Inorganica Chimica Acta, 72 (1983) 253–261

Chiral Metal Complexes. 7*. A Comparison of the Structures of the Two Diastereoisomeric Forms of $[Ru(bipy)_2)L\text{-alanine})]ClO_4 \cdot 0.5H_2O$ as Determined by Single Crystal X-Ray Diffraction

FREDERICK S. STEPHENS, ROBERT S. VAGG**

School of Chemistry, Macquarie University, North Ryde, N.S.W. 2113, Australia

and PETER A. WILLIAMS**

Department of Chemistry, University College, P.O. Box 78, Cardiff CF1 1XL, U.K.

Received November 2, 1982

The complex Δ,Λ-$[Ru(bipy)_2(\text{L-ala})]ClO_4 \cdot 0.5H_2O$ *contains both* Δ,L *and* Λ,L *diastereoisomeric cations in the one crystalline form. The crystals are monoclinic, space group C2, with* a = 32.816 ± 0.004, b = 11.961 ± 0.002, c = 12.368 ± 0.011 Å, $\beta = 94.92 \pm 0.04°$ *and* Z = 8. *The structure was refined by block-matrix least-squares methods to* R = 0.041 *for 3078 non-zero reflexions. A pseudo* c-*glide operation relates the two diastereoisomers.*

The two Ru atoms are each octahedral with small differences in the coordination spheres of the two metals. The bipyridine and L-*alanine molecules are all bidentate. Bond dimensions are:* $Ru–N_{bipy}$ *2.001(8)–2.123(8) Å,* $Ru–N_{amine}$ *2.071(11) and 2.130(11) Å, Ru–O 2.061(7) and 2.095(7) Å,* $N_{bipy}–Ru–N_{bipy}$ *average 78.6(7)° and* $N_{amine}–Ru–O$ *average 79.3(4)°. In the* Λ,L *isomer the amino acid ring is puckered, whereas in the* Δ,L *form this ring is closely planar.*

An analysis of interatomic contact distances and bond-rotational distortions in the cations shows that the Δ,L *isomer is strained due to a steric interaction between the methyl-group of the amino acid and one of the bipyridine rings in that isomer. This observation is related to previously reported chiral discriminations observed for such species. A detailed analysis of angular distortions in the bipyridine groups has been performed.*

The water molecules lie on crystallographic two-fold axes and hydrogen bond symmetry related uncoordinated carboxylic oxygen atoms. The amine protons appear to be involved in weak interactions with the perchlorate oxygen atoms, the latter showing some degree of disorder.

Introduction

We have described previously [1–5] the isolation of a number of complexes of general type $[Ru(\text{diimine})_2(L\text{-aminoacidate})]ClO_4 \cdot nH_2O$ (where the diimine is either 1,10-phenanthroline or 2,2′-bipyridine) and subsequent resolution into their Δ,*L* and Λ,*L* cationic forms. Although apparently very inert in the absence of light these cations are observed to be photochemically labile, and on irradiation equilibrium mixtures often are obtained in which one preferred chiral form predominates. An obvious preference for the Λ-hand of the metal is obtained when the side group of the amino acid is bulky, and this effect has been explained in terms of an intramolecular steric interaction [1, 2, 4].

The corresponding complex of *L*-alanine and 2,2′-bipyridine, Δ,Λ-$[Ru(bipy)_2(L\text{-ala})]ClO_4 \cdot 0.5H_2O$, was observed to crystallise with the Δ,*L* and Λ,*L* forms in equal ratio [4]. When it is dissolved in water a small preference for the Λ-hand results after irradiation [4], indicating an energetic difference of *ca.* 0.5 kJ $mole^{-1}$ between these two solvated diastereoisomeric forms. A significantly smaller energetic difference was observed in D_2O solutions [4], demonstrating that the magnitudes of these discrimination energies are not determined solely by intramolecular steric effects. In the absence of light the diastereotopic amine protons of each isomer were observed to exchange with deuterium of the solvent at vastly different rates, leading

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*Part 6 is reference [12].

