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Chiral Metal Complexes. 4.[1] Stereoselective Deuterium Exchange at the Coordinated NH_2 Group of L-Alanine

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Very recently we reported[1,3,4] the use of some asymmetric α-amino acids to enforce chiral discriminations in ternary complexes of the form Δ,Λ-[Ru(diimine)$_2$(aa)]$ClO_4 \cdot nH_2O$ [where the diimine is either 1,10-phenanthroline (phen) or 2,2′-bipyridine (bpy) and aa represents an L-amino acidate anion]. The Δ,L and Λ,L cationic forms of these complexes were resolved by using cation-exchange chromatography, and subsequent equilibration of each of the pure diastereoisomers to selected Λ/Δ ratios was observed to proceed only under photoinduction.

In the absence of possible hydrogen-bonding effects involving polar groups in the amino acid side chains[1,4] the direction and degree of these observed discriminations appear to be determined largely by intramolecular steric requirements,[3] as has been observed with some related complexes of Co(III).[5] When such a steric interaction is relatively large in one diastereoisomer, spontaneous inversion at the metal center is then observed, resulting in a predominance of the less strained form.

In our reports to date circular dichroism techniques have been used to monitor these unique reactions. The diamagnetic nature of these species in solution allows for a confirmatory and detailed structural investigation by high-resolution nuclear magnetic resonance techniques. This communication details results of our initial ^1H NMR investigations on one of the simplest of these ternary compounds, namely, Δ,Λ-[(L-alaninato)bis(2,2′-bipyridine)ruthenium(II)] perchlorate. The structural formulas of both the Δ,L and Λ,L diastereoisomers of the complex cation are shown in Figure 1, where it may be seen that the Λ form would be the less sterically crowded.

Experimental Section

Δ,Λ-[Ru(bpy)$_2$(L-ala)]$ClO_4 \cdot 0.5H_2O$ was isolated in 63% yield as very dark red needles by following a procedure like that employed for the synthesis of similar amino acid complexes.[1,3,4] Anal. Calcd: C, 45.3; H, 3.8; N, 11.5. Found: C, 45.8; H, 3.8; N, 11.9. Circular dichroism (CD) studies were performed by using a Jobin-Yvon CNRS Dicrographe III instrument. For ^1H NMR investigations a Varian XL-200 spectrometer was used. These spectra were recorded at 25.0 °C in D_2O with some acetone-d_6 added to assist dissolution. Chemical shifts (δ) are reported in parts per million relative to Me_4Si with traces of acetone-d_5 (δ 2.04) used as the internal reference.

Results

The ^1H NMR spectrum of the "racemic"[6] complex immediately after dissolution is shown in Figure 2. Resonance decoupling experiments allow the assignment of methyl and α-methine proton signals as shown. The relative amounts of both diastereoisomeric forms may be most readily assessed from the doublet resonances of their respective methyl groups (CH_{3_Λ} δ 1.20; CH_{3_Δ} δ 1.32).

Figure 3a shows details of the amine and α-methine proton resonances. After several hours of standing at ambient temperature and with light excluded, the two multiplet signals at lower field, each attributable to an amine proton of a different diastereoisomer (H_d and H_e of Figure 1), are seen to disappear (Figure 3b), indicating exchange of these protons with the solvent. The two remaining N–H resonances are observed as doublets, being coupled now solely to each respective α-methine proton. Thus, under these conditions, *each coordinated amine N atom develops opposite asymmetry through formation of a monodeuterated form, I.*

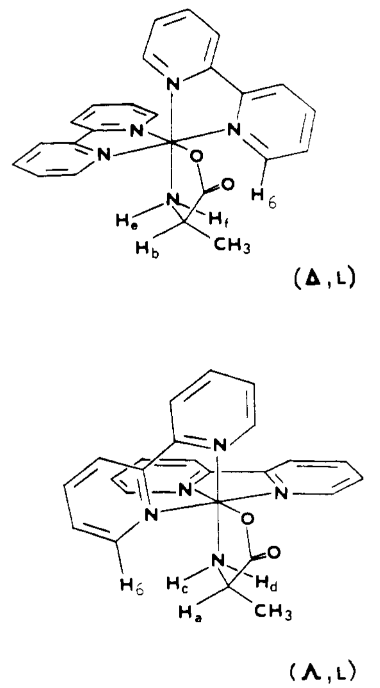


Figure 1. Structural formulas for the Δ,L and Λ,L diastereoisomers of the [Ru(bpy)$_2$(L-ala)]$^+$ cation.

