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# Absolute Configuration of *endo*-Dicyclopentadiene. Crystal and Molecular Structure of (+) (*endo*-Dicyclopentadiene)Platinum Dichloride

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*The absolute configuration of the dissymmetric olefin* endo-*dicyclopentadiene was determined. This was achieved through the determination of the crystal and molecular structure of (+) (endo-dicyclopentadiene) platinum dichloride. The anomalous scattering method was used.*

## Introduction

In the last years the resolution of chiral or prochiral olefins through diastereoisomeric complexes has been the object of considerable studies.[1]

The availability of such optically active olefin complexes offers, *inter alia,* a univoque way to achieve mechanistic informations on reactions of coordinated alkenes. In this connection we can mention as an example the recent elucidation[2] of the stereochemistry of a nucleophilic addition to a π-coordinated olefin.

It must be noted that investigations of the quoted type require the knowledge of the absolute configuration of the chiral or coordinated prochiral alkene.

If the attention is drawn on alkenes with more than one unsaturated bond, it can be remarked that several naturally occurring dienes are optically active and that their absolute configuration is known.

In the case of *endo*-dicyclopentadiene, however, only recently[3] the enantiomeric olefin could be isolated by fractional crystallization of diastereoisomers of platinum(II) complexes.

We examine in this paper the crystal structure of (+) dichloro(*endo*-dicyclopentadiene)platinum(II) for the determination of the absolute configuration of (+) *endo*-dicyclopentadiene,[4] so far not assigned by chemical methods.

This assignement has been instead the object of two separated studies, one[5] based on the exciton theory, the other[6] on ORD and CD spectra of a platinum π-complex of the olefin and the application of the quadrant and octant rules to the coordinated double bonds.

## Experimental Section

(+)-dichloro(*endo*-dicyclopentadiene)Pt$^{II}$ ($[\alpha]_D^{25}$ + 26.2, c 0.5, mehylene chloride) was prepared according to the procedure described.[3] Single crystals were obtained by slow evaporation of methylene chloride from the saturated solution of the enantiomer in a 1:1 v:v mixture of this solvent and acetic acid. A suitable crystal having a tetrahedral shape (edge = 0,02 mm) was mounted on an automated four circle Picker diffractometer.

The crystal is orthorhombic; the unit cell constants were determined by a least square fit from the angular positions of 12 reflections. Crystal data:

$$a = 12.65 \pm 0.05\ \text{Å};\quad b = 12.40 \pm 0.05\ \text{Å};\quad c = 13.07 \pm 0.05\ \text{Å}$$

$$Z = 8;\ d_x = 2.58\ \text{g cm}^{-3};\ d_{exp} = 2.56\ \text{g cm}^{-3}$$

The space group was determined from the systematic extinctions to be $P2_12_12_1$, with 4 general positions per cell; therefore two molecules form the asymmetric unit. The intensities of 1554 independent reflections were measured with a 2ϑ-scanning technique using Zr-filtered Mo-$K_\alpha$ radiation. Of these, 1446 were considered non-zero. The intensities were corrected for the background, for Lorentz and polarization factors and for absorption.

*Structure solution and refinement.* The structure was solved by Patterson methods. The presence of two molecules in the asymmetric unit and the special relationship between the coordinates of the two heavy atoms ($x_1 \simeq x_2$; $y_1 \simeq \frac{1}{2} - y_2$; $z_1 \simeq \frac{1}{2} + z_2$)similated the pseudosymmetry of the space group *Pbca*. This fact made rather difficult to distinguish the light atoms in the first Fourier map. The structure factors calcalculation including only the Pt atoms yielded R

$$= 0.35 \quad (R = \frac{\Sigma||F_o|-|F_c||}{\Sigma|F_o|})$$

We decided to refine the coordinates of the two Pt atoms by least squares methods; the pseudosymmetry *Pbca* disappeared in this way. The R value dropped to 0.17 and the successive Fourier map distinctly show-

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(1) For a review, see G. Paiaro, *Organometal. Chem. Rev.*, (*A*), 6, 319 (1970).

(2) A. Panunzi, A. De Renzi, and G. Paiaro, *J. Amer. Chem. Soc.*, 92, 3488 (1970).

(3) A. Panunzi, A. De Renzi, and G. Paiaro, *Inorg. Chim. Acta, 1,* 475 (1967).

(4) We note that the dextrorotatory free olefin gives rise to the dextrorotatory complex, as described in ref. 3.

(5) B. Bosnich, A. De Renzi, G. Paiaro, J. Himmerleich, and G. Snatzke, *Inorg. Chim. Acta*, 3, 175 (1969).

(6) A.I. Scott and A.D. Wrixon, *Tetrahedr.*, 27, 2339 (1971).

**Table I.** Coordinates and thermal factors of non-hydrogen atoms. The anisotropic thermal factor is in the form exp [—$(h^2a^*\beta_{11}+k^2b^{*2}\beta_{22}+l^2c^{*2}\beta_{33}+2hka^*b^*\beta_{12}+2hla^*c^*\beta_{13}+2klb^*c^*\beta_{23})$]. Standard deviations are given in parentheses; they apply to the last digit.

