Rotatory Dispersions and Circular Dichroisms of Platinum(II) Complexes

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For square-planar complexes, various schemes for orbital energies have been proposed (Fig. 1), but they all make the practical assignment of the absorption bands of platinum(II) complexes difficult. Several attempts have been made to overcome this problem,1) but it still remains unsolved.

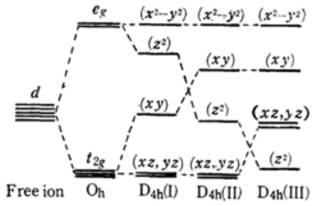

Fig. 1. Probable modes of orbital splitting in square-planar D_{4h} complex.

TABLE I. THE SYMMETRIES OF THE EXCITED STATES, THE MAGNETIC MOMENT AND THE ELECTRIC MOMENT BROUGHT ABOUT BY STRETCHING VIBRATIONS (D_{4h})

	Excited configuration	Magnetic polarization	Vibronic (stretching) polarization
$d_{xy} \rightarrow d_{x^2-y^2}$	A_{2g}	μ_z	r_x, r_y
$d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$	E_g	μ_x, μ_y	r_x, r_y, r_z
$d_{z^2} \rightarrow d_{x^2-y^2}$	B_{1g}	—	r_x, r_y

We have measured the R. D. and C. D. spectra of platinum(II) complexes containing *l*-propylenediamine and studied the splitting of the d orbitals on the basis of an analysis of these spectra. Table I shows the symmetries of the excited states, the magnetic moment, and the electric moment brought about by stretching vibrations for a planar complex with D_{4h} symmetry.

It can be seen that only the $d_{xy} \rightarrow d_{x^2-y^2}$ and d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ transitions have magnetic moments. In the former transition, however, the electric moment and the magnetic moment are perpendicular to each other. This selection rule still holds for symmetries lower than D_{4h}, so far as the stretching vibration alone is considered. Therefore, only the transition to the E_g state should be optically active.

The maxima of the absorption frequencies and the $\varepsilon_l - \varepsilon_r$ values are shown in Table II. The C. D. spectra due to the vicinal effects of propylenediamine have positive signs in all the complexes studied. The fact that only the bands 2 and 4 are optically active supports the idea that both transitions are $A_{1g} \rightarrow E_g$ ($d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$), the lower frequency band involving the triplet, and the other, the singlet state. The ordering of D_{4h}(III) in Fig. 1 can account for these results. The rotatory strength of [Pt *l*-pn$_2$]Cl$_2$ is just twice that of [Pt *l*-pn en]Cl$_2$. This indicates that the magnitude of the Cotton effect due to the vicinal effect is proportional to the number of optically active ligands; there is no apprecialle interaction between the ligands.

TABLE II. EXPERIMENTAL RESULTS

	Band 1		Band 2				Band 3		Band 4			
	Absorption*		Absorption*		C. D.*		Absorption*		Absorption*		C. D.*	
	ν_{max}	log ε	ν_{max}	log ε	ν_{max}	$\varepsilon_l - \varepsilon_r$	ν_{max}	log ε	ν_{max}	log ε	ν_{max}	$\varepsilon_l - \varepsilon_r$
K$_2$[PtCl$_4$]	~18	~0.7	21.0	1.18			25.7	1.78	30.5	1.80		
[PtCl$_2$ *l*-pn]			27.3	1.56	27.0	0.15	33.1	2.37	~37	2.10	37.2	0.38
[Pt *l*-pn$_2$]Cl$_2$			35.7	1.65	35.7	0.54	41.6	1.00**	44.6	2.68	45.2	1.03
[Pt *l*-pn en]Cl$_2$			35.7	1.61	35.7	0.29	~41.7		44.6	2.65	45.1	0.54
[Pt *l*-pn(NH$_3$)$_2$]Cl$_2$			35.2	1.60	35.2	0.22	~41.4		45.3	2.64	44.8	0.51

* ν in 10^3 cm^{-1}, ** Obtained from Gaussian analysis

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1) J. Chatt, G. A. Gamlen and L. E. Orgel, *J. Chem. Soc.*, **1958**, 486; R. F. Fenske, D. S. Martin, Jr., and K. Ruedenberg, *Inorg. Chem.*, **1**, 411 (1962); H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963); D. S. Martin, Jr., and C. A. Lenhardt, *Inorg. Chem.*, **3**, 1368 (1964); D. S. Martin, Jr., M. A. Tucker and A. J. Kassman, ibid., **4**, 1682 (1965); D. S. Martin, Jr., J. G. Foss, M. E. McCarville, M. A. Tucker and A. J. Kassman, ibid., **5**, 491 (1966).