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Optically Active Coordination Compounds.
Part 42.* Optically Active Bis-2,2′- Bipyridyl Complexes of Ru(II) and Ru(III)

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A fast equilibrium exists between $[Ru(bipy)_2Cl_2]^+$ *and* $[Ru(bipy)_2Cl(H_2O)]^{2+}$ *in aqueous solution. Salts containing either cation may consequently be isolated. Reaction of the mixture with (+)-tartrate is stereoselective and partial resolutions of* $[Ru(bipy)_2Cl(H_2O)]^{2+}$ *and* $[Ru(bipy)_2Cl(H_2O)]^+$ *have been achieved. Earlier reports concerning the optical activity of the former complex cation are in error.*

Introduction

Optical activity of diimine complexes of Ru(III) has been studied to a much smaller degree than that of corresponding divalent complexes. Dwyer and Gyarfas [1] found that tris-chelated Ru(III) complexes of 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bipy) were stable enough to permit measurements of rotations by the antipodes, though it has been subsequently shown [2] that the molecules add water to the ligand if they are left in aqueous solution for any time. Contrary to earlier reports [3], these complexes do not racemize, but the optically active spectra change to those of covalently hydrated species. Attempts to resolve $Ru(bipy)_2Cl_2$ and $Ru(phen)_2Cl_2$ have been in the past unsuccessful. It was thought that it might be possible to resolve $Ru(bipy)_2Cl_2$ by reduction of the corresponding optically active Ru(III) monocation.

Partial resolution of $[Ru(bipy)_2Cl_2]^+$ has been achieved through asymmetric induction in a reaction involving optically active tartrate ion. Previous reports [4] concerning the circular dichroism (CD) spectrum of this complex are in error. Several new discoveries concerning the nature of the $[Ru(bipy)_2Cl_2]^+$ ion in aqueous solution have also been made, and are reported here. Although $Ru(bipy)_2Cl_2$ has not been resolved, partial resolution of $[Ru(bipy)_2Cl(H_2O)]^+$ was achieved. This complex cation is optically labile in acid solution.

Experimental

^1H nmr spectra were recorded using a Perkin Elmer R32 90MHz spectrometer and electronic spectra were obtained using Perkin Elmer SP8000 and Beckman DK2A spectrophotometers. Ir spectra were recorded on a Perkin-Elmer 257 grating infrared spectrometer and thermogravimetric analyses carried out using a Stanton Redcroft TG 750 temperature programmed thermogravimetric balance. CD measurements were made using a Jobin–Yvon Dichrographe III.

Cis-$Ru(bipy)_2Cl_2 \cdot 3H_2O$ was prepared according to the method of Krause [5]. *Anal.* Found: C, 44.5; H, 4.3; N, 10.2; $C_{20}H_{22}Cl_2N_4O_3Ru$: Calcd.: C, 44.6; H, 4.1; N, 10.4%. *Cis*-$Ru(bipy)_2(ox) \cdot 4H_2O$ was prepared according to the method of Liu, Liu and Bailar [6]. *Anal.* Found: C, 46.0; H, 4.2; N, 9.6; $C_{22}H_{24}N_4O_8Ru$: Calcd.: C, 46.0; H, 4.2; N, 9.8%. *Cis*-$[Ru(bipy)_2Cl_2]ClO_4$ was prepared according to the method of the same authors [6], using $Ru(bipy)_2Cl_2 \cdot 3H_2O$ as starting material. *Anal.* Found: C, 41.1; H, 3.0; N, 9.7; $C_{20}H_{16}Cl_3N_4O_4Ru$: Calcd.: 41.1; H, 2.8; N, 9.6%. *Cis*-$[Ru(bipy)_2Cl(H_2O)]Cl_2 \cdot 2H_2O$ was prepared using the method of Fergusson and Harris [7], originally given for the preparation of '*cis*-$[Ru(bipy)_2Cl_2]Cl \cdot 3H_2O$'. *Anal.* Found: C, 41.5; H, 4.2; N, 9.7; H_2O, 9.4; $C_{20}H_{22}Cl_3N_4O_3Ru$: Calcd.: C, 41.9; H, 3.9; N, 9.8; H_2O, 9.4%. *Cis*-$[Ru(bipy)_2Cl_2]_2[(AsO\text{-}(+)\text{-tartrate})_2] \cdot 4H_2O$ was made by the dropwise addition of a concentrated solution of sodium arsenyl-(+)-tartrate to an aqueous solution of $[Ru(bipy)_2Cl(H_2O)]Cl_2 \cdot 2H_2O$. The red solid was filtered at the pump as soon as precipitation was complete, washed with ice-cold water and dried *in vacuo* over silica gel. *Anal.* Found: C, 37.9; H, 3.2; N, 7.2; H_2O, 5.0; $C_{48}H_{48}Cl_4N_8O_{18}As_2Ru_2$: Calcd.: C, 38.0; H, 3.2; N, 7.4; H_2O, 4.7%.

