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Chiral Metal Complexes.
12.* Chiroptical, ^{1}H NMR and Crystallographic Studies of the Diastereoisomers Λ- and Δ-[Ru(*diimine*)$_2$(*S*-threonine)]$^+$ and Their *S*-Allothreonine Analogues

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*The four catatopic complexes of general form Δ,Λ-[Ru(*diimine*)$_2$(*aa*)]$ClO_4 \cdot nH_2O$ (where *diimine* is bipy or phen and *aa* is S-threonine or S-allothreonine) have been isolated and each complex resolved into its two diastereoisomeric forms. Each isomer is photo-labile, equilibrating to a definite Λ/Δ ratio on light irradiation, with the resultant equilibrium constants reflecting chiral discrimination energies between isomeric pairs. Equilibration of these species have been followed both by circular dichroism (in H_2O) and ^{1}H NMR (in D_2O) techniques. The NMR spectra have been fully interpreted for each of the eight isomeric forms. The S-threonine complexes equilibrate to Λ/Δ ratios of 0.77(2) H_2O and 0.89(1) D_2O for the phen isomers, and 0.68(1) H_2O and 0.78(1) D_2O for bipy. The corresponding values for the S-allothreonine complexes are 1.15(2) H_2O, 1.09(1) D_2O and 1.12(1) H_2O, 1.02(2) D_2O respectively.*

The crystal and molecular structures of the bipy complexes for both S-threonine and S-allothreonine have been determined. The two complexes are grossly isostructural. Δ,Λ-[Ru(bipy)$_2$(S-thr)]$ClO_4 \cdot 5H_2O$ is monoclinic, space group $P2_1$ *with* $a = 10.165(2)$, $b = 28.220(6)$, $c = 10.896(3)$ Å, $\beta = 104.80(2)°$ *with* $Z = 4$. *Δ,Λ-[Ru(bipy)$_2$(S-allothr)]$ClO_4 \cdot 5H_2O$ is monoclinic, space group* $P2_1$ *with* $a = 10.226(4)$, $b = 27.979(4)$, $c = 10.875(2)$ Å, $\beta = 104.99(2)°$ *with* $Z = 4$. *Both structures were refined by block-matrix least-squares methods to* R *0.042 and 0.037 for 3327 and 4456 non-zero reflexions respectively. A pseudo a-glide operation relates the two Δ and Λ forms in the asymmetric unit of each structure.*

There are no apparent significant differences between corresponding parameters in the four cations. The average bond lengths are Ru–O 2.094(9), $Ru{-}N_{amine}$ *2.128(11) and* $Ru{-}N_{bipy}$ *2.050(20) Å with average bite angles at Ru for the amino acids of 79.7(5) and for bipy ligands of 79.0(4)°. The amino acid chelate rings in the four molecular structures have like conformations, suggesting only minor differences in steric factors within these cations.*

There is evidence in the crystal structures that in the S-allothr complexes an internal H-bond may exist between the β-OH and carboxylic groups which would be unfavourable in the S-thr complexes. This structural difference in the two amino acid side chains is consistent both with observed differences in the NMR spectra of the complexes, and with the different equilibration ratios obtained.

Close linear contacts between the hydroxy oxygen atoms and the 3,3′-protons in the crystals suggest that the latter may have weak carbon acid character.

Introduction

A variety of factors has been observed to influence the chiral discriminations between diastereoisomeric pairs of the form Δ- or Λ-[Ru(*diimine*)$_2$(*aa*)]$^{n+}$, where *diimine* is phen† or bipy and *aa* is an optically active α-amino acidate anion. Among these factors are hydrogen bond formation, differential solvation effects and intramolecular steric interactions [1–3]. The presence in the coordinated amino acid side chain of a polar group capable of hydrogen bonding, as in *S*-serine [3], often leads to an energetic preference for the Δ diastereoisomer on photo-equilibration, a result contrary to that expected from steric considerations alone [1].

Methyl-substitution on the β-carbon of *S*-serine leads to the two diastereoisomeric amino acids *S*-threonine (*I*) and *S*-allothreonine (*II*). If the selec-

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†phen = 1,10-phenanthroline, bipy = 2,2′-bipyridyl, thrH = threonine, allothrH = allothreonine, alaH = alanine, serH = serine.

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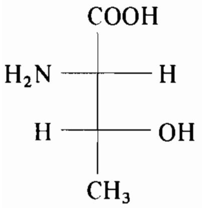
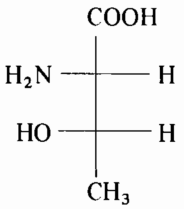
tion of absolute configuration in complexes of these acids were to be determined solely by the overall steric bulk of the side chain then complexes of both *I* and *II* should demonstrate equivalent selectivities. However, restricted rotation around the $C_\alpha-C_\beta$ bonds through intramolecular hydrogen bonding or significant interactions with asymmetric solvent sheaths should lead to observable differences in preferential behaviour on equilibration.



S-threonine
(2*S*-amino-3*R*-hydroxy-butanoic acid)

(*I*)



S-allothreonine
(2*S*-amino-3*S*-hydroxy-butanoic acid)

(*II*)

Here we report the determination by X-ray diffraction of the molecular structures of the four diastereoisomers Δ- and Λ-$[Ru(bipy)_2(S\text{-thr})]^+$ and Δ- and Λ-$[Ru(bipy)_2(S\text{-allothr})]^+$, together with a photo-equilibration study of these cations, and their phen analogues, by circular dichroism and high-resolution ^1H NMR methods.

Experimental

Synthesis of Complexes

The complexes were prepared in a like manner to similar complexes described previously [2] except that longer periods, generally of the order of four to five days, were required for appreciable amounts of material to crystallize from aqueous solutions. Δ,Λ-$[Ru(bipy)_2(S\text{-thr})]ClO_4 \cdot 5H_2O$. Yield: 68%. *Anal.* Found: C, 39.6; H, 4.6; N, 9.4; H_2O, 13.3%. Calcd.: C, 40.0; H, 4.8; N, 9.7; H_2O 12.5%. Δ,Λ-$[Ru(bipy)_2(S\text{-allothr})ClO_4 \cdot 5H_2O$. Yield: 63%. *Anal.* Found: C, 39.7; H, 4.5; N, 9.3; H_2O, 12.6%. Calcd.: C, 40.0; H, 4.8; N, 9.7; H_2O, 12.5%. Δ,Λ-$[Ru(phen)_2(S\text{-thr})]ClO_4 \cdot 5H_2O$. Yield: 42%. *Anal.* Found: C, 43.9; H, 3.1; N, 9.1; H_2O, 12.3%. Calcd.: C, 43.7; H, 4.5; N, 9.1; H_2O, 11.7%.

The low hydrogen analyses obtained may be ascribed to loss of water from the samples prior to combustion, as had been found for related complexes [4]. Δ,Λ-$[Ru(phen)_2(S\text{-allothr})]ClO_4 \cdot 2.5H_2O$. Yield: 40%. *Anal.* Found: C, 46.3; H, 4.1; N, 9.5; H_2O, 7.6%. Calcd.: C, 46.4; H, 4.0; N, 9.7; H_2O, 6.2%.

Physical Methods

Microanalyses were carried out by Mrs A. Dams in the Department of Chemistry, Cardiff. Water of hydration was determined thermogravimetrically using a Stanton-Redcroft TG750 temperature-programmed balance. Pairs of diastereoisomers were resolved chromatographically as described previously, along with the method of determining the equilibrium constants by exposure to light of appropriate isomeric mixtures [1].

Electronic and circular dichroism (CD) spectra were obtained using a Beckman DK2A ratio-recording spectrophotometer and a CNRS Jobin-Yvon Dichrographe III respectively. To record the ^1H NMR spectra, samples of the diastereoisomers were dissolved in water and passed through a Sephadex® A-25 anion exchange resin in the chloride cycle. The chloride salts of these complexes are considerably more soluble in water than the perchlorates. Each complex was flushed from the column with water and the solution evaporated to dryness under reduced pressure at 303 K in the dark. Solutions were prepared in D_2O and 360 MHz ^1H spectra recorded using a Bruker WM360 spectrometer. DSS was used as an internal standard. The 200 MHz spectra were recorded using a Varian XL-200 instrument, of D_2O/acetone-d_6 (4/1; v/v) solutions, using the acetone-d_5 impurity resonance (δ = 2.04 ppm) as the internal reference.

X-Ray Diffraction Analyses

Unit cell parameters were determined initially from single-crystal oscillation, Weissenberg and precession photographs. Accurate cell parameters were obtained from a least-squares fit to diffractometer data. Intensities were collected on an Enraf-Nonius CAD4 diffractometer using Mo-K_α radiation by Dr M. B. Hursthouse at Queen Mary College, London. These were corrected for Lorentz and polarization effects, and for the *S*-threonine complex the data was corrected for absorption.

The similarities in the crystal data of the two complexes, as shown in Table I, suggest that the two compounds are grossly isostructural. Both structures were solved by the heavy-atom method and refined by least-squares techniques in which the function minimised was $\Sigma w\Delta^2$. Weights used were those obtained from counting statistics. During the early stages of isotropic refinement variables for each structure were constrained so as to avoid parameter interaction between the two crystallographically independent molecules in each asymmetric unit.

After isotropic refinement hydrogen atoms were located from difference maps. Their positions were optimised assuming C–H, N–H and O–H to be 1.0 Å and refinement was continued with H atoms held in these positions. Thermal parameters of B = 6.0 Å^2 and 4.5 Å^2 were assigned to H atoms in the *S*-threo-

TABLE I. Crystal Data and Refinement Parameters.

