Circular Dichroism of [PtCl$_2$(R)-pn] and [PtCl$_2$(S)-pn] in Solution and in KCl Matrix

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A technique for quantitative measurement of visible and ultraviolet absorption and circular dichroism spectra of a microcrystalline solid dispersed in an alkali halide matrix is described, and formulae for evaluation of oscillator, dipole and rotatory strengths are given.

The method is applied to [PtCl$_2$(R)-pn] and [PtCl$_2$(S)-pn], pn = 1,2-propanediamine, which are studied in the range $2-4 \times 10^6$ m^{-1}.

Absorption and circular dichroism spectra (ABS and CD) of Pd(II)Cl$_2$ and Pt(II)Cl$_2$ complexes with (R)-1,2-propanediamine ((R)-pn or 1-pn) were measured by Ito et al.[1] and latter by Sullivan[2] who also studied the solid-state CD in a semi-quantitative manner. We report here ABS and CD of the complexes of Pt(II) with both (R)- and (S)-pn in aqueous solution and dispersed in KCl matrix. Our measurements cover the frequency range $1.7-4.5 \times 10^6$ m^{-1}.

These studies were originally undertaken as a prerequisite to similar measurements on [PtCl$_2$en]. One of us proposed on the basis of crystal data,[3] in connection with an infrared study,[4] that [PtCl$_2$en] resolves spontaneously on crystallisation, and that all chelate rings in a single crystal would have identical conformation. This would entail a possibility of studying CD in a d-electron system of purely conformational origin. Exploratory studies on tiny single crystals crushed and pressed with KCl indicated that the effect is real but very weak. In order to develop a proper methodology, we undertook the present study wehere the dissymmetric amine would at the same time lock the chelate ring conformation and enhance the CD but would have little effect on the positions of the ABS bands. The original goal was superseded by Jensen's demonstration of the correctness of the original

proposal, by single crystal CD measurements,[5] but our study revealed some features which hitherto seem to have escaped detection. Also, our description and evaluation of the measurements may be of some interest; earlier measurements on these or similar compounds in KBr or paraffin oil are either qualitative[2] or not described in any detail.[6−8] Recently, the paraffin oil technique was developed into a quantitative procedure by Taniguchi and Shimura.[9]

EXPERIMENTAL

Preparation. Both complexes were prepared according to Werner.[10] [PtCl$_2$(R)-pn]: 0.47 g (1.4 mmol) K$_2$PtCl$_4$ was dissolved in 7 ml H$_2$O, and 0.13 ml (R)-pn solution ($d = 0.678$ g cm^{-3}, 1.2 mmol, $[\alpha]_D^{20} = -31.5°$) was added with stirring. After 24 h the precipitate was recrystallised. Yield: 71%. Analysis: Calc: C 10.62, H 2.95, N 8.26, Cl 20.65, Pt 57.50. Found: C 10.66, H 2.86, N 8.29, Cl 20.85, Pt 57.50, sum 100.16. [PtCl$_2$(S)-pn]: Identically, with $[\alpha]_D^{20} = +32.0°$. Yield: 69%. Analyses: Found: C 10.42, H 2.80, N 8.22, Cl 20.73, Pt 57.45, sum 99.62.

Solution spectra. ABS was recorded on a Cary 11 at $\sim 25°$C in 2 and 5 cm silica cells selected for CD. Solutions were ~ 1 mM in the complex and 60 mM in KCl and in HCl. The same solutions in the same 5 cm cells were used for CD measured with a Roussell-Jouan Dicrographe II.

Solid-state spectra. KCl was used rather than KBr to avoid exchange with the matrix.[11] Preparation of disks: 0.03−2 mg substance was milled with 150 mg KCl dried at 150°C for 16 h in an agate ball mill (RIIC) at speed II for 0.5 min, and then pressed slowly in a 13 mm ø die (RIIC) for 15 min to 6 t under vacuum; if the disk was not satisfactorily clear, it was crushed and the procedure was repeated. A special holder was constructed for use

with both instruments; it allowed for rotating the disk around the optical axis in steps of 90°. This was necessary in order to correct for the strain produced in the pressing. CD recordings were made with the disk in four positions, and the averaged spectra were used. If they differed subjectively too much, the disk was re-made as above. The whole procedure was repeated with a second (or higher) preparation; a final CD was accepted only if it, after evaluation (see below), was identical to within the experimental uncertainty for two different preparations.

