Chiral Metal Complexes

2*. Light-Catalysed Diastereoisomeric Equilibration in Aqueous Solutions of cis-[Ru(phen)₂(L-serine)]⁺ and its 2,2′-Bipyridyl Analogue

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The compounds of general form Δ,Λ-[Ru(diimine)₂(L-ser)] ClO₄·nH₂O where L-ser is the L-serinate anion, diimine is 1,10-phenanthroline and 2,2′-bipyridyl, and n = 1.0 and 0.5 respectively, have been isolated and the complex ions resolved using cation exchange chromatography. The Λ-isomer of the bipy complex and the Δ-isomer of the phen complex spontaneously invert in aqueous solution in the presence of light. The equilibrium constants for the reaction

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

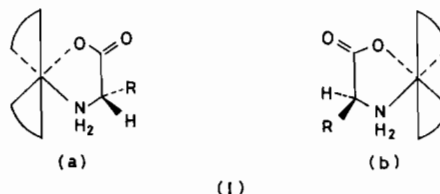$$\Lambda\text{-}[Ru(diimine)_2(L\text{-}ser)]^+_{(aq)}$$
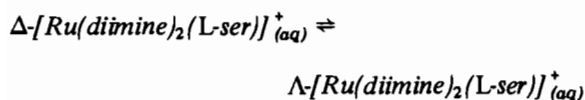
are 1.28(3) and 0.71(5) at 298.2 K for the phen and bipy complex cations respectively. The apparently anomalous behaviour of the bipy complex compared with other related systems indicates that steric factors are not always the most important contributors to chiral discriminations in this class of complexes.

Introduction

We have reported recently [1] the synthesis and separation by chromatographic methods of diastereoisomeric mixtures of complexes of the form *cis*-[Ru(diimine)₂(L-trp)]⁺ where diimine is either phen† or bipy and L-trp is the L-tryptophane anion. In addition it was noted that, in the presence of light, the diastereoisomeric mixtures of these complex cations equilibrate in aqueous solution to give an excess of the Λ-propellor. Furthermore, if the thermodynami-

cally less stable Δ-isomer is separated and its aqueous solution exposed to light, it is observed to spontaneously invert with respect to its absolute configuration at the metal. This reaction is novel in that it is the first inversion reported which involves no overall change in the coordination sphere.

Models of such diastereoisomers suggest that the Λ-isomer, I(a), should be the less sterically strained for any α-amino acid of L-configuration. Accordingly, we have found [1] equilibrium cons-

(a)　　　　　　(b)

(I)

tants for reaction (1) of 4.0 and 2.1 for aa = L-tryptophane and diimine = phen and bipy, respectively.

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

(1)
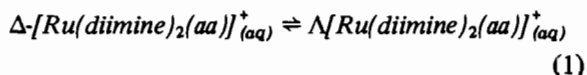
Similarly, the Λ-diastereoisomer is observed to be favoured for other L-amino acids with bulky side groups, such as in L-phenylalanine, L-tyrosine, L-histidine and L-proline [2]. In such complexes each Δ-diastereoisomer, (Ib), with either phen or bipy, inverts its configuration at the metal centre upon exposure to light to give a thermodynamically stable equilibrium mixture in which the Λ-complex is predominant. The magnitude of the equilibrium constant for equation (1) varies both with change in amino acid and heterocyclic base [2].

