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Magnetic Circular Dichroism and Electronic States of Tetrachloroplatinate(II) and Tetrachloropalladate(II) Ions

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The magnetic circular dichroism (MCD) spectra of K_2PtCl_4 and K_2PdCl_4 have been carefully remeasured over the visible-near UV region. The examination of the electronic absorption and the MCD spectra together with their Gaussian analyses strongly suggests that the band of K_2PtCl_4 at $30.3\times10^3\,cm^{-1}$ contains both $\Gamma_5(^1E_g)$ and $\Gamma_3(^1B_{1g})\leftarrow\Gamma_1(^1A_{1g})$ transitions, and the band of K_2PdCl_4 at $21.1\times10^3\,cm^{-1}$ all three spin-allowed d-d transitions. The separation of the $\Gamma_2(^1A_{2g})$ and $\Gamma_5(^1E_g)$ excited states is considerably large with K_2PtCl_4 as compared with K_2PdCl_4. The MCD for the high-intensity absorption bands in K_2PtCl_4 is different from that reported previously. On the basis of new MCD result, the bands at 43.3 and $46.6\times10^3\,cm^{-1}$ have been assigned to d-p transitions, $a_{2u}(p_z)\leftarrow a_{1g}(d_{z^2})$ and $e_g(d_{xz,yz})$, respectively.

The solution MCD spectrum of K_2PtCl_4 was obtained firstly by D. S. Martin, Jr. *et al.*[1] for the d-d transition region, and then by McCaffery *et al.*[2] over the visible-near UV spectral region. That of K_2PdCl_4 was measured partly by the latter group. We have reinvestigated the spectra of these two compounds carefully in order to clarify the electronic states of square-planar complexes, providing more reliable spectra over a broader wave number range.

The electronic states of $PtCl_4^{2-}$ and $PdCl_4^{2-}$ have been studied most extensively by solution, single-crystal, and polarized single-crystal absorption spectra, and moreover polarized single-crystal reflection and MCD spectra, as well as ligand field and molecular orbital theories, angular overlap treatments, and so on; then several different spectral assignments have been made (Tables 1 and 2). One of the major problems remaining unsettled is the position of the d_{z^2} metal orbital, and another is the origins of the high-intensity bands of $PtCl_4^{2-}$. This paper intends to throw light on these problems, together with the assignments of the other bands, consistent with many experimental facts given by previous workers.

Experimental

Materials. Potassium tetrachloroplatinate(II) was purchased from Higuchi Chemical Labolatory Ltd., and was recrystallized from an aqueous solution containing hydrochloric acid.

Potassium tetrachloropalladate(II) was prepared from palladium chloride and potassium chloride.

Measurements. Electronic absorption spectra were recorded with a Hitachi 330 spectrophotometer, and MCD spectra with a JASCO MOE-1 spectropolarimeter in a magnetic field of 1.5 T, being remeasured with inversion of magnetic field in order to obtain a greater precision.[30] Spectral measurements of K_2PtCl_4 and K_2PdCl_4 were made in 0.50 M and 2.0 M HCl aqueous solutions, respectively, at room temperature (1 M=1 mol dm^{-3}).

Gaussian Analyses. Gaussian analyses of absorption and MCD curves were performed using a version of program LGNS[31] adapted to the ACOS computer system. In the MCD curve analysis of K_2PtCl_4, the spectrum was divided into two parts (22.0×10^3—$26.4\times10^3\,cm^{-1}$ and 26.0×10^3—$34.2\times10^3\,cm^{-1}$) in order to keep a precision in weak bands. An A term was analyzed as two B terms with opposite signs. All the calculations were carried out at Computation Center, Osaka University.

Results and Discussion

Ligand-field Absorption Bands. In a square-planar d^8 system (D_{4h}) without spin-orbit coupling, the d-d transitions ($d_{x^2-y^2}\leftarrow d_{xy}$, $d_{xz,yz}$, and d_{z^2}) give rise to six excited states: $^{1,3}A_{2g}$, $^{1,3}E_g$, and $^{1,3}B_{1g}$. These states are split and scrambled under spin-orbit coupling into 12 excited states.

$$d_{x^2-y^2}\longleftarrow d_{xy}\ \begin{cases}^3A_{2g}(\Gamma_1+\Gamma_5)\\ ^1A_{2g}(\Gamma_2)\end{cases},$$

$$d_{x^2-y^2}\longleftarrow d_{xz,yz}\begin{cases}^3E_g(\Gamma_1+\Gamma_2+\Gamma_3+\Gamma_4+\Gamma_5)\\ ^1E_g(\Gamma_5)\end{cases},$$

$$d_{x^2-y^2}\longleftarrow d_{z^2}\ \begin{cases}^3B_{1g}(\Gamma_4+\Gamma_5)\\ ^1B_{1g}(\Gamma_3)\end{cases}.$$

1) K_2PtCl_4: Absorption and MCD data are given in Fig. 1 and Table 3. The assignment of the band at $25.6\times10^3\,cm^{-1}$ has been well established ($\Gamma_2(^1A_{2g})\leftarrow\Gamma_1(^1A_{1g})$) by the polarized absorption spectra.[6—9,28] The band at $30.3\times10^3\,cm^{-1}$ has been assigned to $\Gamma_5(^1E_g)\leftarrow\Gamma_1(^1A_{1g})$ by the MCD spectrum[1,2] and the polarization properties[6,9,28] (Table 1). By careful examination of the band shape, it is found to be unsymmetrical (Figs. 1 and 2), which suggests that there is another component in the higher energy side. The MCD spectrum also

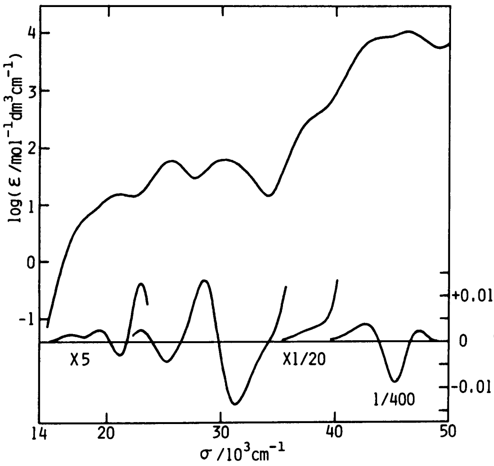

Fig. 1. Absorption and MCD spectra of K_2PtCl_4 in 0.50 M HCl.

