Chiral Metal Complexes.
1. Photochemical Inversion in Ternary Ru(II) Complexes of Diimines and L-Tryptophane

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The compounds Δ,Λ-$[Ru(phen)_2(L$-$trp)]ClO_4 \cdot 3H_2O$ *and* Δ,Λ-$[Ru(bipy)_2(L$-$trp)]ClO_4 \cdot 3H_2O$ *(where* L-trp *is the* L-*tryptophane anion) have been isolated and the complex cations resolved into their diastereoisomeric forms using cation-exchange chromatography. Circular dichroism studies show the* Δ-*isomers to spontaneously invert into the* Λ-*forms in the presence of light in aqueous solution. These novel inversion reactions are the first reported in which substitution in the coordination sphere does not take place. The equilibrium constants for the reaction*

$$\Delta\text{-}[Ru(diimine)_2(L\text{-}trp)]^+_{(aq)} \rightleftharpoons$$

$$\Lambda\text{-}[Ru(diimine)_2(L\text{-}trp)]^+_{(aq)}$$
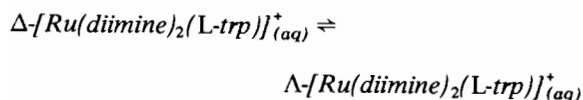
are 4.0 and 2.1 for the phen and bipy compounds respectively.

Introduction

The first report of a reaction with inversion at an octahedral transition metal appeared [1] in 1934, and since that time seven other closely related examples have been discovered, all but two having been found by Bailar and his co-workers. Six of these involved an inverted product resulting from the base hydrolysis of optically active $^+[Co(en)_2Cl_2]^+$ or α-$[Co(trien)Cl_2]^+$. The two remaining examples are those of Gillard and Price [2], who found that

inversion occurs during the acid hydrolysis of Λ-(+)-cis(N)-cis(O)-$[Co(L$-val$)_2CO_3]^-$, and the one example not involving Co(III) reported by Archer *et al.,* [3] in the reaction of Δ-$[Fe(phen)_3]^{2+}$ with cyanide ion to give Λ-$[Fe(phen)_2(CN)_2]$.

Here we wish to report on a unique class of inversions at octahedral centres in reactions which, unlike all previous examples, does not involve substitution in the coordination sphere. These inversions are light-catalysed, and occur during reaction (1), where the diimine

$$\Delta\text{-}[Ru(diimine)_2(aa)]^{n+} \rightleftharpoons \Lambda\text{-}[Ru(diimine)_2(aa)]^{n+} \quad (1)$$
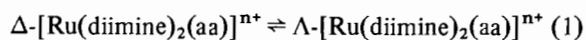
is either phen or bipy and aa is an optically active amino acid. We have found this phenomenon to be quite common in compounds of this type and we present here the results of our studies involving the amino acid L-tryptophane.

Experimental

Microanalyses were determined in this laboratory by A. Dams. Water of hydration analyses were carried out using a Stanton Redcroft TG 750 thermogravimetric balance at temperatures below 120°. Electronic spectra were recorded on a Beckman DK2A recording instrument. Circular dichroism (CD) spectra were recorded on a Jobin-Yvon Dicrographe III.

The bases phen (Lancaster Synthesis) and bipy (BDH) were synthetic grade materials and were used as obtained. L-tryptophane was obtained from Sigma Chemical Company. Sephadex® C25 cation exchange resin obtained from Pharmacia, was used in acid form. $RuCl_3 \cdot 3H_2O$ was obtained from Johnson–Mathey Ltd. All chemicals used were of reagent grade.

Synthesis of Complexes

Cis-[Ru(phen)₂Cl₂] and cis-[Ru(bipy)₂Cl₂]

Cis-[Ru(phen)$_2$Cl$_2$] was prepared by the method of Bosnich and Dwyer [4]. The bipy analogue was prepared by either of the following methods.