	S-thr Complex	*S*-allothr Complex
Formula	$C_{24}H_{34}N_5Cl_1O_{12}Ru$	$C_{24}H_{34}N_5Cl_1O_{12}Ru$
M_r	721.1	721.1
Crystal System	monoclinic	monoclinic
a (Å)	10.165(2)	10.226(4)
b (Å)	28.220(6)	27.979(4)
c (Å)	10.896(3)	10.875(2)
β (°)	104.80(2)	104.99(2)
U (Å^3)	3022.1(23)	3005.6(20)
D_c	1.585	1.594
Z	4	4
$F(000)$	1480	1480
μ(Mo-K$_\alpha$) (mm^{-1})	6.620	not absorption corrected
Systematic Absences	$0k0$ with $k \neq 2n$	$0\ k\ 0$ with $k \neq 2n$
Space Group	$P2_1$ (No. 4)	$P2_1$ (No. 4)
Crystal Habit	deep-red irregular prisms with |0 1 0| elongation	small deep-red plates lying on |0 1 0| with pinacoids {1 0 0} and {0 0 1}
No. of unique reflexions recorded	6715	5397
No. of reflexions with $I > 3\sigma(I)$	3327	4456
No. of h 0 l reflexions with $h \neq 2n$ and $I > 3\sigma(I)$	6	63
No. of varying parameters during anisotropic refinement	775	775
Final R	0.042	0.037
Final R' $(=(\Sigma w\Delta^2/\Sigma w\|F_o\|^2)^{1/2})$	0.037	0.042
Maximum electron density in final difference map	|0.5|e Å^{-3}	|0.7|e Å^{-3}
No. of matrices in block matrix refinement	17	17

nine and *S*-allothreonine structures respectively, these values being consistent with the overall thermal parameters of the two structures. Anisotropic refinement was continued using block matrices, and was terminated in each case when the change in the minimisation function was <0.2%. Other refinement details are given in Table I.

All calculations were carried out on a UNIVAC 1106 computer using programs written by F.S.S. Neutral-atom scattering factors used were taken from *International Tables for X-Ray Crystallography* [5] with corrections being applied for anomalous dispersion. The final atomic coordinates for the two structures are given in Tables II and III. Lists of anisotropic thermal parameters and observed and calculated structure factors have been deposited with the Editor.

Results

Description of the Two Structures

In accord with the crystal data (Table I) the crystal structures of the two complexes are seen to be grossly isostructural. This may readily be seen by reference to the two unit cell diagrams [6] in Fig. 1 and by a comparison of the atomic coordinates for the two structures listed in Tables II and III. It also is apparent here that in each structure a relationship very close to an *a*-glide exists between the two diastereoisomers in the asymmetric unit. This situation is very similar to the pseudo *c*-glide operation observed in the crystal structure of the *S*-alanine analogue [7], and is responsible for the absence of intense reflexions with $h \neq 2n$ in the $h0l$ zone of each reciprocal lattice.

This close structural relationship applies also to the water molecules and the perchlorate anions in the two structures. The suggested hydrogen bonding system involving these groups and the coordinated amino acids (Fig. 1 and Table IV) are necessarily similar, although differences in indicated positions of water H atoms in individual O···H···O bonds of the related *S*-thr and *S*-allothr structures has lead to some differences in the H-atom labelling scheme (Table III). There are necessary differences in the H-bonding scheme involving O(n3) of each

TABLE II. Final Atomic Coordinates (fractional, $\times 10^4$) with Estimated Standard Deviations in Parentheses.

	Λ,Δ-[Ru(bipy)$_2$(*S*-thr)]ClO$_4$·5H$_2$O						Λ,Δ-[Ru(bipy)$_2$(*S*-allothr)]ClO$_4$·5H$_2$O					
	x		*y*		*z*		*x*		*y*		*z*	
	n = 1	*n* = 2	*n* = 1	*n* = 2	*n* = 1	*n* = 2	*n* = 1	*n* = 2	*n* = 1	*n* = 2	*n* = 1	*n* = 2
Ru(*n*)	3653.8(10)	1333.2(10)	1175.4	3842.7(4)	2436.5(9)	7580.2(9)	3660.3(6)	1289.3(6)	1169.6	3846.2(2)	2275.5(6)	7710.0(6)
Cl(*n*)	9756(4)	5281(6)	2199(1)	2865(2)	8623(4)	1404(4)	9760(3)	5115(4)	2181(1)	2878(1)	8393(2)	1431(4)
O(*n*1)	2592(6)	2407(9)	1198(3)	3838(4)	3839(6)	6165(8)	2574(5)	2240(5)	1223(2)	3842(2)	3661(5)	6224(5)
O(*n*2)	1468(9)	4001(10)	1638(3)	3435(4)	4900(8)	5521(9)	1222(7)	3538(8)	1687(2)	3442(3)	4458(6)	5286(8)
O(*n*3)	29(8)	2022(10)	2052(4)	2560(3)	1915(8)	5827(8)	−25(7)	4229(8)	2068(3)	2556(3)	1681(6)	5932(9)
O(*n*A)	11052(14)	4027(19)	2169(6)	2839(8)	9448(10)	618(16)	10880(13)	3764(11)	2287(6)	2950(5)	9276(8)	828(13)
O(*n*B)	9864(11)	5236(14)	2411(4)	2532(4)	7494(9)	2307(16)	9780(8)	5158(12)	2422(3)	2577(4)	7229(6)	2403(13)
O(*n*C)	9277(9)	5551(18)	1715(3)	3304(5)	8206(8)	1703(17)	9543(12)	5738(9)	1701(3)	3293(4)	8091(9)	1855(10)
O(*n*D)	8850(24)	6142(25)	2398(7)	2689(7)	9148(21)	738(26)	8626(12)	5560(33)	2339(5)	2711(10)	8836(14)	601(25)
O(W*n*1)	644(11)	4483(10)	1165(4)	3892(4)	6675(9)	3455(9)	625(8)	4384(8)	1150(3)	3891(3)	6324(7)	3422(8)
O(W*n*2)	3882(8)	1160(10)	578(4)	4446(4)	6020(8)	4170(10)	3932(7)	1052(7)	623(3)	4478(3)	5782(7)	4157(7)
O(W*n*3)	2433(10)	2559(9)	422(4)	4536(3)	7670(11)	2240(8)	2427(7)	2532(8)	487(3)	4612(3)	7552(7)	2415(8)
O(W*n*4)	6630(10)	8323(11)	522(4)	4548(4)	7145(10)	2634(10)	6684(8)	8273(8)	521(3)	4499(4)	7107(7)	2809(9)
O(W*n*5)	8486(11)	6572(11)	479(4)	4508(4)	5938(11)	4352(10)	8460(8)	6501(9)	514(3)	4537(4)	5588(8)	4311(10)
N(*n*)	2783(9)	2220(10)	1861(3)	3151(3)	2140(8)	7900(9)	2813(7)	2179(6)	1862(2)	3153(2)	1890(7)	7958(6)
N(*n*1)	4787(9)	184(9)	1242(3)	3787(3)	1164(9)	8831(8)	4773(6)	222(7)	1234(3)	3772(2)	977(6)	9025(6)
N(*n*2)	5376(10)	−371(9)	1472(4)	3524(3)	3502(9)	6436(8)	5375(6)	−455(6)	1474(2)	3534(2)	3396(6)	6639(6)
N(*n*3)	4287(8)	715(10)	497(3)	4548(4)	2825(8)	7212(10)	4299(6)	670(6)	474(3)	4535(2)	2686(6)	7342(6)
N(*n*4)	2068(8)	2954(11)	807(3)	4218(4)	1268(7)	8753(10)	2070(6)	2910(6)	799(2)	4224(2)	1101(6)	8832(6)
C(*n*11)	6066(10)	−1075(14)	1450(4)	3605(4)	1562(10)	8306(12)	6059(8)	−1020(8)	1425(3)	3568(3)	1449(8)	8608(9)
C(*n*12)	6868(13)	−1962(13)	1494(5)	3508(4)	712(12)	9046(12)	6920(8)	−1802(10)	1501(4)	3488(4)	662(9)	9468(10)
C(*n*13)	6404(13)	−1617(15)	1361(5)	3617(5)	−542(11)	10289(13)	6496(10)	−1342(11)	1376(4)	3602(4)	−594(9)	10721(11)
C(*n*14)	5141(12)	−358(13)	1157(5)	3810(5)	−951(11)	10815(1)	5199(9)	−70(12)	1185(4)	3801(4)	−1066(7)	11142(10)
C(*n*15)	4355(14)	530(11)	1124(5)	3905(4)	−91(11)	10061(11)	4406(8)	684(9)	1117(3)	3879(4)	−235(8)	10261(8)
C(*n*21)	6395(13)	−1400(11)	1558(5)	3457(4)	2920(13)	7003(10)	6410(8)	−1398(8)	1547(3)	3442(3)	2797(8)	7261(8)
C(*n*22)	7648(16)	−2608(11)	1737(6)	3252(4)	3570(14)	6354(12)	7626(8)	−2669(9)	1736(3)	3249(4)	3456(9)	6617(10)
C(*n*23)	7904(12)	−2720(13)	1837(5)	3100(5)	4806(14)	5068(14)	7858(9)	−2909(10)	1864(4)	3155(4)	4709(10)	5354(10)
C(*n*24)	6904(12)	−1698(14)	1760(4)	3170(5)	5415(10)	4495(13)	6812(11)	−1920(10)	1811(4)	3258(4)	5307(10)	4717(9)
C(*n*25)	5628(9)	−524(17)	1594(4)	3398(6)	4750(8)	5188(17)	5623(9)	−705(9)	1601(4)	3437(4)	4624(7)	5414(9)
C(*n*31)	3414(10)	1603(13)	152(4)	4870(5)	2240(10)	7802(12)	3441(8)	1547(8)	134(3)	4881(3)	2088(8)	7935(7)
C(*n*32)	3713(16)	1331(15)	−322(4)	5350(4)	2488(15)	7566(14)	3707(10)	1260(9)	−353(3)	5363(3)	2335(10)	7686(9)
C(*n*33)	4936(18)	145(13)	−446(6)	5479(4)	3328(16)	6699(13)	4894(10)	67(11)	−482(4)	5488(4)	3175(10)	6824(10)
C(*n*34)	5814(13)	−752(15)	−104(5)	5141(6)	3891(12)	6065(17)	5785(10)	−821(10)	−140(4)	5148(4)	3774(10)	6265(9)
C(*n*35)	5450(13)	−477(11)	372(5)	4682(4)	3634(12)	6361(11)	5447(8)	−513(8)	346(3)	4675(3)	3512(8)	6537(9)
C(*n*41)	2203(12)	2824(10)	311(4)	4680(4)	1368(11)	8716(10)	2216(7)	2795(8)	314(3)	4705(3)	1168(8)	8811(8)
C(*n*42)	1218(16)	3801(11)	28(6)	4986(4)	618(17)	9476(11)	1269(10)	3770(9)	4(4)	4992(3)	415(9)	9568(9)
C(*n*43)	21(18)	4880(10)	236(7)	4811(4)	−188(21)	10290(9)	124(10)	4888(10)	196(4)	4796(4)	−397(9)	10377(10)
C(*n*44)	−75(14)	5025(11)	724(5)	4330(4)	−186(13)	10404(9)	−52(10)	5036(9)	685(4)	4309(4)	−464(9)	10374(9)
C(*n*45)	923(13)	4027(12)	1003(5)	4039(4)	534(12)	9628(10)	955(8)	4039(9)	973(3)	4032(3)	328(8)	9615(9)
C(*n*1)	2059(13)	3185(13)	1587(4)	3473(4)	4038(10)	6210(13)	1954(9)	2985(8)	1614(4)	3470(3)	3743(9)	6173(8)
C(*n*2)	2260(12)	3321(12)	2016(4)	3098(4)	3246(11)	7227(12)	2252(9)	3175(9)	2030(3)	3096(3)	2915(8)	7154(9)
C(*n*3)	964(13)	3357(14)	2316(5)	2608(5)	2874(13)	6730(13)	1036(9)	3231(12)	2363(3)	2590(4)	2380(9)	6668(12)
C(*n*4)	1140(14)	3549(14)	2794(4)	2215(4)	2418(12)	7694(14)	583(11)	3565(15)	2665(6)	2217(5)	3323(10)	7657(14)