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*Part 41: L. Vilas Boas, C. A. Evans, R. D. Gillard, P. R. Mitchell and D. A. Phipps, *J. Chem. Soc. Dalton*, 582 (1979).

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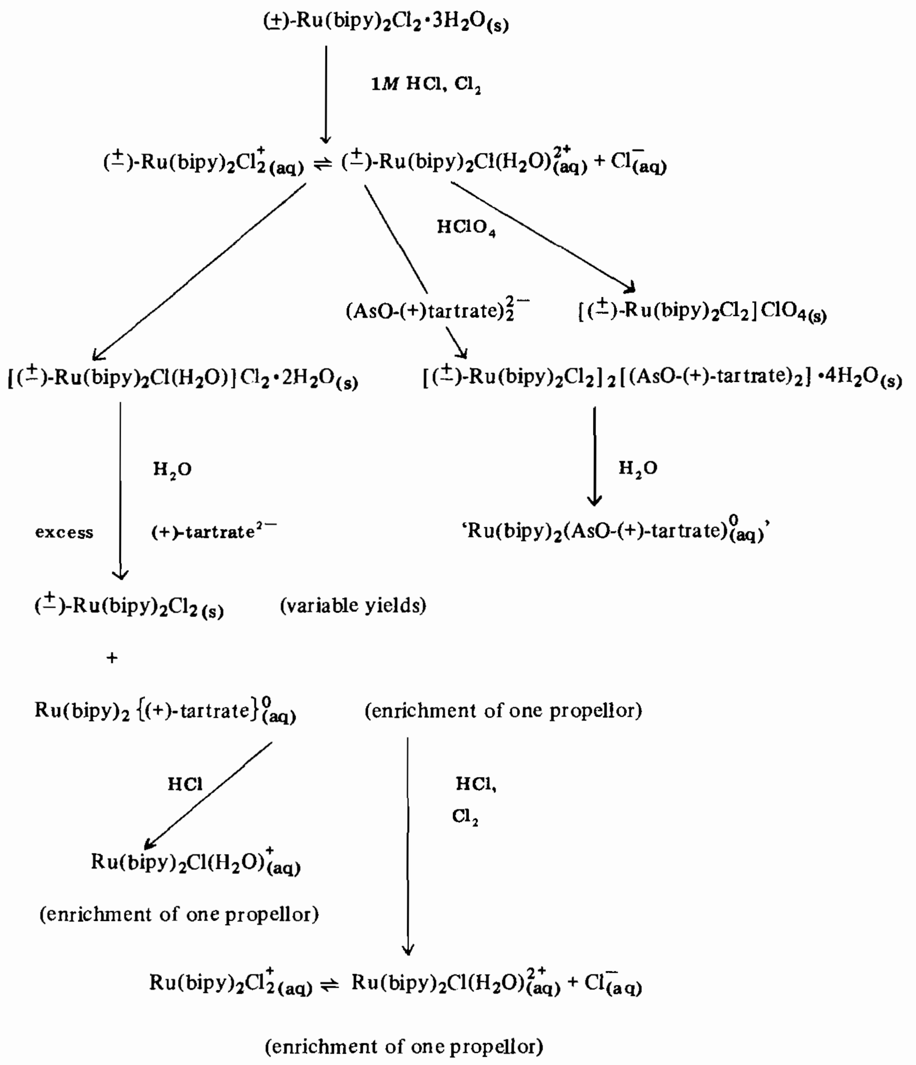
Scheme



