

Some Spectroscopic Properties of Platinum(II) and Palladium(II) Complexes of Aryl Alkyl Sulfides

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Compounds of the $MCl_2(R-S-R_1)_2$ type, where $M = Pt(II)$ and $Pd(II)$, $R = methyl$ and $R_1 = phenyl, o-, m-, p-tolyl$, have been prepared. The trans-structure for some of these compounds was characterized by IR, Raman and ^1H-NMR measurements. Electronic spectra of the mentioned compounds in solid state and solutions were studied. Molecular orbital diagrams were developed for $MCl_2(pms)_2$ where $pms = phenylmethylsulfide$.

The electronic spectra were in reasonable agreement with the proposed diagrams, thus clarifying the electronic structure of the compounds. The shifting of the ligand to metal electron transfer (LMET) transition due to factors such as complex central atoms and different radicals bounded to the sulfur atom, supplied important information, making the interpretation of the data previously obtained from palladium(II) compounds possible. It was also possible to situate the phenylmethylsulfide in the spectrochemical series indicating stronger π bonding and weaker σ bonding for aryl alkyl sulfide complexes as compared to the alkyl sulfide complexes.

Introduction

Electronic spectra of platinum(II) and palladium(II) compounds with aryl alkyl sulfides as ligands have been briefly studied [2, 3].

On previous occasions it was observed that in the palladium(II) compounds the intense band in the near ultraviolet region shifted with the change of aryl or alkyl radicals of the ligands [4]. Now, the characterization of the electronic structure of these compounds, including platinum(II) compounds, was done in order to interpret those facts.

Semi-empirical molecular orbital calculations have been made to determine the energies of the molecular orbital of the nickel(II) maleonitriledithiolate [5], dithioacetylacetonate [6] complexes and others. The optical spectra for these compounds

have been interpreted on the basis of the molecular orbital calculations, and the electronic spectra for analogous complexes of platinum(II) and palladium(II) have been interpreted using as a model a molecular orbital diagram calculated for nickel(II) compounds.

In this work, the interpretation of the electronic spectra data was made on the basis of molecular orbital diagrams that were developed for $MCl_2(pms)_2$ where $M = Pt(II), Pd(II)$. These diagrams were evolved bearing in mind the information for the MCl_4^- ions which have been obtained from self-consistent-field $X\alpha$ -scattered wave calculations (SCF- $X\alpha$ -SW) [7], and the order of energy level provided by photoelectronic spectra for phenylmethylsulfide [8].

Experimental

Materials

The ligands aryl alkyl sulfides were obtained by usual methods [9, 10] or from commercial samples (Eastman Kodak), distilled at low pressure until pure.

BDH tetrachloroplatinate was used to prepare platinum(II) compounds and K & K palladium chloride was used to prepare palladium(II) complexes.

The solvents used to prepare and to recrystallize the complexes were Carlo Erba or Baker.

The solutions for absorption spectra were prepared using acetonitrile and n-hexane spectral grade (Merck-Uvasol).

Preparation of the Complexes

The complexes $PtCl_2L_2$ ($L = phenylmethylsulfide (pms), o-tolylmethylsulfide (o-tms), p-tolylmethylsulfide (p-tms), m-tolylmethylsulfide (m-tms)$) were prepared by the method described by Haake and Turley [11]. The resulting compounds were pale yellow.

TABLE I. Analytical Data.^a

Compounds	M.p. Interval °C	% C		% H		% S		Yield %
		Calcd.	Found	Calcd.	Found	Calcd.	Found	
PtCl ₂ (<i>o</i> -tms) ₂ ^a	154–155	35.4	35.3	3.7	3.6	11.8	11.8	94
PtCl ₂ (<i>p</i> -tms) ₂ ^a	172–176	35.4	35.4	3.7	3.5	11.8	11.7	65
PtCl ₂ (<i>m</i> -tms) ₂ ^b	120–123	35.4	35.1	3.7	3.6	11.8	11.9	81
PdCl ₂ (<i>o</i> -tms) ₂ ^b	141–146	42.3	42.6	4.4	4.7	14.1	14.3	99
PdCl ₂ (<i>p</i> -tms) ₂ ^b	137–139	42.3	42.8	4.4	4.4	14.1	14.1	99
PdCl ₂ (<i>m</i> -tms) ₂ ^b	90–93	42.3	42.0	4.4	4.2	14.1	14.7	99

^aCompounds analysed at the microanalytical laboratory, "Alfred Bernhardt", West Germany.

^bCompounds analysed at the microanalytical laboratory, Instituto de Química-USP.

The complexes PdCl₂L₂ (L = pms, *o*-tms, *p*-tms, *m*-tms) were prepared according to the procedure described by Mann and Purdue [12]. The products were recrystallized from acetone and they were intense yellow.

Analytical data of the compounds obtained for the first time are given in Table I.

Physical Measurements

Electronic spectral data were obtained using a Cary model 17 recording spectrophotometer in the region ranging from 190 to 780 nm for the following compounds: ligands (L = pms, *o*-tms, *p*-tms, *m*-tms) and complexes MCl₂L₂ (M = Pt(II), Pd(II)). The spectra of the solid were obtained by fluorolube mull technique using Hellma 106-QS cells with path length of 0.50 and 0.10 mm [13].

