

Circular Dichroism of Platinum–Olefin Complexes

By E. PREMUZIC and A. I. SCOTT*

(*The Chemical Laboratory, University of Sussex, Brighton, BN1 9QJ*)

RECENT instrumental improvements have allowed the measurement of the circular dichroism of optically active olefins although overlap of $\pi \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ transitions tend to complicate the 200 m μ region and reliable data is still difficult to obtain at 190–200 m μ .^{1,2} Earlier solutions to the problem have utilized the osmate ester³ and destroy the olefinic absorption and geometry. In

principle it is possible to promote a red shift of episulphide chromophores⁴ which necessarily electronic absorption of the ethylenic chromophore whilst observing a concomitant shift of circular dichroism and optical rotary dispersion through complex formation and/or charge-transfer phenomena.† This is now illustrated for two classes of optically active olefin using the

† However, we have observed several optically inactive charge transfer bonds of disymmetric olefins, *e.g.*, with tetracyanoethylene.

transitions of platinum as the chromophore. At the same time the olefinic bond retains its geometry and the ligand can be regenerated from the complex by established methods.⁵

A rapid qualitative assay of platinum complex stability is illustrated for the bicyclic olefin, β -pinene (I). A 3% solution of (+)- β -pinene in 0.1M- Na_2PtCl_4 in n-propanol gives the circular dichroism spectrum shown in Figure 1. The lowest energy $d \rightarrow d$ transition of the trichloro-olefin Pt^{II} complex occurs at 480 $m\mu$ but is optically inactive. The main c.d. band is centred near the second $d \rightarrow d$ transition ($\Delta\epsilon + 0.2$) at 370 $m\mu$, although a small negative maximum $\Delta\epsilon - 0.05$ is also observed at 430 $m\mu$. The corresponding o.r.d. curve shows a simple positive maximum at 420 $m\mu$ and for diagnostic purposes is perhaps a more convenient guide for future absolute configurational comparisons.



In a second example, (+)-limonene (II) was converted into dichloro-(+)-limoneneplatinum(II), whose c.d. spectrum is shown in Figure 2. Again, three distinct optically active transitions of

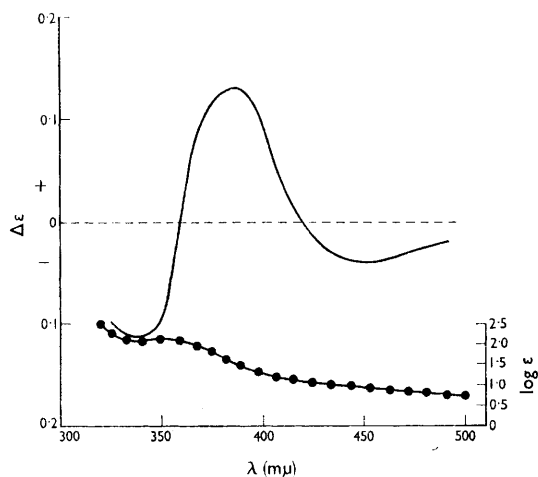


FIGURE 1. Circular dichroism (—) and u.v. (---••---) spectrum of (+)- β -pinene Na_2PtCl_4 solution in n-propanol.

alternating sign occur.[†] The two lowest-energy transitions at 450 $m\mu$ ($[\theta] + 300$) and 370 $m\mu$ ($[\theta] - 400$) are undoubtedly disymmetrically perturbed $d \rightarrow d$ transitions of Pt.⁶ The major circular dichroism band is observed at 274 $m\mu$ ($[\theta] + 3000$) although the absolute configuration of the complex is most probably reflected in the lowest-energy (450 $m\mu$) transition.⁷

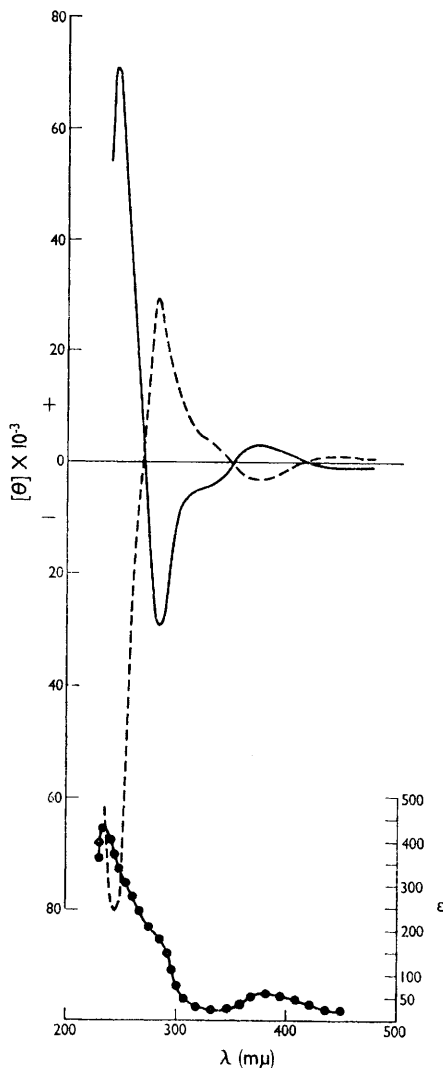


FIGURE 2. Circular dichroism spectra of (a) (+)-dichlorolimoneneplatinum(II) (—), (b) (-)-dichlorolimoneneplatinum(II) (---••---), and the u.v. spectrum of (a) all in (CH_2Cl_2) .

[†] For reasons of clarity the rather complex o.r.d. curve is not included but will be discussed in full elsewhere. (-)-Limonene dichloroplatinum(II) complex gives mirror image c.d. (Figure 2) and o.r.d. data.

These preliminary experiments show that in favourable cases the circular dichroism of olefins can be moved into the convenient instrumental

range for comparative studies of relative and absolute configuration.

(Received, September 7th, 1967; Com. 961.)

¹ A. Yogev, D. Amar and Y. Mazur, *Chem. Comm.*, 1967, 339.

² M. Legrand and R. Viennet, *Compt. rend.*, 1966, **262**, C, 1290.

³ E. Bunnenberg and C. Djerassi, *J. Amer. Chem. Soc.*, 1960, **82**, 5933.

⁴ C. Djerassi, H. Wolf, D. A. Lightner, E. Bunnenberg, K. Taheda, T. Komeno, and K. Kuriyama, *Tetrahedron*, 1963, **19**, 1547; D. E. Bays, R. C. Cookson, R. R. Hill, J. F. McGhie, and G. E. Usher, *J. Chem. Soc.*, 1964, 1563.

⁵ A. C. Cope, C. R. Ganellins, H. W. Johnson, V. Van Auben, and H. J. S. Winkler, *J. Amer. Chem. Soc.*, 1963, **85**, 3276.

⁶ Cf., P. Corradini, G. Paiaro, A. Panunzi, S. F. Mason, and G. H. Searle, *J. Amer. Chem. Soc.*, 1966, **88**, 2863.

⁷ A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 1965, 2883; A. J. McCaffery, S. F. Mason, and B. J. Norman, *ibid.*, p. 5094.