86. *The Visible and Ultraviolet Spectra of Some Platinous Ammines.*

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The visible and ultraviolet spectra of the ions $[Pt(NH_3)_nCl_{4-n}]^{(n-2)+}$ for $n = 0$—4 have been measured and tentatively interpreted in terms of the orbital energy diagram for *d* electrons on the platinous ion. The spread of *d*-orbital energies is greater (30,000—40,000 cm.$^{-1}$) than usual, and appears to be due to electrostatic and σ-bonding effects rather than to π-bonding. The chemical implications of this fact are discussed.

THE spectra of octahedral complexes of the transition metals have often been investigated theoretically and practically. The nature of the weak, long-wavelength absorption bands is now understood fairly well and their detailed assignments to transitions within the d^n configuration of the metal ion have been made for many compounds.[1] The corresponding problem for planar complexes is more difficult since the effect of the ligands on the energies of the different *d*-orbitals is much more complicated. We now study in detail the spectra of a series of platinous ammines and suggest some assignments. These are provisional in that, while they give the best overall interpretation of the available experimental data, other assignments are not excluded.

TABLE 1. *Frequency of maxima* ($\nu_{max.}$),* *maximum extinction coefficients* ($\varepsilon_{max.}$) *and half-widths of the bands* ($\nu_{\frac{1}{2}}$) * *in the absorption spectra of* K_2PtCl_4, *and the derived platinous ammines. The solvent was water, except as indicated.*

	$\nu_{max.}$	$\varepsilon_{max.}$	$\nu_{\frac{1}{2}}$	$\nu_{max.}$	$\varepsilon_{max.}$	$\nu_{\frac{1}{2}}$	$\nu_{max.}$	$\varepsilon_{max.}$	$\nu_{\frac{1}{2}}$
K_2PtCl_4	1·77	2·6	0·10	2·10	15·0	0·203	2·55	59	0·14
$K[NH_3PtCl_3]$	2·07	2·8	0·14	2·41	19·8	0·24	2·89	118	0·15
trans-$(NH_3)_2PtCl_2$	—	—	—	2·68	21·4	0·25	3·17	60	0·17
trans-$[\{(C_5H_{11})_2NH\}_2PtCl_2]$ †	2·26	2·2	0·22	2·64	21·8	0·20	3·12	67·4	—
cis-$[(NH_3)_2PtCl_2]$	2·40	3·2	0·16	2·73	23	0·23	3·31	128	0·22
$[(NH_3)_3PtCl]_2SO_4$	—	—	—	3·10	65	0·27	3·60	80	0·16
$[(NH_3)_4Pt]Cl_2$	—	—	—	3·48	36	0·23	—	—	—
Suggested assignment ...	triplet $d_{xy} \longrightarrow d_{x^2-y^2}$			triplet d_{xy}, $d_{xz} \longrightarrow d_{x^2-y^2}$			singlet $d_{xy} \longrightarrow d_{x^2-z^2}$		

	$\nu_{max.}$	$\varepsilon_{max.}$	$\nu_{\frac{1}{2}}$	$\nu_{max.}$	$\varepsilon_{max.}$	$\nu_{\frac{1}{2}}$	$\nu_{max.}$	$\varepsilon_{max.}$
K_2PtCl_4	3·02	64	0·17	3·79	250	0·03	4·6	9580
$K[NH_3PtCl_3]$	3·33	74	0·21	—	—	—	>4·75	>6000
trans-$(NH_3)_2PtCl_2$	3·67	75	0·25	—	—	—	4·6	2110
trans-$[\{(C_5H_{11})_2NH\}_2PtCl_2$ †	3·71	97·2	—	—	—	—	>4·65	>4000
cis-$[(NH_3)_2PtCl_2]$	3·72	68·5	0·21	—	—	—	>4·76	>4500
$[(NH_3)_3PtCl]_2SO_4$	3·97	233	0·32	—	—	—	>4·8	>6000
$[(NH_3)_4Pt]Cl_2$	—	—	—	—	—	—	>4·87	>3000
Suggested assignment ...	singlet d_{xz}, $d_{yz} \longrightarrow d_{x^2-y^2}$						$d \longrightarrow p$	

* Frequencies are in 10^4 cm.$^{-1}$. † In ethanol.

Spectra.—The spectra of the complexes $[Pt(NH_3)_nCl_{4-n}]^{(n-2)+}$ for $n = 0$—4, measured in aqueous solution, are presented in Figs. 1—3. The spectrum of *trans*-$[\{(n\text{-}C_5H_{11})_2NH\}_2,PtCl_2]$ has been included in Fig. 2 since the long-wavelength region of the spectrum of *trans*-$[Pt(NH_3)_2Cl_2]$ could not be measured accurately on account of the low solubility of the compound. In Fig. 4 we compare the spectra of *trans*-$[\{(n\text{-}C_5H_{11})_2NH\}_2PtCl_2]$ in ethanol and in hexane.

We analysed the measured spectra assuming that they can be represented as sums of Gaussian absorption bands. The results of this analysis are given in Table 1 and the variations of the positions of the various bands with *n* in Fig. 5.

Interpretation.—The transformation properties of the *d*, *s*, and *p* orbitals of the central

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[1] (*a*) Jorgensen, Report of the 10th Solvay Conference in Chemistry, Brussels, 1956; (*b*) Orgel, *J. Chem. Phys.*, 1955, **23**, 1004.

FIG. 1. *Ultraviolet spectra of* $K[NH_3PtCl_3]$ (*solid line*) *and* K_2PtCl_4 (*broken line*).