Results and Discussion

The complex ion $[Ru(bipy)_2Cl_2]^+$ has been reported previously. Liu, Liu and Bailar [6] prepared $[Ru(bipy)_2Cl_2]Cl\cdot 2H_2O$ and $[Ru(bipy)_2Cl_2]ClO_4$. Fergusson and Harris [7] however reported that the chloride salt crystallises as the trihydrate. The differences in these studies are readily rationalized once it is realized that the Ru(III) complex cation participates in the equilibrium (1). Such equilibria have

$$[Ru(bipy)_2Cl_2]^+ + H_2O \rightleftharpoons [Ru(bipy)_2Cl(H_2O)]^{2+} + Cl^- \quad (1)$$

previously been shown [8] to occur extensively in complexes of Ru(II) related to the above. The position of the equilibrium in (2) lies far to the right and

$$[Ru(bipy)(terpy)Cl]^+ + H_2O \rightleftharpoons [Ru(bipy)(terpy)(H_2O)]^{2+} + Cl^- \quad (2)$$

even concentrated solutions of alkali metal halides could not force the equilibrium to any measurable extent in the reverse direction.

When an aqueous 1 mol dm^{-3} HCl suspension of $Ru(bipy)_2Cl_2\cdot 3H_2O$ is oxidized with chlorine gas the solid dissolves, with the initial formation of the deep-red complex cation $[Ru(bipy)_2Cl_2]^+$. With continued bubbling of Cl_2, the solution turns orange and an orange-red solid is precipitated. This solid corresponds to the stoichiometric formula $Ru(bipy)_2Cl_3\cdot 3H_2O$. Thermogravimetric analysis shows that the solid is in fact $[Ru(bipy)_2Cl(H_2O)]Cl_2\cdot 2H_2O$. Two

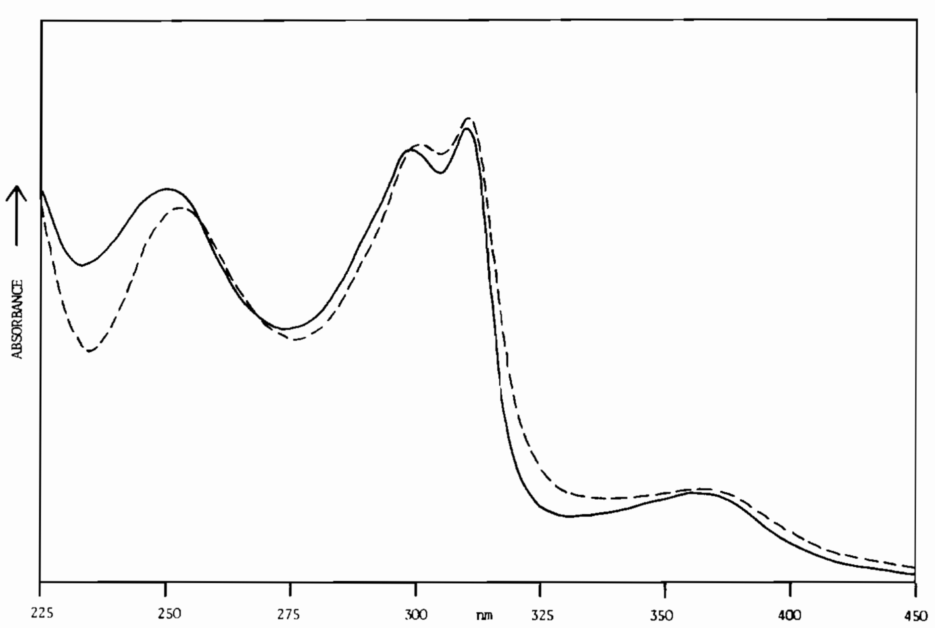


Fig. 1. Electronic spectrum of $[Ru(bipy)_2Cl(H_2O)]Cl_2 \cdot 2H_2O$ dissolved in H_2O (——) and 3 mol dm^{-3} HCl (– – –).

molecules of water are lost* at 95 °C (calculated loss, 6.3; found, 6.4%) and the remaining water molecule is not lost until the temperature reaches 260 °C (calculated loss, 3.1: found, 3.0%). It is assumed that the dihydrate reported by Liu *et al.* [6] contained the $[Ru(bipy)_2Cl_2]^+$ ion, but in our hands, using $Ru(bipy)_2(ox) \cdot 4H_2O$ as starting material, the chloroaquo-species was also obtained.

The presence of equilibrium (1) can also be simply demonstrated by electronic spectral measurements. Fig. 1 shows the spectra of $[Ru(bipy)_2Cl(H_2O)]Cl_2 \cdot 2H_2O$ dissolved in water alone, and in concentrated HCl. The equilibrium constant was not determined, but other studies show that both the dichloro- and chloroaquo- species are present in aqueous solution in significant amounts.