Acetonitrile solution spectra of platinum(II) complexes about 10⁻³ to 10⁻⁴ M were obtained using Hellma 110-QS cells with path length of 1.0 mm and Hellma 114-QS cells with path length of 10.0 mm. For palladium(II) compounds and ligands spectra acetonitrile solutions about 10⁻⁴–10⁻⁵ M, in Hellma 110-QS cells with path length of 1.0 mm, were used.

In *n*-hexane, these compounds have low solubility; the accurate determination of the concentration becomes quite difficult by the usual way. To overcome this problem, a method of determination of the concentration of the studied compounds in *n*-hexane was developed. After recording the spectra of *n*-hexane saturated solutions, the solvent was evaporated and the residue redissolved quantitatively in acetonitrile. The spectrum was recorded again and since the molar absorptivity was known, the concentration of the complex could be calculated.

The infrared spectra were recorded with a Perkin-Elmer model 180 spectrophotometer, using Nujol mulls for the complexes between CsI and polyethylene plates.

The Raman spectra of the solid samples were recorded by a Jarrel-Ash model 25-300 Raman laser

spectrometer, using an argon ion laser (514.5 nm) for excitation.

The N.M.R. spectra were obtained using a Varian T-60 spectrometer at 60 MHz with Me₄Si as an internal standard. Deuteriochloroform was used as a solvent.

Results and Discussion

Characterization of Trans-Structure of MCl₂(pms)₂

For palladium(II) complexes of this type, the *trans*-structure has been proposed [2, 14] through IR and Raman spectroscopy. For the platinum(II) complexes there is evidence of *cis*- and *trans*-isomers and the identification of these isomers was the subject of some studies [15, 16]. For *cis*- complexes with point group C_{2v} there is expected from group-theory analysis one symmetrical stretching ν_s(Pt–Cl) and one antisymmetrical stretching ν_{as}(Pt–Cl) with activity coincident in both infrared and Raman. For *trans*-complexes with point group D_{2h} one expects one symmetrical ν_s(Pt–Cl) Raman active, and one antisymmetrical stretching ν_{as}(Pt–Cl) infrared active. These bands are easily identified because they are very strong. Accordingly, the results obtained indicate a *trans*-structure for PtCl₂(pms)₂. The values for the stretching frequencies ν_s(Pt–Cl) and ν_{as}(Pt–Cl) are respectively 334 cm⁻¹ (R) and 341 cm⁻¹ (IR); these data are in agreement with those of Reed [3] who found 332 (R) and 341 cm⁻¹ (IR).

Proton nuclear magnetic resonance techniques were also used to identify the *cis*- or *trans*-isomers for platinum(II) complexes of the PtCl₂L₂ type where L = dimethylsulfide, dibenzylsulfide, diethylsulfide and phenylmethylsulfide [11, 16–18].

Platinum presents the isotope ¹⁹⁵Pt (I = 1/2) and it is possible to observe the coupling J_{Pt-S-CH}. The spectra of ¹H-NMR show a doublet superimposed to a singlet leading to three peaks with intensity ratios

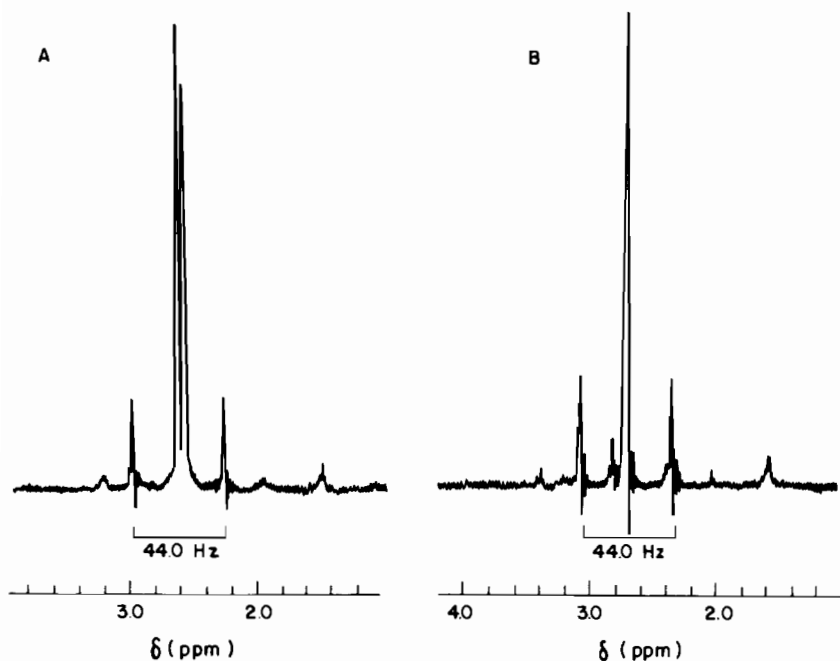


Figure 1. Proton nuclear magnetic resonance spectra. A) $\text{PtCl}_2(o\text{-tms})_2$, B) $\text{PtCl}_2(pms)_2$.