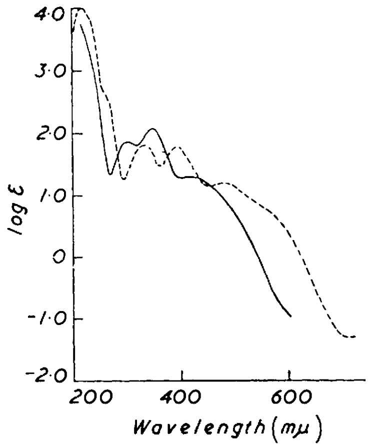


FIG. 2. *Ultraviolet spectra of* cis-$[(NH_3)_2PtCl_2]$ (*solid line*), trans-$[(NH_3)_2PtCl_2]$ (*dotted line*), *and* trans-$[\{(n\text{-}C_5H_{11})_2NH\}_2PtCl_2]$ (*broken line*). *The last plot, taken in ethanol, has been lowered by* 0·5 *log unit.*

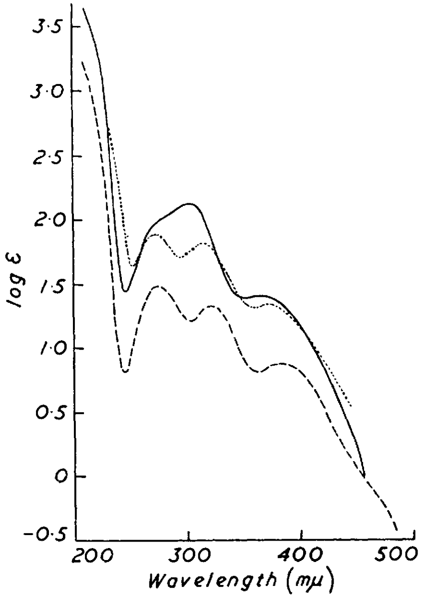


FIG. 3. *Ultraviolet spectra of* $[(NH_3)_4Pt]Cl_2,H_2O$ (*solid line*) *and* $[(NH_3)_3PtCl]_2SO_4$ (*broken line*).

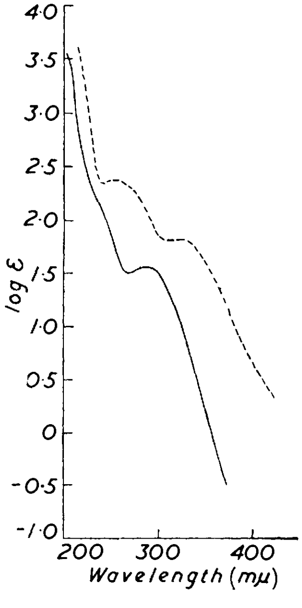
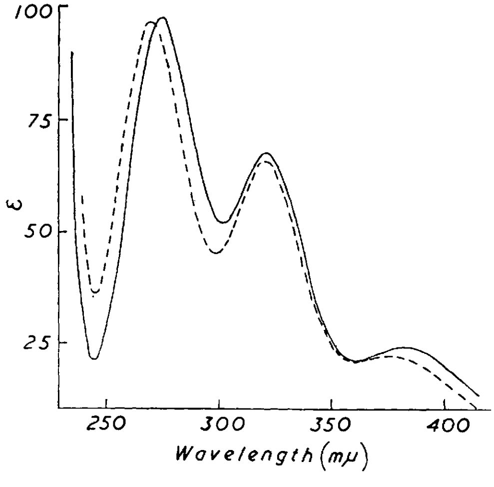


FIG. 4. *Ultraviolet spectrum of* trans $[\{(C_5H_{11})_2NH\}_2PtCl_2]$ *in ethanol* (*solid line*) *and* n-*hexane* (*broken line*).



metal ion in the group D_{4h} of a symmetrical planar MX_4 complex are given in Table 2. The choice of axes is illustrated in Fig. 6.

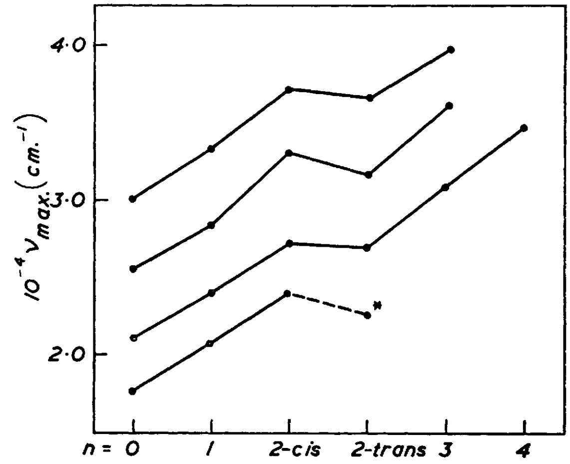
Ligand-field theory shows that the $d_{x^2-y^2}$ orbital, or more correctly the orbital which is largely $d_{x^2-y^2}$ in character, is much less stable than the other *d* orbitals, since it points directly at the ligands and is made less stable by them.[2] The order of stability within the remaining group of *d*-orbitals cannot be settled theoretically.

Electrostatic effects alone would make the d_{xz} and d_{yz} orbitals more stable than the d_{xy} orbital. This may be seen most easily by supposing that the planar complex has been derived from a regular octahedral one by the removal of the ligands lying on the *z* axis. In the original complex the d_{xz}, d_{yz}, and d_{xy} orbitals are degenerate. Since in the octahedral complex the d_{xz} and d_{yz} orbitals are closer to the ligands on the *z* axis than is the d_{xy} orbital, in the planar complex the former orbitals must be more stable than the latter.