**Authors to whom correspondence should be addressed.

0020-1693/83/$3.00

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

	x		*y*		*z*	
	n = 1	*n* = 2	*n* = 1	*n* = 2	*n* = 1	*n* = 2
Ru(*n*)	1169.4(3)	1166.7(3)	–1624.0	1624.0(8)	8688.4(7)	3736.8(7)
O(*n*1)	680(2)	679(2)	–1756(7)	1709(7)	7534(5)	2531(5)
O(*n*2)	234(3)	249(2)	–2901(8)	2851(8)	6648(7)	1615(6)
N(*n*1)	1686(3)	1685(3)	–1601(9)	1585(8)	9714(7)	4748(6)
N(*n*2)	1621(3)	1601(3)	–1468(8)	1509(8)	7601(6)	2700(6)
N(*n*3)	1067(2)	1072(3)	47(8)	–30(9)	8908(6)	3804(7)
N(*n*4)	767(2)	750(3)	–1618(9)	1594(9)	9855(6)	4958(6)
N(*n*)	1173(3)	1141(3)	–3330(9)	3375(9)	8399(7)	3425(6)
C(*n*11)	2046(4)	2042(3)	–1459(13)	1454(8)	9291(8)	4277(9)
C(*n*12)	2426(4)	2414(3)	–1370(12)	1449(10)	9831(10)	4925(8)
C(*n*13)	2454(4)	2401(4)	–1497(12)	1524(12)	10949(9)	6064(8)
C(*n*14)	2084(4)	2048(4)	–1638(13)	1661(12)	11445(9)	6503(8)
C(*n*15)	1725(3)	1686(4)	–1702(11)	1701(11)	10805(8)	5860(7)
C(*n*21)	2003(3)	1990(4)	–1369(8)	1404(11)	8046(7)	3126(9)
C(*n*22)	2344(4)	2305(4)	–1207(11)	1251(11)	7416(10)	2496(9)
C(*n*23)	2275(4)	2223(4)	–1175(14)	1236(10)	6290(10)	1353(9)
C(*n*24)	1862(4)	1852(4)	–1321(14)	1365(10)	5881(10)	881(8)
C(*n*25)	1540(3)	1547(4)	–1461(10)	1472(14)	6568(9)	1522(8)
C(*n*31)	763(3)	803(3)	340(9)	–356(11)	9591(8)	4486(9)
C(*n*32)	650(4)	664(4)	1422(12)	–1452(11)	9634(8)	4628(11)
C(*n*33)	855(6)	825(4)	2214(12)	–2304(10)	8967(14)	4096(9)
C(*n*34)	1152(5)	1126(4)	1924(15)	–1987(9)	8412(11)	3373(8)
C(*n*35)	1240(4)	1236(4)	810(11)	–893(9)	8356(10)	3279(9)
C(*n*41)	638(4)	625(3)	–631(10)	521(11)	10153(9)	5176(8)
C(*n*42)	362(4)	392(4)	–476(12)	347(12)	11039(9)	5971(9)
C(*n*43)	247(4)	239(4)	–1416(13)	1252(13)	11569(9)	6545(11)
C(*n*44)	367(4)	365(4)	–2463(11)	2298(12)	11213(10)	6316(9)
C(*n*45)	638(4)	619(4)	–2491(12)	2513(11)	10364(11)	5505(9)
C(*n*1)	554(4)	536(4)	–2703(10)	2681(12)	7262(8)	2262(11)
C(*n*2)	839(4)	715(4)	–3677(11)	3662(10)	7518(9)	3036(9)
C(*n*3)	618(5)	671(4)	–4738(16)	4782(11)	7855(15)	2443(11)
Cl(*n*)	3324(2)	3326(2)	292(7)	–253(7)	8776(6)	3856(6)
O(*n*A)	3300(4)	3296(8)	–820(14)	853(19)	8475(12)	3665(21)
O(*n*B)	3029(8)	2963(7)	614(19)	–667(20)	9483(22)	4060(25)
O(*n*C)	3319(7)	3487(11)	845(26)	–937(16)	7777(18)	3118(29)
O(*n*D)	3720(7)	3625(10)	555(26)	–277(35)	9378(18)	4543(20)
O(W*n*)	0	0	–4466(15)	4616(16)	5000	0

to the selective formation of mono-N-deuterated forms. Again this effect was explained in terms of steric control of solvent interaction with the coordinated amino acid [4].