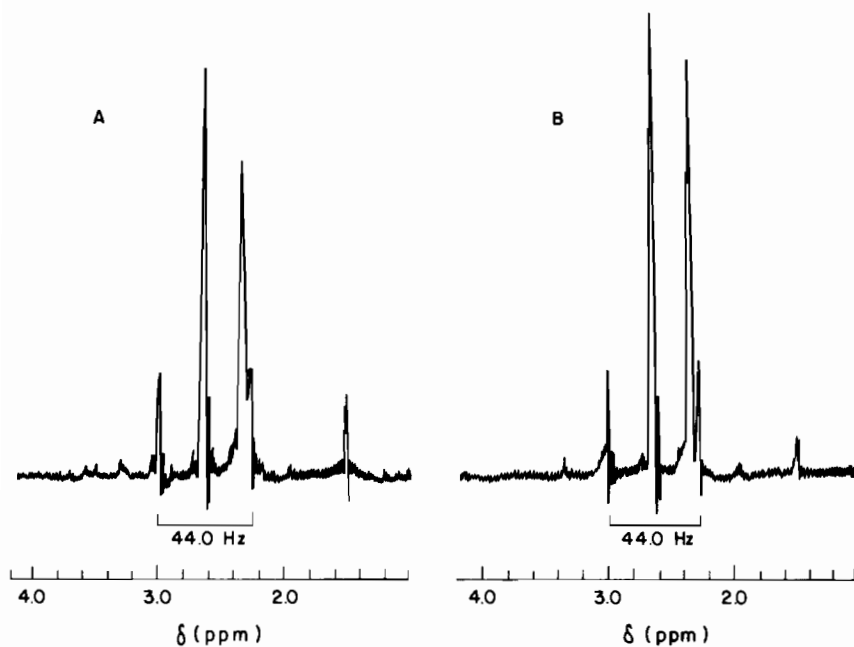


Figure 2. Proton nuclear magnetic resonance spectra. A) $\text{PtCl}_2(p\text{-tms})$, B) $\text{PtCl}_2(m\text{-tms})_2$.

1:4:1. For all the PtCl_2L_2 complexes examined, the platinum-proton coupling constant is greater for the *cis*- compound (about 49.0 Hz) than for the *trans*- form (about 41.0 to 44.0 Hz).

Figures 1 and 2 show the $^1\text{H-NMR}$ spectra of the platinum(II) compounds studied. The values of $J_{\text{Pt-S-CH}}$ coupling (44.0 Hz) observed for these compounds show the *trans*- structure.

Electronic Spectra

Preliminary spectra in the near ultraviolet and visible region of platinum(II) complexes in benzene solutions indicate weak bands, while in the palladium(II) compounds intense bands were observed [4]. The electronic spectra of these compounds are complicated by the existence of several covered bands, which is not easy to resolve into gaussian

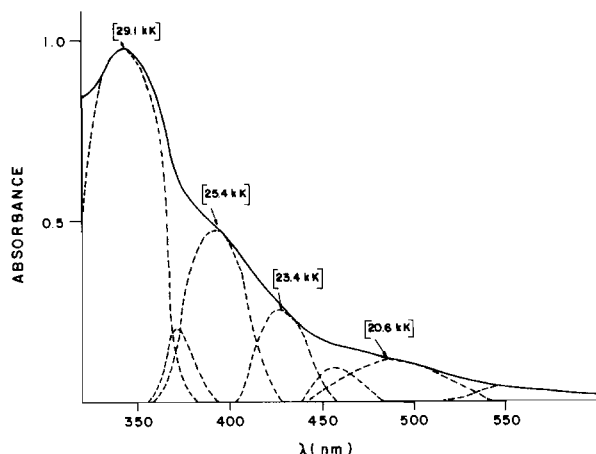


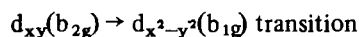
Figure 3. Absorption spectrum of Fluorolube mull of $\text{PtCl}_2(\text{pms})_2$ in the visible and near ultraviolet region, and the gaussian components.

TABLE II. Absorption Spectrum of Fluorolube Mull of the Compound $\text{PtCl}_2(\text{pms})_2$ and the d-d Transition Assignments.^a

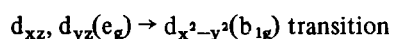
ν , kK	Assignments
b	Singlet $d_{z^2}(a_{1g}) \rightarrow d_{x^2-y^2}(b_{1g})$
29.1	Singlet $d_{xz}, d_{yz}(e_g) \rightarrow d_{x^2-y^2}(b_{1g})$
25.4	Singlet $d_{xy}(b_{2g}) \rightarrow d_{x^2-y^2}(b_{1g})$
23.4	Triplet $d_{xz}, d_{yz}(e_g) \rightarrow d_{x^2-y^2}(b_{1g})$

^aEnergy of the gaussian components as shown in Fig. 3.
^bCovered by intense bands.

components. The study was made in terms of region and it was possible to identify some bands. Figure 3 shows the absorption spectrum for $\text{PtCl}_2(\text{pms})_2$ and the gaussian components in the visible and near ultraviolet region, that permitted the assignment of d-d transitions according to Table II and to discuss ligand field splitting of the d-orbitals. In palladium(II) compounds the intense bands of ligand to metal electron transfer (LMET) transitions cover the d-d bands. The microsymmetry D_{4h} was considered and the ligand field splitting parameters were calculated utilizing equations proposed by Gray and Ballhausen [19].



$$E[{}^1A_{2g} \leftarrow {}^1A_{1g}] = \Delta_1 - C$$

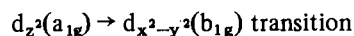


$$E[{}^1E_g \leftarrow {}^1A_{1g}] = \Delta_1 + \Delta_2 - 3B - C$$

TABLE III. Ligand Field Parameters (in kK) for Square Planar Complexes.