TABLE 1. PREVIOUS SPECTRAL ASSIGNMENTS OF K_2PtCl_4 (Wave numbers/10^3 cm^{-1})[a]

Ref. No.[b]	1[c]	2	3	4	5	6	7	8	9	Note
3		17.7 $^3A_{2g}$	21.0 ^3E_g		25.5 $^1A_{2g}$	30.2 ^1E_g	37.9		46 d-p	in 2M HCl
4			[21.6] [22.0] $^3B_{1g}$ $^3A_{2g}$		25.5f $^1A_{2g}$	[29.2] $^1B_{1g}$				LF[d] f: fixed value
5		$^3A_{2g}$	$^1A_{2g}$		$^1B_{1g}$	^1E_g	sfCT[e]		$^1A_{2u}$	MO
6			20.4xy[f] 20.2z $^1B_{1g}$		25.7xy $^1A_{2g}$	28.9xy 29.2z ^1E_g				PAS[g] (r.t.)[h]
7		17.5 17.3xy $^3A_{2g}$	20.4 20.4xy 20.2z $^3E_g/^3B_{1g}$		27.0 26.0xy $^1A_{2g}$	29.0 28.5xy 29.3z $^1E_g/^1B_{1g}$	36.5 $^1B_{1g}/^1E_g$	42.5 $^1A_{2u}$		[i] PAS(r.t.)
8	16.9xy 17.2z Γ_1	18.1xy $\Gamma_2+\Gamma_5$	20.8xy 20.7z $\Gamma_3+\Gamma_5$	24.0xy 23.9z $\Gamma_5(^3B_{1g})$	26.1xy $^1A_{2g}$	29.3xy 29.9z $^1B_{1g}$	^1E_g			PAS(5K)
9	Γ_1	18.0xy 17-19z $\Gamma_2+\Gamma_5$	20.9xy 20.6z $\Gamma_3+\Gamma_5$	24.0xy 24.1z Γ_1	26.3xy $^1A_{2g}$	29.2xy 29.8z ^1E_g	[36.4] $\Gamma_5(^3B_{1g})$		[46.3] $^1B_{1g}$	PAS(15K) [ ]: LF
1						^1E_g				MCD
10	[15.7-16.8] $\Gamma_1+\Gamma_2+\Gamma_5$ [16.8-17.4] $\Gamma_5+\Gamma_1$	[18.2] Γ_2	[19.6-22.1] $\Gamma_3+\Gamma_5+\Gamma_1$ [19.6-20.7] $\Gamma_5+\Gamma_3$	[24.2] $\Gamma_5(^3B_{1g})$ [23.7-24.1] $\Gamma_1+\Gamma_5$	[26.4] $^1A_{2g}$ [26.7] $^1A_{2g}$	[29.6] ^1E_g [29.7] [29.9] $^1B_{1g}$ ^1E_g	[35.3] $^1B_{1g}$			A[j] LF B[j]
11					$^1A_{2g}$					induced CD
12		^3E_g	$^3A_{2g}$	$^3B_{1g}$	$^1A_{2g}$	^1E_g	$^1B_{1g}$	$^1A_{2u}+^1E_u(\pi)$		MO
13			[20.2] [21.8] $^1A_{2g}$ ^1E_g			[29.1] $^1B_{1g}$		[40.4] [42.0] $^1B_{1u}{}^p$ $^1E_u{}^p$	[49.2] $^1A_{2u}{}^p$	MO
14		$^3A_{2g}$	21.0 ^3E_g		25.7 $^1A_{2g}$	30.5 ^1E_g	38.3 ofCT[k]	43.9 $^1A_{2u}+^1E_u(\pi)$	46.5 $^1E_u(\sigma)$	in 2M HCl
15		$^3A_{2g}$	^3E_g	$^3B_{1g}$	$^1A_{2g}$	^1E_g	$^1B_{1g}$		$^1A_{2u}$	[l]
16		17.5 ^3E_g	20.2 $^3A_{2g}$		24.8 $^1A_{2g}$	29.5 ^1E_g	37.0 $^1B_{1g}$		44.1 $^1A_{2u}+^1E_u(\pi)$	in CH_3CN (77K)
2					25.5 $^1A_{2g}$	30.3 ^1E_g		43.4 $^1A_{2u}+^1E_u(\pi)$	46.2 $^1A_{2u}{}^p$	in 0.5M HCl MCD
18		$^3A_{2g}$	^3E_g		$^1A_{2g}$	^1E_g	$^1B_{1g}$	$^1A_{2u}+$ $^1E_u(\pi)/^1E_u{}^p$	$^1A_{2u}$ $/^1A_{2u}{}^p$	review
19								$^1A_{2u}{}^p+^1A_{2u}$	$^1E_u{}^p$	MCD calcn
20	17 $\Gamma_5(^3E_g)$	18 $\Gamma_4(^3E_g)$	20.5 $\Gamma_{5,1}(^3A_{2g})$	24.3 $\Gamma_5(^3B_{1g})$	26.3 $^1A_{2g}$	29.6 ^1E_g	>33 $^1B_{1g}$			single crystal (4K)
21							36.5xy 36.5z $^1B_{1g}$			PAS(15K)
22				[23.4-24.2] $^3A_{2g}+^3E_g$	[28.2] [29.1] $^1A_{2g}$ $^3B_{1g}$	[30.7] ^1E_g	[35.5] $^1B_{1g}$	[37.1-38.7] $^1E_u(\pi)+$ $^1A_{2u}$	[44.4] $^1E_u(\sigma)+$ $^1E_u{}^p$	MO