The crystal structure of Δ,Λ-[Ru(bipy)$_2$(*L*-ala)]-ClO$_4$·0.5H$_2$O now has been determined by X-ray diffraction methods, which permits a comparison of the molecular structures of the two diastereoisomeric cations in the solid state. The results of that analysis are the subject of this article.

Experimental

Crystal Data

$C_{23}H_{23}N_5O_{6.5}ClRu$, M_r = 610.0, Monoclinic, a = 32.816 ± 0.004, b = 11.961 ± 0.002, c = 12.368 ± 0.011 Å, β = 94.92 ± 0.04°, U = 4836.6 ± 5.8 Å^3, D_m = 1.67 (by flotation), Z = 8, D_c = 1.675 Mg m^{-3}, $F(000)$ = 2472, $\mu(\mathrm{M_o}\text{–}K_\alpha)$ = 7.94 mm^{-1}. Systematic absences: *hkl* when $h + k \neq 2n$, space group *C*2 (No. 5), *Cm* (No. 8) or *C*2/*m* (No. 12).

The complex crystallises as very dark-red needles with [001] as the needle axis. Initially, unit cell parameters were determined from single crystal oscillation and Weissenberg photographs using Cu-K_α radiation. 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$_\alpha$ radiation by Dr M. B. Hursthouse at Queen Mary College, London. Of the 4696 reflexions recorded 3078 have $I > 3\sigma(I)$ and these were used for the structure analysis. For the

TABLE II. Final Anisotropic Thermal Parameters ($\times 10^4$) in the Form $\exp-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})$ with Estimated Standard Deviations in Parentheses.[a]

