

Linear and Circular Dichroism in Single Crystals of Dichloro(ethylenediamine)platinum(II) and -palladium(II)

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The linear and circular dichroisms in single crystals of dichloro(ethylenediamine)platinum(II) and dichloro(ethylenediamine)palladium(II), which are isomorphous and crystallize in the orthorhombic space group $C222_1$, are measured and the difference in appearance of the circular dichroism spectra of the two compounds is explained through different distortion of the over-all planar coordination sphere, the Pd(II) complex having the major distortion.

A recent X-ray diffraction study¹ has shown that crystals of *cis*-M(en)Cl₂ (M = Pt, Pd; en = 1,2-ethanediamine) are isomorphous and belong to the orthorhombic system, space group $C222_1(D_2^5)$. The metal atoms are surrounded by two Cl and two N atoms in an almost *cis* square-planar arrangement, and the C atoms in the ethylene bridge are twisted out of this plane, one above and the other below; furthermore the molecules stack in a nearly linear array with a uniform spacing of 3.381 Å (Pt) and 3.369 Å (Pd), respectively.

As indicated by Hald and Rasmussen² and by Berg³ the space group symmetry D_2^5 permits the crystal to rotate the polarization direction of linearly polarized light, *i.e.* the molecular units in the single crystals may be dissymmetric due to the ethylenediamine rings exhibiting only one of the two possible conformations λ or δ . Consequently circular dichroism should be detectable in the crystalline phase as it was also indicated by Hald and Rasmussen² (see the footnote on p. 1412 in Ref. 3), who tried to measure the circular dichroisms having the two complexes diluted through solid dispersion of single crystals in KBr matrices.

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Another way of proceeding for the detection of the inherent circular anisotropy of the M(en)Cl₂ crystals is to measure directly single crystal circular dichroism, which, however, presents the problem of static linear anisotropy coexisting in the crystals.^{4,5} As a matter of fact, the problem of linear dichroism has precluded detection of circular dichroism until very recently, where the questions of instrumentation,⁶ mathematical formulation,^{7,8} measuring conditions and limitations,^{8,9} together with actual experiments^{10,11} were settled.

The crystals M(en)Cl₂ have an exceptionally ideal orientation of the molecular units for the study of polarization directions of transitions through investigation of linear dichroism since the chains of stacked molecules are directed along the orthorhombic *c* axis and the symmetry axis and permanent dipole moment of every molecule are in the $\pm b$ direction. The crystals grow as thin plates with developed face (100) and show under the microscope pronounced fibrous grooves very often along the longest dimension. These grooves were by X-ray diffraction analysis determined to be parallel to the *c* axis,³ a fact which makes orientation of the crystals in an experimental coordinate system very easy.

In this investigation we will choose the same molecular Cartesian coordinate system as Martin *et al.*,^{4,5} *i.e.* with *z* axis normal to the molecular plane and *y* axis along the molecular symmetry axis from which it follows that the axes *x*, *y* and *z* are conveniently directed parallel to the crystallographic axes *a*, *b* and *c*, respectively. As it was also pointed out by Martin *et al.* with this choice of axes the d_{xy} orbital is used for σ bonding, so that the lowest unfilled orbital on the metal center is the antibonding orbital involving d_{xy} .

Among the ligand field transitions three are electric dipole allowed in the symmetry group C_{2v} (which will be used for assigning transitions in the complexes even though $M(en)Cl_2$ strictly possesses only the symmetry C_2), and this is the transitions $A_1 \rightarrow B_1$ ($d_{xz} \rightarrow d_{xy}$) with $z(c)$ polarization and $A_1 \rightarrow B_2$ ($d_{z^2} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{xy}$) with $x(a)$ polarization, but none with $y(b)$ polarization.