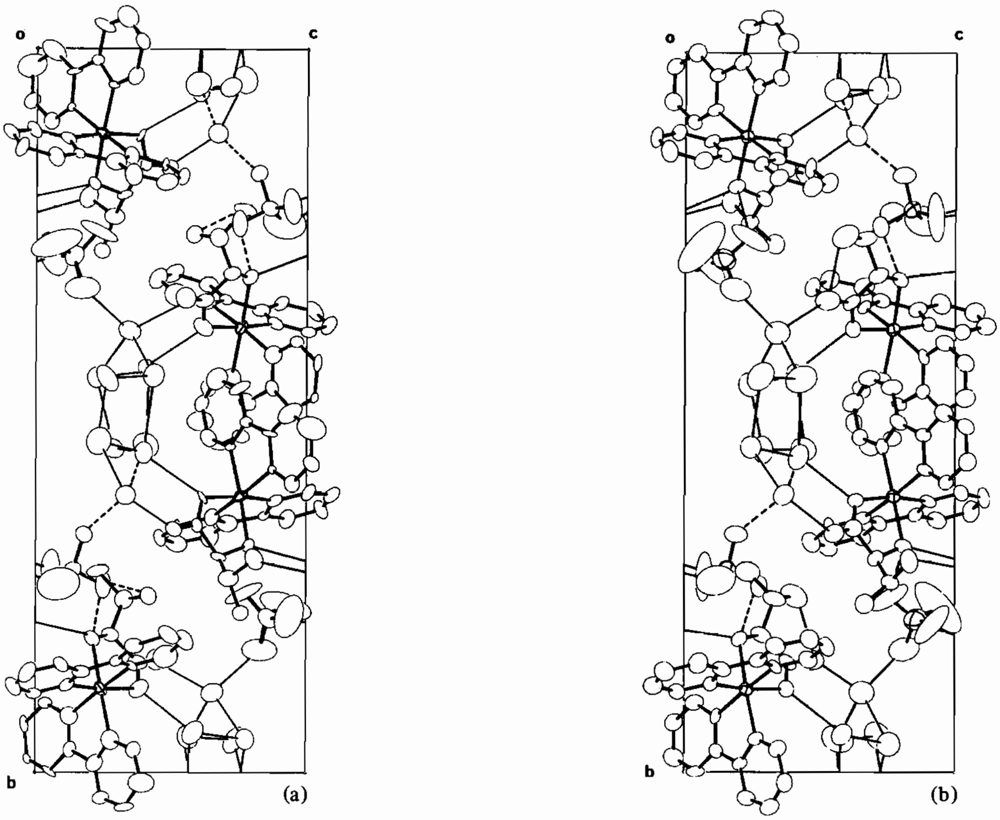


Fig. 1. The packing of the molecular ions in the unit cells of (a) Δ,Λ-[Ru(bipy)$_2$(*S*-thr)]$ClO_4 \cdot 5H_2O$ and (b) Δ,Λ-[Ru(bipy)$_2$-(*S*-allothr)]$ClO_4 \cdot 5H_2O$ projected down the *a* axes. Proposed hydrogen bonds are represented by thin lines.

TABLE III. Hydrogen Atomic Coordinates (fractional, $\times 10^3$).

	Δ-Λ-[Ru(bipy)$_2$(*S*-thr)]$ClO_4 \cdot 5H_2O$						Δ,Λ-[Ru(bipy)$_2$(*S*-allothr)]$ClO_4 \cdot 5H_2O$					
	x		*y*		*z*		*x*		*y*		*z*	
	n = 1	*n* = 2	*n* = 1	*n* = 2	*n* = 1	*n* = 2	*n* = 1	*n* = 2	*n* = 1	*n* = 2	*n* = 1	*n* = 2
H(*n*12)	779	−288	165	336	100	863	784	−275	164	333	107	913
H(*n*13)	699	−227	141	356	−116	1081	714	−190	142	354	−115	1135
H(*n*14)	477	−8	106	388	−186	1173	491	33	109	390	−199	1208
H(*n*15)	342	143	96	405	−40	1047	350	158	98	403	−61	1055
H(*n*22)	838	−338	177	320	308	674	835	−336	179	320	294	708
H(*n*23)	882	−358	197	295	528	456	879	−381	201	302	515	486
H(*n*24)	708	−180	183	308	633	359	705	−205	188	317	625	379
H(*n*25)	491	29	156	344	521	477	496	1	154	349	511	496
H(*n*32)	309	199	−59	560	208	798	304	197	−60	561	188	810
H(*n*33)	519	−12	−79	582	351	650	513	−12	−83	585	339	664
H(*n*34)	672	−163	−18	523	449	545	668	−172	−23	524	443	562
H(*n*35)	613	−114	63	441	404	593	610	−117	59	443	395	614
H(*n*42)	129	368	−32	534	66	938	141	361	−34	536	48	955
H(*n*43)	−72	558	4	503	−54	1080	−59	561	−2	500	−93	1093
H(*n*44)	−94	582	88	420	−73	1104	−87	587	84	415	−107	1096
H(*n*45)	81	416	137	369	52	971	86	414	133	368	28	961
H(*n*2)	310	422	222	320	371	777	278	395	218	308	360	756
H(*n*3)	75	386	233	258	368	605	139	245	263	247	197	610
H(*n*4A)	197	473	286	213	160	816	153	370	276	237	386	847

(continued overleaf)

TABLE III. (*continued*)

	Δ,Λ-[Ru(bipy)$_2$(*S*-thr)]ClO$_4$·5H$_2$O						Δ,Λ-[Ru(bipy)$_2$(*S*-allothr)]ClO$_4$·5H$_2$O					
	x		*y*		*z*		*x*		*y*		*z*	
	n = 1	*n* = 2	*n* = 1	*n* = 2	*n* = 1	*n* = 2	*n* = 1	*n* = 2	*n* = 1	*n* = 2	*n* = 1	*n* = 2
H(*n*4B)	19	310	295	218	177	844	3	443	294	205	298	758
H(*n*4C)	127	364	306	198	323	680	11	283	247	198	389	749
H(O*n*3)	−41	133	215	251	94	634	−18	382	204	274	78	509
H(N*n*1)	341	268	207	312	188	882	353	279	208	315	188	896
H(N*n*2)	192	156	181	290	138	759	212	145	184	292	108	799
H(W*n*11)	89	423	134	372	601	420	82	406	135	371	563	413
H(W*n*12)	54	473	138	364	739	290	23	485	135	368	693	292
H(W*n*21)	346	128	77	411	526	459	346	149	83	426	503	488
H(W*n*22)	484	21	68	430	638	379	339	164	58	453	640	353
H(W*n*31)	162	337	66	432	745	234	175	321	73	436	710	281
H(W*n*32)	320	170	48	447	723	246	218	286	14	497	741	264
H(W*n*41)	716	770	64	438	654	302	732	759	51	451	653	337
H(W*n*42)	675	823	23	488	770	220	569	924	55	449	660	329
H(W*n*51)	941	575	61	430	643	401	923	571	74	430	585	398
H(W*n*52)	897	620	13	482	610	442	862	633	16	489	567	426

TABLE IV. Proposed Hydrogen Bonds. Interatomic distances (A) are given with e.s.d's in parentheses.[a]

	n = 1			*n* = 2	
	S-thr	*S*-allothr		*S*-thr	*S*-allothr
O(13)···O(1A$^{\mathrm{V}}$)[b]	3.14(1)	3.05(1)	O(23)···O(1B$^{\mathrm{I}}$)	3.21(2)	
···O(1D$^{\mathrm{V}}$)	3.10(3)	3.14(2)	O(23)···O(22)		2.62(1)
N(1)···O(2B)	3.08(2)	3.06(1)	N(2)···O(1B$^{\mathrm{I}}$)	3.12(2)	3.13(1)
N(1)···O(1A$^{\mathrm{V}}$)	3.13(1)	3.24(1)	N(2)···O(2A$^{\mathrm{III}}$)	3.18(2)	3.17(2)
O(W11)···O(12)	2.66(1)	2.72(1)	O(W21)···O(22)	2.74(1)	2.71(1)
O(W11)···O(1C$^{\mathrm{I}}$)	2.88(1)	2.90(1)	O(W21)···O(2C)	2.94(2)	2.97(1)
O(W12)···O(11)	2.97(1)	2.90(1)	O(W22)···O(21)	2.80(1)	2.88(1)
O(W12)···O(W14)	2.75(1)	2.83(1)	O(W22)···O(W24$^{\mathrm{VI}}$)	2.96(1)	2.84(1)
O(W13)···O(W11)	2.81(2)	2.71(1)	O(W23)···O(W21)	2.75(1)	2.79(1)
O(W13)···O(W12)	2.64(1)	2.78(1)	O(W23)···O(W22)	2.83(1)	2.74(1)
O(W14)···O(W15)	2.56(1)	2.75(1)	O(W24)···O(W25)	2.90(2)	2.74(1)
O(W14)···O(W23$^{\mathrm{II}}$)	2.93(1)	2.65(1)	O(W24)···O(W13$^{\mathrm{IV}}$)	2.58(2)	2.86(1)
O(W15)···O(W11)	2.88(2)	2.79(1)	O(W25)···O(W21)	2.73(1)	2.79(1)
O(W15)···O(W22$^{\mathrm{II}}$)	2.94(2)	2.94(1)	O(W25)···O(W12$^{\mathrm{IV}}$)	3.07(2)	3.07(1)