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ru(1)	5.1(1)	43.5(5)	33.7(5)	3.8(2)	1.7(1)	4.1(6)
O(11)	8(1)	59(7)	40(5)	−0(2)	−0(2)	7(5)
O(12)	12(1)	77(8)	64(7)	6(2)	−5(2)	−8(6)
N(11)	8(1)	62(8)	47(6)	−8(3)	7(2)	12(7)
N(12)	9(1)	58(8)	26(5)	2(2)	5(2)	−0(6)
N(13)	7(1)	41(7)	9(5)	1(2)	1(2)	4(5)
N(14)	6(1)	46(6)	32(5)	2(2)	4(2)	3(6)
N(1)	6(1)	70(9)	57(7)	8(3)	3(2)	13(7)
C(111)	10(1)	121(15)	20(7)	2(4)	4(2)	2(9)
C(112)	13(2)	97(16)	57(10)	−2(4)	−7(3)	7(10)
C(113)	8(1)	67(11)	75(10)	−3(3)	6(3)	−8(9)
C(114)	10(1)	90(12)	46(8)	10(4)	−5(3)	18(10)
C(115)	6(1)	49(9)	67(9)	−2(3)	4(2)	−0(8)
C(121)	9(1)	55(10)	20(5)	−1(3)	9(2)	−6(6)
C(122)	10(1)	93(13)	55(9)	7(3)	17(3)	5(8)
C(123)	11(2)	141(18)	34(8)	2(4)	6(3)	22(10)
C(124)	13(2)	146(19)	38(8)	14(5)	7(3)	37(10)
C(125)	8(1)	38(9)	57(8)	2(3)	2(2)	11(7)
C(131)	8(1)	39(8)	31(7)	4(3)	8(2)	−11(6)
C(132)	8(1)	91(13)	42(8)	6(3)	9(3)	−0(8)
C(133)	28(3)	40(11)	96(15)	1(5)	−24(6)	11(11)
C(134)	14(2)	137(21)	68(13)	−12(6)	−0(4)	9(13)
C(135)	10(2)	98(14)	35(8)	2(4)	−1(3)	−9(9)
C(141)	8(1)	50(10)	36(8)	−6(3)	3(3)	18(7)
C(142)	7(1)	76(11)	30(7)	−2(3)	7(2)	−11(7)
C(143)	8(1)	112(16)	44(8)	−0(4)	13(3)	16(9)
C(144)	8(2)	77(12)	65(11)	3(3)	3(3)	13(9)
C(145)	8(1)	69(11)	80(11)	−8(3)	8(3)	15(9)
C(11)	10(1)	51(9)	16(6)	3(3)	3(2)	2(6)
C(12)	11(2)	66(11)	45(8)	−8(3)	−0(3)	2(8)
C(13)	14(3)	103(17)	142(18)	−10(5)	−1(5)	7(15)
Cl(1)	18(1)	84(7)	117(6)	−5(2)	17(2)	−8(5)
O(1A)	10(2)	80(15)	116(12)	2(4)	6(3)	−48(10)
O(1B)	48(5)	99(19)	382(35)	−21(8)	121(12)	−80(21)
O(1C)	33(3)	255(32)	114(14)	16(8)	−2(5)	86(17)
O(1D)	25(3)	304(33)	194(21)	−65(8)	39(7)	−172(23)
O(W1)	7(6)	72(15)	62(13)	0	−22(7)	0
Ru(2)	8.6(1)	61.7(7)	27.2(5)	1.5(3)	3.2(2)	−0.5(6)
O(21)	7(1)	60(7)	45(5)	−4(2)	1(2)	2(5)
O(22)	8(1)	100(9)	46(6)	13(2)	−1(2)	3(6)
N(21)	6(1)	48(7)	33(6)	−6(2)	−2(2)	10(6)
N(22)	6(1)	62(8)	34(6)	−1(2)	2(2)	−2(6)
N(23)	8(1)	82(9)	32(6)	3(3)	5(2)	1(7)
N(24)	6(1)	80(9)	39(6)	−1(3)	2(2)	−7(7)
N(2)	11(1)	52(7)	27(6)	4(3)	−2(2)	−4(6)
C(211)	4(1)	16(7)	60(8)	2(2)	−0(2)	2(6)
C(212)	5(1)	61(10)	38(7)	0(3)	6(2)	−4(7)
C(213)	9(1)	95(13)	39(8)	−5(4)	−11(3)	−5(9)
C(214)	12(1)	74(11)	35(7)	3(4)	6(3)	7(8)
C(215)	13(2)	103(13)	8(6)	−7(4)	2(2)	−5(8)
C(221)	4(1)	60(10)	61(9)	−1(3)	−1(2)	−14(8)
C(222)	6(1)	62(10)	47(8)	4(3)	−4(2)	−2(7)
C(223)	10(1)	45(9)	61(9)	−2(3)	18(3)	−1(7)
C(224)	10(1)	52(10)	38(8)	7(3)	10(3)	10(7)
C(225)	13(2)	139(17)	17(7)	−3(5)	−0(3)	2(9)
C(231)	6(1)	71(11)	31(7)	4(3)	−4(2)	−12(7)

(continued overleaf)

TABLE II. *(continued)*

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(232)	13(2)	57(12)	57(9)	–4(4)	–8(3)	17(8)
C(233)	11(2)	49(10)	40(8)	–5(3)	11(3)	12(7)
C(234)	15(2)	36(8)	32(7)	–9(3)	12(3)	–13(6)
C(235)	15(2)	19(7)	33(7)	7(3)	10(3)	–11(6)
C(241)	4(1)	82(11)	40(8)	–8(3)	–1(2)	34(8)
C(242)	7(1)	97(13)	58(10)	7(3)	5(3)	–15(9)
C(243)	10(2)	97(14)	56(10)	2(4)	–2(3)	–2(9)
C(244)	13(2)	99(14)	27(8)	3(4)	12(3)	–17(9)
C(245)	9(1)	82(12)	37(8)	–3(3)	6(3)	–18(8)
C(21)	5(1)	91(13)	77(11)	6(3)	6(3)	–5(10)
C(22)	11(1)	53(11)	38(8)	3(3)	6(3)	–5(7)
C(23)	10(2)	52(11)	96(13)	–3(3)	0(3)	–0(9)
Cl(2)	12(1)	93(7)	115(6)	14(2)	17(2)	58(5)
O(2A)	26(3)	87(20)	272(28)	17(6)	36(8)	24(19)
O(2B)	21(3)	107(20)	449(40)	–7(6)	69(9)	–6(22)
O(2C)	84(8)	66(14)	652(63)	3(9)	214(22)	–13(26)
O(2D)	34(4)	492(62)	133(19)	29(14)	–15(7)	121(28)
O(W2)	41(4)	126(20)	132(18)	0	–42(7)	0