Martin *et al.* present a detailed discussion of the polarized absorption spectra of $Pt(en)Cl_2$; especially they discuss the two b polarized bands at $33\,100\text{ cm}^{-1}$ and $39\,100\text{ cm}^{-1}$, respectively, in terms of ionized excitons (or alternatively $M \leftarrow L$ charge-transfer bands) and acknowledge, on the basis of earlier assignments by Chatt *et al.*,¹² three bands in the ligand field range namely, a c polarized band at $25\,000\text{ cm}^{-1}$ assigned as spin-forbidden $d_{xz} \rightarrow d_{xy}$, a b polarized band at $22\,000\text{--}27\,000\text{ cm}^{-1}$ assigned as a spin-forbidden ligand field transition with vibronic reinforcement and another b polarized band at $28\,000\text{ cm}^{-1}$ assigned as spin-allowed $d_{x^2-y^2} \rightarrow d_{xy}$ with vibronic reinforcement. These three bands are those which will be discussed further in the present paper.

EXPERIMENTAL

Crystals were obtained from Berg, who prepared them as described by him.³ Crystals of suitable thickness ($0.06\text{--}0.01\text{ mm}$) were mounted on microscope slides and centered in the light beam of a microscope built into a phasemodulation spectrophotometer, the construction of which is described elsewhere.^{6,10} The photocurrent is processed and analysed as described by Jensen^{9,10} and Jensen *et al.*⁸ using the intensity ratios of Ref. 10, which are derived under the condition that the Mueller matrix representing the medium has the form presented by Troxell and Scheraga.¹³ This requires that the actual values of the anisotropies are less than 1, a condition which was fulfilled since the measured linear and circular dichroisms never exceeded ~ 0.1 and ~ 0.01 absorbance units, respectively.

The ratios between linear and circular dichroisms around absorption maxima are such that the "true" circular dichroism is obtained, provided the proper correction for linear dichroism in the intensity ratio I_{AC}/I_{DC} is performed. This notion may be gathered in considering an optically active copper(II) complex for which the linear and circular dichroisms of single crystals were also obtained through phase modulation spectroscopy together with the circular dichroism of microcrystals dispersed in KBr matrices.^{10,14}

The signs and the scaling of the spectra were established as described earlier^{10,11} using pseudo-isocyanin- N,N' -diethyl iodide in a stretched PVA-film as standard. Concentrations and molar absorptivities were calculated as described in Ref. 11.

The reproducibility of the spectra was checked from 2–3 single crystals of each compound, and as far as concerns the circular dichroism spectra none of these crystals were enantiometric of each other.

RESULTS AND DISCUSSION

Linear dichroism and circular dichroism spectra of $Pt(en)Cl_2$ and $Pd(en)Cl_2$ in the ligand field range are given in Figs. 1 and 2, respectively. There is a surprising difference between the two sets of spectra, the Pt-compound only showing two bands in the linear dichroism spectrum whereas the Pd-compound has three; furthermore the Cotton effect associated with the c polarized absorption band is ~ 10 times greater for $Pd(en)Cl_2$ than for $Pt(en)Cl_2$. However, with the differences acknowledged it should also be noted that the b polarized bands in the near UV spectral region for both complexes have very similar appearances both in the linear and circular dichroism spectra.

The lack of a second b polarized band in the high wavelength region of the Pt-complex need not be essential, since already Martin *et al.* pointed out that bands of such polarization achieve intensity by vibronic coupling and therefore have fairly low intensity in comparison with the c polarized band

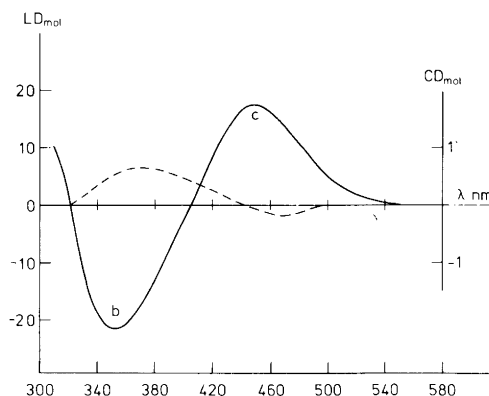


Fig. 1. Linear (—) and circular (---) dichroism in a single crystal of $Pt(en)Cl_2$. The experimental orientation of the crystal is so that $Abs_c - Abs_b$ is obtained.