In the course of our studies, aimed at testing the generality of the above findings, we have found one pair of anomalous diastereoisomers which indicate that steric interactions are not the only important factors which determine the equilibrium direction.
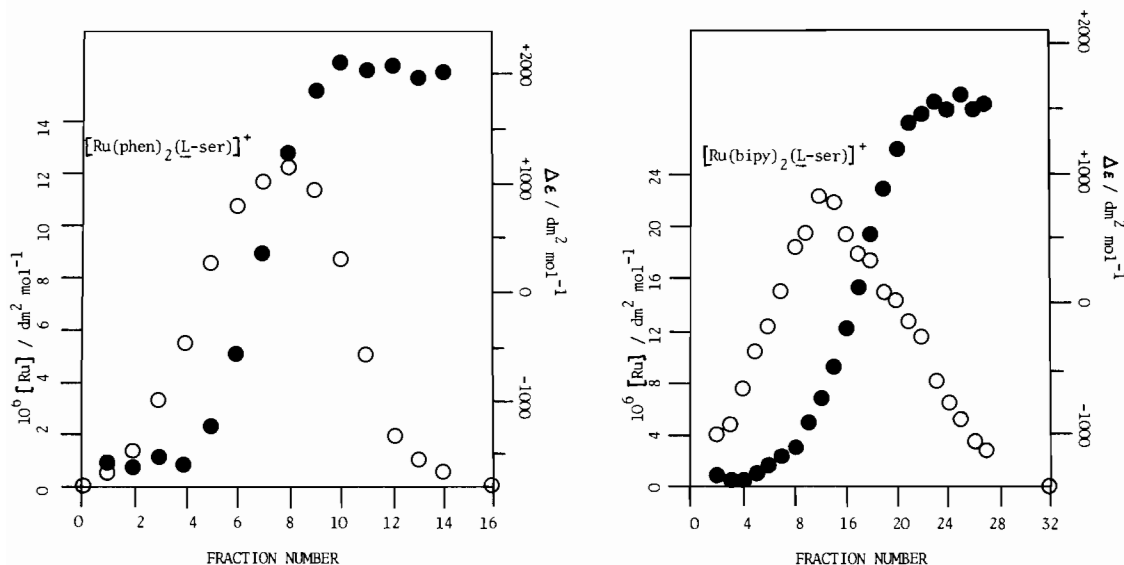
Fig. 1. Course of elution (open circles) and maximum CD (full circles) during chromatography of Δ,Λ-[Ru(phen)$_2$(L-ser)]$^+$, and its bipy analogue.

Here we present the results of our studies on the L-serine-derived complex ions Δ,Λ-[Ru(phen)$_2$(L-ser)]$^+$ and Δ,Λ-[Ru(bipy)$_2$(L-ser)]$^+$.

Experimental

Electronic and circular dichroism (CD) spectra were measured using a Beckmann DK2A ratio recording spectrophotometer and a Jobin–Yvon Dichrographe III, respectively. Elemental analyses were carried out by Mrs. A. Dams in the Department of Chemistry, Cardiff. Water of hydration analysis was performed using a Stanton-Redcroft TG750 thermogravimetric balance. Chromatographic separations of the diastereoisomeric mixtures were performed using Sephadex® C-25 cation exchange resin in the H$^+$ form following earlier reported procedures [1]. Fractions eluted from the columns were collected using an automatic fraction collector.

Δ,Λ-[Ru(phen)$_2$(L-ser)] ClO$_4$ ·H$_2$O

Cis-[Ru(phen)$_2$Cl$_2$], (0.27 g, 0.5 mmol), [3], was dissolved in hot water (50 cm^3) and to the solution of cis-[Ru(phen)$_2$ClH$_2$O]$^+$ thus generated was added L-serine (0.21 g, 2 mmol, Hopkin and Williams Laboratory Reagent), followed by 1.0 mol dm^{-3} NaOH (2 cm^3, 2 mmol). The warm solution was cooled, filtered, and then saturated aqueous NaClO$_4$ solution (10 cm^3) was added. An immediate scarlet precipitate formed in the reaction solution, which was allowed to digest at ambient temperature overnight. The solid product (small dark-red crystals) was then filtered under suction, washed with cold water and dried in vacuo over silica gel. [Yield:

25%. Analyses: Found; C: 47.2; H: 3.7, N: 10.0, H$_2$O: 3.0%. Calc. for [Ru(phen)$_2$(L-ser)] ClO$_4$·H$_2$O; C: 47.5; H: 3.5, N: 10.3; H$_2$O: 2.6%].

Δ,Λ-[Ru(bipy)$_2$(L-ser)] ClO$_4$·0.5H$_2$O

Deep red crystals of the compound were isolated following a procedure identical to that for the phen analogue described above, but starting with cis-[Ru(bipy)$_2$Cl$_2$] prepared as described previously [1]. [Yield: 65%. Analyses: Found; C: 44.0, H: 3.9; N: 11.2, H$_2$O: 1.5%. Calc. for [Ru(bipy)$_2$(L-ser)] ClO$_4$·0.5H$_2$O; C: 44.1; H = 3.7, N: 11.2, H$_2$O: 1.4%].

Absorption coefficients for λ_{max} in the visible regions of electronic spectra were calculated to be 1.284 × 10^5 dm^2 mol^{-1} (482 nm) for Δ,Λ-[Ru(phen)$_2$(L-ser)]$^+$ and 1.013 × 10^5 dm^2 mol^{-1} (494 nm) for Δ,Λ-[Ru(bipy)$_2$(L-ser)]$^+$ in aqueous solution. These absorption coefficients were calculated after the solutions had equilibrated in the presence of light and after addition of hydrazine hydrochloride (20 mg in 100 cm^3) to inhibit photooxidation. The values obtained were used to calculate in turn the concentrations and hence the magnitude of the CD spectra for solutions from both the chromatographic and equilibration studies.

