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Received October 30, 1995

Analysis of chiroptical properties of π-allyl complex $[Pd(\beta\text{-pinenyl})Cl]_2$

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Electronic absorption and circular dichroism spectra of the optically active $[Pd(\beta\text{-pinenyl})Cl]_2$ complex (**1**) have been studied. The assignment of the bands in the circular dichroism spectrum in the d—d-transition region of complex **1** was made within the framework of the one-electron model of optical activity; this assignment is in agreement with the literature data on the analysis of the absorption spectrum of $[Pd(allyl)Cl]_2$. The (1*R*,2*S*,3*S*,5*R*) absolute configuration was suggested for the optical $(+)_{589}$-isomer of **1** studied.

Key words: chirality, absolute configuration; circular dichroism; electronic absorption spectra; Pd(π-allyl) complexes.

π-Allyl complexes of Pd^{II} are widely used in synthesis and catalysis, including their asymmetrical variations.[1,2] However, studies of the relationship between the stereochemistry and the optical activity of complexes, which were started as early as 1970s[3] and which are necessary for performing stereospecific conversions, are not yet widespread. The precise assignment of transitions in the electronic absorption and circular dichroism spectra of compounds is necessary for revealing these correlations. Analysis of electronic absorption and circular dichroism spectra of organometallic compounds may substantially help in the study of the nature of chemical bonds and characteristic features of the structures, which cannot be currently calculated by quantum-chemical methods.

Electron transitions are generally more pronounced in the circular dichroism spectra. Therefore, we use the circular dichroism method for studying chiral π-allyl complex $[Pd(\beta\text{-pinenyl})Cl)]_2$ (**1**). Analysis of the circular dichroism spectrum was carried out within the framework of the one-electron model of optical activity.[4,5] To our knowledge, such analysis of π-allyl complexes has not been previously performed. Interest in chiroptical properties of complex **1** is also associated with the use of this complex in the synthesis of the new chiral $[Fe_3CoCPd(\beta\text{-pinenyl})(CO)_{12}]$ cluster.[6]

Complex **1** was prepared by the reaction of Na_2PdCl_4 with β-pinene ($[\alpha]_D$ −19.7°) using the known procedure.[7] The compound obtained is characterized by a

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 6, pp. 1559—1561, June, 1996.

specific rotation equal to $[\alpha]_D$ +25° (c 6.024 g/100 mL, $CHCl_3$; d = 1 cm).

Optical rotation was measured on a A1-EPO photoelectron polarimeter with an accuracy of ±0.01° (a wavelength 589.3 nm); the electronic absorption spectra were recorded on a Specord UV VIS spectrophotometer; the circular dichroism spectra were obtained on a Marc III dichrograph (Jobin-Yvon).

The optical activity of complex **1** was determined by the planar chirality of the Pd-allyl fragment and asymmetrical C atoms of the initial (−)-(1*S*,5*S*)-β-pinene. In work reported previously,[3] based on the results of studies of chiral olefin complexes of Pt^{II} and allyl complexes of Pd^{II}, it was concluded that coordination of the Pd atom at the sterically less hindered side of the plane of the allyl fragment of complex **1** is highly specific. Besides, these authors reported[3] that only one isomer of complex **1** forms, and its optical activity was studied by the optical rotatory dispersion and circular dichroism methods. More recently, X-ray structural studies of a number of π-allyl complexes containing the β-pinenyl ligand were performed;[8,9] however, the absolute configurations of the asymmetrical centers of the allyl fragments were not considered.

For the sterically less hindered isomer of complex **1**, the absolute configuration may be written as (1*R*,2*S*,3*S*,5*R*) according to the Cahn—Ingold—Prelog nomenclature[10] or (1*R*,5*R*,R_{pl}) according to the Schlogl[11] and Ugi[12] system. The change in notation of the absolute configuration of the asymmetrical C(1) and C(5) atoms of the β-pinenyl ligand in complex **1** as compared to that in (1*S*,5*S*)-β-pinene is associated with the change in seniority of substituents at these asymmetrical centers as a result of coordination of the Pd atom. We suggested that the circular dichroism spectra of complex **1** recorded correspond to this optical isomer.