Table 1. Fractional coordinates and anisotropic temperature factors of Pt(en)Cl₂ according to Benson¹⁸. Space group: C222₁, $a = 12.437 \pm .002$, $b = 8.120 \pm .002$, $c = 6.777 \pm .001$.

	x/a	y/b	z/c	β		
Pt	0.0	0.00247	0.250			
Cl	0.1371	0.1972	0.250			
N	0.1075	-0.1876	0.2262			3.0192
C	0.0492	-0.3439	0.2166			5.898
	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{13}
Pt	0.00342	0.00767	0.01499	0	0	0.0031
Cl	0.00714	0.0159	0.03398	-0.00573	-0.00421	0.00692

$d_{xz} \rightarrow d_{xy}$. This means, small differences in orbital energy between Pt and Pd in the complexes taken into consideration, that the two compounds show linear dichroism spectra which are in accordance with each other and with the polarized spectra of Martin *et al.*^{4,5}

Besides the mere fact that the predicted circular anisotropy of the title compounds is obtainable, a discussion of the intensity difference of the Cotton effects under the c polarized absorption band is relevant. It has above been anticipated that experimental problems exist in attempts to isolate the circular dichroism from a linearly anisotropic system; this mixing of effects in the photocurrent, however, could be less serious than the possibility of a contribution to the rotatory strength from electric quadrupole terms arising from the electric dipole transition and induced by the electric field gradient of the electromagnetic wave.¹⁵⁻¹⁷ That,

however, need not be considered here, as such contributions according to Barron¹⁷ would be greater for a Pt- than for a Pd-compound.

The explanation of the difference in rotatory strength between the two compounds under discussion seems to be that the ethylenediamine group is twisted more with respect to the coordination plane in the Pd-compound than is the case with the Pt-compound, as such a twist would influence the c polarized transition greatly since this transition involves an orbital engaged in σ bonding to the diamine group. This conclusion is in disagreement with the results of Iball *et al.*,¹ which give Pd(en)Cl₂ less twist of the C-C bond than Pt(en)Cl₂. However, the R -value for the refinement of the Pt-compound is considerably greater (0.073) than for the Pd-compound (0.057) and this means that the structural determination of Pt(en)Cl₂ is rather uncertain. Furthermore there exists another X-ray investigation of Pt(en)Cl₂ performed by Benson¹⁸ based on 35% more reflections and with a comparable R -value (0.083) which certainly shows less distortion for Pt(en)Cl₂ than found by Iball *et al.* for both of the complexes M(en)Cl₂ (Table 1).

On these grounds it seems reasonable to accept the ten-fold difference in Cotton effects as due to less distortion from planarity (twist) of the ethylenediamine group in Pt(en)Cl₂ as compared with Pd(en)Cl₂.

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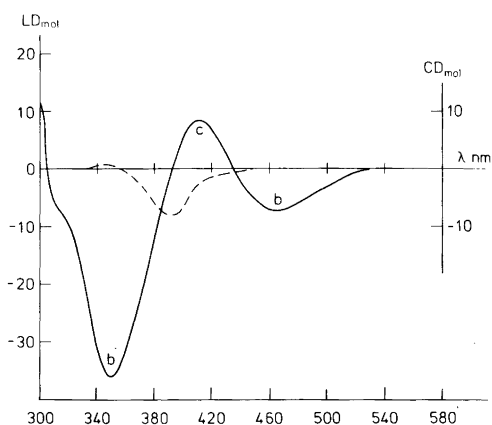


Fig. 2. Linear (—) and circular (---) dichroism in a single crystal of Pd(en)Cl₂. Experimental orientation as in Fig. 1.

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