TABLE 2. *Symmetry classification of orbitals for the group* D_{4h}.

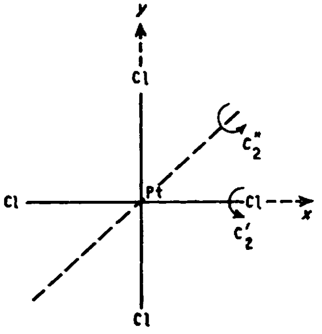
Atomic orbital	s	p_x, p_y	p_z	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}, d_{yz}
Symmetry type	A_{1g}	E_u	A_{2u}	A_{1g}	B_{1g}	B_{2g}	E_g

FIG. 5. *Values of* $\nu_{max.}$ *for the spectra of* $[Pt(NH_3)_nCl_{4-n}]^{(n-2)+}$, *where* n = 0—4.



* This point is taken from the spectrum of *trans*-$[\{(C_5H_{11})_2NH\}_2PtCl_2]$ which is almost identical with that of the ammine.

FIG. 6. *Choice of axes for planar complexes. The z axis is perpendicular to the molecular plane.*



The problem is complicated by the ability of some ligands to form π bonds involving the d_{xy}, d_{xz}, and d_{yz} orbitals. In the complexes now discussed, we can neglect double-bonding to the ammonia molecules, since this is only possible through interaction with the hydrogen atoms,[3] but the double-bonding to the chloride ions cannot be ignored.

The chloride ion, with the closed-shell structure . . . $(3s)^2(3p)^6$, has available for double-bonding the filled 3*p* and the empty 3*d* orbitals. Interaction with the former makes the metal d_{xy}, d_{xz}, and d_{yz} orbitals less stable, while interaction with the latter stabilises them. In any given transition-metal complex the relative importance of these two effects depends on the electronegativity of the metal. If the metal *d* electrons are loosely held they are likely to be stabilised, and if tightly held made less stable by π-bonding. Thus while the influence of the chlorine *p* orbitals must be large in $[PtCl_6]^{2-}$, that of the chlorine *d* orbitals probably outweighs it in $[PtCl_4]^{2-}$, leading to a net stabilisation by π-bonding.[4] These relations are illustrated in Fig. 7.

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[2] Orgel, *J.*, 1952, 4756.

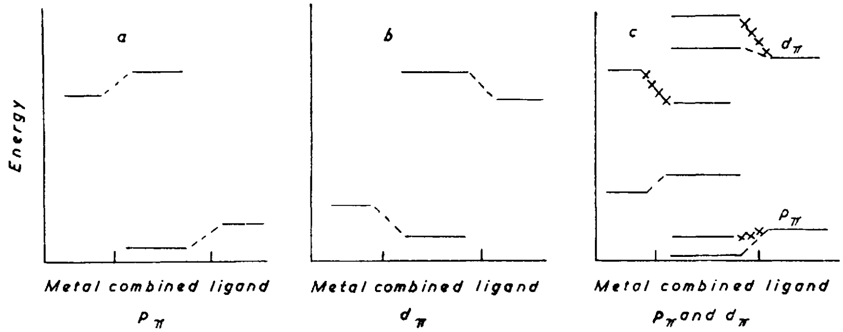
[3] Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461.

[4] (*a*) Chatt, Duncanson, and Venanzi, *J.*, 1956, 2712; (*b*) Chatt and Wilkins, *J.*, 1956, 525.

In the case of the $[PtCl_4]^{2-}$ ion, the metal d_{xz} and d_{yz} orbitals can each interact with the two $d\pi$ orbitals on the chloride ions. The d_{xy} orbitals, however, can interact with four chlorine $d\pi$ orbitals, and so should be stabilised a little more, as shown in Fig. 8. We do not believe that this effect is very large, certainly not large enough to disturb the order of levels determined by the electrostatic effect.

The d_{z^2} orbital is much more difficult to place on an energy scale for several reasons. First, simple electrostatic calculations do not lead to unambiguous conclusions, for the order of the d_{xy}, d_{xz}, and d_{yz} orbitals on the one hand and the d_{z^2} orbital on the other depends critically on the details of the model chosen. Secondly, molecular-orbital theory shows that the d_{z^2} and s orbitals can become mixed together in a planar complex. One combination, being concentrated in the molecular plane, is ideal for bond formation while the other is kept well away from the ligands and is ideal for housing a pair of non-bonding electrons. As a working hypothesis we shall adopt the energy level scheme given in Fig. 9, the main uncertainty being in the position of the d_{z^2} orbital.

FIG. 7. *Atomic d, ligand π, and molecular orbitals for a planar complex.*



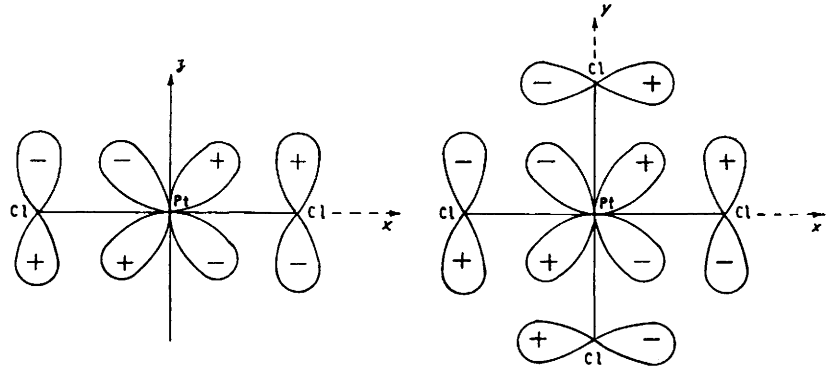
a, Only ligand $p\pi$ orbitals included; *b*, only ligand $d\pi$ orbitals included; *c*, ligand $p\pi$ and $d\pi$ orbitals included for high electronegativity (— — —) or low electronegativity (× × ×) of the metal orbitals.