[a] For all H atoms $B = 4.5$ Å^2.

hOl zone with *l* odd only 41 reflexions gave significant counts and this is consistent with the precursory photographic investigation. Intensities were corrected for Lorentz, polarization and absorption effects.

Structure Determination

Only the space group *C*2 allows the amino acid to be present in the *L*(*S*) form and hence it was adopted in the analysis. The structure was solved by the heavy atom method and refined by least-squares calculations in which the function minimised was $\Sigma w\Delta^2$. The weight used for each reflexion was that obtained from counting statistics.

After isotropic refinement a difference synthesis indicated the positions of all the hydrogen atoms. These were optimised assuming C–H, N–H and O–H to be 1.0 Å and refinement was continued with H atoms being located in these positions with B = 4.5 Å^2, their parameters not being varied.

Due to the large number of variable parameters (659) block matrices were used during anisotropic refinement. The ten matrices used contained (1) the overall scale and thermal parameters, and the parameters for (2) and (3) the two Ru atoms and their coordination spheres, (4)–(7) the carbon atoms of the four bipyridine groups, (8) and (9) the uncoordinated atoms of each amino acid molecule together with the associated water molecule, and (10) the two perchlorate groups.

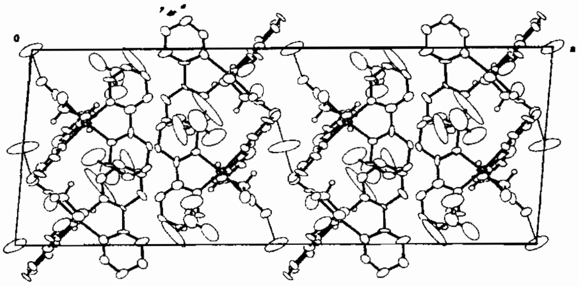

Fig. 1. The packing of the molecular ions in the cell viewed down *b*. Thermal ellipsoids are scaled to include 50% probability. Narrow lines represent hydrogen bonds between water molecules and carboxylic O atoms.

The refinement process was terminated when the change in the minimization function was <1%, at which stage only the oxygen atom O(2D) showed positional oscillation and the maximum shift in the parameters for the other atoms was <0.5σ. A final difference map showed no unusual features, with maximum positive electron densities of 0.8–0.9 eÅ^{-3} being associated with the Ru atoms. The final value for R, based on 3078 reflexions, was 0.041 and for R' $[=(\Sigma w\Delta^2/\Sigma w|F_o|^2)^{1/2}]$ was 0.046.

All calculations were carried out on a UNIVAC 1106 computer using programmes written by F.S.S. Scattering factors used were taken from *International Tables for X-Ray Crystallography* [6], with corrections being applied for anomalous dispersion. The final atomic parameters are given in Tables I, II and III. A list of observed and calculated structure factors (18 pages) has been deposited with the Editor.