Evaluation of ABS. In an isotropic disk we write the measured absorbance A as the sum of two quantities, eqn. (1), where g is a constant characterising the disk (the manufacturing), $f(v)$ describes the dispersion and $a(v)$ is the true absorbance of the disk. In an empty disk with no absorbing material we have eqn. (2) and in another disk containing an absorbing substance eqn. (3).

$$A(v) = a(v) + f(v)g \tag{1}$$

$$A_e(v) = f(v)g_e \tag{2}$$

$$A_s(v) = a(v) + f(v)g_s \tag{3}$$

If there is a frequency v_o where $a(v)_o = 0$ we have eqns. (4) and (5). The ratio g_s/g_e is thus measurable. From eqns. (5) and (3) we get eqn. (6) and thus eqn. (7).

$$A_s(v_o) = f(v_o)g_s \tag{4}$$

$$\frac{A_s(v_o)}{A_e(v_o)} = \frac{g_s}{g_e} \tag{5}$$

$$A_s(v) = a(v) + f(v)\frac{A_s(v_o)}{A_e(v_o)}g_e =$$

$$a(v) + \frac{A_s(v_o)}{A_e(v_o)}A_e(v) \tag{6}$$

$$a(v) = A_s(v) - \frac{A_s(v_o)}{A_e(v_o)}A_e(v) \tag{7}$$

It is thus possible to correct for a difference in dispersion between two almost identical disks, provided the dispersion is reasonably unchanged. To test this assumption we measured the absorbance of three disks without sample. In this case, with $a(v) = 0$ and $f(v)$ the same for the three disks, we should have $A_1(v)/A_2(v) = g_1/g_2$, that is, independent of v. Plotting the three ratios against σ should then give three horizontal lines. Fig. 1 shows that such is not the case, but that the ratios are constant to within about 30%. We may therefore reckon with an uncertainty of about 50% in the solid state ABS spectra. The crucial assumption that $f(v)$ is unchanged from one disk to another is probably the most inaccurate. It is our experience that differences due to the presence of sample are no bigger than between empty disks.

The molar absorbance $\varepsilon = a/cl$ is found as follows. The number of mol in the disk is given by eqn. (8), where m_s, m_{KCl} and m_d are the masses of substance, KCl and the finished disk, and M is the molar weight of the substance. The n mol are dissolved in a volume V, eqn. (9), and the molar absorbance is therefore, as $c = n/V$ and $d = 0.013$ m; $[\varepsilon]$ is $m^2\ mol^{-1}$ if $[m]$ is mg mol^{-1} and $[M]$ g mol^{-1}.

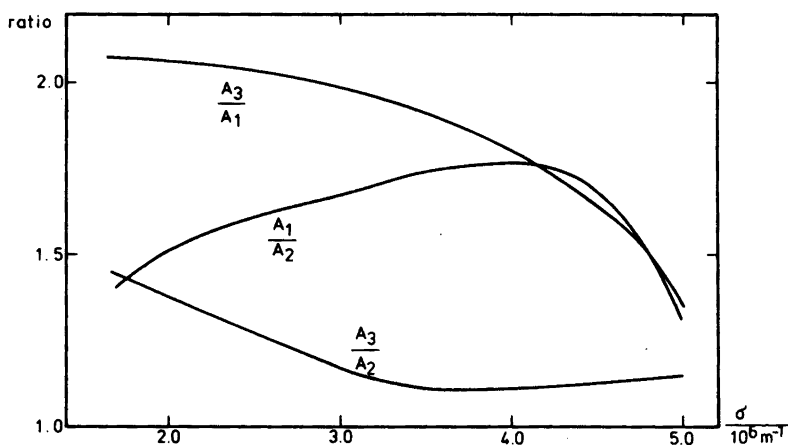*Fig. 1.* Ratios of measured absorbances of three KCl disks without sample.

$$n = \frac{m_s m_d}{(m_s + m_{KCl})M} \quad (8)$$

$$V = (d/2)^2 \pi l \quad (9)$$

$$\varepsilon = aV/nl = a\frac{m_s + m_{KCl}}{m_s m_d} M \times 0.1327 \quad (10)$$

In order to get reasonable accuracy for both strong and weak bands, disks containing from 0.1 to 5 mmol substance were prepared.