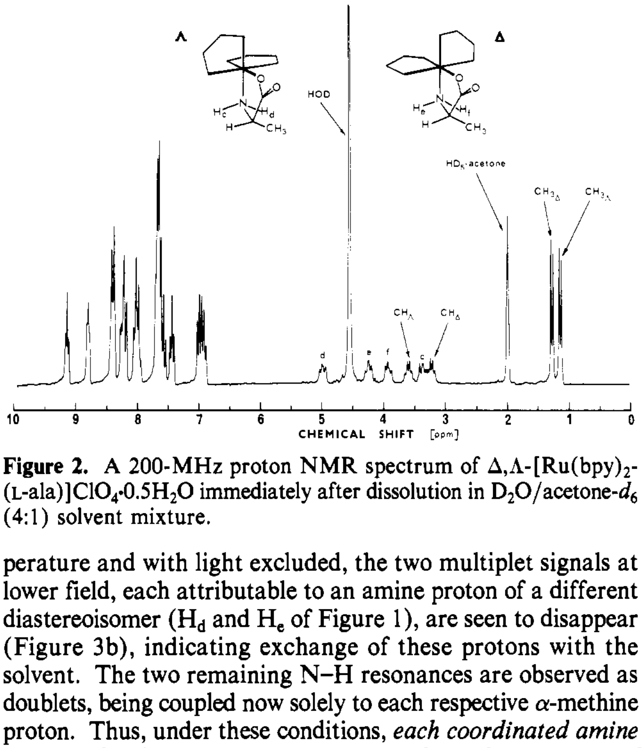
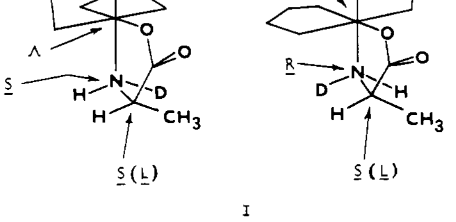


Figure 2. A 200-MHz proton NMR spectrum of Δ,Λ-[Ru(bpy)$_2$-(L-ala)]$ClO_4 \cdot 0.5H_2O$ immediately after dissolution in D_2O/acetone-d_6 (4:1) solvent mixture.



I

After the solution was allowed to stand for several days, the remaining N–H proton of each diastereoisomer exchanges,

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[1] Part 3: Vagg, R. S.; Williams, P. A. *Inorg. Chim. Acta* **1982**, *58*, 101.

[2] (a) Macquarie University. (b) University College.

[3] Vagg, R. S.; Williams, P. A. *Inorg. Chim. Acta* **1981**, *51*, 61.

[4] Vagg, R. S.; Williams, P. A. *Inorg. Chim. Acta* **1981**, *52*, 69.

[5] Fujii, Y.; Matsufuru, M.; Saito, A.; Tsuchiya, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2029.

[6] An X-ray crystal structure analysis of the complex has begun (F. S. Stephens, R. S. Vagg, and P. A. Williams). Both Λ,L and Δ,L forms are present in the crystal in equal ratio.

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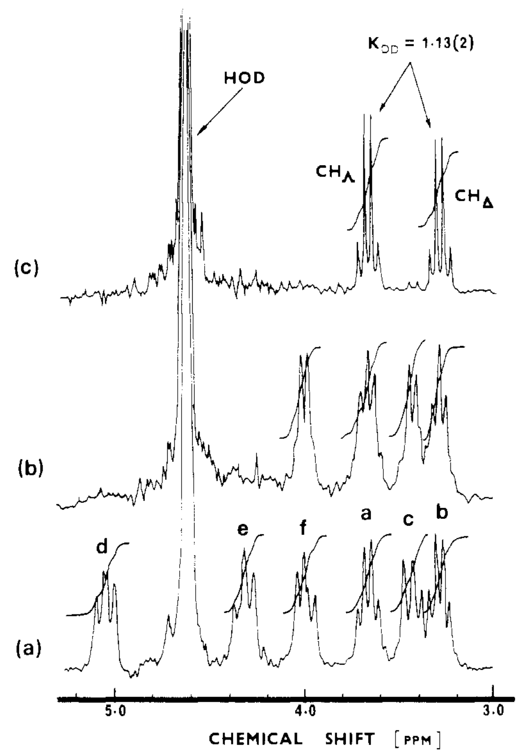