Compounds	Δ_1	Δ_2	Δ_3	Ref.
$\text{PtCl}_2(\text{pms})_2$	28.4	5.7	a	—
PtCl_4^{2-}	28.2	6.2	8.0	20
PtBr_4^{2-}	26.6	5.2	3.6	20
$\text{Pt}(\text{NH}_3)_4^{2+}$	46.6	1.5	3.5	20

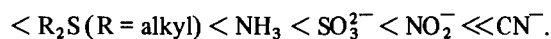
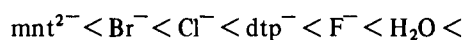
^aInsufficient experimental data.



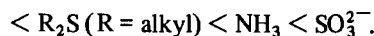
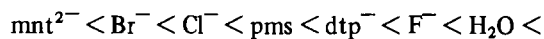
$$E[{}^1B_{1g} \leftarrow {}^1A_{1g}] = \Delta_1 + \Delta_2 + \Delta_3 - 4B - C$$

The results compared with other data are presented in the Table III.

Studies accomplished by Jørgensen [21] about the position of R_2S (R = alkyl) in spectrochemical series show that it is located between H_2O and NH_3 in this series:



Applying the rule average environment [22] Δ_1 was calculated for the hypothetical $\text{Pt}(\text{dms})_4^{2+}$ using experimental data of the compounds $[\text{PtBr}_3(\text{dms})]^-$ and $[\text{PtCl}(\text{dms})_3]^+$ [3]. The values obtained were 38.8 kK and 38.4 kK respectively. If dialkylsulfide was of the same nature as the phenylmethylsulfide, Δ_1 for $\text{PtCl}_2(\text{pms})_2$ would be expected at about 35.5 kK; however the result was 28.4 kK, as shown in the Table III. This value could be interpreted by the presence of the aromatic ring: the sulfur of the phenylmethylsulfide has two lone pairs and one of these participates in a molecular orbital with the π system of the aromatic ring. This facts causes a delocalization of the lone pairs, resulting in the weakening of the $\sigma\text{L} \rightarrow \text{M}$ bond. Consequently $d_{x^2-y^2}$ is decreased and d_{xy} energy level is increased and therefore $d_{xy} \leftarrow d_{x^2-y^2}$ transition has the energy lowered. As a result, the pms can be located near to the chloride and the following spectrochemical series is suggested:



This result made it possible to evolve a molecular orbital diagram using the sequence of the orbital energy levels in the MCl_4^- ions. These tetrachloride ion systems were extensively studied by several methods of molecular orbital calculations [20, 23, 24] including the SCF-X α -SW [7]. This method is today indicated as the best one, and offers results

TABLE IV. Allowed Transitions and Range of Energies for $\text{PtCl}_2(\text{pms})_2$.

Spectral Region	Transition	Transition Character
I 32 kK (310 nm) to 38 kK (263 nm)	$3b_u \rightarrow 6a_g(B_u \leftarrow)$	$\text{Cl}_{\pi} n^b \rightarrow \text{Md}_{x^2-y^2}$
	$5b_g \rightarrow 4b_u(A_u \leftarrow)$	$\text{Md}_{xy} \rightarrow \text{Mp}_z$
	$4b_g \rightarrow 4b_u(A_u \leftarrow)$	$\text{Md}_{xz} \rightarrow \text{Mp}_z$
	$5b_g \rightarrow 2a_u(B_u \leftarrow)$	$\text{Md}_{xy} \rightarrow \text{Mp}_x$
II 38 kK (263 nm) to 40 kK (250 nm)	$5a_g \rightarrow 4b_u(B_u \leftarrow)$	$\text{Md}_{yz} \rightarrow \text{Mp}_z$
	$5b_g \rightarrow 2a_u(B_u \leftarrow)$	$\text{Md}_{xy} \rightarrow \text{Mp}_x$
	$4b_g \rightarrow 2a_u(B_u \leftarrow)$	$\text{Md}_{xz} \rightarrow \text{Mp}_x$
	$5a_g \rightarrow 2a_u(A_u \leftarrow)$	$\text{Md}_{yz} \rightarrow \text{Mp}_x$
	$3b_g \rightarrow 4b_u(A_u \leftarrow)$	$\text{Cl}_{\pi} n^b \rightarrow \text{Mp}_z$
III 40 kK (250 nm) to 44 kK (228 nm)	$4a_g \rightarrow 4b_u(B_u \leftarrow)$	$\text{Md}_z^2 \rightarrow \text{Mp}_z$
	$4b_g \rightarrow 5b_u(A_u \leftarrow)$	$\text{Md}_{xz} \rightarrow \text{Mp}_y$
	$3b_g \rightarrow 2a_u(B_u \leftarrow)$	$\text{Cl}_{\pi} n^b \rightarrow \text{Mp}_x$
	$3b_u \rightarrow 7a_g(B_u \leftarrow)$	$\text{Cl}_{\pi} n^b \rightarrow \text{Ms}$
	$5a_g \rightarrow 5b_u(B_u \leftarrow)$	$\text{Md}_{yz} \rightarrow \text{Mp}_y$
IV 44 kK (228 nm) to 48 kK (208 nm)	$4a_g \rightarrow 2a_u(A_u \leftarrow)$	$\text{Md}_z^2 \rightarrow \text{Mp}_x$
	$3b_g \rightarrow 5b_u(A_u \leftarrow)$	$\text{Cl}_{\pi} n^b \rightarrow \text{Mp}_y$
	$4a_g \rightarrow 5b_u(B_u \leftarrow)$	$\text{Md}_z^2 \rightarrow \text{Mp}_y$
	$2b_u \rightarrow 6a_g(B_u \leftarrow)$	$\text{Cl}, \text{S}, \pi \rightarrow \text{Md}_{x^2-y^2}$