Results and Discussion

Figure 1 shows the course of elution from the Sephadex® column of the complexes [Ru(phen)$_2$(L-ser)]$^+$ and [Ru(bipy)$_2$(L-ser)]$^+$ with time, using aqueous 1% NaClO$_4$ solution as eluant. Superimposed on the figure are the magnitudes of the high-wave-
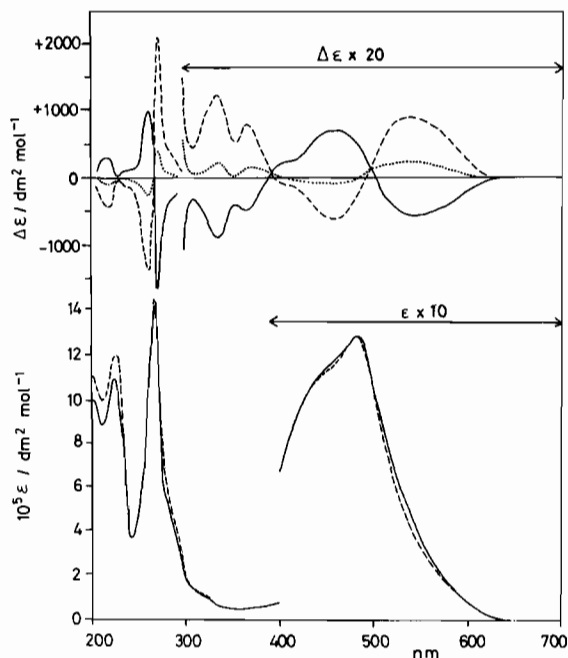
Fig. 2. Electronic and CD spectra of (———) Δ-[Ru(phen)$_2$-(L-ser)]$^+$, (------) Λ-[Ru(phen)$_2$(L-ser)]$^+$, and (......) CD spectrum of the diastereoisomeric equilibrium mixture in aqueous solution exposed to light.

Fig. 3. Electronic and CD spectra of (———) Δ[Ru(bipy)$_2$-(L-ser)]$^+$, (------) Λ-[Ru(bipy)$_2$(L-ser)]$^+$, and (......) CD spectrum of the diastereoisomeric equilibrium mixture in aqueous solution exposed to light.

length long-axis-polarized $\pi \rightarrow \pi^*$ CD transition for each fraction collected. While complete separation of the diastereoisomers was not achieved, the constant CD of the leading and trailing fractions in both cases shows that, like the L-tryptophane analogues [1], complete resolution was attained for these solutions. Apart from instrumental sources during the recording of spectra no light was admitted at any time to the solutions during the course of separation and subsequent spectral characterization. A check was made that light from the spectrophotometer sources had negligible effect on the concentrations and optical activity of species in solution during a period of 2 hours. Molar concentrations were calculated after each fraction was allowed to equilibrate in the light, and after addition of solid hydrazine hydrochloride (see above). The $\Delta\epsilon$ value of pure Δ-[Ru(phen)$_2$(L-ser)]$^+$ for the high wavelength $\pi \rightarrow \pi^*$ transition is observed to be $-1.65(6) \times 10^3$ dm^2 mol^{-1}. This species is eluted first from the column and the absolute configuration is assigned [1] on the basis of the calculations of Bosnich [4, 5] for closely related complexes. For the same electronic transition as that above, $\Delta\epsilon$ of pure Λ-[Ru(phen)$_2$(L-ser)]$^+$ is found to be $+2.05(5) \times 10^3$ dm^2 mol^{-1}. Corresponding values of $\Delta\epsilon$ calculated for pure Δ-[Ru(bipy)$_2$(L-ser)]$^+$ (also eluted first from the column) and Λ-[Ru(bipy)$_2$(L-ser)]$^+$ are $-1.33(3) \times 10^3$ and $+1.53(5) \times 10^3$
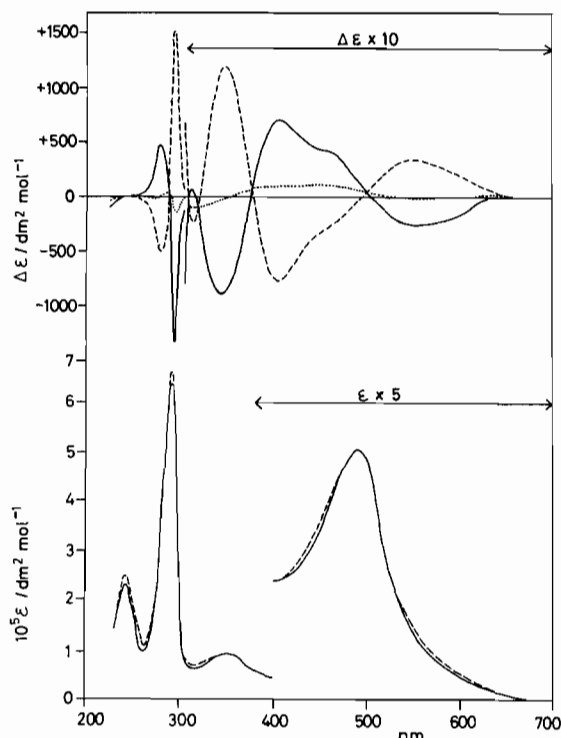
dm^2 mol^{-1} respectively. The CD spectra of the pure diastereoisomers are shown in Figs. 2 and 3, together with their electronic spectra. In both phen and bipy complexes the value for $\Delta\epsilon_{max}$ for the above transition is lower for the Δ- than for the Λ-isomer. This may reflect slightly different degrees of distortion between diastereoisomeric pairs. The observation cannot be due, however, to partial inversion of the Δ-diastereoisomer, since it is also found for the bipy-L-serine case (see below).