In the $^1A_{1g}$ ground state of the complexes the Pt^{2+} ion has the $5d$-electron configuration

$$(d_{z^2})^2\ (d_{xz},\ d_{yz})^4\ (d_{xy})^2\ (d_{x^2-y^2})^0$$

The spectrum should include three fairly strong singlet–singlet transitions ($\varepsilon \approx 50$) in which an electron is removed from one of the filled d orbitals and placed in the $5d_{x^2-y^2}$ orbital and three or four somewhat weaker transitions to the corresponding triplets. The situation differs from that in the first transition series, because the spin–orbit coupling is so strong for platinum that the intensity of the singlet–triplet transitions may approach that for the spin-allowed transitions (the approximation of Russell–Saunders coupling is not really

FIG. 8. *Bonding combinations of d_{xz} and d_{xy} orbitals with chlorine π orbitals in* $[PtCl_4]^{2-}$.



valid, and the classification of states into singlets and triplets is only meant in an approximate sense). In the first two columns of Table 3 we classify the states of the d^8 configuration to which one-electron transitions are possible. By $d_{xy} \longrightarrow d_{x^2-y^2}$ we denote the sub-configuration arising from the ground-state configuration by the promotion of an electron from the d_{xy} to the $d_{x^2-y^2}$ orbital, etc. The ^3E_g state is split by spin-orbit interaction and could conceivably give rise to two absorption bands.

The energies of the excited states relative to the ground state do not correspond directly to the separations in Fig. 9, for the latter do not allow for the changes in the d-electron repulsion energy which accompany excitation. This quantity, together with the energies of the various relevant states, was calculated in terms of Slater–Condon or Racah parameters by methods already described.[5,6] The various energy terms are collected together in Table 4 together with some rough guesses at their numerical values.

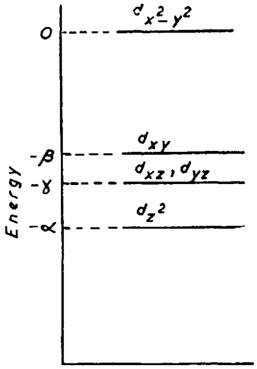


FIG. 9. *Provisional energy-level scheme for d orbitals in* $[PtCl_4]^{2-}$.

TABLE 3. *Symmetries of the excited states of* $[PtCl_4]^{2-}$ *and of the vibrations making transitions to them allowed.*

Transition	Symmetry of upper state	Vibration making singlet–singlet transition allowed	Polarisation of singlet–singlet transition
$d_{z^2} \longrightarrow d_{x^2-y^2}$	$^{1,3}B_{1g}$	B_{2u}	z
		E_u	x, y
$d_{xy} \longrightarrow d_{x^2-y^2}$	$^{1,3}A_{2g}$	A_{1u}	z
		E_u	x, y
d_{xz}, $d_{yz} \longrightarrow d_{x^2-y^2}$	$^{1,3}E$	E_u	z
		A_{1u} A_{2u} B_{1u} B_{2u}	x, y

TABLE 4. *Energies of states obtained by one-electron transitions from the ground state of* $[PtCl_4]^{2-}$. *Configurative interaction has been neglected, and we have assumed* B = 750 *cm.*$^{-1}$, C = 3000 *cm.*$^{-1}$.

State	Energy relative to ground state in terms of Racah parameters [5,6] and crystal-field splittings (see Fig. 9)	Estimate of Racah term (cm.$^{-1}$)	State	Energy relative to ground state in terms of Racah parameters [5,6] and crystal-field splittings (see Fig. 9)	Estimate of Racah term (cm.$^{-1}$)
$^1B_{1g}$	$\alpha - 4B - C$	-6000	$^3B_{1g}$	$\alpha - 12B - 3C$	$-18{,}000$
$^1A_{2g}$	$\beta - C$	-3000	$^3A_{2g}$	$\beta - 3C$	-9000
^1E_g	$\gamma - 3B - C$	-5250	^3E_g	$\gamma - 9B - 3C$	$-15{,}750$

The additional term has the effect of complicating the assignments, since the upper singlet states corresponding to the $d_{z^2} \longrightarrow d_{x^2-y^2}$, and $d_{xz}, d_{yz} \longrightarrow d_{x^2-y^2}$ transitions are lowered relative to that of the $d_{xy} \longrightarrow d_{x^2-y^2}$ transition by 2000—3000 cm.$^{-1}$. This again raises

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[5] Orgel, *J. Chem. Phys.*, 1955, **23**, 1819.

[6] Griffith, *J. Inorg. Nuclear Chem.*, 1956, **2**, 1.

doubts about the order of the ${}^1A_{2g}$ and ${}^1E_g$ upper states which, together with our uncertainty of the position of the ${}^1B_{1g}$ state, prevent our making any firm predictions on the basis of purely theoretical considerations. To make any further progress we have to consider the experimental data in greater detail.