[a] Roman numerical superscripts refer to the following equivalent positions relative to x, y, z: I: $x - 1, y, z$; II: $1 - x, y - ½, 1 - z$; III: $x, y, z + 1$; IV: $1 - x, y + ½, 1 - z$; V: $x - 1, y, z - 1$; VI: $1 + x, y, z$. [b] Bifurcated bond.

of the four isomers due to the different chirality of C(*n*3) in the two crystal structures. The molecular structures of these four cations are shown in Figs. 2 and 3 together with the atomic labelling scheme [6]. For each of the *S*-thr and *S*-allothr Δ cations the O(13)–H(O13) group appears to be involved in a bifurcated interaction with perchlorate oxygen atoms (Table IV). The β–OH group of the Λ-*S*-thr cation also is seen to H-bond a perchlorate O atom, but in the *S*-allothr analogue an internal H-bond to the carboxylic O(22) atom is apparent (see Fig. 3(b)). Again as in the crystal structure of the *S*-alanine analogue reported earlier [7], the amine protons H(N*n*1) and H(N*n*2) of each molecule are weakly H-bonded to perchlorate ions (Table IV).

The close similarities in the molecular structures of the cations may be seen in Figs. 2 and 3. The

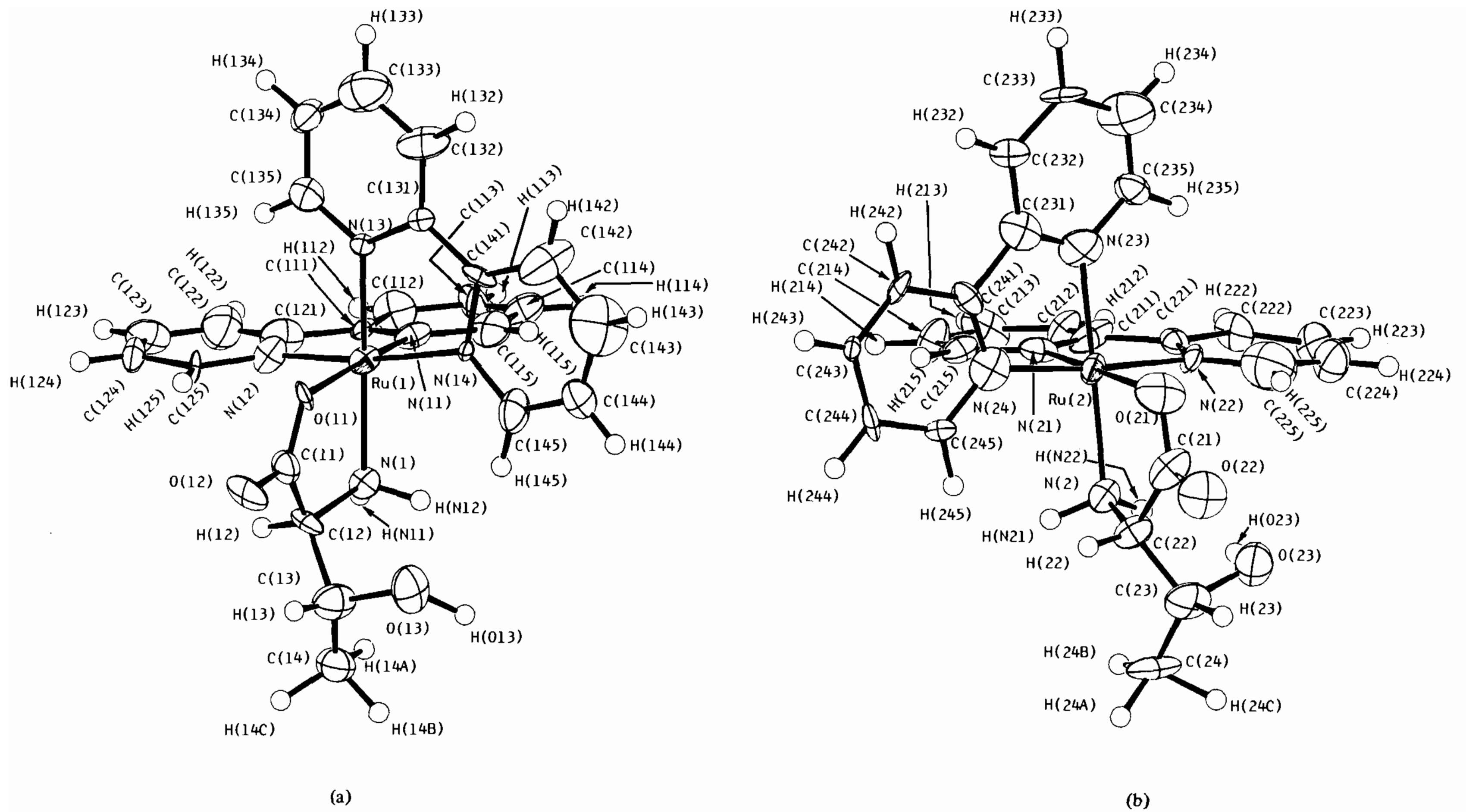
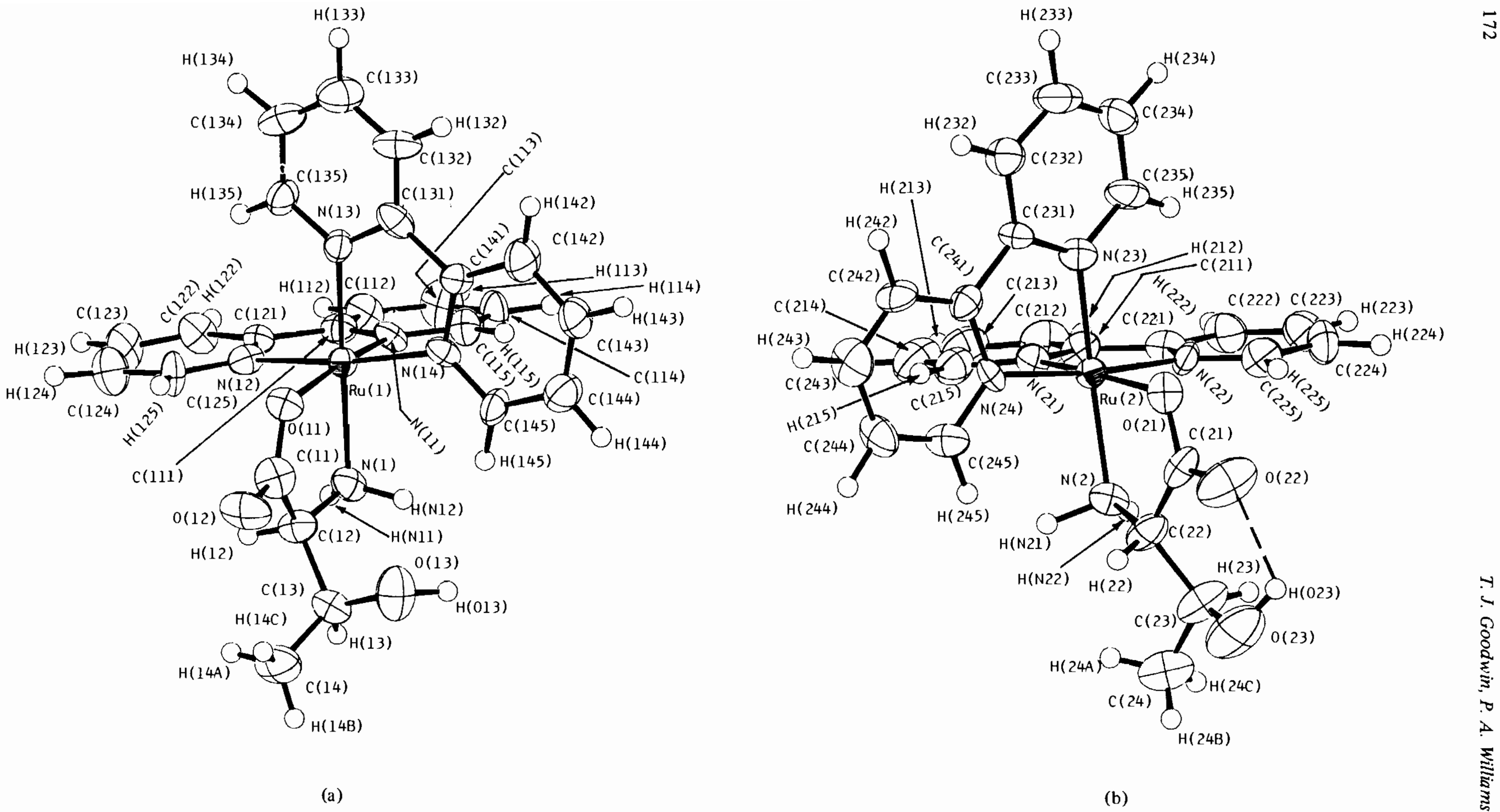


Fig. 2. Perspective drawings of (a) the Δ-[Ru(bipy)$_2$(*S*-thr)]$^+$ and (b) the Λ-[Ru(bipy)$_2$(*S*-thr)]$^+$ diastereoisomeric cations showing the atomic labelling. Thermal ellipsoids are scaled to include 50% probability. Hydrogen atoms have been included with a thermal parameter $B = 1.0$ Å^2.



(a)

(b)

Fig. 3. Perspective drawings showing the atomic labelling of (a) the Δ-[Ru(bipy)$_2$(*S*-allothr)]$^+$ cation and (b) the Λ-[Ru(bipy)$_2$(*S*-allothr)]$^+$ cation showing the proposed intramolecular hydrogen bond. Thermal ellipsoids are scaled to include 50% probability. Hydrogen atoms have $B = 1.0$ Å^2.