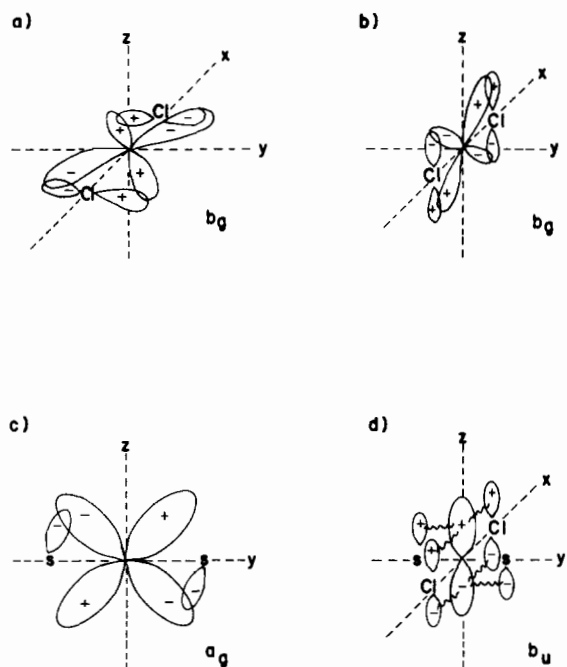


Figure 4. Overlap of a) d_{xy} with $\pi_h(\text{Cl})$ functions; b) d_{xz} with $\pi_v(\text{D1})$ functions; c) d_{yz} with $\pi^*(\text{pms})$ functions; d) p_z with $\pi_v(\text{Cl})$ and $\pi^*(\text{pms})$ functions.

that confirm experimental data of photoelectronic spectra [25].

Electronic Structure and Spectra

To discuss and to interpret the most intense bands as electron transfer transitions, molecular orbital diagrams for the $\text{PtCl}_2(\text{pms})_2$ and $\text{PdCl}_2(\text{pms})_2$ compounds were evolved. Figures 4-c and d show the overlap of the d_{yz} and p_z of the metal with π anti-bonding orbitals of the phenylmethylsulfide. The π anti-bonding orbital of the ligand has its origin in the overlap of one of the two lone pairs with the π system of the aromatic ring. The symmetry group for these compounds is normally D_{2h} , but it can be seen in Figure 4-d that the C_2 axis perpendicular to the principal axis C_2 (which contain Cl-M-Cl) disappears and for the sake of discussion the point group C_{2h} is considered.

Figures 5 and 6 show the molecular orbital diagrams of the compounds $\text{PtCl}_2(\text{pms})_2$ and $\text{PdCl}_2(\text{pms})_2$ respectively. Energy levels of the tetrachloride ions (SCF-X α -Sw) [7] and some data of photoelectronic spectra of phenylmethylsulfide [8] were used. Every combinations of the metal orbitals with the ligands σ and π molecular orbitals were analysed, and the changes expected with the substitution of the chloride by phenylmethylsulfide were considered. For example, to establish the sequence of the $2b_u(\pi)$