Figure 3. Details of proton NMR spectra in the range δ 3.0–5.2: (a) immediately after dissolution; (b) after formation of mono-N-deuterated species in the absence of light; (c) after complete exchange of amine protons in sunlight. Proton assignments are given in Figure 1.

leaving a simple quartet pattern for each of the two α-methine protons. The isomeric ratio, indicated by both these and the methyl resonances, remains as unity throughout.

The stereoselective exchange reaction described above is not observed in the presence of light. If the same experiment is performed under conditions of bright sunlight, all four amine protons exchange at a relatively fast rate, and there is a corresponding change in the diastereoisomeric Λ/Δ ratio to 1.13 (2) once equilibrium is reached, demonstrated by the ratios of both the α-methine (Figure 3c) and methyl resonances.

Prolonged standing (1–2 months) results in the formation of an appreciable quantity of a decomposition product, indicated by the appearance of a doublet at δ 1.97, which has not yet been identified. Accompanying this final reaction is the disproportionate loss of signals attributable to the Δ isomer.

Discussion

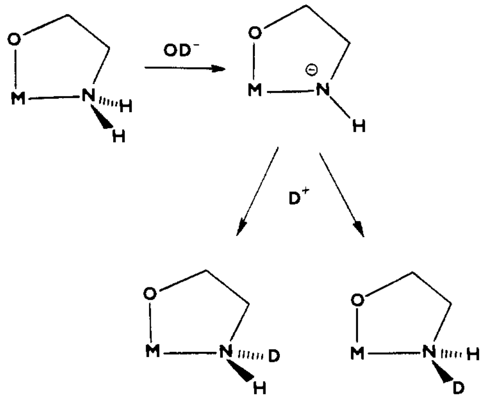
An inspection of the molecular structures of the two diastereoisomers (Figure 1) allows an assessment of the different intramolecular electronic effects that would be felt by the amino acid protons. van der Waals deshielding[7] would result from steric interactions with the bipyridine proton (H_6) in each isomer. In addition, in the Λ isomer the α-methine proton (H_a) would be in the aromatic deshielding region of this interacting bipyridine ring, while in the Δ form the methyl group would feel this deshielding effect. As a result, the signals for each of these protons would occur at lower field compared with those of the corresponding protons in the other isomer, and the spectra have been interpreted on this basis.

This interpretation was confirmed by partial resolution of the two diastereoisomers by using cation-exchange chromatography.[3,4] The ^{1}H NMR spectra of the initial fractions collected show a high concentration of the isomer here formulated as Δ, and their CD spectra showed a strong negative maximum at 290 nm. This is fully consistent with previous assignments based on enhanced steric interactions.[3,4] The small discriminations observed for these deuterated L-alanine species, with the Λ form predominant at equilibrium, may be ascribed to a steric interaction involving the methyl group in the less favored Δ isomer (Figure 1). The indicated free energy difference between these solvated species[8] therefore is ~0.3 kJ mol^{-1}.

Resonance-decoupling experiments on the α-methine proton signals both confirm the methyl resonance assignments and also permit assignment of the pairs of N–H resonances for each diastereoisomer. The respective chemical shifts of these amine protons, however, may not be explained solely in terms of intramolecular electronic effects. An inspection of the molecular structures (Figure 1) shows that the two less hindered amine protons (H_e and H_d) would be the more accessible to interaction with the solvent through hydrogen bonding. This then would account for their observed low-field positions[7] as well as their increased lability, evidenced by their selective exchange with deuterons in the absence of light. In contrast, the nonselective nature of this exchange in sunlight demonstrates the fluxional or labile character of the central metal atom on irradiation, which would allow the inversion reactions previously described.[1,3,4]

The stereoselective exchange effects described above, which reflect an asymmetric solvation of the coordinated NH_2 group due to a steric cause, are analogous to the selective exchange of α-methylene protons in complexes of N-substituted glycines that has been reported recently.[9] We have found that these effects are not confined to the L-alanine species alone but have been observed with several other such amino acid complexes.[10] The exchange rates, as expected, are [OD$^-$] dependent, increasing with higher pD.