(a) RuCl$_3$·3H$_2$O (5.2 g, 20 mmol) was dissolved in 6 *M* HCl (50 cm^3) and a solution of bipy (3.1 g, 20 mmol) in 6 *M* HCl (70 cm^3) was added. The dark brown-green solution was filtered immediately then allowed to stand for 3–4 days. The brown crystalline solid which formed (8.44 g) was filtered off, washed with a little cold water then with acetone and air-dried. Microanalysis suggested the formula [bipyH$_2$] [RuCl$_5$H$_2$O] for this salt [found: C: 26.2, H: 2.6, N: 6.0%. Calc.: C: 26.4, H: 2.7, N: 6.2%], although repeated syntheses yielded products of variable composition. The substance was dissolved in warm dimethylformamide (80 cm^3) and to this solution was added bipy (2.8 g, 18 mmol). The dark orange solution was heated under reflux for 30 min, during which time the colour changed to a deep purple and similarly coloured crystals began to deposit from the hot solution. The mixture was allowed to stand for 3 days then the solid product was filtered off, washed well with acetone and air-dried. [Yield: 3.15 g (33%). *Analyses*: Found: C: 49.2, H: 3.6, N: 11.4%. Calc. for *cis*-[Ru(bipy)$_2$Cl$_2$]: C: 49.6; H: 3.3, N: 11.6%].

(b) To a solution of RuCl$_3$·3H$_2$O (0.52 g, 2 mmol) in warm dimethylformamide (50 cm^3) was added bipy (0.62 g, 4 mmol). The dark green solution was heated under reflux for 15 min, the colour changing progressively to dark red then a deep purple. The solution was allowed to cool and was filtered. The filtrate was reduced in volume on a hotplate to 25 cm^3 and was then allowed to cool and stand overnight. The dark purple crystals which formed were filtered off, washed with acetone and air-dried [Yield: 0.35 g (36%). *Analyses*: Found: C: 49.4; H: 3.4, N: 11.7%].

Δ,Λ-[Ru(phen)₂(L-trp)] ClO₄·3H₂O and Δ,Λ-[Ru(bipy)₂(L-trp)] ClO₄·3H₂O

A mixture/suspension of *cis*-[Ru(phen)$_2$Cl$_2$] (0.18 g, 0.33 mmol) and *L*-tryptophane (0.20 g, 1 mmol) in water (50 cm^3) was heated to just below boiling then 1 *M* NaOH (1 cm^3) was added. After maintaining this temperature for 5–10 min, the hot orange-red reaction solution was filtered and a saturated aqueous solution of NaClO$_4$ (2 cm^3) was added. A red-brown solid formed immediately. The mixture was allowed to cool and stand overnight, then the solid product was filtered off, washed with water and dried under vacuum [Yield: 0.10 g (37%). *Analyses*: Found: C: 51.4, H: 3.6, N: 10.2, H$_2$O: 6.2%. Calc. for [Ru(phen)$_2$(*L*-trp)] ClO$_4$· 3H$_2$O: C: 51.4, H: 4.2, N: 10.3, H$_2$O: 6.6%]. Δ,Λ-[Ru(bipy)$_2$(*L*-trp)] ClO$_4$·3H$_2$O was isolated as a fine red precipitate by employing synthetic procedure similar to that for the phen analogue described above. [Yield: 43%. *Analyses*: Found: C: 48.4, H: 3.6, N: 11.3, H$_2$O: 6.3%. Calc.: C: 48.4, H: 4.3, N: 10.9, H$_2$O: 7.0%.]

Resolution of Diastereoisomers

A small sample (1–2 mg) of either amino acid chelate was dissolved in 95% ethanol (0.5 cm^3) and water (3 cm^3) was added to the resulting deep red solution. The dissolved sample was then placed on a column (30 cm × 1.5 cm) of Sephadex® C25 resin with deionized water as supporting solvent. The adsorbed complex cation was washed well with deionized water then eluted with either 1% w/w sodium chloride or 1% w/w sodium perchlorate solutions. The coloured eluents were collected in several fractions each of 5 cm^3. During the separation process the column and resulting collected fractions were kept fully covered with aluminium foil in order to exclude light.

