Determination of Absolute Configuration of Platinum–Olefin Complexes by Circular Dichroism

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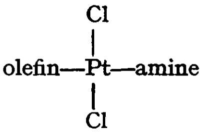
FOLLOWING our initial study of the circular dichroism of optically active olefins complexed to divalent platinum,[1] we have now examined the relationship between the circular dichroism and absolute configuration of a series of dissymmetric cycloalkenes. The resolution of the *trans*-olefins cyclo-octene,[2] cyclononene,[3] and cyclodecene[3] as their *trans*-dichloro-α-methylbenzylamine–olefin platinum(II) complexes [*e.g.* (I)] led to isolation of (*R*)- and (*S*)-*trans*-cyclo-octene, and the allocation of the (*R*)-configuration to (—)-*trans*-cyclo-octene[4] by chemical methods. However, the liberated *trans*-cyclononene racemised rapidly at room temperature and *trans*-cyclodecene could not be recovered in an optically active form.

When the c.d. spectra (Figure 1) of *trans*-dichloro-(—)-*trans*-cyclo-octene-*R*-amineplatinum(II) and of the less soluble *trans*-dichlorocyclodecene-*R*-amineplatinum(II) complex are compared, the correspondence of the lowest energy optically active $d \rightarrow d$ transition at 390 mμ ([θ] *ca.* + 2500) implies that the same absolute configuration (*S*,*S*)† obtains for the co-ordinated olefinic centres in both complexes. Similarly the c.d. curve of *trans*-dichloro-(+)-*trans*-cyclononene-*S*-amineplatinum(II) (Figure 1) is antipodal (θ 390 mμ *ca.* 2500) requiring (*R*,*R*) configuration in the ligand and hence the *S*-configuration for the liberated (+)-*trans*-cyclononene.



$$\text{olefin}-\overset{\displaystyle \text{Cl}}{\underset{\displaystyle \text{Cl}}{\text{Pt}}}-\text{amine}$$

(I)

The possible contribution of the optically active amine to the lowest-energy transition was examined and, as shown in Figure 2, the sign of the

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† When the R. S. Cahn, C. K. Ingold, and V. Prelog (*Angew. Chem.*, 1966, 78, 385) system of nomenclature is applied to such complexes, it is important to note that a dissymmetric olefin of *R* absolute stereochemistry will become *S* with respect to both carbon centres of the olefin co-ordinated with platinum and *vice versa*.

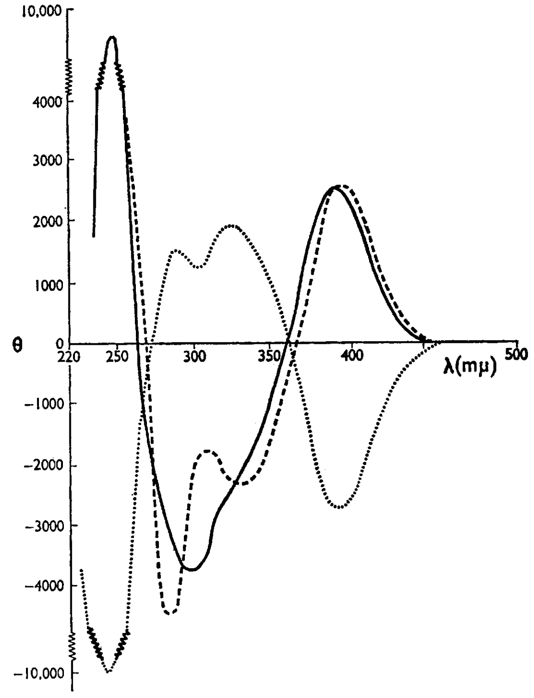


FIGURE 1. *The c.d. spectra of* (a) *trans*-dichloro-(*S*,*S*)-*trans*-cyclo-octene-*R*-α-methylbenzylamineplatinum(II) (———) (b) *trans*-dichloro-(*R*,*R*) *trans*-cyclononene-*S*-α-methylbenzylamineplatinum(II) (· · · · · ·), (c) *trans*-dichloro-(*S*,*S*)-*trans*-cyclodecene-*R*-α-methylbenzylamineplatinum(II) (- - - - - -).