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

	x		*y*		*z*	
	n = 1	*n* = 2	*n* = 1	*n* = 2	*n* = 1	*n* = 2
H(*n*2)	97	55	−391	375	685	366
H(*n*3A)	87	87	−520	524	788	286
H(*n*3B)	49	39	−467	508	854	248
H(*n*3C)	40	74	−499	471	725	169
H(N*n*1)	112	123	−374	379	909	411
H(N*n*2)	144	134	−357	356	817	286
H(*n*12)	267	269	−125	138	940	463
H(*n*13)	273	265	−147	148	1138	657
H(*n*14)	204	205	−173	175	1226	729
H(*n*15)	147	142	−172	176	1111	618
H(*n*22)	263	259	−112	116	779	282
H(*n*23)	251	245	−106	113	583	86
H(*n*24)	180	180	−133	139	505	10
H(*n*25)	125	126	−156	152	625	117
H(*n*32)	43	45	168	−159	1010	515
H(*n*33)	78	75	304	−308	894	425
H(*n*34)	128	123	244	−257	786	285
H(*n*35)	146	144	54	−65	787	268
H(*n*42)	28	31	29	−42	1127	617
H(*n*43)	4	6	−138	108	1213	714
H(*n*44)	28	25	−318	291	1155	675
H(*n*45)	73	71	−324	329	1012	533
H(W*n*)	8	9	−392	397	559	55

Results and Discussion

One striking aspect of the crystal structure is the close proximity to a *c*-glide relationship between the two diastereoisomeric forms which is consistent with the observed lack of reflexions for the *h*0*l* zone with *l* odd. This relationship may be seen in the packing diagram (Fig. 1) and is evident from an inspection of the fractional atomic coordinates listed in Tables I and III.. The arbitrary choice of the origin in *y* was made after completion of refinement so as to emphasise this relationship.

The molecular structures of the two cations, together with the atomic labelling scheme [7], are shown in Figs. 2 and 3. Bond lengths and angles are given in Table IV. The apparently close mirror relationship between the two cations is only broken by the like chirality of the amino acid α-carbon atom in each molecule.

In the Λ,L form (Fig. 3) the bipyridine hydrogen atom H(245) makes a close van der Waals contact (Table V) with both H(N21) and H(22) on one side of the amino acid chelate ring. For the Δ,L form (Fig. 2) the corresponding contacts are H(145) to H(N11) and to the methyl group defined by C(13). The latter is pushed down away from the interacting bipyridine group such that the resulting twist around the Ru(1)–N(1) bond brings H(N11) into a particularly close contact with H(145). Resulting differences between the two amino acid chelate ring conformations are demonstrated by the projections along the

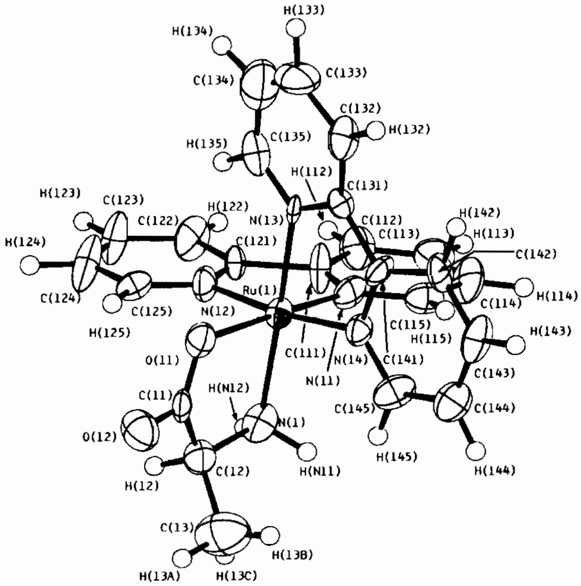

Fig. 2. A perspective drawing of the Δ,L diastereoisomeric cation showing the atomic labelling. Thermal ellipsoids are scaled to include 50% probability. Hydrogen atoms have been included with a thermal parameter $B = 1.0$ Å^2.