The obtained data of the electronic absorption and circular dichroism spectra for complex **1** are given in Fig. 1 and in Table 1. The circular dichroism spectrum of complex **1** that we recorded shows a greater number of Cotton effects in the visible and near-UV regions as compared to the circular dichroism spectrum of complex **1** reported previously;[3] however, the positions and signs of the principal Cotton effects (*B*, *D*, and *F*) coincide. Moreover, the shapes and half-widths ($\Delta_{1/2}$) of the low-energy positive and negative Cotton effects ($\Delta_{1/2}$ = 2.6 and 3.5 κK, respectively)[3] make it possible to suggest that several electron transitions will appear in this region. The data of the circular dichroism spectrum of complex **1** obtained in these work agree well with the results of detailed analysis[13] of the electronic absorption spectra for $[Pd(allyl)Cl]_2$ (**2**).

In the absorption spectrum of compound **2** in an aqueous 4 *M* KCl solution expanded in Gaussian components, three bands (29.3, 34.5, and 40.5 κK) were assigned to d—d transitions:[13] from three MOs consisting mainly of the d_{xz}-, d_{yz}-, and $d_{x^2-y^2}$ AOs, respectively, to the MO consisting predominantly of the d_{z^2}-AO.

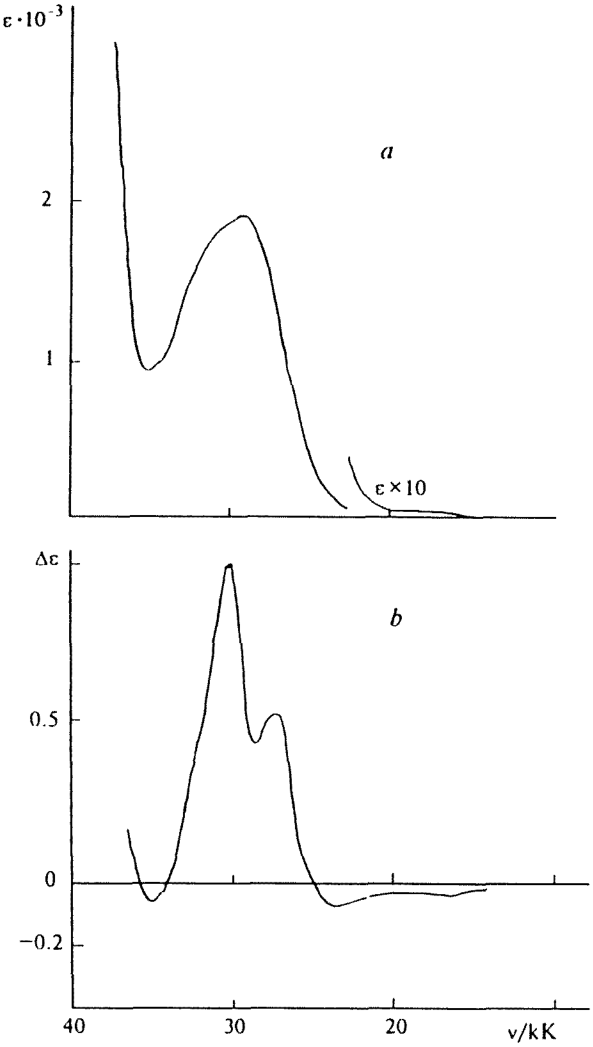

Fig. 1. Absorption spectrum (*a*) and circular dichroism spectrum (*b*) of a solution of complex **1** in CH_2Cl_2.