The spectrum of $[PtCl_4]^{2-}$ beyond 300 mμ consists of four bands. The two at 331 mμ and 392 mμ ($3{\cdot}02 \times 10^4$ and $2{\cdot}55 \times 10^4$ cm.$^{-1}$ respectively) are clearly due to singlet–singlet transitions, since they have just the expected intensity. The weak band at 565 mμ ($1{\cdot}77 \times 10^4$ cm.$^{-1}$) is equally clearly due to a singlet–triplet transition, for the first excited state must be a triplet. The intensity of this transition is, if anything, a little small for a spin-forbidden band in a platinum complex.

The assignment of the band at 476 mμ ($2{\cdot}10 \times 10^4$ cm.$^{-1}$), which has intermediate intensity, is less clear. We believe that it is another triplet, for the following reasons. First, each band at 331 mμ and 392 mμ must have a corresponding triplet band at longer wavelengths. We can see no trace of weak bands except at 476 mμ and 565 mμ. Secondly, the energy separations between the 331 mμ and 476 mμ bands and between the 392 mμ and 565 mμ bands seem very reasonable if they are corresponding pairs of singlets and triplets (see Table 4). Finally the longest-wavelength band of $[Pt(NH_3)_4]^{2+}$, which must correspond to a transition to a triplet upper state, is even more intense than that of the 476 mμ band, showing that the moderate intensity of the band is not inconsistent with our assignment. These arguments are all rather indirect, so that the assignment may have to be reversed in the light of further experiments on related compounds, particularly if our guess at the position of the d_{z^2} orbital proves incorrect.

In crystals of K_2PtCl_4 there are two fairly strong absorption bands, one at 375 mμ which has its transition vector in the plane of the molecule and the other at 340 mμ with its transition vector perpendicular to that plane.[7] There is a much weaker transition at 500 mμ which is not polarised. It seems natural to associate these bands with the solution bands at 392 mμ, 331 mμ, and 476 mμ, respectively. In order to interpret these polarisation data we have to discuss the mechanism by which the forbidden *g*–*g* electronic transitions are made allowed.

TABLE 5. *Symmetry of* $[PtCl_4]^{2-}$ *vibrations.*

Type of vibration	Stretching	Bending in plane	Bending out of plane
Symmetry type	A_{1g} B_{1g} E_u	B_{2g} E_u	A_{2u} B_{2u}

The usual mechanism by which *g*–*g* transitions become allowed in molecules is by vibrational perturbation.[8] In Table 5 we list the symmetry characters of the proper vibrations of the $[PtCl_4]^{2-}$ group, and in Table 3 the way in which the different electronic transitions may be made allowed by vibrations. Now the electronic energy of the $[PtCl_4]^{2-}$ ion is particularly sensitive to the Pt–Cl distances, and hence the stretching frequencies should play a dominant rôle in making the transitions allowed. Since the only *u* stretching frequency has the symmetry class E_u, transitions to A_{2g} or B_{1g} states should be polarised parallel, and transitions to the E_g state perpendicular, to the molecular plane. This suggests that the band at 375 mμ has an upper state of A_{2g} or B_{1g} symmetry, while the upper state of the 340 mμ band has E_g symmetry. The most probable assignment of the singlets is thus 375 mμ $\approx d_{xy} \longrightarrow d_{x^2-y^2}$ and 340 mμ $\approx d_{xz},d_{yz} \longrightarrow d_{x^2-y^2}$. If this is so, the triplets at 565 mμ and 476 mμ correspond to the same pair of sub-configurations.

In the series of compounds $[Pt(NH_3)_nCl_{4-n}]^{(n-2)+}$ it is possible to recognise a steady evolution of the position of the absorption bands with increasing *n*, as shown in Fig. 5. The regularities indicated in the Figure allow us to take over our tentative assignments

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[7] Yamada, *J. Amer. Chem. Soc.*, 1951, **73**, 1182.

[8] Moffitt and Ballhausen, *Ann. Rev. Phys. Chem.*, **1956**, **7**, **107**.

from $[PtCl_4]^{2-}$ to the whole group of ions. While the group-theoretical classification will be different in the lower symmetry groups of many of the molecules, the character of the orbitals involved must be only slightly modified. It follows that the designations such as $d_{xy} \longrightarrow d_{x^2-y^2}$ retain their original meanings.

The establishment of a simple correspondence between the bands of $[PtCl_4]^{2-}$ and $[Pt(NH_3)_2Cl_2]$ allows us further to test our assignments. By working with $[\{(n\text{-}C_5H_{11})_2NH\}_2PtCl_2]$, which has a spectrum closely similar to that of the simple ammine, we can study the effect of different solvents on the absorption bands. The band at 321 mμ is unaffected by the change from hexane to ethanol as solvent (Fig. 4), while those at about 270 mμ and 374 mμ are definitely shifted to longer wavelengths.

The effect of a polar solvent can be understood if it is realised that the positive charge on the Pt^{II} ion will lead to an orientation of the dipole moment of the solvent so that the negative end is close to the molecular plane. This type of residual interaction can even lead to the formation of compounds as Harris, Nyholm, and Stephenson [9] showed in the case of $[Pd(diarsine)_2I_2]$. The presence of very weakly attracted dipolar molecules of this sort makes the d_{z^2}, d_{xz}, and d_{yz} orbitals less stable relative to the d_{xy} and $d_{x^2-y^2}$ orbitals, while affecting the latter pair equally. Thus the $d_{z^2} \longrightarrow d_{x^2-y^2}$ and $d_{xz},d_{yz} \longrightarrow d_{x^2-y^2}$ transitions should show a red shift in a polar solvent, while the $d_{xy} \longrightarrow d_{x^2-y^2}$ transitions should be unchanged.[10] Thus our assignment does predict correctly the red-shift of the 270 mμ and 374 mμ bands and the unchanged position of the 321 mμ band when ethanol is used instead of hexane as a solvent.