TABLE 1. (Continued)

Ref. No.[b)]	1[c)]	2	3	4	5	6	7	8	9	Note
23								[43.6] $^1A_{2u}^p$	[44.3] ^1E_u	polarized reflection
24					$^1A_{2g}$	^1E_g	$^1B_{1g}$			oscillator strength
27	m)				$^1A_{2g}$	28.5 29.3 $^1B_{1g}$ ^1E_g	$^1B_{1u}^p$	$^1E_u^p$	$^1A_{2u}^p$	ligand substitution and l)
28	17.5z $\Gamma_{4,5}(^3B_{1g})$	18.0xy	20.9xy 20.7z $^1B_{1g}$	24.0xy 24.0z $\Gamma_2+\Gamma_5(^3A_{2g})$	26.2xy $^1A_{2g}$	28.7xy 29.3z ^1E_g				PAS(10K)
29	[17.1] Γ_1	[18.0] $\Gamma_2+\Gamma_5$	[20.8] [21.0] Γ_5 Γ_3	[24.3] $\Gamma_5(^3B_{1g})$	[26.0] $^1A_{2g}$	[30.2] ^1E_g	[34.2] $^1B_{1g}$			AOM

a) Superscripts p's denote d-p transitions; bracketed values represent calculated ones (the remains all experimental ones). b) References are arranged chronologically. c) Band number. d) Ligand field theory. e) A spin-forbidden charge transfer. f) xy: In-plane polarized; z: out-of-plane polarized. g) Polarized single-crystal absorption spectra. h) Room temperature. i) Diffuse reflectance spectrum. j) See Ref. 10. k) An orbitally-forbidden charge transfer. l) Assigned on the basis of experimental facts reported before that time. m) As alternative B in Ref. 10.

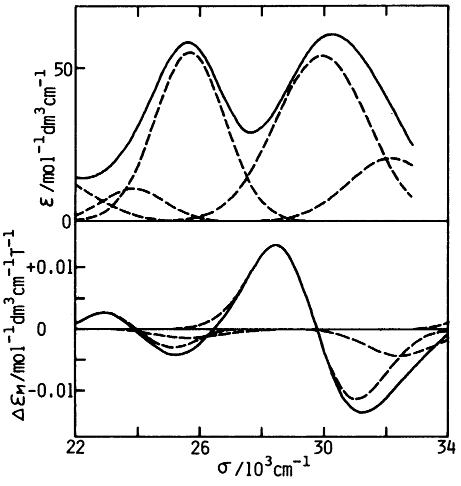

Fig. 2. Gaussian analyses of K_2PtCl_4. ------ : Gaussian components and —— : sum of them. The sum fits in very closely with the experimental curve to such an extent that it is impossible to show the difference between them in this figure. An A-term curve is given by a sum of two B terms with opposite signs (See Experimental). Standard deviations are 0.11 $mol^{-1} dm^3 cm^{-1}$ for the absorption curve, and 3.4×10^{-5} (in $(22.0—26.4)\times10^3 cm^{-1}$) and 1.3×10^{-4} $mol^{-1} dm^3 cm^{-1} T^{-1}$ (in $(26.0—34.2)\times10^3$ cm^{-1}) for the MCD one.

suggests the presence of a positive B term for the component. The results of Gaussian analyses for the absorption and MCD curves support this expectation (Fig. 2 and Table 5).[32)] It seems reasonable to assign the component to the third spin-allowed d-d transition, $\Gamma_3(^1B_{1g})\leftarrow\Gamma_1(^1A_{1g})$.

Gaussian analysis of the absorption curve indicates the existence of a minor component under the lower edge of the band at 25.6×10^3 cm^{-1}. This component has been detected in the polarized single-crystal spectra at liquid helium temperature,[8,9,28)] and assigned to $\Gamma_5(^3B_{1g})\leftarrow\Gamma_1(^1A_{1g})$. The MCD exhibits a negative A term in the transition region (Fig. 1), compatible with an assignment to a degenerate excited state; moreover it has the same sign as the A term for the $\Gamma_5(^1E_g)$ state with which the excited state is mixed. This interpretation can explain the MCD band at 22.9×10^3 cm^{-1} near the valley of the absorption spectrum, and leads to the result that the MCD band at 25.2×10^3 cm^{-1} primarily consists of the negative part of the negative A term for $\Gamma_5(^3B_{1g})\leftarrow\Gamma_1(^1A_{1g})$ rather than the positive B term for $\Gamma_2(^1A_{2g})\leftarrow\Gamma_1(^1A_{1g})$ as mentioned previously.[2)] Thus the latter is considerably smaller than the appearance (Fig. 2 and Table 5). This is consistent with the fact that the MCD under the absorption band at 30.3×10^3 cm^{-1} resembles that in the spin-allowed d-d transition region of K_2PdCl_4, very closely in shape, or the ratio of the positive band to the negative one (*vide infra*, Figs. 1 and 3).

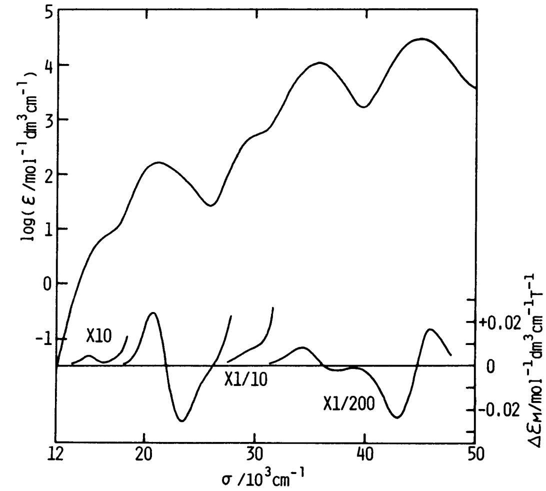

Fig. 3. Absorption and MCD spectra of K_2PdCl_4 in 2.0 M HCl.

