167. *Ligand Field Strengths of the Halide, Methyl, Phenyl, and Hydride Anions.*

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The visible and ultraviolet spectra of compounds of the formula *trans*-[$RuXY\{C_2H_4(PMe_2)_2\}_2$] ($X = Y =$ Cl, Br, I, or CN; $X =$ H, Me, Ph, or *p*-tolyl, and $Y =$ Cl) have been determined and interpreted to show that the ligand field strengths of hydrogen and the organic groups are large, but less than that of cyanide ion.

Much is known about the relative crystal field (or ligand field) splittings of the halide ions and ligands containing oxygen and nitrogen as ligand atoms,[1,2] but nothing about the splittings caused by methyl or aryl groups and hydrogen atom when they take the place of anions in transition-metal complexes.

This arises because very few transition-metal complexes containing these groups as anionic ligands are known and even fewer provide the required information. However, the recently discovered alkyl, aryl, and hydrido-complexes of ruthenium [3] furnish useful material and here we record and discuss the ultraviolet spectra (Figs. 1—3) of the compounds *trans*-[$RuXY\{C_2H_4(PMe_2)_2\}_2$] ($X = Y =$ Cl, Br, I, CN; $X =$ H, Me, Ph or *p*-tolyl, and $Y =$ Cl).

It will be seen that the spectra have a number of intense bands at <340 mμ and in the case of the dihalides a further weak band ($\varepsilon < 100$) was resolved from the main bands. In the methyl, aryl, and hydrogen complexes the weak band has undergone a hypsochromic shift so that in the methyl and aryl compounds it is partially obscured by the intense bands and in the hydride it is completely obscured. By Gaussian analysis of the spectra,[4] the weak band in the methyl complex has been found exactly, and that in the phenyl complex rather less accurately, owing to an intense overlapping band ($\varepsilon_{max.}$ 8000). These " weak " bands are more intense than usual for internal *d–d*-transitions, but this may be due to mixing of the energy levels with those corresponding to the neighbouring intense bands. In the hydrogen complex, it is only possible to place a lower limit of 27,500 cm.$^{-1}$ on the energy of the weak band. In the spectra of the dichloro- and dibromo-complexes, the weak band fits a single Gaussian curve.

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[1] Jorgensen, Report on the 10th Solvay Conference in Chemistry, Brussels, 1956.
[2] Orgel, (*a*) *J. Chem. Phys.*, 1955, **23**, 1004; (*b*) *J.*, 1952, 4756.
[3] Chatt and Hayter, *Proc. Chem. Soc.*, 1959, 153, and unpublished work.
[4] Chatt, Gamlen, and Orgel, *J.*, 1958, 486.

The intense bands may be due to charge transfer and for the present study only the weak singlet bands (see Table) are of interest.

Wavelength ($\lambda_{max.}$; mμ), *energy E* (cm.$^{-1}$), *and intensity* ($\varepsilon_{max.}$) *of the lowest-energy singlet transition in the complexes* trans-[MXY{$C_2H_4(PMe_2)_2$}$_2$] (M = Ru, Os).

Compound	$\lambda_{max.}$	*E*	ε	Solvent
For M = Ru:				
X = Y = Cl	407	24,600	—	n-Hexane
	411	24,300	56	Benzene
	417	24,000	56	Ethanol
X = Y = Br	435	23,000	64	Ethanol
X = Y = I	455	22,000	87	Ethanol
X = Me, Y = Cl	348 *	28,700	123·5	Ethanol
X = Ph, Y = Cl	<344 *†	>29,100	280	Benzene
X = *p*-tolyl, Y = Cl	<352 †‡	>28,400	280	Benzene
X = H, Y = Cl	<364 *†	>27,500	—	n-Hexane
For M = Os:				
X = Y = Cl	350	28,600	88	Ethanol

* Estimated from Gaussian analysis. † These analyses consisted of complex overlapping bands, so that the values, although safely upper limits, are not certain. ‡ Estimated by comparison with corresponding phenyl compound.

Interpretation.—The ruthenium(II) complexes under study are diamagnetic and isoelectronic in the valency shell with cobalt(III) complexes. Thus their spectra should have two weak bands ($^1\Gamma_4$ and $^1\Gamma_5$) due to the forbidden $t_{2g} \longrightarrow e_g$ transition if all the ligand atoms were identical. In fact, our complexes are of the type *trans*-[RuA_4B_2] and *trans*-[RuA_4BC], so that we may expect the lower energy band ($^1\Gamma_4$) to be split in two.[2b] The amount of splitting is determined by the differences in the sum of the crystal-field contributions along each axis.[5] For the dihalogen complexes, these differences are probably large and the completely resolved band (Fig. 1) will be the lower-energy component $^1\Gamma_{5t}$. If we assume that the partly obscured band in the spectrum of the dichloro- and dibromo-complexes is the higher-energy component $^1\Gamma_{2t}$, the splitting is 9000—10,000 cm.$^{-1}$ and, in any case, this represents a lower limit. This splitting is larger than is observed for related complexes, where the differences between the ligands are less marked, for example, *trans*-[$CoCl_2(NH_3)_4$]$^+$ (5100 cm.$^{-1}$) and *trans*-[$CoCl_2$ en$_2$]$^+$ (6400 cm.$^{-1}$).[6]

The spectrum of the corresponding osmium complex, *trans*-[$OsCl_2${$C_2H_4(PMe_2)_2$}$_2$] (Fig. 3) was also examined. However, the separation between the weak and intense bands was too small to permit the determination of the relative ligand-field splittings of the hydride and organic anions. The singlet $\longrightarrow$ triplet transition expected to accompany the $^1\Gamma_4$ singlet $\longrightarrow$ singlet transition was, in general, not observed in the spectra of the ruthenium complexes. It was, however, visible in the spectrum of the osmium compound as a weak shoulder ($\varepsilon \sim 13$) on the low-energy side of the weak resolved band. This accords with the general observation that the triplet band is more intense in the complexes of the very heavy metals.

