214. *Ligand-field Splittings due to Organic Amines, Phosphines, Arsines, Sulphides, Selenides, and Tellurides.*

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The ultraviolet and visible spectra of a series of complexes of the type *trans*-[L,piperidine$PtCl_2$] have been measured. In these the ligands L are aliphatic amines, phosphines, etc. Their ligand-field splittings, inferred from the energies of the $d_{xy} \longrightarrow d_{x^2-y^2}$ transition, decrease in the sequence $P(OMe)_3 > PPr^n_3 >$ piperidine $> AsPr^n_3 > Et_2S > Et_2Se > Et_2Te$. This is unlikely to be a universal sequence but will depend to some extent on the π-bonding capacities of the metals. The total range of energy of the transitions is small, varying from 33,400 cm.$^{-1}$ in the $P(OMe)_3$ compound to 29,400 cm.$^{-1}$ in its Et_2Te analogue.

Spectra.—While a great deal of information is available concerning the crystal- or ligand-field splittings (Δ) produced by oxygen- and nitrogen-containing ligands, virtually nothing has been written about the corresponding splittings in phosphine, arsine, sulphide, selenide, and telluride complexes. Here we interpret the ligand-field bands in the spectra of a series of planar complexes of the type *trans*-[L,piperidine$PtCl_2$] (Figs. 1—3). In Fig. 4 we reproduce three related spectra which are relevant to the present work.

Interpretation.—In the Table are listed the values of $\lambda_{max.}$, the energy E, and $\varepsilon_{max.}$ for what we believe to be the first spin-allowed transition. This assignment is based on a previous study of the spectra of the platinous chloro-ammines,[1] and the transition is probably that which is predominantly $d_{xy} \longrightarrow d_{x^2-y^2}$. The total range of energy of this transition is seen to be quite small, the $d_{xy} \longrightarrow d_{x^2-y^2}$ transition frequency varying from 33,400 cm.$^{-1}$ in the $P(OMe)_3$ compound to 29,400 cm.$^{-1}$ in the Et_2Te compound. The intensities are undoubtedly substantially higher in these compounds than in the chloro-ammines, but the values given are not very significant, since we have not carried out Gaussian analyses of the spectra.

Wavelength $\lambda_{max.}$, *energy* E, *and intensity* $\varepsilon_{max.}$ *of the first spin-allowed transition in the complex trans*-[L,piperidine$PtCl_2$].

L	$\lambda_{max.}$ (mμ)	E (cm.$^{-1}$)	$\varepsilon_{max.}$	L	$\lambda_{max.}$ (mμ)	E (cm.$^{-1}$)	$\varepsilon_{max.}$
Piperidine	315	31,750	78	Et_2S	330	30,300	136
$P(OMe)_3$	299	33,400	319	Et_2Se	335	29,850	160
PPr^n_3	307	32,600	303	Et_2Te	340	29,400	350
$AsPr^n_3$	321	31,150	310				

Before we draw deductions from these results about the ligand-field splittings in other complexes there are two problems to be considered. First, there is the special problem of extrapolating from planar to octahedral complexes and, secondly, the more general

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[1] Chatt, Gamlen, and Orgel, *J.*, 1958, 486.

FIG. 1.

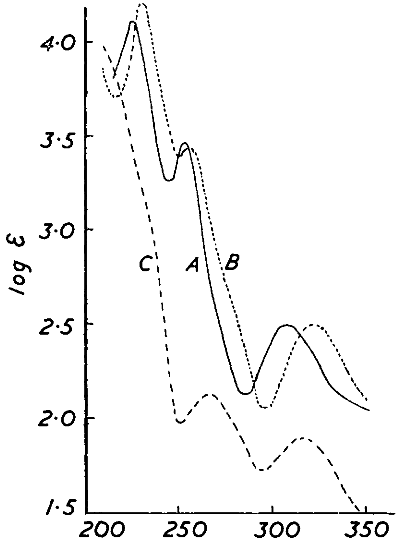

FIG. 2.

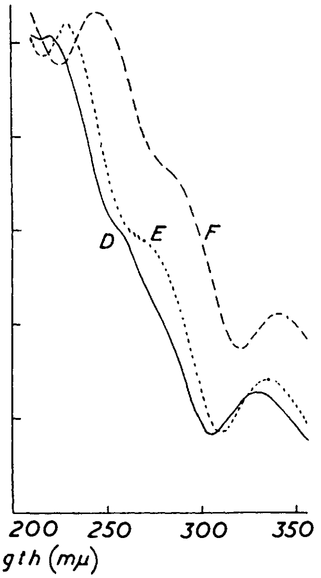

FIG. 1. *Ultraviolet spectra of* (*A*) *trans*-[PPr$^n_3$,pipPtCl$_2$], (*B*) *trans*-[AsPr$^n_3$,pipPtCl$_2$], *and* (*C*) *trans*-[pip$_2$PtCl$_2$].

FIG. 2. *Ultraviolet spectra of* (*D*) *trans*-[Et$_2$S,pipCl$_2$], (*E*) *trans*-[Et$_2$Se,pipPtCl$_2$], *and* (*F*) *trans*-[Et$_2$Te,pipPtCl$_2$].