Evaluation of CD. $\Delta\varepsilon$ is found from Δa precisely as ε from a. Δa is given by the dichrographe, after correction for instrumental sensitivity. The dispersion cancels out, and the strain is corrected for by the averaging procedure of measuring in four positions described above.

$$f = 4\pi\varepsilon_o m_e c^2 \ln 10/\pi Ne^2 \times I =$$
$$4\pi m_e \ln 10/\mu_o \pi Ne^2 \times I \quad (11)$$

$$D = \varepsilon_o 3\hbar c \ln 10/\pi N \times a/\sigma_o \times I =$$
$$3\hbar \ln 10/\mu_o c\pi N \times a/\sigma_o \times I \quad (12)$$

$$R = 3\hbar \ln 10/4\pi\mu_o cN \times b/\sigma_o \times J \quad (13)$$

Evaluation of $\hbar$, D and R. The oscillator, dipole and rotatory strengths are found from the observed ABS and CD using the formulae [12] (11)−(13), where σ_o is the wavenumber in m^{-1} of the absorption peak, I is the integral (first moment) over the band approximated as $\varepsilon\delta\sigma$, $\delta\sigma$ being the halfwidth, and J is the analogous integral approximated as $\Delta\varepsilon\delta\sigma$. a and b take account of the refractive index of the medium; we use the approximations [12] $a = 9n_o/(n_o^2 + 2)^2$ and $b = 3/(n_o^2 + 2)$ with $n_o = 1.38$ for H$_2$O [13] and 1.55 for KCl. [14]

The data, as presented in the tables, also include the dissymmetry ratio $g = \Delta\varepsilon/\varepsilon$ and the ratio $4R/D$

$= bJ/aI$, which is a more basic dissymmetry ratio than g, as it is corrected for the influence of the medium.

The unit for both R and D is m^{2}s^{2}A^2 or (Cm)^2, the square of an electric dipole moment. Perhaps a more logical choice for R would be m^{3}sA^2 or (Cm)(Am·m) or (Cm)(JT^{-1}), the product of an electric and a magnetic dipole moment. Because of the wish for the undimensioned dissymmetry ratio R/D the former is chosen; hence the division by c in the formula for R above. The relationships to formerly used units are 1 Cm $= 3 \times 10^{11}$ esu cm and 1 J T$^{-1} = 10^3$ erg G^{-1}; in the tables, 1 unit for $D = 9 \times 10^{-38}$ esu and 1 unit for $R = 0.9 \times 10^{-40}$ esu or 0.9 Biot.

RESULTS

Solution spectra. The ABS are presented in Fig. 2 and the CD in Fig. 3. SI units are used for σ, ε and $\Delta\varepsilon$. Overlapping bands are resolved graphically. Within the limits of error, ABS are identical for the two compounds, and CD are mirror images. Uncertainties are very large in regions 2.0 − 2.5 and $> 3.7 \times 10^6$ m^{-1}.

Numerical data derived from the spectra are given in Table 1; values are averaged over the two compounds and, where possible, over ABS and CD. Signs of $\Delta\varepsilon$, g, R and R/4D are positive overall for the (R), negative for the (S) compound. The tiny ABS band at 2.37×10^6 m^{-1} is badly determined, and so is the CD band at 3.32×10^6 m^{-1}. If the former is real it has $\Delta\varepsilon < 0.002$ m^2 mol^{-1}.

Solid state spectra. ABS are shown in Figs. 4 and 5. They are not identical, but very much alike; they certainly do not differ within the accuracy of measurement. Three concentrations, here called strong, medium and weak, were used to get also
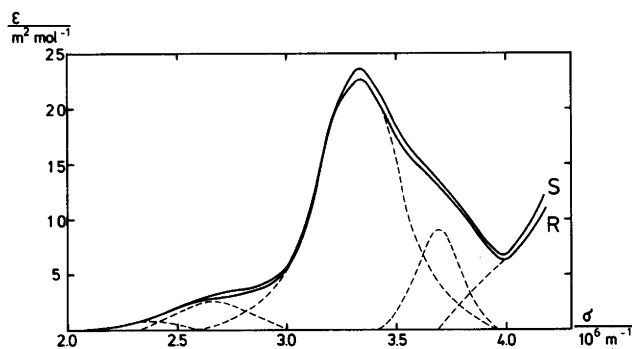

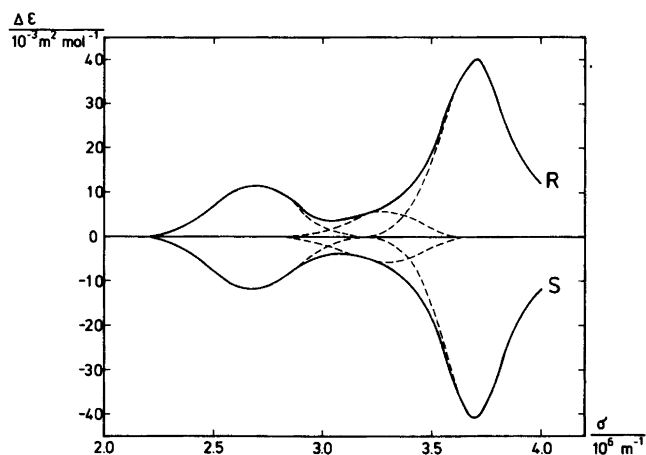*Fig. 2.* Absorption spectra of [PtCl$_2$(R)-pn] and [PtCl$_2$(S)-pn] in aqueous solution.