TABLE V. Torsion Angles (°) Along the C–C Bonds in the Coordinated Amino Acids.

	S-thr		*S*-allothr	
	n = 1	*n* = 2	*n* = 1	*n* = 2
C(*n*1)–C(*n*2)–N(*n*)–Ru(*n*)	+19.2	+18.1	+20.4	+15.9
C(*n*3)–C(*n*2)–N(*n*)–Ru(*n*)	+144.9	+144.3	+149.1	+146.9
O(*n*3)–C(*n*3)–C(*n*2)–C(*n*1)	+73.4	+62.8	+56.7	–52.4
C(*n*4)–C(*n*3)–C(*n*2)–C(*n*1)	–164.3	–177.6	–68.3	–173.8
O(*n*3)–C(*n*3)–C(*n*2)–N(*n*)	–52.0	–62.1	–70.9	+178.5
C(*n*4)–C(*n*3)–C(*n*2)–N(*n*)	+70.4	+57.5	+164.2	+57.1

TABLE VI. Least-Squares Planes Data.

a) Least-squares planes and their equations given by $lX' + mY' + nZ' - p = 0$ where X′, Y′ and Z′ are orthogonal coordinates (A) derived with respect to the orthogonal axes a', b, c. Deviations (A) of relevant atoms from the planes are given in square brackets.

	l	*m*	*n*	*p*
(i) *S-Threonine Complex*				
Plane (1): Ru(1), O(11), C(11), N(1) [Ru(1) 0.035, O(11) –0.057, C(11) 0.048, N(1) –0.026, C(12) 0.26]	0.8343	0.3587	0.4186	4.8650
Plane (2): Ru(2), O(21), C(21), N(2) [Ru(2) 0.033, O(21) –0.053, C(21) 0.046, N(2) –0.025, C(22) 0.25]	0.7716	0.4039	0.4914	9.2466
Plane (3): N(11), C(111) – C(115) [N(11) –0.022, C(111) 0.013, C(112) –0.008, C(113) 0.010, C(114) –0.018, C(115) 0.024, Ru(1) –0.01, C(122) –0.11]	–0.3852	0.9109	–0.1482	1.3976
Plane (4): N(12), C(121)–C(125) [N(12) –0.021, C(121) 0.005, C(122) 0.007, C(123) –0.002, C(124) –0.014, C(125) 0.026, Ru(1) –0.13, C(112) 0.05]	–0.3331	0.9313	–0.1478	1.7730
Plane (5): N(13), C(131)–C(135) [N(13) –0.001, C(131) 0.008, C(132) –0.006, C(133) –0.004, C(134) 0.011, C(135) –0.009, Ru(1) –0.08, C(142) 0.14]	0.4418	–0.0209	–0.8969	0.0704
Plane (6): N(14), C(141)–C(145) [N(14) 0.028, C(141) –0.028, C(142) 0.010, C(143) 0.008, C(144) –0.009, C(145) –0.010, Ru(1) –0.004, C(132) –0.16]	0.4495	0.0352	–0.8926	0.2119
Plane (7): N(21), C(211) – C(215) [N(21) –0.020, C(211) 0.017, C(212) –0.008, C(213) 0.004, C(214) –0.007, C(215) 0.015, Ru(2) –0.13, C(222) –0.12]	–0.3888	0.9147	–0.1100	8.6724
Plane (8): N(22), C(221) – C(225) [N(22) –0.016, C(221) –0.005, C(222) 0.018, C(223), C(224) –0.010, C(225) 0.023, Ru(2) –0.03, C(212) –0.21]	–0.3794	0.8963	–0.2294	7.4379
Plane (9): N(23), C(231) – C(235) [N(23) –0.002, C(231) –0.011,.C(232), C(233) 0.008, C(234) –0.022, C(235) 0.019, Ru(2) –0.16, C(242) 0.09]	–0.4696	0.0422	0.8819	6.9805
Plane (10): N(24), C(241) – C(245) [N(24) –0.026, C(241), C(245) 0.016, C(242), C(244) 0.004, C(243) –0.014, Ru(2) 0.07, C(232) 0.005]	–0.5142	–0.0127	0.8576	5.9041
Plane (11): O(11), O(12), C(12) [Ru(1) 0.06, C(11) –0.03]	0.8590	0.2325	0.4561	4.5753
Plane (12): O(21), O(22), C(22) [Ru(2) 0.12, C(21) –0.06]	0.7132	0.5154	0.4751	10.1646
(ii) *S-Allothreonine Complex*				
Plane (13): Ru(1), O(11), C(11), N(1) [Ru(1) 0.011, O(11) –0.018, C(11) 0.016, N(1) –0.008, C(12) 0.27]	0.8128	0.3847	0.4375	4.8453

(continued overleaf)

TABLE VI. *(continued)*

	l	*m*	*n*	*p*
Plane (14): Ru(2), O(21), C(21), N(2) [Ru(2) 0.024, O(21) −0.039, C(21) 0.033, N(2) −0.019, C(22) 0.22]	0.8076	0.3957	0.4373	8.7798
Plane (15): N(11), C(111) – C(115) [N(11) 0.006, C(111) −0.003, C(112) 0.003, C(113) −0.006, C(114) 0.008, C(115) −0.009, Ru(1) 0.05, C(122) −0.002]	−0.3773	0.9180	−0.1220	1.4084
Plane (16): N(12), C(121)–C(125) [N(12) −0.002, C(121) 0.012, C(122) −0.003, C(123) −0.015, C(124) 0.025 C(125) −0.016, Ru(1) −0.04, C(112) 0.21]	−0.3502	0.9151	−0.1997	1.4631
Plane (17): N(13), C(131) – C(135) [N(13) −0.004, C(131) 0.011, C(132) −0.010, C(133) 0.001, C(134) 0.007, C(135) −0.006, Ru(1) −0.09, C(142) 0.15]	0.4558	−0.0262	−0.8897	0.3176
Plane (18): N(14), C(141) – C(145) [N(14) 0.013, C(141) −0.010, C(142) 0.004, C(143) <|0.001|, C(144) 0.003, C(145) −0.010, Ru(1) 0.06, C(132) −0.16]	0.4761	0.0460	−0.8782	0.4922
Plane (19): N(21), C(211) – C(215) [N(21) 0.009, C(211) −0.007, C(212) 0.001, C(213) 0.004, C(214) −0.002, C(215) −0.004, Ru(2) −0.08, C(222) −0.02]	−0.4107	0.9118	−0.0848	8.6991
Plane (20): N(22), C(221)–C(225) [N(22) 0.005, C(221) 0.001, C(222) <|0.001|, C(223) −0.006, C(224) 0.012, C(225) −0.012, Ru(2) 0.10, C(212) −0.02]	−0.3642	0.9242	−0.1146	8.4568
Plane (21): N(23), C(231)–C(235) [N(23) −0.016, C(231) 0.007, C(232) 0.008, C(233) −0.014, C(234) 0.004, C(235) 0.011, Ru(2) −0.15, C(242) 0.11]	−0.4425	0.0382	0.8959	7.2031
Plane (22): N(24), C(241)–C(245) [N(24) 0.010, C(241) −0.006, C(242) −0.008, C(243) 0.017, C(244) − 0.013, C(245) <|0.001|, Ru(2) 0.13, C(232) − 011]	−0.4713	−0.0559	0.8802	5.7519
Plane (23): O(11), O(12), C(12) [Ru(1) −0.19, C(11) −0.03]	0.7840	0.2874	0.5502	4.7927
Plane (24): O(21), O(22), C(22) [Ru(2) −0.08, C(21) −0.005]	0.7996	0.4841	0.3553	9.1675

b) Dihedral angles (°) between relevant planes

1–11,	7.7;	2–12,	7.3;	13–23,	8.7;	14–24,	6.9;
3–4,	3.2;	7–8,	7.0;	15–16,	4.7;	19–20,	2.8;
5–6	3.2;	7–10,	4.3;	17–18,	4.4;	21–22,	5.7.

only obvious differences in these structures, both between Λ and Δ pairs and between *S*-thr and *S*-allothr ions of like hand, are derived from the enforced chiralities of the C$_\alpha$ and C$_\beta$ atoms (C(*n*2) and C(*n*3)). These differences are highlighted by a comparison of the torsion angles around the C–N$_{amine}$ and C$_\beta$–C$_\alpha$ bonds, which are given in Table V. The five-membered amino acid chelate rings have a very similar conformation in both the Λ and Δ forms of each complex; this is demonstrated by the like torsion angles around each of the C(*n*2)–N(*n*) bonds and by the displacements of the C(*n*2) atoms from the planes defined by the remaining four atoms of the rings (Table VI, planes 1, 2, 13 and 14). Differences seen in the torsion angles around the C(*n*3)–C(*n*2) bonds reflect the rotation allowed around them and the differing H-bonding requirements of the β-OH groups.

The pyridyl rings each show the expected planarity (Table VI, planes 3–10 and 15–22) with each of the bipy groups being closely coplanar (Table VI(b)). There are some distortions of the metal atoms out of their respective carboxylic acid planes (Table VI, planes 11, 12, 23 and 24).

The bond lengths and angles in the molecular ions of both structures are given in Table VII. There are no apparent significant differences between corresponding bonding parameters in the four cations. The average bond lengths are Ru(*n*)–O(*n*1) 2.094(9), Ru(*n*)–N(*n*) 2.128(11) and Ru(*n*)–N(*n*1–4) 2.050(2) Å with average bite angles at the Ru(*n*) atoms for the amino acids of 79.7(5) and for bipy ligands of 79.0(4)°. Again these parameters are closely comparable with those of the *S*-alanine analogue [7]. There is some evidence of flattening at the C$_\alpha$ and C$_\beta$ atoms in the side chains of the two

TABLE VII. Bond Lengths (A) and Angles (°) with Estimated Standard Deviations in Parentheses.