Finally we discuss the magnitude of the ligand-field effects. In octahedral complexes of bivalent transition-metal ions of the first series the energy difference between the stable t_{2g} and the less stable e_g orbitals is about 10,000 $cm.^{-1}$. In corresponding complexes of the third transition series somewhat larger values of about 15,000—20,000 $cm.^{-1}$ would be expected. In the complexes which we have studied the spread of the *d*-orbital energies is much greater, perhaps 30,000—40,000 $cm.^{-1}$. Planar Cu^{2+} complexes also have *d*-orbital energy splittings greater than those for similar octahedral complexes. An interpretation of this fact has been suggested.[11]

Our results enable us to make a number of deductions of chemical interest about the electronic structure of platinous and related complexes. First, the fact that there is no sign of a splitting of the $d_{xz},d_{yz} \longrightarrow d_{x^2-y^2}$ transition in *trans*-$[PtCl_2(NH_3)_2]$ suggests strongly that the energy of the $d_{x^2-y^2}$ orbital is much more sensitive to the nature of the ligands than are those of the d_{xz} and d_{yz} orbitals. (One cannot exclude the possibility that the effects of the Cl^- and NH_3 on the d_{xz} or d_{yz} orbitals are large but equal; however this seems improbable in view of the general tendency of NH_3 to produce much greater splittings than does Cl^-.) This implies that electrostatic and σ-bond effects are more important than π-bonding. This conclusion agrees with much qualitative physical and chemical evidence on the nature of the bonding in platinous and related complexes.[3, 12] While we cannot separate rigorously the electrostatic from the σ-bonding effects on the basis of optical spectra, on general grounds we believe the σ-bonding to be important in platinous compounds and responsible for a significant part of the *d*-orbital splitting.

Secondly, the ligand-field splitting is much greater for NH_3 than it is for Cl^-. This is the order found for compounds of the first transition series and also for Rh^{3+} and Ir^{3+} complexes. Furthermore, the observed crystal-field splittings for Br^- are always somewhat smaller than those for Cl^- in corresponding compounds. It seems, therefore, that small ligand-field splittings are characteristic of the heavier halogen ions in all their complexes.

If this generalisation is reliable it raises a very important question. Is it true that chloride complexes tend to be more " covalent " than hydrates or ammines in the sense

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[9] Harris, Nyholm, and Stephenson, *Nature*, 1956, **177**, 1127.

[10] McGarvey, *J. Phys. Chem.*, 1956, **60**, 71.

[11] Orgel, Report of the 10th Solvay Conference in Chemistry, Brussels, 1956.

[12] Ahrland and Chatt, *J.*, 1957, 1379.

implied by Pauling,[13] *i.e.*, do they tend to have low spin values? There does not seem to be any experimental evidence that this is so. Chloride complexes of the second and third sub-group elements such as $[IrCl_6]^{2-}$ have low spin values, but so also do the corresponding hydrates, etc. No significant comparisons have been made for the complexes of the first series in solids or in solution. The magnetic susceptibilities of binary halides are certainly unusual, but in all the cases studied in detail this is due to antiferromagnetic interactions rather than to spin pairing on a single ion. While it is possible that the halides of certain ions will be found to have low spin although the corresponding hydrates have high spin, for example, if delocalisation is much more extensive in the former than in the latter, in the absence of experimental evidence this should not be taken for granted.

The intense absorption which sets in at about 230 mμ for most of these compounds is believed to be connected with charge-transfer and $d \longrightarrow p$ transitions. It will be the subject of a subsequent communication.

EXPERIMENTAL

Microanalyses (C, H, N) are by Messrs. W. Brown and A. G. Olney of these laboratories.

Platinum Complexes.—These were obtained as described in the references.

Potassium chloroplatinite, K_2PtCl_4. Commercial material was recrystallised from 0·75N-hydrochloric acid, washed with ice-cold water, and dried (Found: Pt, 47·00, 46·99. Calc. for Cl_4K_2Pt: Pt, 47·00%).

Potassium amminotrichloroplatinite,[14] $K[NH_3PtCl_3],H_2O$, was recrystallised from water and air dried (Found: H, 1·4; N, 3·8; Pt, 52·0. Calc. for H_5ONCl_3KPt: H, 1·4; N, 3·7; Pt, 51·9%).

cis-Diamminodichloroplatinum,[15] *cis*-$[(NH_3)_2PtCl_2]$, was thrice recrystallised from water (Found: H, 1·95; N, 9·6; Pt, 65·0. Calc. for $H_6N_2Cl_2Pt$: H, 2·0; N, 9·3; Pt, 65·0%). The *trans*-isomer [15] was thrice recrystallised from 0·3N-hydrochloric acid (Found: H, 2·0; N, 9·5; Pt, 64·8%).

Triamminochloroplatinum sulphate,[16] $[(NH_3)_3PtCl]_2SO_4,H_2O$. The corresponding chloride prepared by Tschugaev's method had the correct analysis but was faintly yellow (Found: H, 2·8; N, 13·15. Calc. for $H_9N_3Cl_2Pt$: H, 2·9; N, 13·2%). This colour could not be removed by recrystallisation, and was probably caused by contamination with yellow *trans*-$[(NH_3)_2PtCl_2]$, which may be produced during the recrystallisation. The less soluble sulphate was therefore prepared from the sparingly soluble pink $[(NH_3)_3PtCl]_2[PtCl_4]$ by reaction with boiling silver sulphate solution, and obtained as the white monohydrate after recrystallisation from water (Found: H, 2·95; N, 12·65; Pt, 57·3. Calc. for $H_{20}O_5N_6Cl_2SPt_2$: H, 3·0; N, 12·4; Pt, 57·6%).