As was found previously [1] the optical activity of solutions of each of these diastereoisomers remains constant indefinitely if stored in the dark. When exposed to laboratory lighting an aqueous solution of Δ-[Ru(phen)$_2$(L-ser)]$^+$ spontaneously inverts over a period of two hours at room temperature to yield an equilibrium solution enriched in the Λ-isomer. The CD spectrum of the equilibrium mixture also is shown in Fig. 2. A corresponding solution of the Λ-isomer loses CD intensity until the same equilibrium spectrum is obtained, for which $\Delta\epsilon$ of the high-wavelength $\pi \rightarrow \pi^*$ transition is $+4.27(8) \times 10^2$ dm^2 mol^{-1}. Thus the equilibrium constant for equation (1) above has a value of 1.28(3). From this result the difference in free energies of formation of the two diastereoisomers is $-0.61(6)$ kJ mol^{-1}.

By comparison with results found [1] for the analogous L-tryptophane complexes, the equilibrium shift to the right in equation (*1*) is here less pronounced. The side chain of L-serine is less bulky than that of L-tryptophane, and hence if steric effects alone are considered, it might be expected that the discrimination would be smaller in complexes of the former amino acid. Notwithstanding this smaller discrimination, the results obtained for the equilibration of the Δ,Λ-[Ru(phen)$_2$(L-ser)]$^+$ solutions are fully in accord with previous findings [1, 2] and indicate that steric factors are important in the determination of the equilibrium concentrations of the two propellor molecules.

The results for the equilibration of aqueous solutions of the bipy species in the light, are however, at variance with the above findings. Δ-[Ru(bipy)$_2$(L-ser)]$^+_{(aq)}$ partially racemizes whilst Λ-[Ru(bipy)$_2$(L-ser)]$^+_{(aq)}$ spontaneously inverts in the presence of light, both yielding solutions in which the Δ-isomer is enriched preferentially. The effect is demonstrated in Fig. 3. For this pair of diastereoisomers the equilibrium constant with respect to equation (*1*) is 0.71(5), the corresponding difference in free energy being 0.85(18) kJ mol^{-1}. At the higher-wavelength long-axis-polarized $\pi \rightarrow \pi^*$ transtion $\Delta\epsilon$ of the equilibrium solution is calculated to be $-1.45(11) \times 10^2$ dm^2 mol^{-1}.

With the exception of [Ru(bipy)$_2$(L-ser)]$^+$, it has been found to be true that with the general species Δ,Λ-[Ru(diimine)$_2$(aa)]$^{n+}$, the Λ-isomer is thermo-dynamically more stable in aqueous solution when the amino acid has the L-configuration [1, 2]. However, the exception described above indicates that steric factors are not always overwhelming in their influence on the inversion of these diastereoisomeric complexes. Craig and Mellor [6] have reviewed possible interactions which might lead to discrimination in, and between, chiral molecules. The influences of chiral systems may be propagated by short range interactions through one or more layers of solvent; so also may differential hydrogen bonding be a chemical source of discrimination. Contact terms which are electrostatic in nature may be dominated by long-range forces, dispersion interactions or extremely short-range repulsions. The apparently anomalous higher stability of the Δ-hand of [Ru(bipy)$_2$(L-ser)]$^+$ no doubt represents a case where simple repulsive interactions are outweighed by other discriminating forces, the importance of which, in part, is the subject of our continuing studies.

References

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