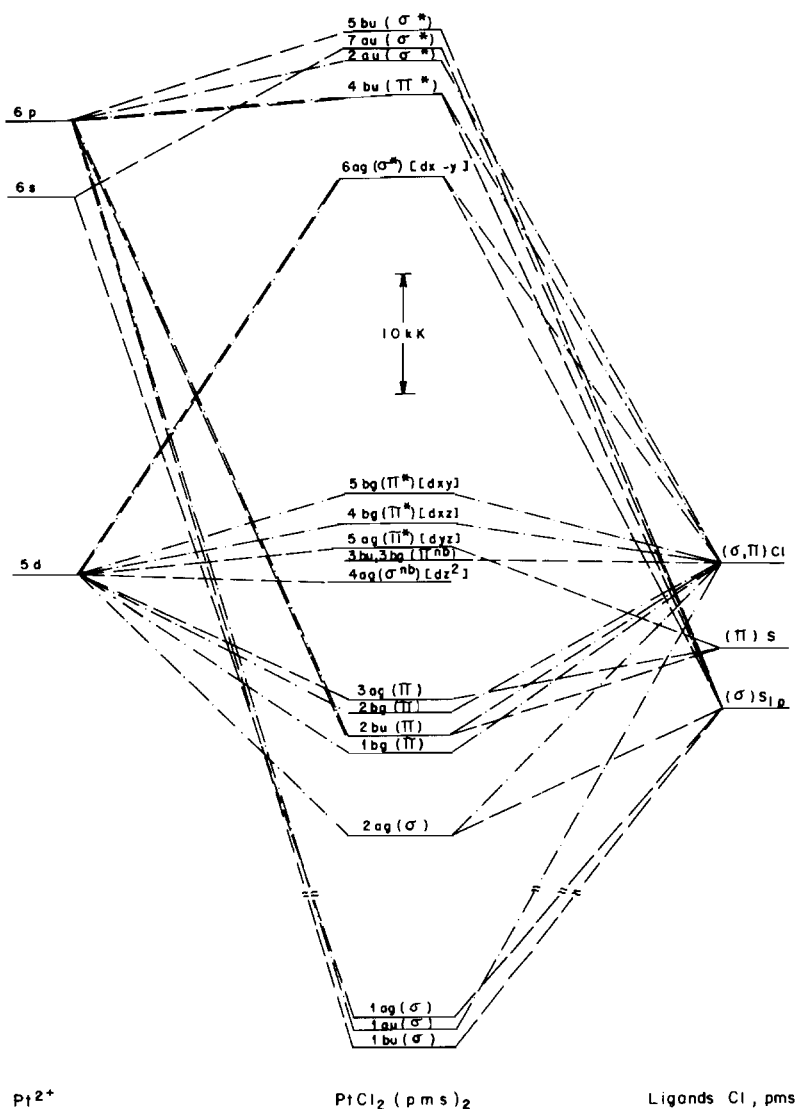


Figure 5. Molecular orbital diagram of $\text{PtCl}_2(\text{pms})_2$.

(Figure 4-d) in the complexes $\text{MCl}_2(\text{pms})_2$, the ionization energy data of higher energy of π^* filled of the free pms could not be considered (8.07 eV) [8]. When the phenylmethylsulfide was complexed, the ionization energy was lowered, consequently the orbital $2b_u(\pi)$ was located at higher energy. This fact agrees with experimental data of electronic spectra of $\text{PdCl}_2(\text{pms})_2$. The intense band at 332 nm (Figure 7) is typically LMET transition ($2b_u \rightarrow 6a_g$ ($B_u \leftarrow$)) which indicates the high energy of $2b_u$ orbital. According to the analysis of d-d transitions (Table IV) the energy level of the molecular orbital $6a_g$ with $d_{x^2-y^2}$ character is similar to the tetrachloride ions.

Some generalizations can be considered regarding the electronic structures of these compounds. Observing the Figure 7, differences are visible between palla-

dium(II) and platinum(II) compounds. The $5d_{x^2-y^2}$ orbital of the platinum(II) has greater participation in the σ bond than $4d_{x^2-y^2}$ orbital of the palladium(II), thus d splitting is smaller in the latter, consequently $4d_{x^2-y^2}$ is at lower energy. Accordingly, the experimental results of electronic spectra show the LMET transition located at lower energy for the palladium(II) compound (Figure 7).

The separation $5d-6p$ in platinum(II) is smaller than $4d-5p$ in palladium(II) by about 5 kK [26], and Figure 7 shows d-p transitions (Rydberg transitions) for platinum(II) compound at about 300 to 220 nm, while for palladium(II) compound these bands are located between 250 and 200 nm.

Selection rules were considered for the C_{2h} symmetry. Tables IV and V show attempts to locate the allowed transitions according to the relative

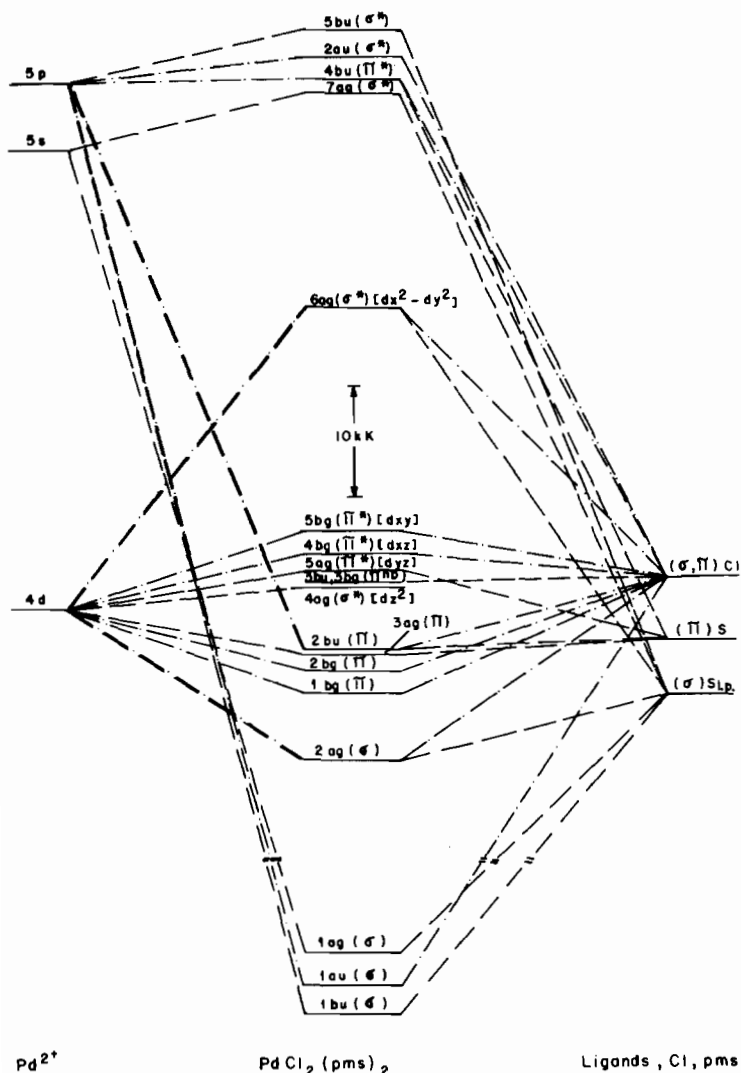


Figure 6. Molecular orbital diagram of PdCl₂(pms)₂.