Tetra-amminoplatinum chloride,[17] $[(NH_3)_4Pt]Cl_2,H_2O$, recrystallised from 3N-ammonia solution in pure white needles which were dried in air (Found: H, 3·5; N, 15·8; Pt, 55·7. Calc. for $H_{14}ON_4Cl_2Pt$: H, 4·0; N, 15·9; Pt, 55·4%).

trans-Bis(di-*n*-pentylamine)dichloroplatinum, *trans*-$[\{(C_5H_{11})_2NH\}_2PtCl_2]$, was kindly supplied by Dr. L. M. Venanzi who prepared it as follows. *trans*-Bis(dimethyl sulphide)dichloroplatinum (2·0 g.) was suspended in di-*n*-butyl ether (*ca.* 50 c.c.) containing di-*n*-pentylamine (2·3 c.c.) and refluxed (2½ hr.). The hot reaction mixture was filtered, and the yellow *product* separated from the filtrate as it cooled. Recrystallised thrice from light petroleum (b. p. 60—80°), it had m. p. 195—197° (Found: C, 41·15; H, 7·7; N, 4·7. $C_{20}H_{46}N_2Cl_2Pt$ requires C, 41·4; H, 8·0; N, 4·8%).

Measurement of Ultraviolet Absorption Spectra.—These were determined on a Unicam S.P. 500 spectrophotometer, modified to take 10 cm. cells. The spectra of two or three different solutions of each substance were determined. When the solutions were stable the extinction coefficients were accurate to about ±1%. All measurements were made at 23° ± 1°.

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[13] Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, 1945.

[14] Cossa, *Ber.*, 1890, **23**, 2503.

[15] "Handbuch der Präparativen Anorganischen Chemie," Ed. Bauer, Enke, Stuttgart, 1953, p. 1181, Method II.

[16] Tschugaev, *J.*, 1915, 1247.

[17] *Inorganic Syntheses*, 1946, **2**, 250.

The aqueous solutions of K_2PtCl_4 and the ammines, except $[(NH_3)_4Pt]Cl_2$, were not stable and their spectra slowly changed on ageing. These changes were suppressed by hydrochloric acid. They are most probably caused by slow aquations such as those described by Grantham, Elleman, and Martin [18] for the $[PtCl_4]^{2-}$ ion and by K. A. Jensen [19] for the *cis*-diammine, *e.g.*, $[PtCl_4]^{2-} + H_2O \rightleftharpoons [H_2OPtCl_3]^- + Cl^-$. The addition of hydrochloric acid to stabilise the solutions has the danger that chloride ion may add to one or both of the octahedral positions of the platinous complex or replace water molecules already there. This has been observed in solutions containing the $[PdCl_4]^{2-}$ ion,[20] *e.g.*, $[PdCl_4]^{2-} + Cl^- \rightleftharpoons [PdCl_5]^{3-}$. Such reactions should reach equilibrium almost instantaneously. The acid might also abstract ammonia from the ammines, *e.g.*, $[(NH_3)_3PtCl]^+ + HCl \rightleftharpoons [(NH_3)_2PtCl_2] + NH_4^+$, but this reaction should be measurably slow. The fact that 2·0N-hydrochloric acid as solvent gave solutions which were optically stable, or almost so, for the duration of the measurements indicates that neither aquation nor deammination was significant at the the temperatures and concentrations of acid used.

That the addition of chloride ion was also insignificant, if it occurred at all, was shown by observing the wavelengths where the greatest changes in the spectrum of each substance occurred when it was dissolved in pure water. These changes, being reasonably slow, could be accurately extrapolated to zero time. The extrapolated values were in every case identical with those observed in hydrochloric acid solution. General notes on the spectra and stability of the solutions are given below.

Potassium chloroplatinite.[21] Our results are in substantial agreement with those of Babaeva. Solutions of potassium chloroplatinite in 2·0N-hydrochloric acid are stable. Those in weaker acid undergo slow aquation [18] and those in much stronger acid are oxidised to potassium chloroplatinate by air; the rate of oxidation increases with increasing concentration of the acid. The oxidation product was identified by its low solubility and ultraviolet spectrum.

Potassium amminotrichloroplatinite. In neutral solution its spectrum changed for about 19 hr. but in 2·04N-hydrochloric acid the spectrum of a $2{\cdot}76 \times 10^{-3}$M-solution changed only very slowly. The " zero time " spectrum in water and that in 2·04N-hydrochloric acid were in excellent agreement.

cis-*Diamminodichloroplatinum.* In neutral solution the spectrum changed for 7 hr., and it appeared that only one aquated species was formed since there is an isosbestic point at 278 mμ. In 2·0N-hydrochloric acid very little change occurred and in 2·3N-hydrochloric acid the solution was stable. The spectrum in 2·36N-hydrochloric acid was in excellent agreement with the " zero time " spectrum in water.

trans-Diamminodichloroplatinum is so very slightly soluble in water that an accurate spectrum was difficult to obtain, even with 10 cm. cells. It was measured in water by the extrapolation method and in 2N-hydrochloric acid.

Triamminochloroplatinum sulphate. The spectrum of its neutral aqueous solution changed only very slowly as compared with the compounds described above, and so the " zero time " spectrum was obtained accurately without recourse to hydrochloric acid solution.