The CD and electronic spectra of each fraction were recorded as soon as practical after collection, and each fraction was then stored in the dark. The
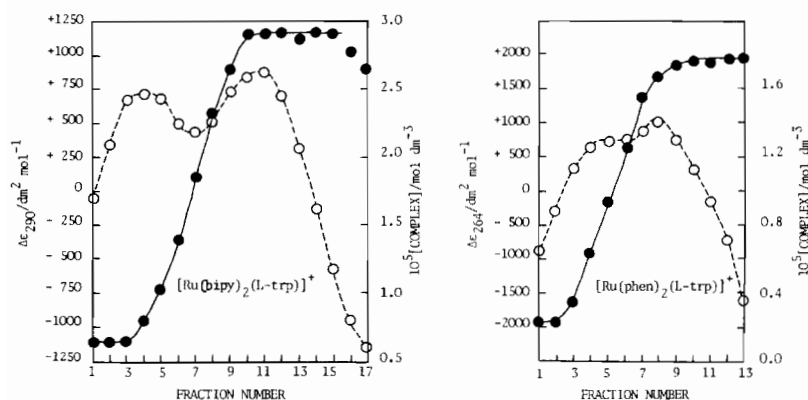

Fig. 1. Profiles of separations of diastereoisomers, using cation-exchange chromatography.
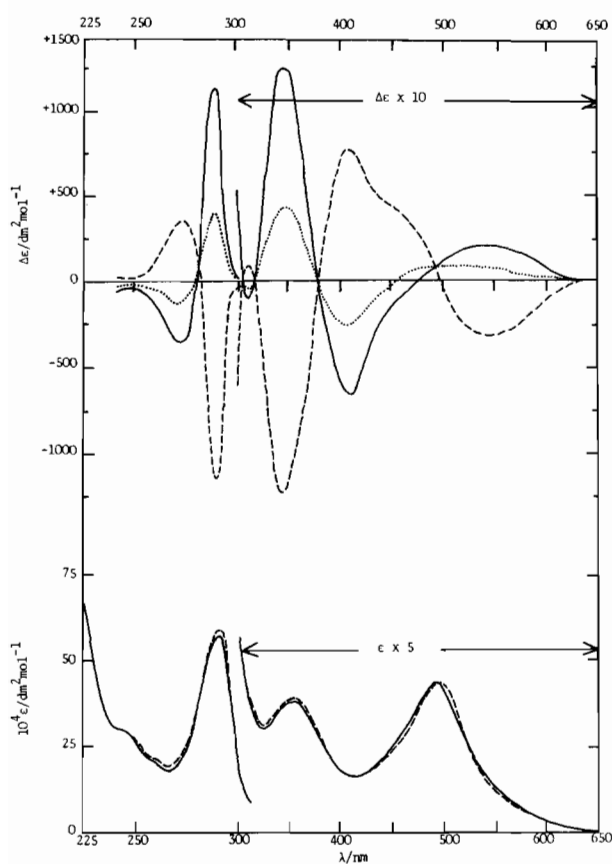
Fig. 2. Electronic and CD spectra of the Λ-, (———), and Δ-, (-----), diastereoisomers of $[Ru(phen)_2(L\text{-trp})]^+$, together with the CD spectrum (······) of the equilibrium mixture in H_2O after exposure to light.

Fig. 3. Electronic and CD spectra of the Λ-, (———), and Δ-, (-----), diastereoisomers of $[(Ru(bipy)_2(L\text{-trp})]^+$, together with the CD spectrum (······) of the equilibrium mixture in H_2O after exposure to light.

concentration of a sample of each solution was determined after exposure to light by comparison with the visible absorption spectrum of a solution of known concentration prepared from the relevant solid perchlorate salt.