TABLE 2. PREVIOUS SPECTRAL ASSIGNMENTS OF K_2PdCl_4 (Wave numbers/10^3 cm^{-1})[a)]

Ref. No.[b)]	1[c)]	2	3	4	5	6	7	8	Note
5		16.7 $^1A_{2g}$	21.5 $^1B_{1g}$	23.3 ^1E_g			36.0 $^1A_{2u}$	44.9 $^1E_u(\pi)$	nujol mull[d)] MO
7		18.0 18.0xy[f)] 17.0z $^3E_g/^3B_{1g}$	21.5 20.0xy $^1A_{2g}$	22.6xy 23.0z $^1E_g/^1B_{1g}$		31.5 29.5xy $^1B_{1g}/^1E_g$	36.5		i) PAS[g)] (r.t.)[h)]
12		$^3B_{1g}$	$^1A_{2g}$	^1E_g		$^1B_{1g}$	$^1A_{2u}+^1E_u(\pi)$	$^1E_u(\sigma)$	MO
14		^3E_g	21.0 $^1A_{2g}$	23.7 ^1E_g		30.5 ofCT[k)]	35.7 $^1A_{2u}+^1E_u(\pi)$	45.1 $^1E_u(\sigma)$	in 1M HCl
15		^3E_g	$^1A_{2g}$	^1E_g		$^1B_{1g}$	$^1A_{2u}$		l)
2			21.1 ^1E_g			30.2	35.8 $^1A_{2u}+^1E_u(\pi)$	44.9 $^1E_u(\sigma)$	in 2M HCl MCD
17		17.7xy 17.2z $^3A_{2g}+^3E_g$	21.0xy $^1A_{2g}$	22.5xy 23.3z ^1E_g	28.5xy $^3B_{1g}$	33.0xy $^1B_{1g}$	intense xy 37.3z $^1A_{2u}+^1E_u$		PAS (12K)
19								$^1E_u(\pi)$	MCD calcn
22			[20.2] [21.0] $^3A_{2g}$ ^3E_g	[25.8] $^3B_{1g}$	[28.2] $^1A_{2g}+^1E_g$	[34.7] $^1B_{1g}+^1E_u(\pi)$	[37.1] $^1A_{2u}$	[43.6–46.0] $^1E_u(\pi\text{-s},\sigma,\text{d-p})$[e)]	MO
23							36.8 $^1E_u(\pi)$	41.5 $^1E_u(\sigma)$	polarized reflection
25	15.4	17.0 17.7xy 17.0z $^3A_{2g}+^3E_g$	20.8 21.7xy $^1A_{2g}$	22.4 23.2xy 23.2z ^1E_g		30.1 j)	35.7 40.8 intense xy 37.4z $^1E_u(\pi)+^1A_{2u}$	45.0 $^1E_u(\sigma)$	in 2M KCl PAS(15K)
26		17.5 18.9 $\Gamma_1(^3A_{2g})+\Gamma_5(^3B_{1g})$	20.5 21.5 $^1A_{2g}$	23.3 22.5 25.6 ^1E_g j)	28.0 28.9 $^1B_{1g}$		35.8 ^1E_u		single crystal (4K) in Cs_2ZrCl_6 (2K)
27		$^3A_{2g}+^3E_g$	$^1A_{2g}$	22.6 23.0 $^1B_{1g}$ ^1E_g	$^1B_{2g}$(CT)		$^1A_{2u}+^1E_u(\pi)$	$^1E_u(\sigma)$	ligand substitution and l)
28		17.7xy 17.1z $\Gamma_{4,5}(^3B_{1g})$	21.8xy $^1A_{2g}$	23.4xy 23.4z $^1B_{1g}$		^1E_g			PAS(10K)
29		[17.9] $\Gamma_5(^3B_{1g})$	[21.1] $^1A_{2g}$	[23.4] ^1E_g	[26.8] $^1B_{1g}$				AOM

a—c, f—i, k, l) As in Table 1. d) For the bands 7 and 8, in an aqueous solution containing Cl^-. e) π-s: $Pd(5s)\leftarrow Cl(\pi)$. j) Not $PdCl_4^{2-}$.

The assignments for the bands at *ca.* 18×10^3 and 21×10^3 cm^{-1} are not straightforward because of many possibilities of spin-triplet excited states, the MCD spectrum also indicating the presence of more than two components in the region. However, it is likely that these bands are tentatively assigned to $\Gamma_1(^3A_{2g}+^3E_g)+\Gamma_2(^3E_g)+\Gamma_5(^3A_{2g}+^3E_g)$ and $\Gamma_3(^3E_g)+\Gamma_5(^3A_{2g}+^3E_g)$ respectively, on the basis of the polarized absorption spectra[9,11)] and the available energy calculations.[10,29)] (The Γ_4 components arising from $^3B_{1g}$ and ^3E_g are expected to have almost zero intensity since no Γ_4 state is produced from spin- or orbitally-allowed one-electron-transitions with close transition energies).

2) K_2PdCl_4: In general, square-planar palladium(II) complexes have remarkably reduced intensities of the spin-triplet transitions relative to those of the spin-singlet ones, in comparison with the platinum analogs; so, for simplicity we may neglect spin-orbit coupling for palladium(II) complexes in a discussion of the electronic states.

Absorption and MCD data are given in Fig. 3 and Table 4. The shoulder centered at *ca.* 16.9×10^3 cm^{-1} is roughly assigned to the spin-forbidden d-d transitions, $^3A_{2g}$, ^3E_g, and/or $^3B_{1g}\leftarrow{}^1A_{1g}$. Further details of these transitions will not be discussed.