Tetra-amminoplatinum chloride was stable in neutral aqueous solution and no special precautions were necessary.

trans-*Bis*-(*di*-n-*pentylamine*)*dichloroplatinum.* The spectrum was measured in ethanol and in *n*-hexane (" special for spectroscopy ") to observe the effect of solvent on the spectrum.

The Analysis of the Spectra into Gaussian Curves.—The absorption spectra, plotted on a frequency scale, were analysed into a small number of Gaussian error curves, which are known to approximate closely in shape to single absorption bands of transition-metal salts in solution.[22] In this way absorption bands of low intensity, which are concealed by more intense overlapping bands, can be found. The analysis was carried out by trial and error.

The general equation to the Gaussian in terms of extinction coefficient (ε) and frequency (ν) is $\varepsilon = \varepsilon_{\text{max.}} \exp[-a(\nu - \nu_0)^2]$, where $\varepsilon_{\text{max.}}$, the maximum intensity, occurs at ν_0. Tabulated values of x and z for the equation $z = (2\pi)^{-\frac{1}{2}} \exp(-\frac{1}{2}x^2)$ were taken from mathematical tables,[23]

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[18] Grantham, Elleman, and Martin, *J. Amer. Chem. Soc.*, 1955, **77**, 2965.
[19] Jensen, *Z. anorg. Chem.*, 1939, **242**, 87.
[20] Sundaram and Sandell, *J. Amer. Chem. Soc.*, 1955, **77**, 855.
[21] Babaeva, *Doklady Akad. Nauk S.S.S.R.*, 1943, **40**, 61.
[22] Jørgensen, *Acta Chem. Scand.*, 1954, **8**, 1495 and references therein.
[23] Chambers's Six-figure Mathematical Tables, Vol. II, Natural Values, L. J. Comrie, Chambers, Edinburgh and London, 1949, p. 520.

and the most intense peaks were fitted first (*e.g.*, peaks *A* and then *A'*, Figs. 10 and 11). A trial $\varepsilon_{\text{max.}}$ was chosen (slightly less than the observed $\varepsilon_{\text{max.}}$ if there were neighbouring bands) and the ordinate at $\nu_{\text{max.}} = 0$ to plot the Gaussian curve $\varepsilon = \varepsilon_{\text{max.}} (2\pi)^{\frac{1}{2}}z = \varepsilon_{\text{max.}} \exp(-\tfrac{1}{2}x^2)$. The scale of the abscissa was chosen to give the best fit to the peak of the experimentally observed spectral band independently of the actual frequency scale, so allowing for the constant (*a*). If a good fit is obtained, the band is evidently single, but if the experimental curve deviates from the Gaussian of best fit, the difference between the Gaussian and experimental curve is plotted (*e.g.*, peaks *B*, Figs. 10 and 11) and a Gaussian fitted to the difference curve. Having obtained the best fit to these curves, we can then make a proper allowance for them in fitting the first more intense peaks, and so by repeated approximation the whole absorption curve can be fitted.

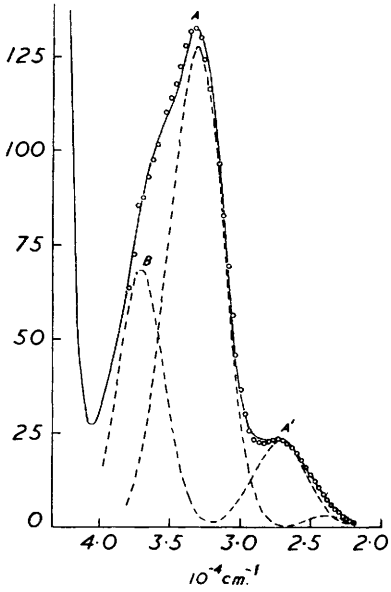

FIG. 10. *Gaussian analysis of the spectrum of* cis-$[(NH_3)_2PtCl_2]$.

——— Experimental. — — — Component Gaussian curves. ○ ○ ○ Sum of Gaussian curves.

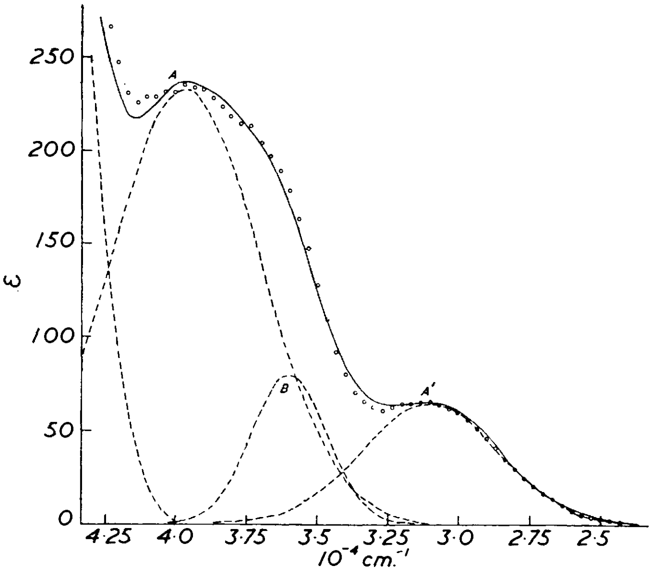

FIG. 11. *Gaussian analysis of the spectrum of* $[(NH_3)_3PtCl]_2SO_4$.

——— Experimental.
— — — Component Gaussian curves.
○ ○ ○ Sum of Gaussian curves.

Generally the experimental curves were fitted remarkably closely by the sum of a small number of Gaussian error curves and Fig. 10 and 11 show the best and the worst fittings respectively.

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