^{-1} in the Raman, characteristic of *cis*-$Pt(Ph_3P)_2Cl_2$.[44]

The cis dibromide complex was produced by metathesis of the dichloride with excess LiBr (1:24, mol) in refluxing chloroform to give a yellow powder, mp 307–309° (lit.,[45] 300° dec), showing no Pt–Cl stretching band in the infrared. An unidentified colorless solid was isolated from the mother liquor.

The cis diiodide was produced by metathesis of the dichloride with excess KI (1:50, mol) in a refluxing equivolume mixture of ethanol, acetone, water, and chloroform to give a bright yellow powder, mp 303–304° (lit.,[45] orange-yellow, 285°), and a prismatic

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[34] Similar to the delocalized system in acetylacetone.

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orange solid, mp 314–316°, also shown to be the cis diiodide.[46] These two polymorphs were separated by fractional recrystallization from chloroform. No Pt–Cl stretching band was observed in the infrared spectrum of the yellow powder; the rest of the spectrum was nearly identical with that of *cis*-$Pt(Ph_3P)_2Cl$.

Preparation of ***trans*****-$Pt(Ph_3P)_2X_2$.** The trans isomer of $Pt(Ph_3P)_2Cl_2$ was prepared from the cis isomer by photochemical methods.[13] Lemon-yellow crystals, mp 306–309° (lit.,[47] 307–310°), were produced by recrystallization from benzene. A single strong Pt–Cl stretching band at 344 cm^{-1} was observed in the infrared.[46]

The trans dibromide was prepared by metathesis of the trans dichloride with excess LiBr (1:100, mol) in refluxing ethanol–water (100:1, v/v) with periodic addition of small portions of chloroform, to give a dark yellow solid, mp 309–310°, with no Pt–Cl band in the infrared. The remaining infrared spectrum was nearly identical with that of the trans dichloride.

Metathesis of the trans dichloride with excess NaI (1:500, mol) in a refluxing mixture of water, acetone, ethanol, and chloroform (2.5:1:1:1, v/v) gave a yellow-orange powder, mp 296–299°, on evaporation of the chloroform layer; no Pt–Cl band was found in the infrared.

Acknowledgments. We wish to thank Dr. P. A. Turley for providing samples of *cis*- and *trans*-$Pt(NH_3)_2Cl_2$ and $Pt(bipy)Cl_2$, Dr. K. Stark for the sample of $Pt(dpm)Cl_2$, Mrs. Sharon M. Jones and Dr. M. Haugh for assistance in obtaining the mass spectra, and Drs. D. A. Lightner and R. A. Kent for many helpful discussions.

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An Oxygen-17 Nuclear Magnetic Resonance Study of Nickel(II)–Ethylenediaminetetraacetate Complexes in Aqueous Solution

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Received March 9, 1971

Abstract: At pH 2 the nickel(II)–EDTA complex appears to exist as $Ni(H_2O)HEDTA^-$ with one (protonated) acetate arm replaced by a water molecule. Kinetic parameters for water exchange with this species are $k_1(25°) = (2.0 \pm 0.1) \times 10^5$ sec^{-1}, $\Delta H^{\ddagger} = 9.8 \pm 0.3$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -1.5 \pm 2$ cal mol^{-1} deg^{-1}. The scalar coupling constant A/h for the Ni–O interaction is $(2.3 \pm 0.1) \times 10^7$ Hz. At pH 6–7, evidence for significant amounts of an aquo–EDTA complex was found. It was concluded that a six-coordinate species, $Ni(H_2O)(EDTA)^{2-}$, with one unprotonated acetate arm off, best explains the observations. Kinetic parameters for this species are $k_1(25°) = (7 \pm 0.5) \times 10^5$ sec^{-1}, $\Delta H^{\ddagger} = 8.0 \pm 0.5$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -7.0 \pm 2$ cal mol^{-1} deg^{-1}. The scalar coupling constant A/h is $(2.6 \pm 0.2) \times 10^7$ Hz. Effects of substitution on water lability are discussed as well as structural implications. The nickel(II)–ethylenediaminedisuccinic acid (EDDS) complex also appears to have a small percentage of aquo form present at high pH.

The crystallographic studies on transition metal–EDTA (ethylenediamine-*N*,*N*,*N′*,*N′*-tetraacetate, H_4Y) complexes by Hoard and his group[1] showed structural possibilities A–D in the solid state (Figure 1). Except in the case of substitution-inert cobalt(III) compounds,[2] the structure of these complexes in solution is still an unsettled question.

The common p*K* value exhibited toward protonation led Higginson[3] to postulate that the divalent metal complexes had structure B both in the protonated and unprotonated forms. Colorimetric studies of Nancollas[4] shed doubt on this conclusion. Bhat and Krishnamurthy[5] deduced from the pH dependence of the electronic spectra of Ni(II), Co(II), and Cu(II) complexes that at neutral pH at least some of the EDTA was hexadentate (structure A) and that one carboxylate arm was removed by protonation. The predominant outer-sphere oxidation[6] of Co(II)–EDTA solution to the inert Co(III)–EDTA ion (Fig. 1A) suggests that in neutral solution Co(II)–EDTA has structure A also. Margerum and Rosen[7] have observed temperature-jump relaxation of Ni(II)–EDTA solutions at pH 8 and conclude that there is a coordinated water molecule present. Matwiyoff,[8] from a combination of ^{13}C and ^{17}O nmr data, concluded that the nickel–EDTA complex has structure A in neutral solution and B in acid solution. Higginson and Samuel,[9] on the other hand, deduce from the formation constants of monodentate ligands with EDTA complexes in neutral solution that for several divalent metals an equilibrium exists between hexadentate (structure A) and pentadentate (structure B) forms.

We have used ^{17}O nmr to investigate the structures and water-exchange kinetics of Ni(II)–EDTA solutions.

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