Addition of $HClO_4$ to a solution of $[Ru(bipy)_2Cl(H_2O)]Cl_2 \cdot 2H_2O$ in water yields the complex salt $[Ru(bipy)_2Cl_2]ClO_4$. Similarly, during an attempt to resolve the Ru(III) complex using the (AsO-(+)-tartrate)$_2^{2-}$ dimer, the salt (±)-$[Ru(bipy)_2Cl_2]_2$-[(AsO-(+)-tartrate)$_2$]$\cdot 4H_2O$ was obtained. All the water in this compound is lost at 90 °C. This shows the above formula, rather than $[Ru(bipy)_2Cl(H_2O)]_2$-[(AsO-(+)-tartrate)$_2$]$Cl_2 \cdot 2H_2O$, to be correct. The attempted resolution using arsenyl-(+)-tartrate was unsuccessful, the solid salt which was obtained containing both antipodes of the Ru(III) cation. The above reactions, together with subsequent ones, in which partial resolution was achieved, are summarized in the Scheme.

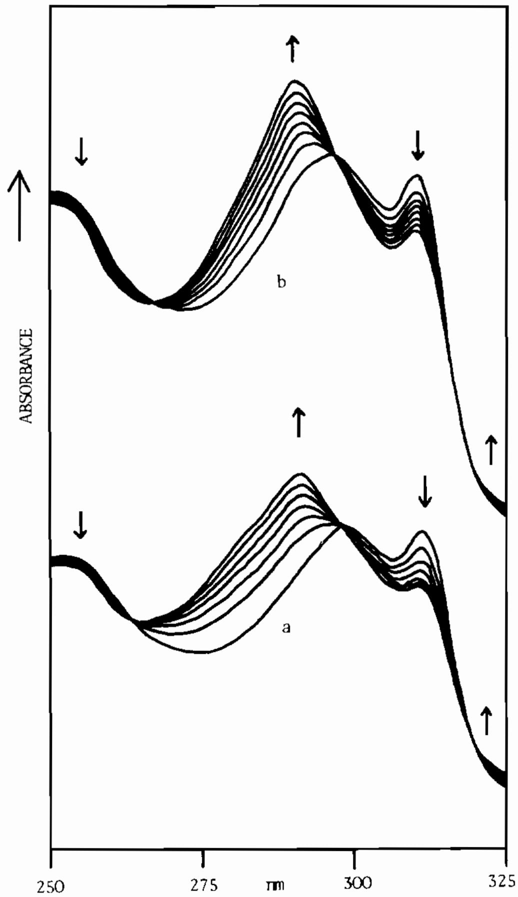


Fig. 2. (a) Change of spectrum with time (20 minute intervals) of $[Ru(bipy)_2Cl_2]_2$[(AsO-(+)-tartrate)$_2$]$\cdot 4H_2O$ in aqueous solution. (b) as for (a), but with 10 minute intervals for $[Ru(bipy)_2Cl(H_2O)]Cl_2 \cdot 2H_2O$ dissolved in aqueous Na_2(+)-tartrate solution. Arrows indicate the change of spectra with time, recorded at 20 °C.

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*Temperatures are given for the mid-points of the transition.