	$[Ru(bipy)_2(S\text{-thr})]ClO_4 \cdot 5H_2O$		$[Ru(bipy)_2(S\text{-allothr})]ClO_4 \cdot 5H_2O$	
	n = 1	*n* = 2	*n* = 1	*n* = 2
(a) *Distances (A)*				
Ru(*n*)–O(*n*1)	2.084(6)	2.104(9)	2.096(5)	2.090(5)
Ru(*n*)–N(*n*)	2.118(9)	2.142(10)	2.121(7)	2.130(7)
Ru(*n*)–N(*n*1)	2.025(10)	2.015(9)	2.037(6)	2.021(7)
Ru(*n*)–N(*n*2)	2.019(10)	2.064(8)	2.044(6)	2.055(6)
Ru(*n*)–N(*n*3)	2.030(8)	2.094(11)	2.065(7)	2.035(7)
Ru(*n*)–N(*n*4)	2.062(7)	2.095(11)	2.068(6)	2.075(6)
C(*n*11)–C(*n*21)	1.46(2)	1.44(2)	1.46(1)	1.46(1)
C(*n*31)–C(*n*41)	1.42(2)	1.48(2)	1.48(1)	1.47(1)
C(*n*11)–C(*n*12)	1.39(1)	1.38(2)	1.39(1)	1.40(1)
C(*n*12)–C(*n*13)	1.38(2)	1.35(2)	1.37(1)	1.36(1)
C(*n*13)–C(*n*14)	1.37(2)	1.37(2)	1.40(1)	1.38(2)
C(*n*14)–C(*n*15)	1.38(2)	1.39(2)	1.37(1)	1.39(1)
N(*n*1)–C(*n*11)	1.39(1)	1.36(2)	1.39(1)	1.36(1)
N(*n*1)–C(*n*15)	1.37(2)	1.34(1)	1.31(1)	1.34(1)
C(*n*21)–C(*n*22)	1.38(2)	1.38(1)	1.37(1)	1.41(1)
C(*n*22)–C(*n*23)	1.34(2)	1.44(2)	1.37(1)	1.36(1)
C(*n*23)–C(*n*24)	1.37(2)	1.36(2)	1.40(1)	1.40(1)
C(*n*24)–C(*n*25)	1.39(1)	1.39(2)	1.38(1)	1.37(1)
N(*n*2)–C(*n*21)	1.37(2)	1.36(1)	1.39(1)	1.34(1)
N(*n*2)–C(*n*25)	1.36(1)	1.38(2)	1.34(1)	1.32(1)
C(*n*31)–C(*n*32)	1.38(2)	1.39(2)	1.40(1)	1.39(1)
C(*n*32)–C(*n*33)	1.39(2)	1.38(2)	1.37(1)	1.38(1)
C(*n*33)–C(*n*34)	1.35(2)	1.38(2)	1.37(1)	1.35(1)
C(*n*34)–C(*n*35)	1.40(2)	1.35(2)	1.41(1)	1.37(1)
N(*n*3)–C(*n*31)	1.36(1)	1.33(2)	1.34(1)	1.36(1)
N(*n*3)–C(*n*35)	1.33(1)	1.38(2)	1.33(1)	1.35(1)
C(*n*41)–C(*n*42)	1.37(2)	1.41(1)	1.40(1)	1.38(1)
C(*n*42)–C(*n*43)	1.43(2)	1.32(1)	1.38(1)	1.36(1)
C(*n*43)–C(*n*44)	1.38(2)	1.37(1)	1.38(1)	1.37(1)
C(*n*44)–C(*n*45)	1.36(2)	1.41(1)	1.41(1)	1.37(1)
N(*n*4)–C(*n*41)	1.41(1)	1.31(2)	1.37(1)	1.35(1)
N(*n*4)–C(*n*45)	1.35(1)	1.35(2)	1.32(1)	1.36(1)
C(*n*1)–O(*n*1)	1.27(1)	1.29(2)	1.28(1)	1.30(1)
C(*n*1)–O(*n*2)	1.25(1)	1.26(1)	1.23(1)	1.24(1)
C(*n*1)–C(*n*2)	1.53(2)	1.51(2)	1.55(1)	1.47(1)
C(*n*2)–N(*n*)	1.50(1)	1.49(2)	1.46(1)	1.51(1)
C(*n*2)–C(*n*3)	1.53(2)	1.49(2)	1.54(1)	1.52(1)
C(*n*3)–C(*n*4)	1.46(2)	1.51(2)	1.49(1)	1.47(2)
C(*n*3)–O(*n*3)	1.43(1)	1.46(2)	1.42(1)	1.45(1)
Cl(*n*)–O(*n*A)	1.40(1)	1.34(2)	1.32(1)	1.38(1)
Cl(*n*)–O(*n*B)	1.40(1)	1.39(1)	1.44(1)	1.34(1)
Cl(*n*)–O(*n*C)	1.48(1)	1.29(1)	1.39(1)	1.35(1)
Cl(*n*)–O(*n*D)	1.33(2)	1.37(2)	1.44(1)	1.20(2)
(b) Angles (°)				
O(*n*1)–Ru(*n*)–N(*n*)	79.0(2)	80.7(4)	79.1(2)	79.9(3)
O(*n*1)–Ru(*n*)–N(*n*1)	172.1(3)	173.7(4)	170.7(2)	172.1(3)
O(*n*1)–Ru(*n*)–N(*n*2)	95.8(3)	93.9(4)	94.2(2)	93.9(3)
O(*n*1)–Ru(*n*)–N(*n*3)	94.1(3)	93.0(4)	96.3(2)	92.1(2)
O(*n*1)–Ru(*n*)–N(*n*4)	90.0(3)	88.6(4)	90.1(2)	89.9(2)
N(*n*)–Ru(*n*)–N(*n*1)	95.7(4)	96.4(4)	93.2(2)	96.2(3)
N(*n*)–Ru(*n*)–N(*n*2)	88.6(4)	87.4(3)	88.9(2)	88.0(3)
N(*n*)–Ru(*n*)–N(*n*3)	172.5(3)	172.2(4)	174.1(2)	171.2(2)
N(*n*)–Ru(*n*)–N(*n*4)	97.8(3)	97.4(4)	96.9(2)	98.0(3)

(continued overleaf)

TABLE VII. *(continued)*

	[Ru(bipy)$_2$(*S*-thr)]ClO$_4$·5H$_2$O		[Ru(bipy)$_2$(*S*-allothr)]ClO$_4$·5H$_2$O	
	n = 1	*n* = 2	*n* = 1	*n* = 2
N(*n*1)–Ru(*n*)–N(*n*2)	78.1(4)	80.4(4)	80.2(3)	79.0(3)
N(*n*1)–Ru(*n*)–N(*n*3)	91.4(3)	90.4(4)	91.8(3)	92.2(3)
N(*n*1)–Ru(*n*)–N(*n*4)	96.6(4)	97.4(4)	96.1(2)	97.5(3)
N(*n*2)–Ru(*n*)–N(*n*3)	95.1(4)	97.7(4)	95.1(3)	96.3(3)
N(*n*2)–Ru(*n*)–N(*n*4)	172.1(4)	174.9(4)	173.3(3)	173.4(3)
N(*n*3)–Ru(*n*)–N(*n*4)	79.0(3)	77.8(4)	79.4(2)	78.1(3)
Ru(*n*)–O(*n*1)–C(*n*1)	118.4(7)	113.8(8)	118.4(5)	115.6(5)
Ru(*n*)–N(*n*)–C(*n*2)	111.3(6)	110.4(7)	111.3(5)	110.6(5)
Ru(*n*)–N(*n*1)–C(*n*11)	118.4(7)	113.0(8)	115.0(5)	115.8(5)
Ru(*n*)–N(*n*1)–C(*n*15)	124.6(8)	127.5(8)	127.4(5)	125.0(6)
Ru(*n*)–N(*n*2)–C(*n*21)	117.1(8)	114.3(6)	114.8(5)	115.4(5)
Ru(*n*)–N(*n*2)–C(*n*25)	126.4(8)	125.2(9)	128.1(6)	125.0(6)
Ru(*n*)–N(*n*3)–C(*n*31)	116.3(6)	115.2(8)	115.6(5)	116.5(5)
Ru(*n*)–N(*n*3)–C(*n*35)	124.7(8)	124.0(9)	125.2(6)	125.6(6)
Ru(*n*)–N(*n*4)–C(*n*41)	114.1(6)	115.3(8)	114.1(5)	116.4(5)
Ru(*n*)–N(*n*4)–C(*n*45)	125.4(7)	127.6(8)	128.2(6)	126.1(6)
O(*n*1)–C(*n*1)–O(*n*2)	122.6(11)	122.3(12)	125.5(9)	118.3(9)
O(*n*1)–C(*n*1)–C(*n*2)	117.6(10)	121.8(11)	115.3(8)	120.5(7)
N(*n*)–C(*n*2)–C(*n*1)	110.4(9)	110.5(10)	112.3(7)	111.2(7)
N(*n*)–C(*n*2)–C(*n*3)	113.9(10)	111.3(10)	110.1(6)	113.0(8)
O(*n*2)–C(*n*1)–C(*n*2)	119.6(11)	115.3(12)	119.1(9)	121.2(9)
C(*n*1)–C(*n*2)–C(*n*3)	111.0(11)	112.9(11)	114.4(7)	114.9(8)
C(*n*2)–C(*n*3)–C(*n*4)	115.4(12)	116.2(12)	116.5(8)	115.4(10)
C(*n*2)–C(*n*3)–O(*n*3)	105.7(10)	103.0(10)	106.3(7)	110.4(9)
O(*n*3)–C(*n*3)–C(*n*4)	110.4(11)	109.5(12)	111.5(5)	107.0(10)
N(*n*1)–C(*n*11)–C(*n*12)	119.5(10)	120.9(12)	121.3(8)	119.5(8)
N(*n*1)–C(*n*11)–C(*n*21)	111.0(10)	118.6(11)	115.1(7)	114.8(7)
C(*n*12)–C(*n*11)–C(*n*21)	129.4(11)	120.0(12)	123.5(8)	125.8(8)
C(*n*11)–C(*n*12)–C(*n*13)	121.8(12)	120.0(12)	119.1(8)	121.5(10)
C(*n*12)–C(*n*13)–C(*n*14)	119.4(12)	119.1(12)	119.3(8)	118.6(10)
C(*n*13)–C(*n*14)–C(*n*15)	117.6(12)	120.3(11)	118.5(7)	118.5(10)
C(*n*14)–C(*n*15)–N(*n*1)	124.6(12)	119.9(10)	124.1(8)	122.8(9)
C(*n*11)–N(*n*1)–C(*n*15)	116.8(10)	119.6(10)	117.6(6)	119.0(7)
N(*n*2)–C(*n*21)–C(*n*22)	122.3(13)	121.0(12)	120.6(8)	120.9(8)
N(*n*2)–C(*n*21)–C(*n*11)	115.3(10)	113.6(9)	114.7(7)	115.0(7)
C(*n*22)–C(*n*21)–C(*n*11)	122.5(12)	125.4(12)	124.7(8)	124.1(8)
C(*n*21)–C(*n*22)–C(*n*23)	120.7(15)	117.5(12)	121.4(8)	118.5(9)
C(*n*22)–C(*n*23)–C(*n*24)	118.5(13)	121.7(11)	118.7(8)	119.9(9)
C(*n*23)–C(*n*24)–C(*n*25)	120.7(11)	117.9(14)	118.0(9)	118.0(9)
C(*n*24)–C(*n*25)–N(*n*2)	121.1(10)	121.3(15)	124.2(8)	123.0(8)
C(*n*21)–N(*n*2)–C(*n*25)	116.5(10)	120.5(10)	117.1(4)	119.6(6)
N(*n*3)–C(*n*31)–C(*n*32)	121.1(11)	120.0(12)	121.7(9)	121.1(7)
N(*n*3)–C(*n*31)–C(*n*41)	115.8(9)	115.4(11)	114.9(8)	115.1(7)
C(*n*32)–C(*n*31)–C(*n*41)	123.1(12)	124.7(12)	123.4(8)	123.8(8)
C(*n*31)–C(*n*32)–C(*n*33)	119.2(14)	118.8(12)	118.8(10)	118.9(8)
C(*n*32)–C(*n*33)–C(*n*34)	119.8(15)	120.8(12)	120.0(10)	120.2(9)
C(*n*33)–C(*n*34)–C(*n*35)	118.9(13)	118.4(14)	118.7(9)	119.5(9)
C(*n*34)–C(*n*35)–N(*n*3)	122.1(12)	121.2(12)	121.6(8)	122.4(9)
C(*n*31)–N(*n*3)–C(*n*35)	118.9(9)	120.7(11)	119.2(4)	117.9(7)
N(*n*4)–C(*n*41)–C(*n*42)	119.3(11)	122.7(10)	122.4(8)	121.7(8)
N(*n*4)–C(*n*41)–C(*n*31)	114.6(9)	116.2(11)	115.9(7)	113.8(7)
C(*n*42)–C(*n*41)–C(*n*31)	126.0(11)	121.1(11)	121.7(8)	124.5(8)
C(*n*41)–C(*n*42)–C(*n*43)	120.2(15)	120.4(10)	118.6(9)	120.5(9)
C(*n*42)–C(*n*43)–C(*n*44)	117.2(15)	119.0(10)	119.8(9)	118.2(9)
C(*n*43)–C(*n*44)–C(*n*45)	122.3(14)	118.7(10)	118.0(9)	119.8(9)