Results and Discussion

The two solids isolated, $\Delta,\Lambda\text{-}[Ru(phen)_2(L\text{-trp})]\text{-}ClO_4\cdot 3H_2O$ and $\Delta,\Lambda\text{-}[Ru(bipy)_2(L\text{-trp})]ClO_4\cdot 3H_2O$, contain approximately equal mixtures of diastereoisomers. These isomeric pairs may be resolved by cation exchange chromatography as described above. A profile of the separation of each mixture is demonstrated in Fig. 1. It may be seen that, under the conditions employed, incomplete separation in both cases is obtained overall. However, as the consistent $\Delta\epsilon$ values indicate, optical purity is obtained for each diastereoisomer in the leading and trailing fractions, and the collection of these fractions constitutes an effective resolution of the complex cations.
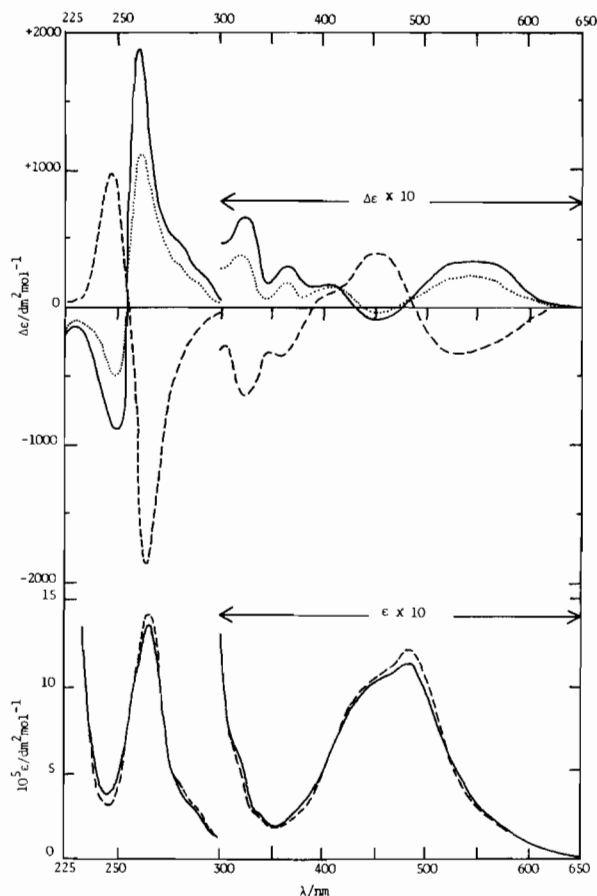
The electronic and CD spectra of the pure diastereoisomers of $[Ru(phen)_2(L\text{-trp})]^+$ thus obtained are shown in Fig. 2, and the analogous definitive spectra for the bipy species are presented in Fig. 3. There are differences in spectral features for each pair of isomers, as might be expected for species which are not enantiomorphous.

The absolute configurations of the various species have been assigned throughout on the basis of predictions [5, 6] derived from exciton theory using the sign of the long-axis-polarized $\pi \to \pi^*$ transitions in coordinated phen moieties. The rotational strength observed for these transitions also is in accord with the predictions of Bosnich [5] who found comparable results for the resolved complex cation $[Ru(phen)_2(py)_2]^{2+}$; The Λ-isomer, which is the more stable, is eluted from the column last in both cases.

Although many examples of the separation of diastereoisomeric species are known, the findings reported here are unique in that a facile light-catalysed mechanism for interconversion is available.
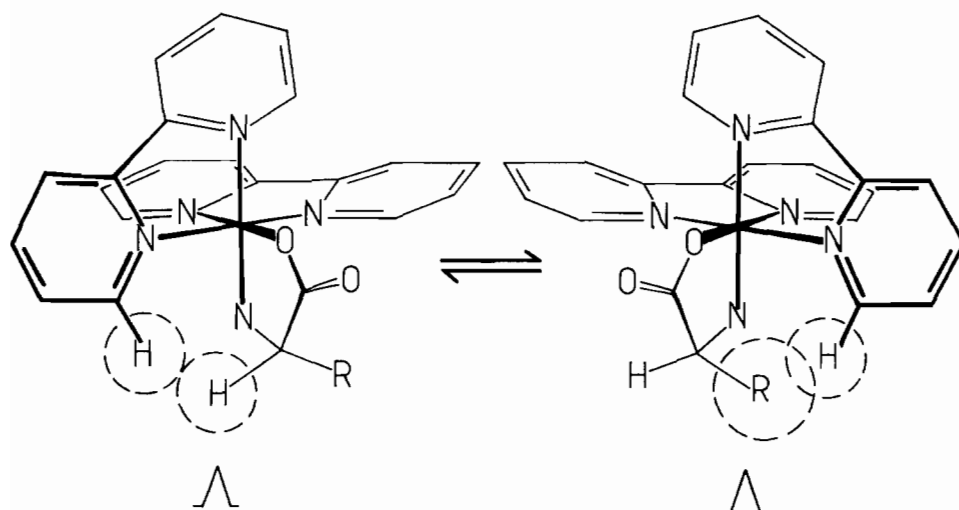
Fig. 4. Schematic representation of steric interactions involving the amino acid in the complexes Δ- and Λ-[Ru(diimine)$_2$(aa)]$^{n+}$.