FIG. 3.

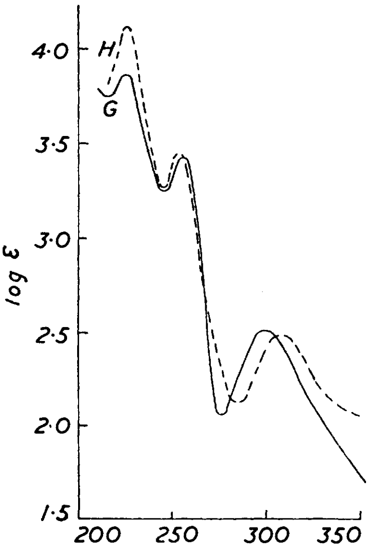

FIG. 4.

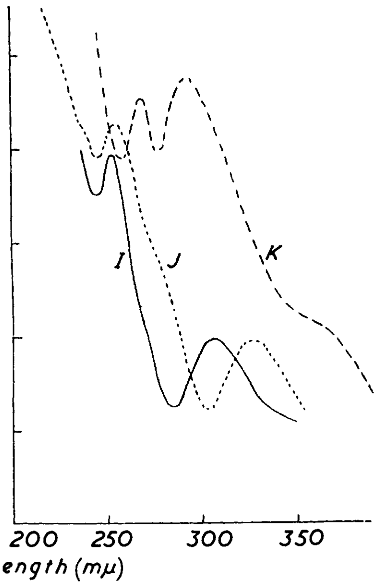

FIG. 3. *Ultraviolet spectra of* (*G*) *trans*-[P(OMe)$_3$,pipPtCl$_2$] *and* (*H*) *trans*-[PPr$^n_3$,pipPtCl$_2$].

FIG. 4. *Ultraviolet spectra of* (*I*) *trans*-[PPr$^n_3$,pipPtCl$_2$], (*J*) *trans*-[PPr$^n_3$,pipPtBr$_2$], *and* (*K*) *trans*-[PPr$^n_3$,pipPtI$_2$].

problem of telling how the relative sizes of the splitting produced by different ligands vary from one metal ion to another.

Fortunately the $d_{xy} \longrightarrow d_{x^2-y^2}$ transition is the one most closely related to the $t_2 \longrightarrow e$ transition (*i.e.*, $d_{xy},d_{yz},d_{zx} \longrightarrow d_{x^2-y^2},d_{z^2}$) of an octahedral complex, because the non-cubic component of the ligand field in a square complex to a first approximation affects the d_{xy} and the $d_{x^2-y^2}$ orbitals equally. The values of E in the Table differ from the energy separation between the $d_{x^2-y^2}$ and the d_{xy} orbitals by an electrostatic energy term which should not vary much from compound to compound.[1] For this reason the results presented probably give reliable information about relative Δ values also for octahedral complexes.

We believe that the fact that Δ is larger for phosphines than for amines indicates that double bonding is important in the former,[2] *i.e.*, that the larger d_{xy}–$d_{x^2-y^2}$ separation is due to the stabilisation of the d_{xy}-orbital by π-bonding rather than the destabilisation of the $d_{x^2-y^2}$-orbital by σ-bonding. This suggestion is supported by the larger separation in the $P(OMe)_3$ than in the PPr^n_3 complex. Presumably the former ligand forms weaker σ- and stronger π-bonds to the Pt^{++} ion and the latter effect is more important than the former.

If we accept this explanation then it is clear that the relative value of Δ for phosphines, etc., compared with that for aliphatic amines must decrease as the d_π donor property of the metal decreases. Thus the order, $P(OMe)_3 > PPr^n_3 >$ piperidine $> AsPr^n_3 > Et_2S > Et_2Se > Et_2Te$, can only be expected to hold for complexes to transition metals in relatively low valencies. In complexes of higher valency the *relative* Δ values for simple amines would increase while in zero-valent compounds it would decrease still further. Nevertheless, it appears that for the heavier ligand atoms in analogous complexes the ligand-field splittings will normally decrease as each Group is ascended, *i.e.*, P > As; S > Se > Te; Cl > Br > I.

The shift of the $d \longrightarrow d$ transitions to lower energy in bromide and iodide complexes relative to that in the chloride complex (Fig. 4) is consistent with the lower Δ values usually found for the heavier halogens.

The intense bands usually beyond 240 mμ we believe to be connected with charge transfer and $d \longrightarrow p$ transitions.

Experimental.—Platinum complexes. The preparation and analysis of the substances used in these experiments have been described by Chatt, Duncanson, and Venanzi.[3]

Measurement of the absorption spectra. These were determined on a Unicam S.P. 500 spectrophotometer modified to take 10 cm. cells,[4] with *n*-hexane " Special for Spectroscopy " as solvent. The solutions were accurately prepared to be about 10^{-3}M, and the spectra measured at 23° ± 1°.

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[2] Cf. Chatt, Duncanson, and Venanzi, *J.*, 1958, 3203, and references therein.

[3] Chatt and Venanzi, *J.*, 1955, 3858; Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461.

[4] Gamlen, Photoelectric Spectrometry Group Bulletin No. 11, 1958, 286.