The specific nature of these reactions has interesting connotations not only for the mechanism of exchange but also for the mechanism of diastereoisomeric equilibration. The possible processes involved are represented in Figure 4. Nonselective deuterium exchange on coordinated ammonia and substituted amines is well-known, and planar deprotonated amido intermediates, II, have been postulated.[11] If such an intermediate



II

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(7) Williams, D. H.; Fleming, I. "Spectroscopic Methods in Organic Chemistry", 2nd ed.; McGraw-Hill: London, 1973; p 74 ff.

(8) The equilibrium constant determined from CD measurements in D_2O is consistent with that reported here. A higher value of 1.24 (4) was obtained in H_2O by the same technique, indicating that the magnitude of the discrimination energies is not determined by this steric interaction alone.

(9) Golding, B. T.; Ioannou, P. V.; Sellars, P. J. *Inorg. Chim. Acta* **1981**, *56*, 95. Golding, B. T.; Gainsford, G. J.; Herlt, A. J.; Sargeson, A. M. *Angew. Chem.* **1975**, *14*, 495. Golding, B. T.; Gainsford, G. J.; Herlt, A. H.; Sargeson, A. M. *Tetrahedron* **1976**, *32*, 389.

(10) Vagg, R. S.; Williams, P. A., unpublished results.

(11) See for example: Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967.

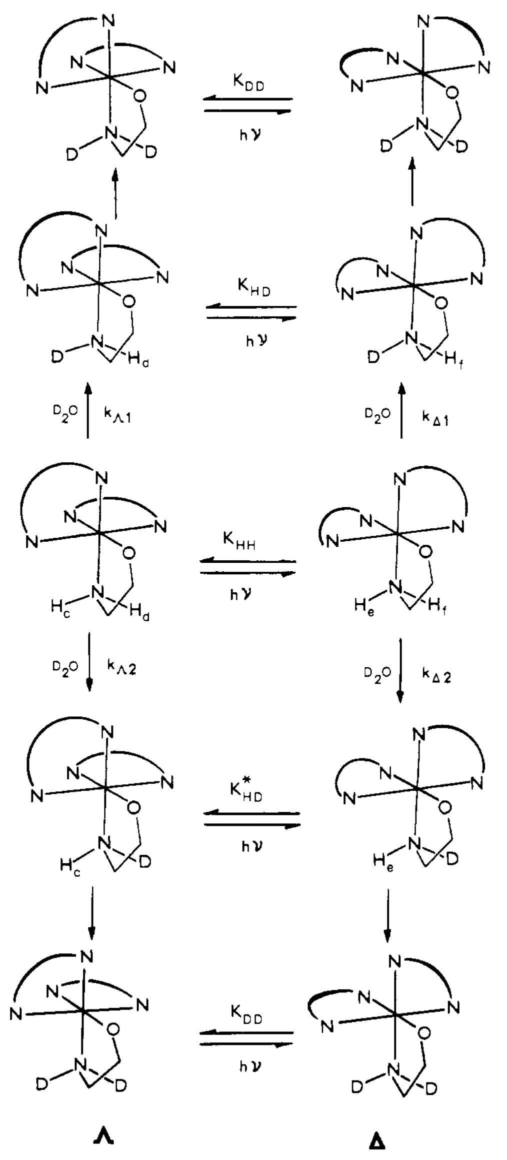

Figure 4. Possible deuterium-exchange processes and photocatalyzed chiral equilibria. Results indicate $k_{\Delta 1} > k_{\Lambda 2} >> k_{\Delta 2} > k_{\Lambda 1}$, K_{HH} = 1.24 (4), and K_{DD} = 1.13 (2). K_{HD} and K^*_{HD} are indeterminant.

were to form in the reaction reported here, with the deprotonation step being stereospecific and assisted by a solvent (or OD^-) interaction, then attack at that intermediate by D_2O also must be sterically controlled so as to allow complete formation of the mono-N-deuterated forms as observed (Figure 3).