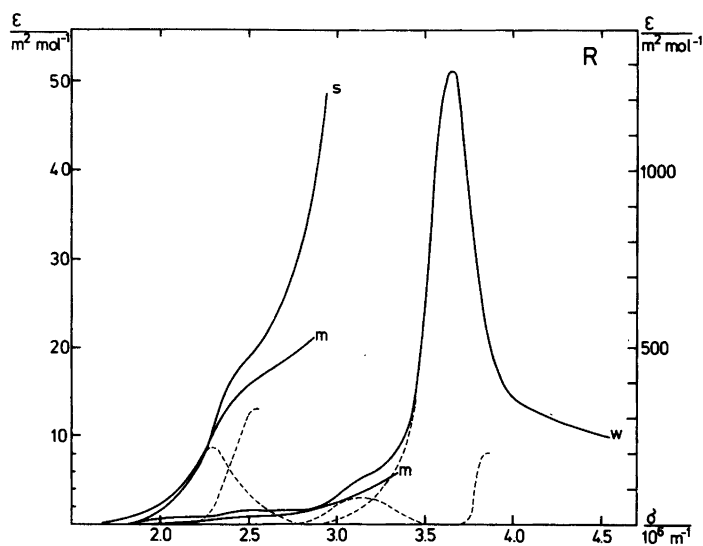*Fig. 3.* Circular dichroism spectra of $[PtCl_2(R)\text{-pn}]$ and $[PtCl_2(S)\text{-pn}]$ in aqueous solution.

Fig. 4. Absorption spectra of $[PtCl_2(R)\text{-pn}]$ in KCl matrix. s, m and w denote high, medium and low concentration in the disk.

Table 1. Absorption and circular dichroism spectra of $[PtCl_2pn]$ in aqueous solution.

σ_o 10^6 m^{-1}	ε m^2 mol^{-1}	$\Delta\varepsilon$ 10^{-3} m^2 mol^{-1}	g 10^{-3}	f	D 10^{-60} m^2 s^2 A^2	R 10^{-63} m^2 s^2 A^2	$4R/D$ 10^{-3}
2.37	0.8	<2	<2.0	0.0001	0.08		
2.68	2.6	12	4.6	0.00043	0.31	0.38	4.9
3.32	22.6	6	0.27	0.0041	2.36	0.13	0.22
3.70	9.0	40	4.4	0.0009	0.47	0.76	6.5

Table 2. Absorption and circular dichroism spectra of [PtCl$_2$(R)-pn] and [PtCl$_2$(S)-pn] in KCl matrix.

σ_0 10^6 m^{-1}	ε m^2 mol^{-1}	$\Delta\varepsilon$ 10^{-3} m^2 mol^{-2}	g 10^{-3}	f	D 10^{-60} m^2 s^2 A^2	R 10^{-63} m^2 s^2 A^2	$4R/D$ 10^{-3}
R							
2.30	8.7	−3.65	−0.42	0.0013	0.95	−0.058	−0.24
2.55	13.2	+3.70	+0.28	0.0018	1.22	+0.048	+0.16
3.15	75	−49.5	−0.66	0.014	7.6	−0.63	−0.33
3.64	1285	−2300	−1.79	0.167	78	−13.2	−0.68
3.83	200	+1120	+5.6	0.016	27	+5	+0.7
S							
2.27	8.9	+3.40	+0.38	0.0014	1.01	+0.060	+0.24
2.55	16.0	−3.65	−0.23	0.0026	1.75	−0.053	−0.12
3.14	80	+49.5	+0.62	0.015	8.3	+0.71	+0.34
3.66	1110	+2500	+2.25	0.106	49	+19.1	+1.56
3.89	200	−700	−3.5	0.024	41	−5	−0.5

minor details. CD are given in Fig. 6. They are almost as perfect mirror images as the solution CD.