The main band with a peak at 21.1×10^3 cm^{-1} is apparently unsymmetrical, which indicates the presence of transition components more than one. The MCD under the band is very similar to that for the band at 30.3×10^3 cm^{-1} of K_2PtCl_4 as described in the

TABLE 3. ABSORPTION AND MCD DATA OF K_2PtCl_4

σ_{max} $10^3 cm^{-1}$	ε $mol^{-1} dm^3 cm^{-1}$	σ_{ext} $10^3 cm^{-1}$	$\Delta\varepsilon_M$ $mol^{-1} dm^3 cm^{-1} T^{-1}$
18.5sh$^{a)}$	7.2	16.7	+0.0003
		19.3	+0.0005
21.03	15.4	21.1	−0.0006
		22.9	+0.0026
25.62	58.3	25.2	−0.0042
30.31	61.7	28.5	+0.014
		31.2	−0.014
38.4sh	380	38.3sh	+0.06
43.5sh	7600	42.6	+1.5
46.19	10000	45.2	−3.6
		47.3	+0.90

a) sh: shoulder (ε is for the value of σ given).

TABLE 4. ABSORPTION AND MCD DATA OF K_2PdCl_4

σ_{max} $10^3 cm^{-1}$	ε $mol^{-1} dm^3 cm^{-1}$	σ_{ext} $10^3 cm^{-1}$	$\Delta\varepsilon_M$ $mol^{-1} dm^3 cm^{-1} T^{-1}$
16.8sh$^{a)}$	8.7	15.0	+0.0005
21.11	162	20.7	+0.024
		23.3	−0.025
30.0sh$^{b)}$	510	29.7sh	+0.075
35.73$^{c)}$	10400	34.2	+1.7
		37.3	−0.44
44.92$^{d)}$	28000	42.9	−4.7
		45.9	+3.3

a) sh: shoulder (ε is for the value of σ given). b) $^1B_{2g} \leftarrow {}^1A_{1g}$ (CT). c) $^1A_{2u} + {}^1E_u(\pi) \leftarrow {}^1A_{1g}$. d) $^1E_u(\sigma) \leftarrow {}^1A_{1g}$.

previous section. From this observation it is reasonable to consider that the band at 21.1×10^3 cm^{-1} includes the same transition components (^1E_g and $^1B_{1g} \leftarrow {}^1A_{1g}$) as the latter band. The cross point (or zero point) of the apparent A term exists at higher energy than the absorption peak; therefore, it can be predicted that there is another absorption component at lower energy than the cross point. Then the component should correspond to the band at 25.6×10^3 cm^{-1} of K_2PtCl_4, being assigned to the $^1A_{2g} \leftarrow {}^1A_{1g}$ transition. This prediction is supported by the polarized absorption spectra.[17,25] The MCD for the transition is expected to be considerably weak from a comparison between two MCD curves of the Pd and Pt compounds in the spin-allowed d-d transition region.

The absorption band at 21.1×10^3cm^{-1} consequently contains all three spin-allowed d-d transitions. On the basis of this conclusion, the Gaussian analyses of the absorption and MCD curves were carried out (Fig. 4), the numerical data being given in Table 5 together with the assignments. These are compatible with the polarized absorption spectra.[17,25]

3) Comparison of Two Compounds: The electronic structures of the two compounds are different in two points. Firstly, the separation of the $\Gamma_2(^1A_{2g})$ and $\Gamma_5(^1E_g) \leftarrow \Gamma_1(^1A_{1g})$ transitions is considerably large with K_2PtCl_4 as compared with K_2PdCl_4. This seems to be primarily due to the high π-bonding character of Pt-Cl over Pd-Cl bonds.[29] Secondly, the electronic spectrum of K_2PtCl_4 exhibits a structure in the region of the spin-triplet transitions, for which the MCD is also complicated. This fact can be attributed to the substantial spin-orbit coupling. In K_2PdCl_4 the electronic and MCD spectra are simplified because of a minor spin-orbit coupling as assumed previously.

Considering the above two points, the absorption and MCD spectra of K_2PdCl_4 can be easily correlated with those of K_2PtCl_4 and in fact they correspond to each other very well. That the $\Gamma_3(^1B_{1g}) \leftarrow \Gamma_1(^1A_{1g})$

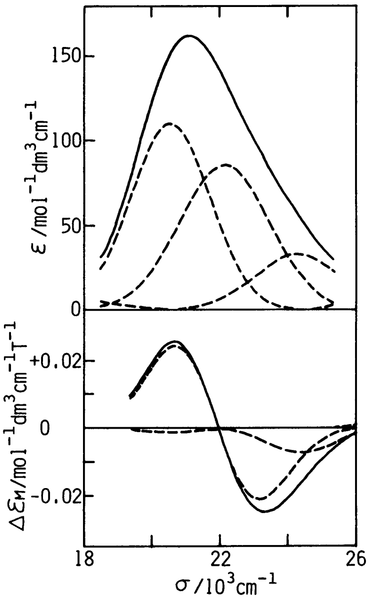

Fig. 4. Gaussian analyses of K_2PdCl_4. See the figure caption of Fig. 2. Standard deviations are 0.27 mol^{-1} dm^{3}cm^{-1} and 2.1×10^{-4} mol^{-1}dm^{3}cm^{-1}T^{-1} for the absorption and MCD curves, respectively.

Table 5. The results of Gaussian analyses for K_2PtCl_4 and K_2PdCl_4

Absorption					MCD			
σ_{max}	ε	$\Delta\sigma_{1/2}$ a)	S b)	σ_{ext}	$\Delta\varepsilon_M$	$\Delta\sigma_{1/2}$	Term	Assignments
10^3 cm^{-1}	mol^{-1} dm^3 cm^{-1}	10^3 cm^{-1}		10^3 cm^{-1}	mol^{-1} dm^3 cm^{-1} T^{-1}	10^3 cm^{-1}		$\leftarrow\Gamma_1(^1A_{1g})$
			K_2PtCl_4					
21.00f c)	15.2f	3.41	55.1	21.10f	−0.0006	1.39		d)
23.84	10.6	2.38	26.8	22.95 25.15	+0.0027 −0.0030	1.59 1.77	−A	$\Gamma_5(^3B_{1g})$
25.67	55.1	2.68	157	25.67f	−0.0014	2.67	+B	$\Gamma_2(^1A_{2g})$
29.92	54.0	3.49	201	28.64 30.77	+0.0155 −0.0127	2.47 2.69	−A	$\Gamma_5(^1E_{1g})$
32.11	20.5	3.24	70.8	32.41	−0.0042	2.67	+B	$\Gamma_3(^1B_{1g})$
43.28	6330	3.25	21900				−B	$^1A_{2u}$(d-p)
46.54	9470	3.60	36300				+A	^1E_u(d-p)
			K_2PdCl_4					
16.90f	8.1f	3.60	31.0					$^3A_{2g}$, ^3E_g, $^3B_{1g}$
20.55	109.8	2.74	320	20.54	−0.0013	2.27	+B	$^1A_{2g}$
22.14	85.2	3.13	284	20.86 22.97	+0.0283 −0.0233	2.32 2.48	−A	^1E_g
24.27	33.1	2.92	103	24.38	−0.0073	2.33	+B	$^1B_{1g}$