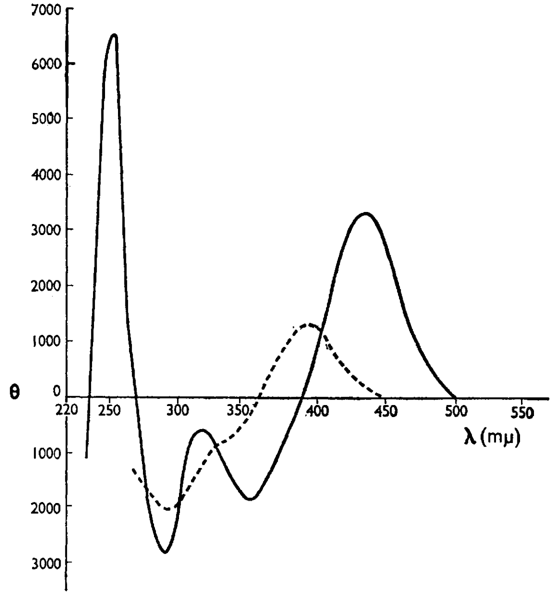


FIGURE 2. *The c.d. spectra of* (a) di-μ-chloro-1,3-dichloro-2,4-bis-(*S*,*S*)-*trans*-cyclo-octenediplatinum(II) (———), (b) *trans*-dichloro-(*S*,*S*)-*trans*-cyclo-octene-*S*-α-methylbenzylamineplatinum(II) (- - - - - -).

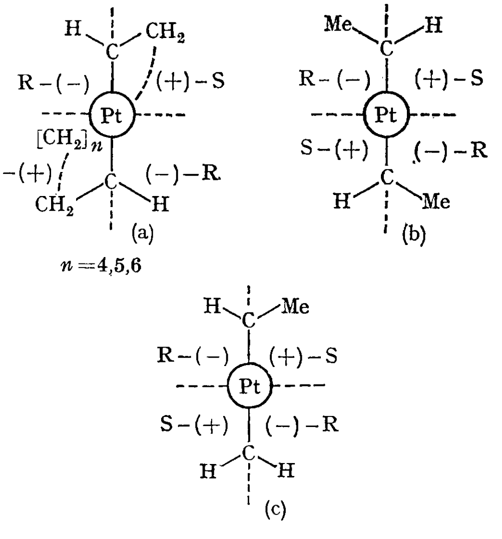
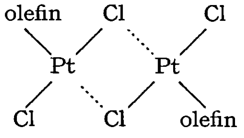


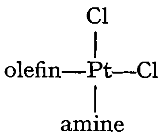
FIGURE 3. *Quadrant rule diagram. R, S* refer to absolute configuration of complexed olefin: +, − to observed sign of the c.d. maximum at 375—425 mμ.

first $d \rightarrow d$ transition is unaltered by a change in the configuration (*R*)-amine → (*S*)-amine. Although a shift to longer wavelength is observed in di-μ-chloro-1,3-dichloro-2,4-bis-(—)-*trans*-cyclooctenediplatinum(II) [as (II)] the magnitude and sign of the dichroism is virtually unaffected by complete removal of the ligand amine. Further support for the premise that the sign of the Cotton effect of the lowest energy Pt $d \rightarrow d$ transition is independent of the relative positions of amine and olefin on the square plane of platinum and reflects the absolute configuration of the co-ordinated olefin[5] comes from the observation that *cis*-dichloro-(+)-*trans*-cyclo-octene-(*S*)-amineplatinum(II) (as III) is laevorotatory.[6] These results and the assignment[7] by *X*-ray methods of the (*R*,*R*) configuration to the olefinic ligand (—)-*cis*-dichloro-*trans*-2-butene-(*S*)-α-methylbenzylamine (negative c.d. at *ca.* 375 mμ)[6] suggest that the



(II)

absolute configuration of the co-ordinated olefinic centres can be derived directly from the sign of the optically active $d \rightarrow d$ transition at 375—425 mμ using the known absolute configuration and c.d. spectra of the *trans*-cyclo-octene complexes as references.



$$\text{olefin}-\underset{\underset{\text{amine}}{|}}{\overset{\overset{\text{Cl}}{|}}{\text{Pt}}}-\text{Cl}$$

(III)

It is found that a general Quadrant Rule predicts the absolute configuration from the sign of the c.d. maximum near 400 mμ. As shown in Figure 3 the chirality of the complexed olefinic carbon centres is related to the location of substituents or ring residues in quadrants of alternating sign formed by the intersection of the platinum square plane and the vertical plane normally corresponding[8,9] to the olefinic C–C bond viewed along the platinum x-axis. The quadrant diagram for the (R)-*trans*-cycloalkenes [S,S-*trans*-cycloalkeneplatinum(II)] is shown in Figure 3a and the case of laevorotatory‡ R,R-*trans*-2-butene (*cis*- or *trans*[11]-amine complex) is demonstrated in Figure 3b. In Figure 3c it is shown that (+)-*cis*-dichloropropylene-S-α-methylbenzylamine-platinum(II)[6] and the (+)-*trans*-propylene-R-amine[10] complex both possess the S-configuration (positive c.d. at *ca.* 375 mμ in both cases).

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‡ Negative c.d. curves have been found for both the *cis*-[6] and the *trans*-amine[10] complex.

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