(continued overleaf)

TABLE VII. *(continued)*

	$[Ru(bipy)_2(S\text{-thr})]ClO_4 \cdot 5H_2O$		$[Ru(bipy)_2(S\text{-allothr})]ClO_4 \cdot 5H_2O$	
	$n = 1$	$n = 2$	$n = 1$	$n = 2$
C(*n*44)–C(*n*45)–N(*n*4)	120.4(2)	122.4(10)	123.4(8)	122.3(9)
C(*n*41)–N(*n*4)–C(*n*45)	120.4(9)	116.7(10)	117.4(4)	117.4(5)
O(*n*A)–Cl(*n*)–O(*n*B)	108.6(8)	102.5(10)	109.1(6)	106.9(7)
O(*n*A)–Cl(*n*)–O(*n*C)	108.9(8)	108.6(13)	116.4(10)	111.2(8)
O(*n*A)–Cl(*n*)–O(*n*D)	113.2(13)	106.0(15)	108.0(10)	103.1(16)
O(*n*B)–Cl(*n*)–O(*n*C)	102.6(6)	122.1(11)	106.5(5)	110.7(8)
O(*n*B)–Cl(*n*)–O(*n*D)	114.7(11)	105.4(13)	110.3(7)	114.0(17)
O(*n*C)–Cl(*n*)–O(*n*D)	108.2(11)	111.1(11)	106.5(7)	110.7(15)

amino acids. The average C(*n*1)–C(*n*2)–C(*n*3) observed bond angle is 113.3(12)° and the average C(*n*2)–C(*n*3)–C(*n*4) angle is 115.9(12)°, each being greater than an undistorted tetrahedral angle.

Equilibrium Studies

The phen and bipy complexes of Ru(II) with either *S*-threonine or *S*-allothreonine were resolved chromatographically using Sephadex® C-25 cation exchange resin. Chiroptical and electronic spectral data for the complexes are given in Table VIII. The circular dichroism spectra for the isolated diastereoisomers are shown in Fig. 4. Assignments of absolute configuration have been made on the basis of the sign of the lower energy π–π* transitions in the ultraviolet region of the spectra [8, 9]. The spectra of the phen and bipy series of isomers are similar to those of related complexes [1, 2]. Also shown in Fig. 4 are the circular dichroism spectra of solutions containing equilibrated mixtures of diastereoisomers, and from this data we have been able to calculate

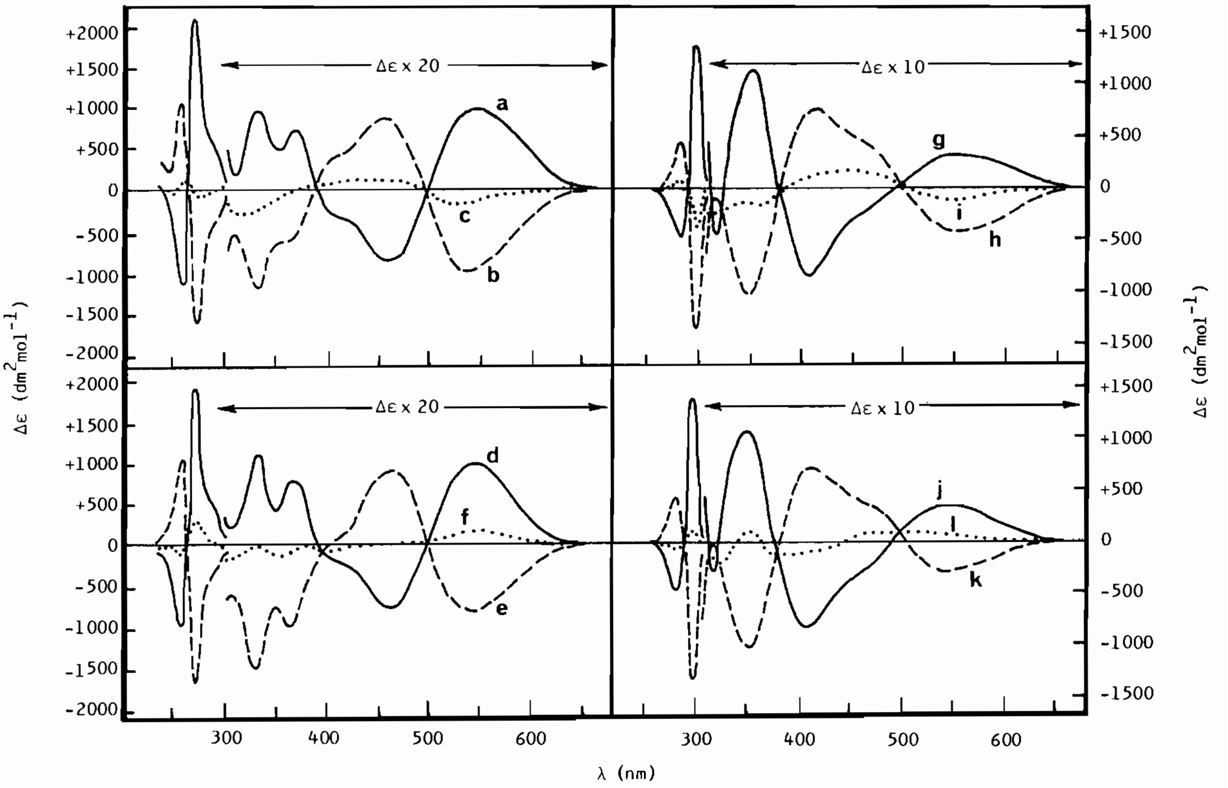


Fig. 4. Circular dichroism spectra of: (a) Λ-, (b) Δ- and (c) an equilibrated solution of Δ,Λ-$[Ru(phen)_2(S\text{-thr})]^+$; (d) Λ-, (e) Δ- and (f) an equilibrated solution of Δ,Λ-$[Ru(phen)_2(S\text{-allothr})]^+$; (g) Λ-, (h) Δ- and (i) an equilibrated solution of Δ,Λ-$[Ru(bipy)_2(S\text{-thr})]^+$; and (j) Λ-, (k) Δ- and (l) an equilibrated solution of Δ,Λ-$[Ru(bipy)_2(S\text{-allothr})]^+$.

TABLE VIII. Circular Dichroism and Electronic Spectral Data[a] for the Complexes in Aqueous Solution at 298 K.