a) Half-value widths. b) Band area=1.0645×(ε_{max}/mol^{-1} dm^3 cm^{-1})×($\Delta\sigma_{1/2}$/10^3 cm^{-1}). c) f: Fixed values. d) See text.

transition has never been evidently identified seems to be ascribed to its low intensity, which is valid for both compounds (Figs. 2 and 4, and Table 5). A combination of this deduction with the data of the polarized single-crystal absorption spectra[9,28] leads to the following result: the low transition-probability with in-plane polarized light is responsible for the low intensity of the $\Gamma_3(^1B_{1g})\leftarrow\Gamma_1(^1A_{1g})$ transition, at least in K_2PtCl_4. That is to say, the transition does not largely couple with the e_u molecular vibration, but with the b_{2u} one to gain the intensity. This interpretation can also explain the difference in the peak-positions at *ca.* 29—30×10^3 cm^{-1} between the in- and out-of-plane polarized spectra,[8,9,28] which had been a troublesome problem in an assignment of the absorption bands. In brief, the band at 29.2×10^3 cm^{-1} in the in-plane polarized spectrum[9] is composed mainly of the $\Gamma_5(^1E_g)\leftarrow\Gamma_1(^1A_{1g})$ transition, whereas the band at 29.8×10^3 cm^{-1} in the out-of-plane polarized spectrum[9] includes the $\Gamma_3(^1B_{1g})\leftarrow\Gamma_1(^1A_{1g})$ transition to a considerable extent in addition to the $\Gamma_5(^1E_g)\leftarrow\Gamma_1(^1A_{1g})$ one. As to K_2PdCl_4, a similar discussion cannot be made owing to the smaller splitting between the $^1A_{2g}$ and $^1E_g+^1B_{1g}\leftarrow{}^1A_{1g}$ transitions.[17,25]

High-intensity Absorption Bands. 1) *K_2PtCl_4*: The MCD above 35×10^3 cm^{-1} is different from that reported by McCaffery *et al.*[2] in two substantial points. First, they had observed a shoulder at *ca.* 44×10^3 cm^{-1}, whereas we have never detected it in spite of careful measurements. Secondly, they had observed a positive B term coinciding with the absorption peak at 46.2×10^3 cm^{-1}; however, we have done a positive A term corresponding to the absorption peak. From the facts that we have measured the MCD spectrum in the same solvent as used by McCaffery *et al.*, and that no difference is found between both absorption spectra; low resolving power of their CD instrument seems to have precluded accurate recordings.

The Gaussian analysis of the absorption curve above 42×10^3 cm^{-1} indicates the presence of absorption components at *ca.* 43.3×10^3 cm^{-1} and 46.5×10^3 cm^{-1} (Table 5). McCaffery *et al.* assigned the 43.3×10^3-cm^{-1} band to $^1A_{2u}+{}^1E_u(\pi)\leftarrow{}^1A_g$ ($b_{1g}(d_{x^2-y^2})\leftarrow b_{2u}(\pi)+e_u(\pi)$), and the 46.5×$10^3$-cm^{-1} one to $^1A_{2u}\leftarrow{}^1A_{1g}$ ($a_{2u}(p_z)\leftarrow a_{1g}(d_{z^2})$) (Fig. 5). Kroening *et al.*[21] and Elding and Olsson[27] assigned the former band to $^1E_u\leftarrow{}^1A_{1g}$ ($a_{2u}(p_z)\leftarrow e_g(d_{xz,yz})$). Both assignments are based on the MCD result of McCaffery *et al.*; however, these assignments should be reconsidered from the situation described above.

The main band at 46.6×10^3 cm^{-1} shows an A-term MCD, which requires an assignment to a degenerate

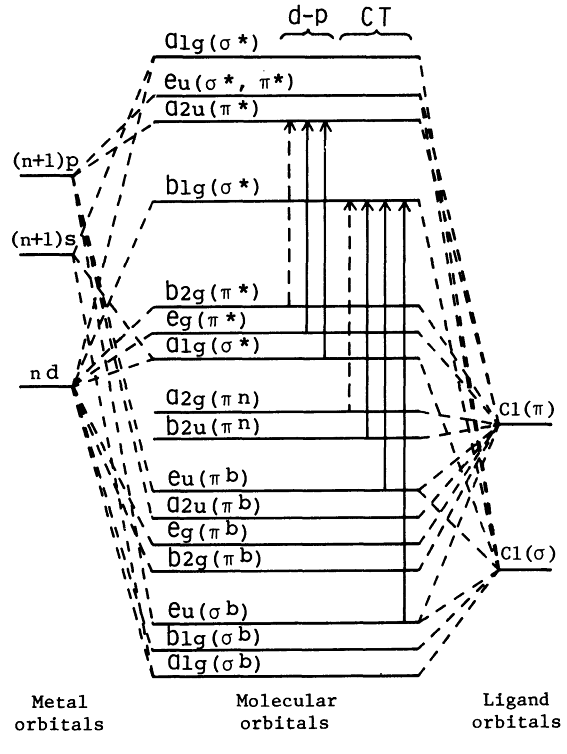

Fig. 5. Relative molecular orbital energy levels for square-planar MCl_4^{2-} complexes (D_{4h}). In a d^8 system, the $b_{2g}(\pi^*)$ and all the orbitals below it are doubly occupied. Transitions to be considered in the assignments of high-intensity bands are shown with full-drawn (for allowed transitions) and dashed (for orbitally-forbidden ones) arrows.