It may be suggested that bands *C*, *D*, and *E* (26.9, 29.9, and 35.0 κK) in the circular dichroism spectrum of complex **1** correspond to dipole-allowed $^1A_1 \rightarrow ^1B_1$, $^1B_2$,

Table 1. Absorption spectra and circular dichroism spectra of a solution of complex **1** in CH_2Cl_2

Electronic absorption spectrum		Circular dichroism spectrum			Circular dichroism spectrum[3]	
ν/kK	ε	ν/kK	Δε	Band	ν/kK	Δε
18.50 sh	5	17.86 sh	−0.002	*A*		
		23.81	−0.060	*B*	23.75	−0.021
		26.88	+0.527	*C*		
29.50	1903	29.94	+1.0	*D*	28.99	+0.735
		34.96	−0.064	*E*		
>37.0	>3000	>35.7	+CE	*F*	42.37	+10.61

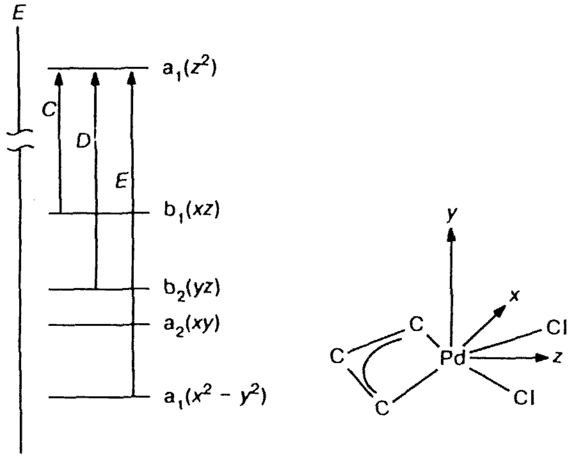

Fig. 2. Scheme of MOs involved in the d—d transitions of complex **1** (the principal components of MOs are given in parentheses) and the system of coordinates used.

and $^1A_1$ transitions. Our analysis of the circular dichroism spectrum of complex **1**, as well as the assignment of bands in the electronic absorption spectrum of complex **2**,[13] was carried out under the assumption that the metallochromophore [(allyl)PdCl$_2$] has C_{2v} symmetry: the directions of the axes of coordinates are shown in Fig. 2. The choice of the mononuclear fragment for analysis is justified[13—15] by the absence of the interaction between the Pd atoms in the Pd$_2$X$_6$ dimers and by the similarity in the spectra in the region of d—d transitions for PdX$_4$$^{2-}$ and Pd$_2$X$_6$.

The rather uniform bathochromic shift of bands *C*, *D*, and *E* in the spectrum of complex **1** relative to the positions of the corresponding bands in the spectrum of compound **2** is most probably due to the weaker bonding of the Pd atom to the sterically hindered β-pinenyl ligand although the effect of the stronger electron-donor character of this ligand is also not ruled out. Note also that in the electronic absorption spectra of a solution of complex **2** in CHCl$_3$, substantial bathochromic shifts (1.0—1.5 кK) are observed for the bands discussed[13] as compared to the above-mentioned values for this complex.

Band *B* may be assigned to the *y*-polarized magnetic-allowed $d_{xz}\rightarrow d_{z^2}$ transition associated with the $d_{yz}\rightarrow d_{z^2}$ dipole-allowed transition (band *D*). Apparently, the *z*-polarized magnetic-allowed $d_{xy}\rightarrow d_{z^2}$ transition also contributes to band *D*. The $d_{x^2-y^2}\rightarrow d_{z^2}$ dipole-allowed transition, which is associated with the *z*-polarized magnetic-allowed $d_{xy}\rightarrow d_{z^2}$ transition and to which the negative Cotton effect corresponds (band *E*), is compensated to a large degree by the positive Cotton effects in the region of the charge transfer $p\pi_{Cl}\rightarrow d_{z^2}$ transition (band *F*) and the d—d transition (band *D*).

Analysis of the circular dichroism spectrum of complex **1** performed (for the first time for π-allyl complexes) confirms the possibility of using the one-electron model of optical activity for metallochromophores.[16] In the future, we plan to draw up the sector rules within the framework of this model as well as rules[16] supplemented with the nodal planes of the orbitals involved in the electronic transitions.

This work was supported by the International Science Foundation (Grants J88 100 and N91 000) and the Russian Foundation for Basic Research (Project No. 93-03-5705).

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Received December 14, 1995