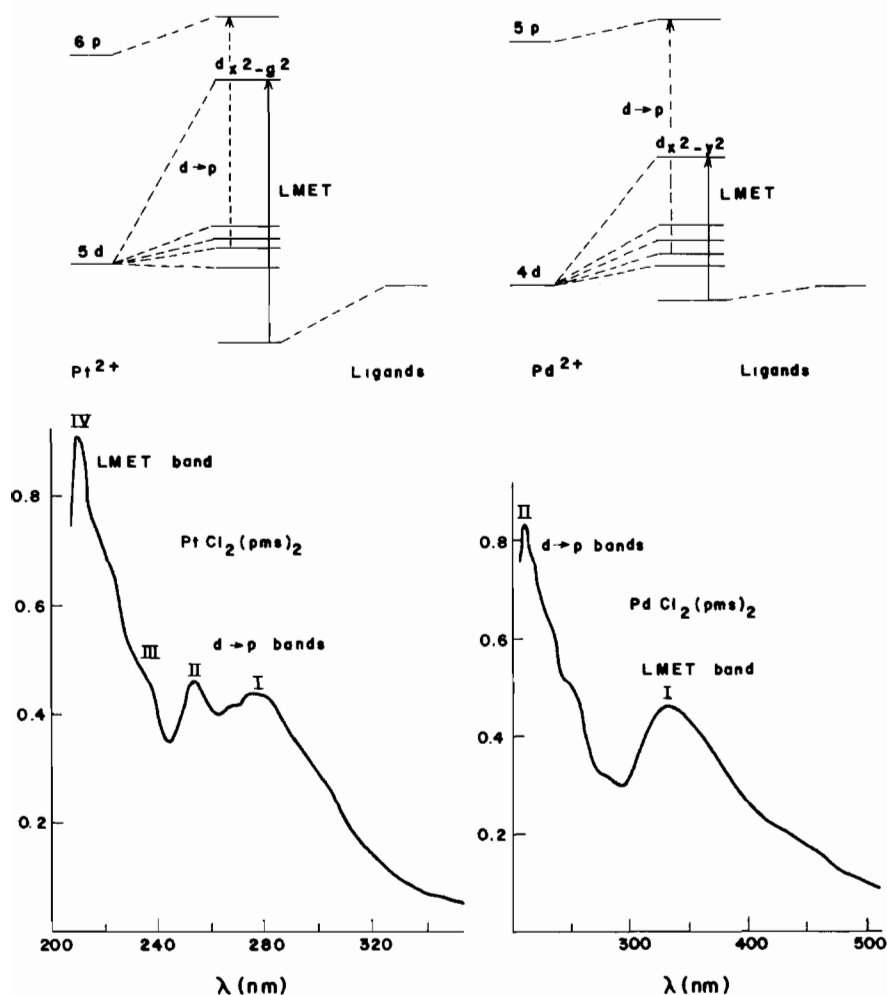
TABLE V. Allowed Transitions and Range of Energies for PdCl₂(pms)₂.

Spectral Region	Transition	Transition Character
I 22.2 kK (450 nm) to 33.3 kK (300 nm)	3b _u → 6a _g (B _u ←)	Cl _π n ^b → Md _{x²-y²}
	2b _u → 6a _g (B _u ←)	Cl, S, π → Md _{x²-y²}
	5b _g → 4b _u (A _u ←)	Md _{xy} → Mp _z
	5b _g → 2a _u (B _u ←)	Md _{xy} → Mp _x
	4b _g → 4b _u (A _u ←)	Md _{xz} → Mp _z
	3b _u → 7a _g (B _u ←)	Cl _π n ^b → Ms
	5a _g → 4b _u (B _u ←)	Md _{yz} → Mp _z
	4b _g → 2a _u (B _u ←)	Md _{xz} → Mp _x
	5b _g → 2a _u (B _u ←)	Md _{xy} → Mp _x
	3b _g → 4b _u (A _u ←)	Cl _π n ^b → Mp _z
II		

(continued on facing page)

TABLE V. (continued)

Spectral Region	Transition	Transition Character
33.3 kK (300 nm) to 50.0 kK (200 nm)	$4a_g \rightarrow 4b_u(B_u \leftarrow)$	$Md_{z^2} \rightarrow Mp_z$
	$5a_g \rightarrow 2a_u(A_u \leftarrow)$	$Md_{yz} \rightarrow Mp_x$
	$3b_g \rightarrow 2a_u(B_u \leftarrow)$	$Cl_{\pi n^b} \rightarrow Mp_x$
	$4b_g \rightarrow 5b_u(A_u \leftarrow)$	$Md_{xz} \rightarrow Mp_y$
	$4a_g \rightarrow 4a_u(A_u \leftarrow)$	$Md_{z^2} \rightarrow Mp_x$
	$5a_g \rightarrow 5b_u(B_u \leftarrow)$	$Md_{yz} \rightarrow Mp_y$
	$3b_g \rightarrow 5b_u(A_u \leftarrow)$	$Cl_{\pi n^b} \rightarrow Mp_y$
	$4a_g \rightarrow 5b_u(A_u \leftarrow)$	$Cl_{\pi n^b} \rightarrow Mp_y$

Figure 7. Electronic structure and spectra of $PtCl_2(pms)_2$ and $PdCl_2(pms)_2$.

energies estimated, starting from the molecular orbital diagrams. These data agree reasonably with the regions of electronic spectra (Figure 7) in the solid state in both platinum(II) and palladium(II) compound.