excited state. Considering simply, there are three candidates: $b_{1g}(d_{x^2-y^2}) \leftarrow e_u(\sigma)$, $b_{1g}(d_{x^2-y^2}) \leftarrow e_u(\pi)$, and $a_{2u}(p_z) \leftarrow e_g(d_{xz,yz})$ (Fig. 5). This band is the lowest dipole-allowed transition correlated to a degenerate excited state, and a $b_{1g} \leftarrow e_u(\sigma)$ transition generally occurs in higher energy than the corresponding $b_{1g} \leftarrow e_u(\pi)$ one; therefore the assignment to the former is excluded. In K_2PdCl_4 a negative A term has been observed for the $b_{1g} \leftarrow e_u(\pi)$, transition (*vide infra*). If this is the case with K_2PtCl_4, the assignment to it is also excluded, since the MCD for the band of interest exhibits a positive A term. On the other hand, the band which has been assigned to $a_{2u} \leftarrow e_g$ in $[Pt(NH_3)_4]^{2+}$,[33,34] $[Pt(en)_2]^{2+}$,[34] and $[Pt(tn)_2]^{2+}$,[34] shows a positive A term. Thus, the band at 46.6×10^3 cm^{-1} can be reasonably assigned to the d-p transition, $a_{2u} \leftarrow e_g$ (Fig. 5).

The component at 43.3×10^3 cm^{-1} shows a B-term MCD. Although it is impossible to say definitely that the band exhibits only a B term from the MCD feature alone, the polarized reflection spectra by Anex and Takeuchi[23] indicate the existence of an out-of-plane polarized band with an in-plane polarized one in the region under consideration; therefore, the band should be assigned to a $^1A_{2u} \leftarrow {}^1A_{1g}$ transition. There are two transitions which agree with the excited state: $b_{1g}(d_{x^2-y^2}) \leftarrow b_{2u}(\pi)$ and $a_{2u}(p_z) \leftarrow a_{1g}(d_{z^2})$ (Fig. 5). In K_2PdCl_4 the former transition has a remarkably low intensity as a dipole-allowed transition,[25] as expected for a pure $\sigma^* \leftarrow \pi$ transition by Jφrgensen.[35] If this is also the case with K_2PtCl_4, the band at 43.3×10^3 cm^{-1} is too intense to be assigned to $b_{1g} \leftarrow b_{2u}$. The assignment $a_{2u} \leftarrow a_{1g}$, combined with that of the band at 46.6×10^3 cm^{-1} seems at a glance to be inconsistent with the corresponding d-d transitions. However, this might be rationalized by the difference in interelectronic repulsion and configuration interaction between the d-d and d-p transitions.[25] Particularly, the $^1A_{2u}(p_z \leftarrow d_{z^2})$ excited state is presumed to be lowered in energy by configuration interaction with the $^1A_{2u}(b_{1g}(d_{x^2-y^2}) \leftarrow b_{2u}(\pi))$ one close to it.[21] Therefore, the band at 43.3×10^3 cm^{-1} is also assigned to a d-p transition ($a_{2u} \leftarrow a_{1g}$; Fig. 5).

The above assignments are not in conflict with the experimental results of Anex and Takeuchi,[23] who observed two bands, of which one is out-of-plane and the other is in-plane polarized around 44×10^3 cm^{-1}, the former occurring in lower energy. This order of two components agrees with our assignment. In the previous assignments,[23,27] the 43.3×10^3-cm^{-1} band in solution had been correlated with the higher-energy band (at 44.3×10^3 cm^{-1}) in crystal, and the 46.6×10^3-cm^{-1} band in solution with the lower-energy one (at 43.6×10^3 cm^{-1}) in crystal; then the difference in their relative positions between solution and crystal spectra had been explained by exciton theory.[23] However, our assignment makes the explanation needless.

Finally, the assignment of the shoulder at *ca.* 38×10^3 cm^{-1} remains. Most of the previous workers have assigned it to a d-d transition ($^1B_{1g} \leftarrow {}^1A_{1g}$). On the other hand, Gray and Ballhausen[5] have done it to a spin-forbidden charge-transfer (CT) transition, Ito *et* al.[14] to an orbitally-forbidden d-p one ($a_{2u}(p_z) \leftarrow b_{2g}(d_{xy})$; Fig. 5). In addition to these, there is also a possibility of a spin-forbidden d-p transition. The assignment to a d-d transition is easily excluded on the basis of the discussion made in the previous section. The MCD for the shoulder shows a negative B term, resembling apparently that for the band at *ca.* 29×10^3 cm^{-1} of K_2PdCl_4 (Figs. 1 and 3). However, the shoulder seems to be too remote from a dipole-allowed ligand-to-metal CT band (which is absent below 50×10^3 cm^{-1}) to be assigned to the orbitally-forbidden CT transition ($b_{1g}(d_{x^2-y^2}) \leftarrow a_{2g}(\pi)$) as in K_2PdCl_4 (*vide infra*). A similar difficulty arises for the possible assignment to a spin-forbidden CT transition. The single-crystal polarized spectra by Kroening *et al.*[21] have shown a band at *ca.* 36.5×10^3 cm^{-1} in both polarizations. The band has so low intensity that it is not likely to have the same origin as the shoulder at 38×10^3 cm^{-1} in solution. Their data suggest that the neighboring band at higher energy which is presumed to correspond to the shoulder also appears in both polarizations. If the presumption is valid, the assignment to the orbitally-forbidden d-p transition ($a_{2u} \leftarrow b_{2g}$) is unreasonable. It is because that the transition is vibronically allowed by a coupling only with the b_{2g} molecular vibration, being out-of-plane polarized. On the other hand, the assignment to a spin-forbidden d-p transition can be a candidate if spin-orbit coupling is taken into account, although the assignment cannot explain the very simple MCD feature. As has been discussed so far, the assignment of the shoulder at 38×10^3 cm^{-1} is still ambiguous and thus further details will be deferred.