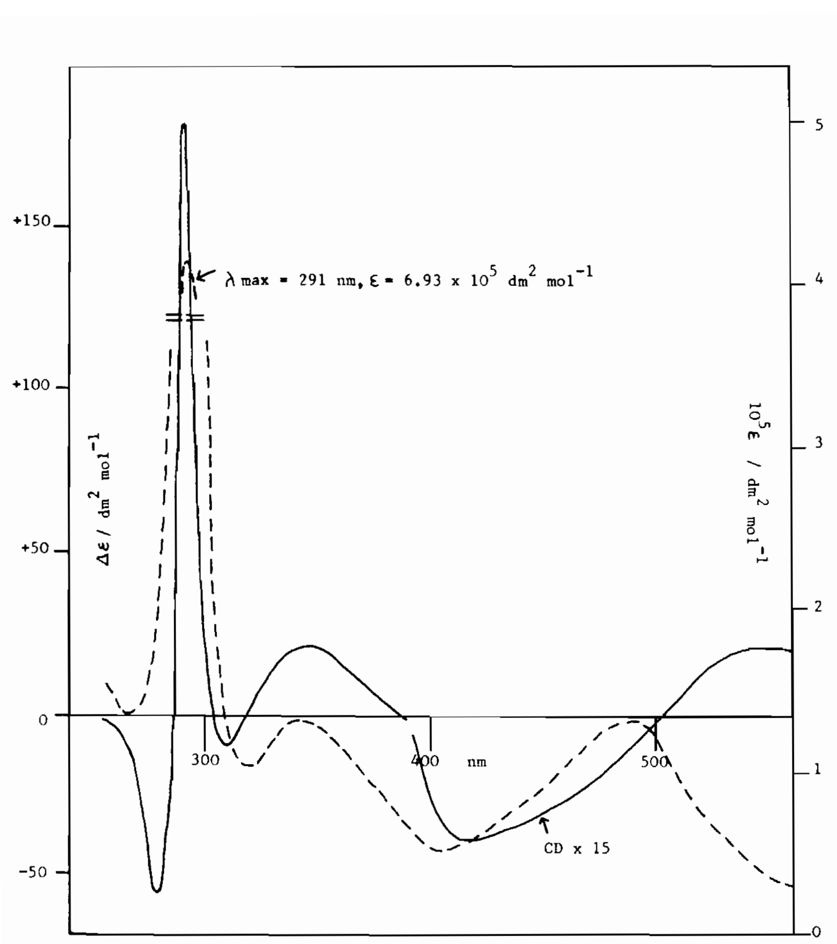

Fig. 3. Electronic (– – –) and CD (——) spectra of the mixture of diastereoisomers of $[Ru(bipy)_2\{(+)\text{-tartrate}\}]^\circ$ in aqueous solution.

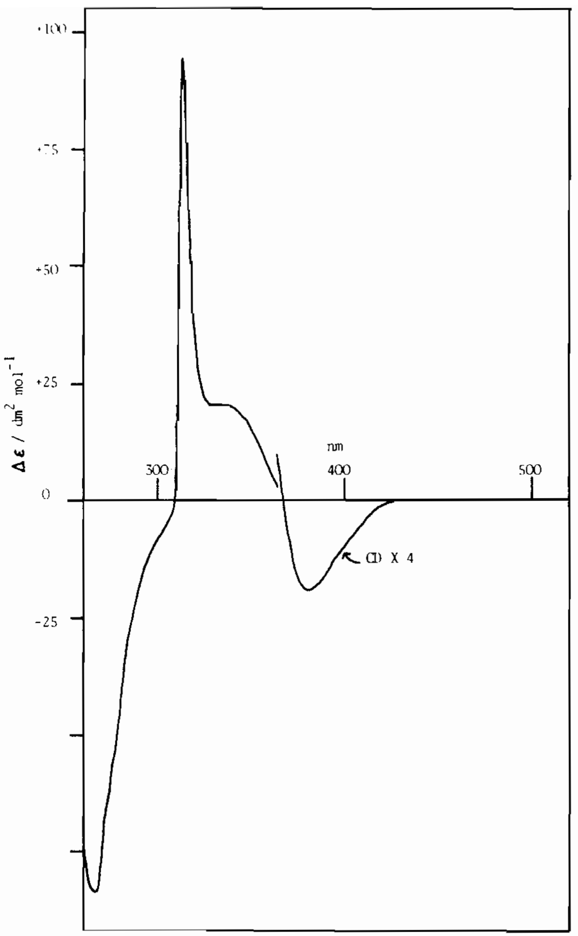

Fig. 4. CD spectrum of partially resolved $[Ru(bipy)_2Cl_2]^+$ and $[Ru(bipy)_2Cl(H_2O)]^{2+}$ generated from the solution of Fig. 3 which was made 3 mol dm^{-3} in HCl and oxidized with chlorine gas, immediately.

The precipitation of the racemic complex as the arsenyl-(+)-tartrate is a kinetic phenomenon. When aqueous solutions of this salt initially optically inactive with reference to the Ru(III) cation, * were allowed to stand, optical activity developed in the transitions of the ruthenium cation. No doubt this is due to an interaction of the anion with the cation and the reaction follows constant stoichiometry as evidenced by isosbestic points in the electronic spectra, as shown in Fig. 2a. The nature of this reaction was not fully investigated because entirely analogous observations are made when (+)-tartrate is allowed to react with $[Ru(bipy)_2Cl(H_2O)]^{2+}$ or $[Ru(bipy)_2Cl_2]^+$, as shown in Fig. 2b. While some very slight difference in the positions of the isosbestic points and intensities of the transitions are apparent, both reactions (with (+)-tartrate and with (+)-arsenyl tartrate) clearly follow the same general path.