| Atom | x/a | y/b | z/c | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ | B |
|---|---|---|---|---|---|---|---|---|---|---|
| Pt | 0.6177(1) | 0.6219(1) | 0.4312(1) | 1.90(5) | 1.47(5) | 2.05(5) | 0.01(5) | 0.00(5) | —0.22(6) | |
| Pt′ | 0.5939(1) | 0.8698(1) | 0.9382(1) | 2.17(6) | 1.93(6) | 2.94(6) | 0.38(6) | 0.54(6) | 0.22(7) | |
| Cl(1) | 0.5650(10) | 0.6701(9) | 0.5962(9) | 4.4(5) | 3.1(5) | 3.8(5) | 0.4(4) | 0.4(5) | —1.0(4) | |
| Cl(2) | 0.4689(9) | 0.7059(9) | 0.3703(10) | 2.8(5) | 3.2(5) | 5.0(6) | 0.4(4) | —1.6(5) | 0.4(5) | |
| Cl(1′) | 0.5790(12) | 0.8081(13) | 0.1034(10) | 6.2(8) | 7.3(8) | 3.3(6) | 1.1(7) | 1.7(6) | 1.1(6) | |
| Cl(2′) | 0.4369(10) | 0.7811(11) | 0.8980(12) | 2.7(5) | 4.4(6) | 8.3(9) | —0.9(5) | 0.4(6) | 1.2(6) | |
| C(1) | 0.711(3) | 0.620(4) | 0.288(3) | | | | | | | 3.3(8) |
| C(2) | 0.618(4) | 0.550(4) | 0.279(3) | | | | | | | 3.4(9) |
| C(3) | 0.661(4) | 0.430(4) | 0.291(3) | | | | | | | 3.4(9) |
| C(4) | 0.777(4) | 0.435(4) | 0.319(4) | | | | | | | 4.5(11) |
| C(5) | 0.811(3) | 0.563(3) | 0.302(3) | | | | | | | 2.4(7) |
| C(6) | 0.796(3) | 0.434(3) | 0.451(3) | | | | | | | 2.8(8) |
| C(7) | 0.727(4) | 0.510(4) | 0.509(4) | | | | | | | 4.4(11) |
| C(8) | 0.775(3) | 0.612(4) | 0.483(3) | | | | | | | 3.0(8) |
| C(9) | 0.863(3) | 0.598(3) | 0.414(3) | | | | | | | 2.3(7) |
| C(10) | 0.911(4) | 0.483(4) | 0.460(3) | | | | | | | 3.3(9) |
| C(1′) | 0.591(3) | 0.975(3) | 0.801(3) | | | | | | | 2.3(7) |
| C(2′) | 0.618(4) | 0.866(4) | 0.771(4) | | | | | | | 4.3(10) |
| C(3′) | 0.732(4) | 0.856(4) | 0.743(4) | | | | | | | 4.3(11) |
| C(4′) | 0.783(3) | 0.953(3) | 0.791(3) | | | | | | | 2.7(8) |
| C(5′) | 0.694(3) | 0.038(3) | 0.806(3) | | | | | | | 1.9(7) |
| C(6′) | 0.839(4) | 0.946(4) | 0.895(4) | | | | | | | 4.3(11) |
| C(7′) | 0.758(4) | 0.897(4) | 0.979(4) | | | | | | | 4.0(10) |
| C(8′) | 0.685(4) | 0.004(4) | 0.003(4) | | | | | | | 3.9(10) |
| C(9′) | 0.721(4) | 0.085(4) | 0.922(4) | | | | | | | 3.9(10) |
| C(10′) | 0.847(4) | 0.076(4) | 0.916(4) | | | | | | | 4.1(10) |

ed all the light atoms. Subsequent refinements by least squares using anisotropic temperature factors for Pt and Cl atoms and isotropic temperature factors for C atoms brought the R value to 0.066. The hydrogens were not considered.

At this point anomalous scattering factors were used for Pt and Cl. For the two enantiomorphous molecular structures we obtained the R value 0.063 and 0.072. According to the Hamilton test[7] the best solution has a significance degree greater than 0.995.

In table I are reported the coordinates and the temperature factors together with the corresponding standard deviations of the atoms of the two molecules forming the asymmetric unit. The observed and calculated structure factors are available on application to the authors.

## Results and Discussion

Figure 1 shows the absolute molecular structure of the complex averaged over the two molecules of the structural unit. The geometrical parameters are not reported; owing to the high standard deviations of the coordinates the bond lengths in the olefin are deviated from the normal values up to ± 0.15 Å and the bond angles up to 5°-6°. The location of the coordinated double bonds of the olefin can be determined on the basis of their distances from platinum. The absolute configuration of the olefin illustrated in figure 2 can be assigned in this way.

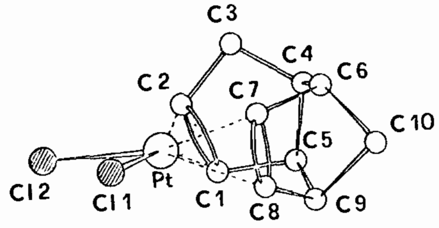

Figure 1.

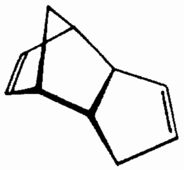

Figure 2. (+) *endo*-dicyclopentadiene.

Our results, which have undoubtedly a great confidence degree, confirm the absolute configuration previously assigned by Scott and Wrixon.[6]

On the other hand, the exciton analysis by Bosnich *et al.*[5] is to be considered correct, if allowance is made for a sign reversing which altered the conclusive assignment.[8]

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(7) W.C. Hamilton, *Acta Cryst.*, *18*, 502 (1965).

(8) A recent private communication by G. Paiaro informed us that the disagreement between our results (as well as those by Scott and Wrixon) and those reported in ref. 5 is actually only apparent. In fact, the CD curve of the (+) isomer of the olefin was ascribed to the (—) isomer: this caused the inverse absolute configuration to be assigned to the latter in the conclusion of ref. 5.