In the compounds $PtCl_2L_2$ ($L = o\text{-tms}$ or $p\text{-tms}$) great differences are not observed in the electronic spectra, as shown in Figure 8. Some differences probably are due to electronic effects, but these cannot be identified in the LMET transition, which

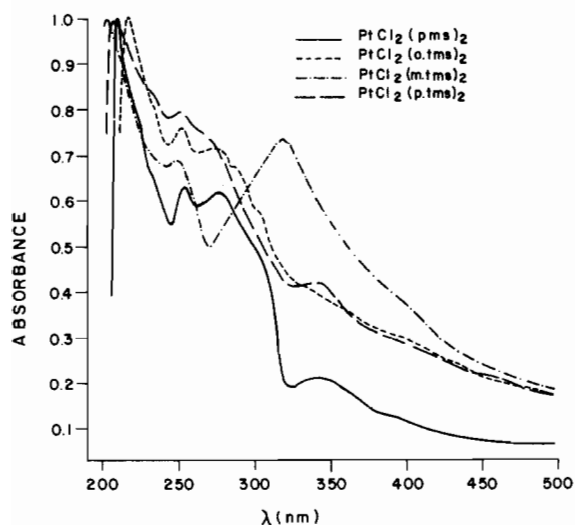


Figure 8. Absorption spectra of platinum(II) compounds in Fluorolube mull.

is covered by other intense $d \rightarrow p$ transitions (see Table V, $2b_u \rightarrow 6a_g(B_u \leftarrow)$ transition). Only *m*-tolylmethylsulfide complex showed a peculiar spectrum (Figure 8), probably due to the different conformation in the solid state. Spectra in solvents of the *m*-compound did not show differences in relation to analogous *o*-, or *p*-compounds.

Figure 9 presents the absorption spectra of $PdCl_2$ - L_2 type compounds and the shift of LMET transi-

TABLE VI. ν_{max} of the LMET Transition for $PdCl_2L_2$ Type Compounds.

L	Fluorolube ν_{max} , kK	n-hexane ν_{max} , kK
pms	30.1	31.3
<i>p</i> -tms	27.8	30.9
<i>m</i> -tms	26.0	31.0
<i>o</i> -tms	23.8	30.7

tion is observed when L is changed. This is probably due to steric effects. The energy of the LMET transition is affected by the position of the methyl group in the ligand L. The shift to low energy is observed in the following sequence: $pms < p\text{-tms} < m\text{-tms} < o\text{-tms}$, (Table VI). It seems that the bulk of the ligands causes stabilization in the molecular orbital $6a_g$ of character $d_{x^2-y^2}$, which is due to the weakening of the σ bond between metal and ligand L. Electronic effects probably are present but the steric effects mask these in the solid state. In solvents as n-hexane steric effects are smaller and electronic effects are approximately of the same extent, and it becomes more difficult to identify these effects as shown in Table VI. In acetonitrile solution the LMET disappears from this region, and it is doubtful if a large shift is due to the donor effect of the solvent as in the halopalladate ions [26]. Justification of the

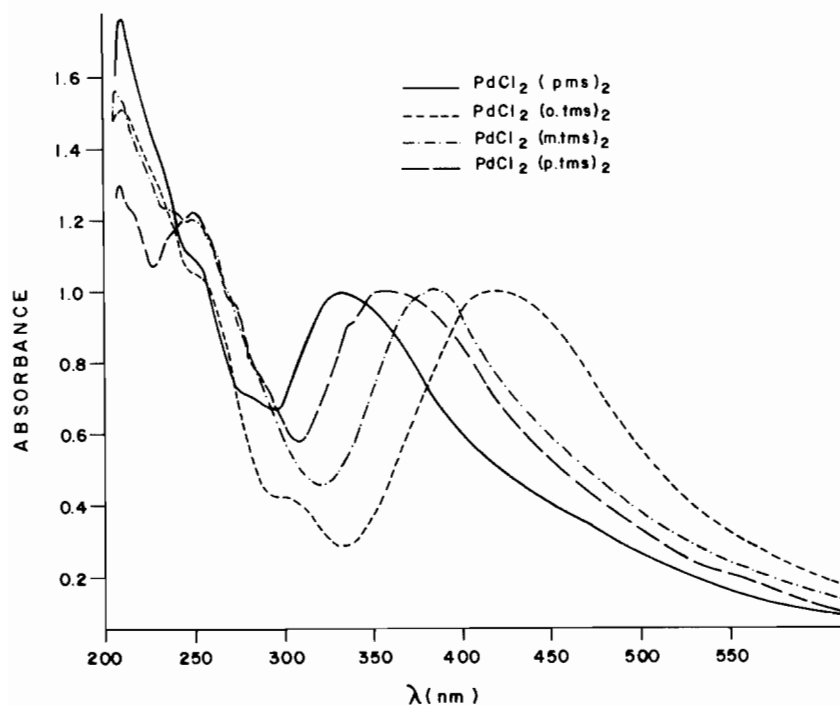


Figure 9. Absorption spectra of palladium(II) compounds in Fluorolube mull.

above phenomenon requires further study and experimentation.

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