2) K_2PdCl_4: It has been found that both bands at 35.7 and 44.9×10^3 cm^{-1} are in-plane polarized, by the polarized reflection spectra;[23] and that in addition, the former includes a $^1A_{2u}$ component, by the polarized absorption spectra.[17,25] The MCD result is consistent with these facts. Therefore, the lower-energy band can be assigned to $^1A_{2u} + {}^1E_u(\pi) \leftarrow {}^1A_{1g}$ ($b_{1g}(d_{x^2-y^2}) \leftarrow b_{2u}(\pi) + e_u(\pi)$), and the higher-energy one to $^1E_u(\sigma) \leftarrow {}^1A_{1g}$ ($b_{1g} \leftarrow e_u(\sigma)$) (Fig. 5). In view of MCD, the $^1A_{2u}$, $^1E_u(\pi)$, and $^1E_u(\sigma) \leftarrow {}^1A_{1g}$ transitions correspond to a negative B term, a negative A term, and a positive A term, respectively.

The assignments to be considered for the shoulder at *ca.* 29×10^3 cm^{-1} are ones to spin-forbidden and orbitally-forbidden CT transitions.[14,27] In K_2PdBr_4 there is another band, which is assigned to a spin-forbidden CT transition,[25] in addition to the band corresponding to the shoulder of K_2PdCl_4; thus, the former assignment is excluded. The orbitally-forbidden CT transition ($b_{1g} \leftarrow a_{2g}$) is expected to be allowed *via* an e_u vibration, being in-plane polarized. This has been confirmed for the shoulder,[7,17] which supports the latter assignment.

The above all assignments (Tables 4 (footnotes) and 5) have been made on the basis of our MCD data and many experimental ones reported by previous workers. The study on the electronic spectra of square-planar complexes (particularly palladium(II)) with nitrogen and oxygen in addition to chlorine as coordinating atoms will be reported in the near future.

References

1) D. S. Martin, Jr., J. G. Foss, M. E. McCarville, M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, **5**, 491 (1966).

2) A. J. McCaffery, P. N. Shatz, and P. J. Stephens, *J. Am. Chem. Soc.*, **90**, 5721 (1968).

3) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, **1958**, 486.

4) R. F. Fenske, D. S. Martin, Jr., and K. Ruedenberg, *Inorg. Chem.*, **1**, 441 (1962).

5) H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963).

6) D. S. Martin, Jr., and C. J. Lenhardt, *Inorg. Chem.*, **3**, 1368 (1964).

7) P. Day, A. F. Orchard, A. J. Thomson, and R. J. P. Williams, *J. Chem. Phys.*, **42**, 1973 (1965).

8) O. S. Mortensen, *Acta Chem. Scand.*, **19**, 1500 (1965).

9) D. S. Martin, Jr., M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, **4**, 1682 (1965).

10) D. S. Martin, Jr., M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, **5**, 1298 (1966).

11) B. Bosnich, *J. Am. Chem. Soc.*, **88**, 2606 (1966).

12) H. Basch and H. B. Gray, *Inorg. Chem.*, **6**, 365 (1967).

13) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **6**, 369 (1967).

14) H. Ito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **40**, 2584 (1967).

15) P. Day, M. J. Smith, and R. J. P. Williams, *J. Chem. Soc., A*, **1968**, 668.

16) W. A. Mason, III and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 5721 (1968).

17) E. Francke and C. Moncuit, *C. R. Acad. Sci., Ser. B*, **271**, 741 (1970).

18) D. S. Martin, Jr., *Inorg. Chim. Acta Rev.*, **5**, 107 (1971).

19) H. Kato, *Bull. Chem. Soc. Jpn.*, **45**, 1281 (1972).

20) H. H. Patterson, J. J. Godfrey, and S. M. Khan, *Inorg. Chem.*, **11**, 2872 (1972).

21) R. F. Kroening, R. M. Rush, D. S. Martin, Jr., and J. C. Clardy, *Inorg. Chem.*, **13**, 1366 (1974).

22) R. P. Messmer, L. V. Interrante, and K. H. Johnson, *J. Am. Chem. Soc.*, **96**, 3847 (1974).

23) B. G. Anex and N. Takeuchi, *J. Am. Chem. Soc.*, **96**, 4411 (1974).

24) C. Moncuit, *Theor. Chim. Acta*, **39**, 255 (1975).

25) R. M. Rush, D. S. Martin, Jr., and R. G. Legrand, *Inorg. Chem.*, **14**, 2543 (1975).

26) T. G. Harrison, H. H. Patterson, and J. J. Godfrey, *Inorg. Chem.*, **15**, 1291 (1976).

27) L. I. Elding and L. F. Olsson, *J. Phys. Chem.*, **82**, 69 (1978).

28) W. Tuszynski and G. Gliemann, *Z. Naturforsch., A*, **34**, 211 (1979).

29) L. G. Vanquickenborne and A. Ceulemans, *Inorg. Chem.*, **20**, 796 (1981).

30) H. Kobayashi, M. Shimizu, and Y. Kaizu, *Bull. Chem. Soc. Jpn.*, **43**, 2321 (1970).

31) D. B. Siano and D. E. Metzler, *J. Chem. Phys.*, **51**, 1856 (1969).

32) When the band at 30.3×10^3 cm^{-1} was assumed to consist of only one component, the Gaussian curve did not fit in very closely with the experimental one, and furthermore the half-value width was too wide compared with those of other components.

33) H. Isci and W. R. Mason, *Inorg. Nucl. Chem. Lett.*, **8**, 2321 (1972).

34) K. Nakayama, T. Komorita, and Y. Shimura, unpublished work.

35) C. K. Jϕrgensen, *Prog. Inorg. Chem.*, **12**, 130 (1970).