Complex	λ^b (nm)	$10^{-4} \times \epsilon$ (dm^2 mol^{-1})	λ^b (nm)	$\Delta\epsilon$ (dm^2 mol^{-1})
Δ-[Ru(phen)$_2$(S-thr)]$^+$			531	−53
			455	+44
			360	−31
			272	−1636(11)
			260	+1050
Λ-[Ru(phen)$_2$(S-thr)]$^+$			544	+48
			458	−44
			366	+36
			331	+48
			271	+2068(28)
			259	−1175
Δ,Λ-[Ru(phen)$_2$(S-thr)]$^+$	482	11.6^c	272	−20(1)^c
	264	81.5^c	260	+80^c
Δ-[Ru(phen)$_2$(S-allothr)]$^+$			538	−41
			462	+45
			365	−49
			333	−79
			272	−1693(12)
			260	+1075
Λ-[Ru(phen)$_2$(S-allothr)]$^+$			540	+50
			461	−39
			366	+39
			331	+56
			271	+1846(13)
			259	−1060
Δ,Λ-[Ru(phen)$_2$(S-allothr)]$^+$	482	11.5^c	271	+205(1)^c
	264	81.4^c	259	−67^c
Δ-[Ru(bipy)$_2$(S-thr)]$^+$			547	−44
			414	+78
			350	−106
			296	−1373(7)
			284	+480
Λ-[Ru(bipy)$_2$(S-thr)]$^+$			550	+32
			405	−90
			354	+116
			296	+1360(15)
			284	−500
Δ,Λ-[Ru(bipy)$_2$(S-thr)]$^+$	494	9.2^c	296	−253(2)^c
	292	58.0^c	284	+80^c
Δ-[Ru(bipy)$_2$(S-allothr)]$^+$			547	−29
			412	+73
			354	−104
			296	−1363(9)
			284	+460
Λ-[Ru(bipy)$_2$(S-allothr)]$^+$			543	+34
			405	−84
			350	+109
			296	+1350(11)
			284	−480
Δ,Λ-[Ru(bipy)$_2$(S-allothr)]$^+$	494	9.3^c	296	+67(2)^c
	292	58.1^c	284	−37^c

[a] Errors in ϵ values are $\pm 0.1 \times 10^4$. Standard deviations given in parentheses for CD extrema were calculated from multiple measurements; other CD values reported for each spectrum have similar precision. [b] Wavelengths reported are for maxima in the electronic spectra and for extrema in the CD spectra. [c] Values for light-equilibrated solutions.

TABLE IX. Values of Equilibrium Constants[a] for the Complexes Δ,Λ-[Ru(diimine)$_2$(aa)]$^+$ at 298 K.

Diimine	Amino Acid	K_{H_2O}[b]	K_{D_2O}[c]
phen	*S*-thr	0.77(2)	0.89(1)
phen	*S*-allothr	1.15(2)	1.09(1)
bipy	*S*-thr	0.68(1)	0.78(1)
bipy	*S*-allothr	1.12(1)	1.02(2)
phen	*S*-ser	1.28(3)[d]	1.23(5)
bipy	*S*-ser	0.78(5)[d]	0.94(5)

[a] Standard deviations in parentheses are derived from a number (>10) of measurements. [b] Determined chiroptically in H_2O. [c] From ^1H NMR measurements in D_2O. [d] Taken from ref. [3].

values for the equilibrium constants with reference to eqn. (1).

$$\Delta\text{-[Ru}(\textit{diimine})_2(\textit{aa})]^+ \rightleftharpoons \Lambda\text{-[Ru}(\textit{diimine})_2(\textit{aa})]^+ \quad (1)$$

These values are presented in Table IX, and refer to normal aqueous solutions, as contrasted with D_2O solutions (*vide infra*). It is found that both phen and bipy complexes with *S*-threonine give equilibrium mixtures of isomers which are enriched in the Δ-hand, but corresponding complexes of *S*-allothreonine give mixtures slightly favouring the Λ-diastereoisomer. Calculated chiral discrimination energies between pairs of diastereoisomers range from 0.3 to 1.0 kJ mol^{-1}.

TABLE X. ^1H NMR Data for the Complexes Λ,Δ-[Ru(diimine)$_2$(aa)]$^+$ in D_2O Solution at 298 K.[a]

Diimine	δ (ppm)	J (Hz)	*S*-thr Complexes[b]		*S*-allothr Complexes[b]	
			$n = 1(\Delta)$	$n = 2(\Lambda)$	$n = 1(\Delta)$	$n = 2(\Lambda)$
bipy	$H(n45)$		9.402	9.245	9.289	9.209
	$H(n25)$		8.978	8.978	8.916	8.933
	$H(n2)$		3.273	3.707	3.335	3.842
	$H(n3)$		4.573	4.499	4.233	4.219
	$C(n4)H_3$		1.252	1.240	1.298	1.042
		$J_{n44,n45}$	5.46	5.57	6.57	5.36
		$J_{n24,n25}$	5.52	5.52	5.92	5.98
		$J_{n2,n3}$	<0.02	<0.02	4.28	4.59
		$J_{n3,n4}$	6.56	6.60	6.55	7.53
phen	$H(n45)$		9.927	9.754	9.925	9.822
	$H(n25)$		9.522	9.522	9.572	9.605
	$H(n2)$		3.484	3.962	3.665	4.223
	$H(n3)$		4.718	4.649	4.498	4.506
	$C(n4)H_3$		1.348	1.331	1.560	1.274
		$J_{n44,n45}$	5.25	5.17	5.16	5.17
		$J_{n24,n25}$	5.30	5.30	5.19	5.17
		$J_{n2,n3}$	<0.02	<0.02	4.23	4.50
		$J_{n3,n4}$	5.47	6.30	6.50	6.52

Diimine	δ (ppm)	J (Hz)	*S*-ser Complexes[c]	
			$n = 1(\Delta)$	$n = 2(\Lambda)$
bipy	$H(n45)$		9.23	9.16
	$H(n25)$		8.83	8.83
		$J_{n44,n45}$	6.0	6.0
	H_A		3.95	3.84
	H_B		3.58	3.57
	H_X		3.27	3.69
		J_{AB}	−12.8	−13.2
		J_{AX}	2.8	3.0
		J_{BX}	2.8	3.0
phen	$H(n45)$		9.71	9.63
	$H(n25)$		9.29	9.29
		$J_{n44,n45}$	5.2	5.2

[a] Chemical shifts (δ) are reported in ppm downfield from DSS. Chemical shifts are ±0.002 ppm, coupling constants (J) are ±0.02 Hz for 360 MHz spectra; corresponding values for 200 MHz spectra are ±0.02 ppm and ±0.2 Hz. [b] Recorded at 360 MHz. [c] Recorded at 200 MHz.

We have also carried out equilibrium studies in D_2O, and monitored changes in isomer concentrations using ^1H NMR spectroscopy. Selected and pertinent ^1H NMR data for the complexes are listed in Table X. Solutions of pairs of diastereoisomers were allowed to equilibrate in sunlight until all amine hydrogen atoms were exchanged for deuterium and equilibrium had been reached. It was noticed that prolonged irradiation (several weeks) caused some decomposition of the complexes, giving rise to free amino acid and Δ,Λ-$[Ru(\textit{diimine})_2Cl(D_2O)]^+$ in D_2O solution. However, equilibrium between pairs of isomers was attained in all cases before any significant amount of decomposition had occurred.

Equilibrium constants were estimated by integration of the amino acid proton signals where appropriate, and by integration of the H(*n*45) proton signals for each diastereomer. These signals are both well-resolved and separated in all complexes, and are the signals occurring furthest downfield in the ^1H NMR spectra. Their resonance positions are considerably different to those of H(*n*25) and H(*n*35) since these protons experience considerable shielding by adjacent pyridyl rings [10]. Signals corresponding to H(*n*15) occur slightly upfield from those of H(*n*45) as they are somewhat shielded by the coordinated carboxyl group of the amino acid. Values for the equilibrium constants for eqn. (1) in D_2O solution, with all labile protons exchanged, are also listed in Table X. In general, similar trends are found as for H_2O solutions in that the *S*-threonine complexes favour the Δ-diastereoisomer and the converse is true for the *S*-allothreonine complexes. However, in all cases the values in D_2O solutions are much closer to unity, and the variations found from solvent to solvent may reflect slightly different hydrophobic bonding effects under changing conditions [11].

Discussion

The crystal structures of the *S*-threonine and *S*-allothreonine complexes are similar and the molecular structures of the diastereoisomeric cations also are closely related to those found for the *S*-alanine analogue [7]. In the *S*-alanine structure [7] there was an obvious difference in the conformations of the amino-acid chelate rings. This was attributed to unequal intramolecular steric factors. In the present structures the amino-acid chelate rings have like conformations which are intermediate between those observed in the *S*-alanine analogue (see Table V). This suggests that differences in steric factors within these cations are minor.

The preference for the Δ-hand on photo-equilibration observed for the *S*-threonine species may be compared with the CD study of the *S*-serine analogue [2]. Again a preference towards the Δ-hand is more pronounced in the bipy species, an effect that has been attributed to the greater flexibility of the bipy ligand, since on steric arguments the Λ-isomer should be favoured for an *S*-amino acidate complex of this type.

Unlike the above mentioned complexes the *S*-allothreonine analogues each equilibrate to give mixtures of diastereoisomers showing a slight preference for the Λ-hand. In the crystal structures here reported only in Λ-$[Ru(bipy)_2(S\text{-allothr})]^+$ is an intramolecular hydrogen bond indicated which links the β-OH group with the coordinated carboxylic acid group. Molecular models suggest that for the other isomer such a hydrogen bond would be feasible even though not observed in the solid state. However for the *S*-threonine species its formation would lead to an unfavoured conformation with the methyl group being *gauche* to both the amino- and carboxy-substituents on the α-carbon atom. These conclusions would apply equally well to the analogous phen complexes.

In the NMR spectra of the *S*-threonine complexes (Table X) the methyl resonances in both the phen and bipy pairs of isomers almost overlap, indicating a similar average chemical and magnetic environment in each isomer. However for the *S*-allothreonine complexes the methyl resonance for each Δ-isomer is found about 0.3 ppm downfield from that of its corresponding Λ-form. This difference in the methyl group environments suggests some structuring in the side chain of the amino acid which would be consistent with the intramolecular hydrogen bond discussed above. The importance of intramolecular hydrogen bonding in enforcing chiral discriminations in these types of complexes, depending of course on the nature of the amino acid employed, is again demonstrated. The role of such interactions was first suggested [4] in complexes of *S*-aspartic acid analogous to those reported above, for which similar results were obtained.

The solid state environments of the β-OH atoms O(13) in these two structures include close contacts to hydrogen atoms H(112) and H(122) of neighbouring molecules. These O···H distances range from 2.42 to 2.54 Å with angles subtended at these hydrogens lying between 166 and 175°. These are the 3,3′-protons of a bipy ligand which are known to be weak carbon acids in analogous complexes [10]. The presence of such interactions in the solid state has interesting implications for solvated structures in donor solvents.

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