Mixtures consisting of aqueous solutions of $[Ru(bipy)_2Cl(H_2O)]Cl_2 \cdot 2H_2O$ with a ten-fold excess of sodium (+)-tartrate were allowed to react to completion (*ca.* 24 hours). A series of repeat experiments showed that constant stoichiometry over this period of time was not always followed and that variable amounts of $Ru(bipy)_2Cl_{2(s)}$ could be filtered from the final mixture. This Ru(II) salt was invariably racemic. At the end of the reaction with (+)-tartrate, all of the Ru(III) is reduced to Ru(II). This corresponds with previous observations [6] concerning tartrate and oxalate as reducing agents in these kinds of reaction. The deep-red solution at the end of the experiment contains the complex $[Ru(bipy)_2(+)\text{-tartrate}]^\circ$, the *cis*-configuration of the bipy ligands being confirmed by ^1H nmr studies. The electronic spectrum of the complex and its CD are shown in Fig. 3.

An optically active spectrum is only to be expected for this complex mixture since, at the very least, the species $\Delta\text{-}[Ru(bipy)_2\{(+)\text{-tartrate}\}]^\circ$ and $\Lambda\text{-}[Ru(bipy)_2\{(+)\text{-tartrate}\}]^\circ$ are not enantiomorphous. Most interestingly, this simple analysis is not sufficient to describe all of the reactions which have taken place.

If the solution containing the tartrato-complexes is made acidic with HCl and oxidized with chlorine, the mixture of cations $[Ru(bipy)_2Cl_2]^+$ and

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**i.e.* an equal mixture of the two diastereoisomeric salts with arsenyl (+)-tartrate.