Moreover, the fact that the equilibrium constants for reaction (1) are observed to be greater than unity means that inversion at the metal centre is readily obtainable.

Separation of the diastereoisomers was carried out in the absence of light. When visible light is allowed to fall upon a solution of the Λ-diastereoisomer over an extended period the optical activity is observed only to decrease. However when visible light is admitted to a solution of the Δ-diastereoisomer the ion inverts spontaneously, resulting in a spectrum identical to that obtained with the solution of the other propellor. In addition, freshly prepared solutions of the solid mixtures of diastereoisomerism equilibrate in the light to give CD spectra corresponding to the same degree of selectivity as that obtained with the pure isomers.

The CD spectra of the equilibrium solutions are included in Figs. 2 and 3. These equilibrium positions correspond to values of the equilibrium constant for equation (1) of 4.0 and 2.1 for the phen and bipy analogues respectively. From those values the difference in the free energies of formation, $\Delta\Delta G_f^o$, (2), for the phen isomers

$$\Delta\Delta G_f^o = \Delta G_f^o \left\{ \Lambda\text{-[Ru(phen)}_2(L\text{-trp)]}^+_{(aq)} \right\} -$$

$$-\Delta G_f^o \left\{ \Delta\text{-[Ru(phen)}_2(L\text{-trp)]}^+_{(aq)} \right\} \qquad (2)$$

is -3.43 kJ mol^{-1}. The corresponding parameter for the bipy analogues is -1.84 kJ mol^{-1}. Models of pairs of diastereoisomers for this class of compounds, Fig. 4, indicate a sterically more favoured configuration for the Λ-propellor, which is in agreement with the above findings based on exciton theory. It is possible therefore that steric factors play a

prominent role in the determination of the preferred stereochemistry.

The facile inversion of the Δ-isomers to the Λ-forms is unusual in that complexes of bivalent ruthenium of this type are usually kinetically inert towards racemization [7], especially compared with similar complexes of Ru(III), and indeed any distribution of the diastereoisomers in solution remains completely unaltered in the absence of light. It has been reported [8] that cis–trans-photoisomerization of related Ru(II) complexes (3) takes place, and that the

$$cis\text{-[Ru(bipy)}_2(H_2O)_2]^{2+} \xrightleftharpoons{h\nu}$$

$$-trans\text{-[Ru(bipy)}_2(H_2O)_2]^{2+} \qquad (3)$$
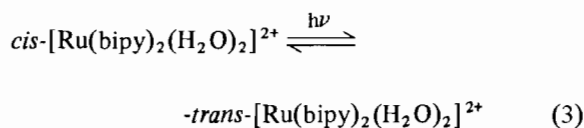
complexes are photochemically oxidised to Ru(III) in the presence of perchlorate ion. Similarly, cis and trans-[Ru(en)$_2$(H$_2$O)Cl]$^{2+}$ are known to be photochemically interconvertable [9] with comparable quantum yields. Therefore the possibility that the isomeric inversions reported here might take place via a light-catalysed redox mechanism involving Ru(III) was investigated. Some decomposition of the complexes occurs in aqueous solution with prolonged light exposure, but at a much slower rate than the inversion. In this connection it may be worthy of note that tryptophane alone undergoes a photochemical intramolecular reaction [10]. We have found that the observed decomposition may be arrested by the addition of hydrazine, while the inversion continues. This seems to suggest that the light-

catalysed inversion proceeds with the ruthenium atom retaining the bivalent oxidation state.

Those reactions are unique in that they are the first reported inversions which do not involve substitution in an octahedral coordination sphere. Similar behaviour has been observed with each of the Ru(II)/ aminoacid chelates investigated thus far [11], and, in addition, resolution of like complexes with other metals has been obtained. The results of these studies will be communicated in future articles.

Acknowledgements

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