Numerical data extracted from the graphs are given in Table 2. Wavenumbers are averaged over ABS and CD; otherwise the data are kept separate as the spectra are rather more complicated than for the solutions. The far UV band at about 3.85 × 10^6 m^{-1} or 260 nm is badly determined in both ABS and CD, but is probably real. It is possible to resolve the solution ABS in an analogous way, but the solution CD does not support this.

For all spectra, D and R are determined through integrals I and J as described above, $\delta\sigma$ being read off the respective graphs.

DISCUSSION

Comparison with earlier work. Ito et al.[1] found for PtCl$_2$(R)-pn in dilute HCl (σ, ε, $\Delta\varepsilon$, g): (2.73, 3.63, +0.015, 0.00041), (3.31, 23.4, not meas.), (3.7, 12.6, +0.038, 0.00030) for the second, third and fourth
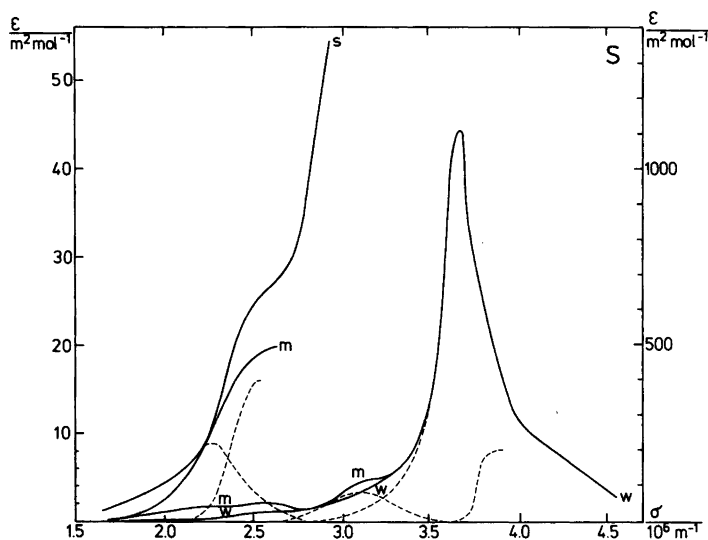

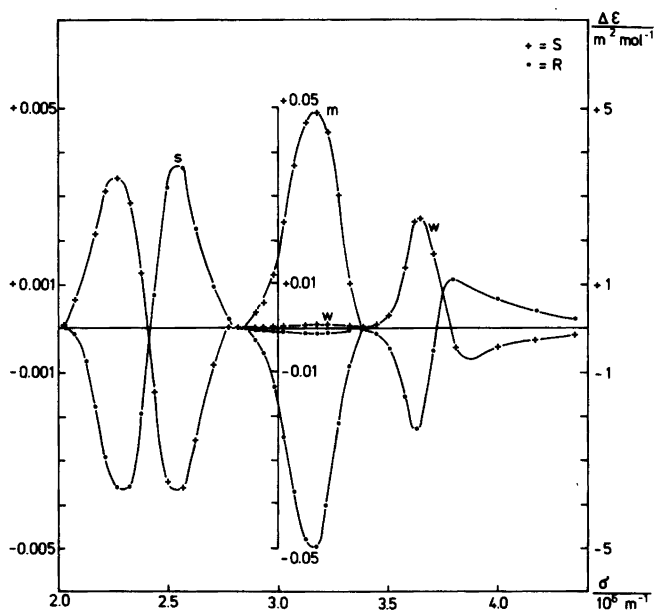*Fig. 5.* Absorption spectra of [PtCl$_2$(S)-pn] in KCl matrix.

Fig. 6. Circular dichroism spectra of [PtCl$_2$(R)-pn] and [PtCl$_2$(S)-pn] in KCl matrix.

band. The values are close to ours through not identical.

Sullivan[2] did not give numerical data, but his graphs of ABS in solution and solid and CD in solution are very much like ours. For CD in solid we disagree: Sullivan misses the first band and shows a positive $\Delta\varepsilon$ at 3.4×10^6 m^{-1}; we find no indication of this.

Solid versus *solution.* The phenomenological differences are striking. On going from solution to solid there are noticeable bathochromic changes in the wavenumbers of the near UV bands between 2.6 and 3.3×10^6 m^{-1}. For the UV bands, extinction and CD increase drastically; and CD changes sign. An interpretation shall not be attempted here.

CONCLUSION

We have demonstrated that it is practicable though tedious to measure and evaluate absorption and circular dichroism spectra of microcrystalline samples. We have, in a quantitative manner, employed the methods to a complete study of the ABS and CD of the title pair of compounds and have derived dipole and rotatory strengths of all observable transitions in the VIS and UV.

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