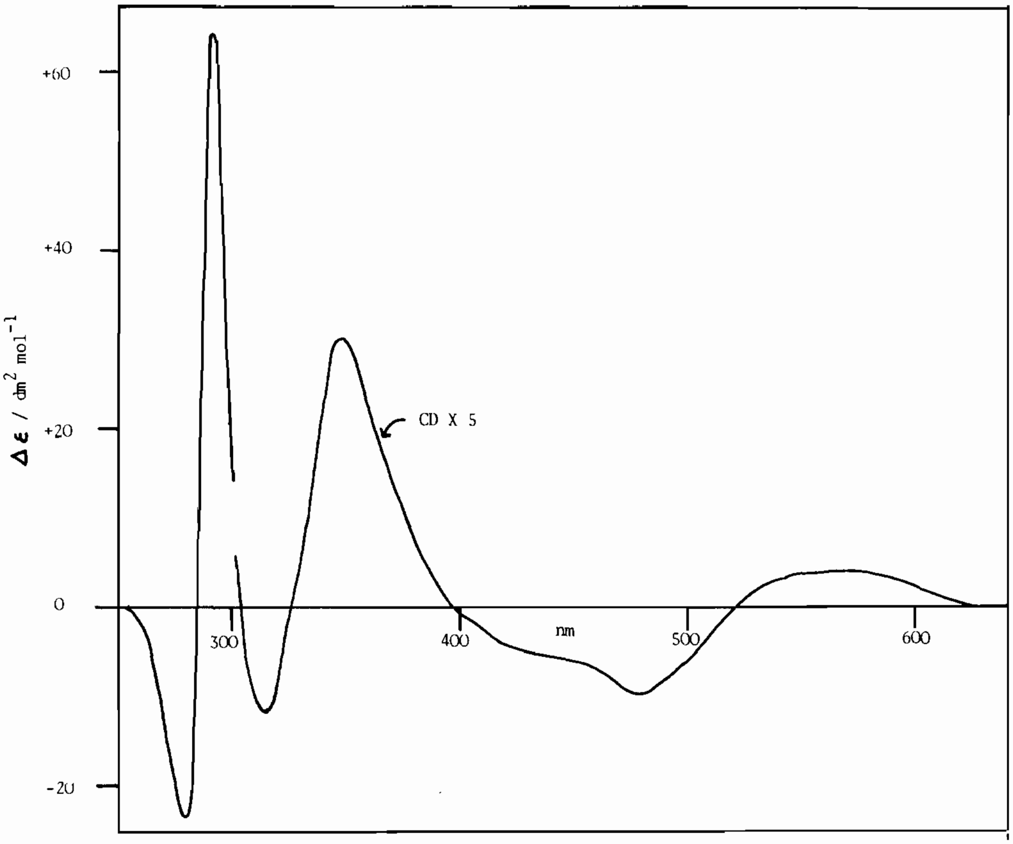

Fig. 5. CD spectrum of partially resolved $[Ru(bipy)_2Cl_2]^\circ$ and $[Ru(bipy)_2Cl(H_2O)]^+$ generated from the solution of Fig. 3 which was made 5 mol dm^{-3} in HCl. The spectrum was measured immediately after acidification (12 nm min^{-1} from 700 nm), and is somewhat dependent upon acid concentration and exposure to light [12].

$[Ru(bipy)_2Cl(H_2O)]^{2+}$ is again obtained. This solution is *also* optically active (Fig. 4). Only one explanation is possible. One hand of the complex has been selectively enriched during the reaction with (+)-tartrate. Furthermore, this enrichment of propellors must also be reflected in the CD spectrum of the Ru(II) tartrato-diastereoisomers. With reference to the magnitude of the CD observed by Bosnich [9] for fully resolved related bis-2,2′-bipyridyl complexes, if this case is taken to be analogous, a partial resolution of the order of about 5% has been achieved.

This is the first time either $[Ru(bipy)_2Cl_2]^+$ or $[Ru(bipy)_2Cl(H_2O)]^{2+}$ has been resolved. An earlier report of Wajda *et al.* [4] is in error. The complex in that study was *not* resolved. Neither was the *cis*-$[Ru(bipy)_2(SCN)_2]$ complex whose CD spectrum was also reported by Wajda *et al.* [10]. The same workers have also reported [11] the CD spectrum of the $[Ru(SCN)_2(NCS)_2(NH_3)_2]^-$ ion which has *2mm* symmetry and cannot exist in enantiomorphous forms. We attribute all of the above results to errors of measurement, since no optically active species of any kind was added at any point.

One further observation, and in addition, the first occurrence of optical activity for the Ru(II) complex with chloride, was noted. When the red solution containing the $[Ru(bipy)_2\{(+)\text{-tartrate}\}]^\circ$ species is not oxidized with chlorine but made strongly acidic (5 mol dm^{-3} HCl) tartrate is lost and a mixture of species largely comprising the ion $[Ru(bipy)_2Cl(H_2O)]^+$ with minor $[Ru(bipy)_2Cl_2]^\circ$ is obtained. This solution too is optically active; the CD spectrum is shown in Fig. 5. The rotational strengths of the visible bands are very weak, and much weaker than is the case with the Ru(III) analogues. Slow racemization occurs. It may well be that the resolutions of $Ru(bipy)_2Cl_2$ is an intractable problem, but solutions of $[Ru(phen)_2Cl_2]^+$ undergo reduction in aqueous solution to Ru(II) much more readily. Preliminary results, which will be communicated in full in the near future, indicate similar behaviour to the bipy complexes, and it appears that the phen analogue can be resolved.

References

1 F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. New South Wales, 83,* 174 (1949).

2 J. A. Arce Sagüés, R. D. Gillard, R. J. Lancashire and P. A. Williams, *J. Chem. Soc. Dalton,* 193 (1979).

3 F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions', Interscience, New York (1959).

4 S. Wajda, K. Rachlewicz and E. Krawczyk, *Bull. Acad. Pol. Sci., 26,* 399 (1978).

5 R. A. Krause, *Inorg. Chim. Acta, 31,* 241 (1978).

6 C. F. Liu, N. C. Liu and J. C. Bailar, *Inorg. Chem., 3,* 1197 (1964).

7 J. E. Fergusson and G. M. Harris, *J. Chem. Soc. (A),* 1293 (1966).

8 N. R. Davies and T. L. Mullins, *Aust. J. Chem., 20,* 657 (1967).

9 B. Bosnich, *Inorg. Chem., 7,* 178 (1968).

10 S. Wajda and K. Rachlewicz, *Inorg. Chim. Acta, 31,* 35 (1978).

11 S. Wajda and K. Rachlewicz, *Inorg. Chim. Acta, 31,* 25 (1978).

12 B. Bosnich and F. P. Dwyer, *Aust. J. Chem., 19,* 2229 (1966).