Discussion.—The very large hypsochromic shift (>4100 cm.$^{-1}$) of the low-energy band when chlorine is replaced by alkyl or aryl as ligand indicates the much greater ligand-field strengths of the organic groups than of chloride ion. Similarly, the replacement of chlorine by hydrogen caused a shift of at least 2900 cm.$^{-1}$, indicating that the latter also has a strong ligand field. A direct comparison between, say, methyl and cyanide ion is not possible owing to failure to prepare a *trans*-halide cyanide. However, a rough estimate of the minimum energy of the $^1\Gamma_{5t}$ transition in the (unknown) complex *trans*-[RuCl·CN{$C_2H_4(PMe_2)_2$}$_2$] can be made from the spectra of the corresponding dicyano- and dichloro-complexes, since ligand-field effects in mixed complexes can be averaged.[1] The weak band in *trans*-[$Ru(CN)_2${$C_2H_4(PMe_2)_2$}$_2$],H_2O probably does not occur at any energy lower than that corresponding to $\varepsilon = 50$ (34,400 cm.$^{-1}$) in its spectrum. This fixes

[5] Basolo, Ballhausen, and Bjerrum, *Acta Chem. Scand.*, 1955, **9**, 810, and references therein.

[6] Linhard and Weigel, *Z. anorg. Chem.*, 1952, **271**, 101.

the minimum energy for the corresponding band in the chloride cyanide at $\frac{1}{2}(34{,}400 + 24{,}000) = 29{,}200$ cm.$^{-1}$, which is close to, but greater than, that of the lowest-energy band in the spectrum of the methyl complex (28,700 cm.$^{-1}$). It appears that the methyl group, although it has a large ligand field strength, is weaker than cyanide ion.

Now the position of a ligand in the spectrochemical series is determined[1] mainly by the ligand atom nearest to the metal, the ligand field strength increasing halogen $<$ O $<$ N $<$ C. The current results indicate that alkyl and aryl groups as ligands may be grouped with cyanide, previously the only ligand with carbon as ligand atom to have been placed in the series. The higher ligand field strength of cyanide ion might be attributed to its capacity to form double bonds with metals such as ruthenium(II). Nevertheless the identity of the ligand atom itself, as required by the older electrostatic concept of crystal field theory, must be a major factor, since methyl, which could not form strong double bonds, has a high strength. This suggests that all ligands with carbon as ligand atoms may have high ligand field strengths.

Ultraviolet and visible spectra.

FIG. 1. FIG. 2. FIG. 3.

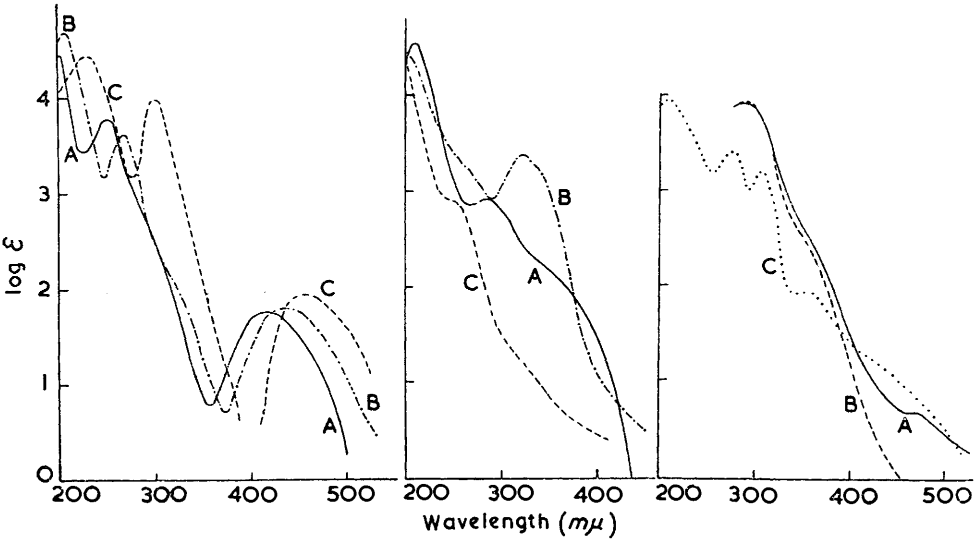

FIG. 1. *trans*-[RuXY{$C_2H_4(PMe_2)_2$}$_2$]: A, X = Y = Cl; B, X = Y = Br; C, X = Y = I. (All in EtOH.)

FIG. 2. *trans*-[RuXY{$C_2H_4(PMe_2)_2$}$_2$]: A, X = Me, Y = Cl (in EtOH); B, X = H, Y = Cl (in n-hexane); C, X = Y = CN (in EtOH).

FIG. 3. *trans*-[MXY{$C_2H_4(PMe_2)_2$}$_2$]: A, M = Ru, X = Cl, Y = *p*-tolyl (in C_6H_6); B, M = Ru, X = Cl, Y = Ph (in C_6H_6); C, M = Os, X = Y = Cl (in EtOH).

Experimental.—Preparation of the compounds studied in this paper will be detailed later.[3]

The spectra were measured on a Unicam S.P. 500 spectrophotometer with n-hexane ("Special for Spectroscopy"), absolute ethanol (Burrough's), and benzene (dried with calcium chloride and by distillation from phosphorus pentoxide) as solvents. The solutions were accurately prepared to be about 10^{-3}M and the spectra measured at 21° ± 1°.

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