If the mechanism for the photoinduced chiral equilibration were to involve "bond rupture",[11,12] then the rotations thus allowed should mean that exchange at the amine group would be nonspecific. If the Ru-NH_2 bond in particular were to break, then H-D exchange with the solvent should be rapid, and the rate of disappearance of the amine proton signals would be determined by that of the equilibration process at the metal. A fluxional "twist" mechanism,[11,12] if slow, would demonstrate a constant equilibrium ratio of all four N-H ^{1}H NMR signals until complete exchange is observed, with this ratio reflecting to a large extent the relative rates of the two processes. However, if the "twist" process were comparatively rapid, then an approximately equal amine proton ratio would persist until exchange is complete. At this stage of our investigations no distinction can be made between these two mechanisms. However, as the rate of attainment of chiral equilibrium may be controlled by the incident light intensity[10] and the rate of proton-deuteron exchange is pD dependent, then manipulation of these parameters should allow a distinction to be made between the two mechanisms. Such a study has begun.

Acknowledgment. The authors are indebted to Mr. A. Tseng of the School of Chemistry, Macquarie University, for the recording of ^{1}H NMR spectra. P.A.W. wishes to thank the British Council for a travel grant.

Registry No. Λ-[(L-Alaninato)bis(2,2′-bipyridine)ruthenium(II)] perchlorate, 83692-85-7; Δ-[(L-alaninato)bis(2,2′-bipyridine)ruthenium(II)] perchlorate, 83730-07-8; hydrogen, 1333-74-0.

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(12) Serpone, N.; Bickley, D. G. *Prog. Inorg. Chem.* **1972**, *17*, 391 and references therein.

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Reinvestigation of 18-Crown-6 Ether/Potassium Superoxide Solutions in Me_2SO

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It was recently reported[1] that optical absorption measurements are unsatisfactory for determining superoxide ion (O_2^-) concentrations in dimethyl sulfoxide (Me_2SO) solutions. Solutions of KO_2 in Me_2SO are often prepared with use of 18-crown-6 ether to increase the solubility of the salt.[2] The concentrations of these solutions are measured spectroscopically.[3] Spectra of KF, KCl, KCN, and KH_2PO_4 in 0.3 M 18-crown-6 ether in Me_2SO were published,[1] showing a large maximum at ~275 nm with $\epsilon \approx 3000$ M^{-1} cm^{-1}. If such a spectral band did arise from 18-crown-6 ether potassium complexes in Me_2SO, spectrophotometric determinations of the superoxide concentrations in crown ether solubilized KO_2 used in many laboratories including our own[4] would be unreliable. We were therefore prompted to undertake this reinvestigation of potassium crown ether complexes and of the stability of superoxide ion in Me_2SO.

Experimental Section

Potassium chloride (Fisher Certified) and potassium bromide (Baker Analyzed) were finely ground in a mortar, dried at 150 °C, and stored under vacuum. Potassium fluoride (Baker Analyzed) was heated in a platinum crucible over a Bunsen burner for 2 h and finely ground after cooling. Potassium superoxide (Alfa, 95%, stored under N_2) was finely ground and kept in a Vacuum Atmospheres drybox. 18-Crown-6 ether (Aldrich, Recrystallized[4]) was dissolved in Me_2SO (Aldrich spectrophotometric grade, freshly distilled over CaH_2 at a reduced pressure of N_2) to give a 0.08 M stock solution. Weighed amounts of KF, KCl, KBr, and KO_2 were dissolved in this crown ether solution in a glovebag filled with dry N_2. For the solutions of KCl and KBr, the concentration of potassium was determined by atomic absorption spectroscopy (Galbraith Laboratories, Knoxville, TN).

UV spectra were recorded at 25 °C with use of a Cary 118C spectrophotometer and 0.1-mm path length matched quartz cells. Dimethyl sulfone was determined by gas chromatography on a Varian Aerograph 1400. The carrier gas was N_2, Carbowax 20 M on Chromosorb was used as the column material, and the column temperature was 150 °C.

Results

The spectra of 18-crown-6 ether and its complexes of KCl, KBr, and KO_2 in Me_2SO are shown in Figure 1. They clearly

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