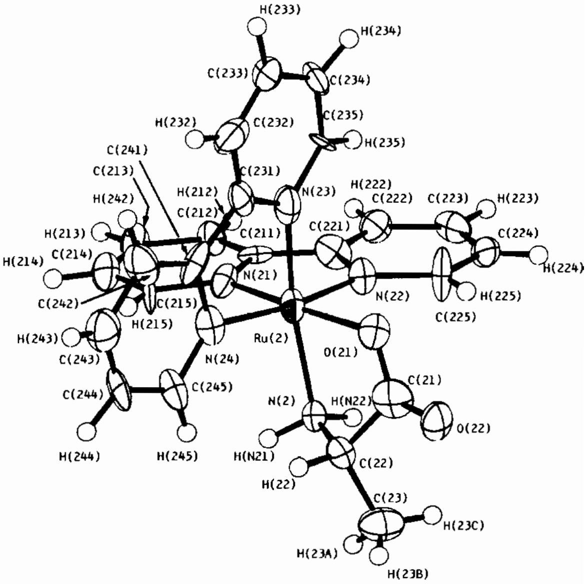

Fig. 3. A perspective drawing of the Λ,L diastereoisomeric cation showing the atomic labelling. Thermal ellipsoids are scaled to include 50% probability. Hydrogen atoms have been included with a thermal parameter $B = 1.0$ Å^2.

TABLE IV. Bond Lengths and Angles with Estimated Standard Deviations in Parentheses.

a) Distances (Å)

	n = 1	*n* = 2
Ru(*n*)–O(n1)	2.061(7)	2.095(7)
Ru(*n*)–N(*n*)	2.071(11)	2.130(11)
Ru(*n*)–N(*n*1)	2.028(9)	2.024(8)
Ru(*n*)–N(*n*2)	2.094(8)	2.001(8)
Ru(*n*)–N(*n*3)	2.048(8)	2.005(11)
Ru(*n*)–N(*n*4)	2.038(7)	2.123(8)
C(*n*11)–C(*n*21)	1.54(1)	1.42(1)
C(*n*31)–C(*n*41)	1.43(1)	1.50(2)
C(*n*11)–C(*n*12)	1.37(2)	1.40(1)
C(*n*12)–C(*n*13)	1.39(2)	1.42(1)
C(*n*13)–C(*n*14)	1.41(2)	1.33(2)
C(*n*14)–C(*n*15)	1.37(1)	1.37(2)
N(*n*1)–C(*n*15)	1.35(1)	1.38(1)
N(*n*1)–C(*n*11)	1.35(1)	1.36(1)
C(*n*21)–C(*n*22)	1.43(1)	1.36(1)
C(*n*22)–C(*n*23)	1.39(2)	1.41(2)
C(*n*23)–C(*n*24)	1.42(2)	1.33(2)
C(*n*24)–C(*n*25)	1.42(2)	1.34(2)
N(*n*2)–C(*n*25)	1.28(1)	1.45(1)
N(*n*2)–C(*n*21)	1.33(1)	1.35(1)
C(*n*31)–C(*n*32)	1.35(2)	1.40(2)
C(*n*32)–C(*n*33)	1.46(2)	1.35(2)
C(*n*33)–C(*n*34)	1.29(2)	1.44(1)
C(*n*34)–C(*n*35)	1.37(2)	1.36(2)
N(*n*3)–C(*n*35)	1.30(2)	1.36(1)
N(*n*3)–C(*n*31)	1.40(1)	1.33(1)
C(*n*41)–C(*n*42)	1.49(1)	1.31(1)
C(*n*42)–C(*n*43)	1.37(2)	1.41(2)
C(*n*43)–C(*n*44)	1.40(2)	1.36(2)
C(*n*44)–C(*n*45)	1.43(2)	1.38(2)
N(*n*4)–C(*n*45)	1.31(2)	1.38(2)
N(*n*4)–C(*n*41)	1.32(2)	1.38(2)
C(*n*1)–O(*n*1)	1.24(1)	1.29(2)
C(*n*1)–O(*n*2)	1.26(1)	1.20(1)
C(*n*1)–C(*n*2)	1.51(2)	1.59(2)
C(*n*2)–N(*n*)	1.54(2)	1.48(2)
C(*n*2)–C(*n*3)	1.54(2)	1.53(2)
Cl(*n*)–O(*n*A)	1.38(2)	1.35(2)
Cl(*n*)–O(*n*B)	1.41(1)	1.34(2)
Cl(*n*)–O(*n*C)	1.40(2)	1.37(2)
Cl(*n*)–O(*n*D)	1.48(2)	1.24(2)

Angles (°)

TABLE IV. *(continued)*

	n = 1	*n* = 2
O(*n*1)–Ru(*n*)–N(*n*)	79.6(3)	78.9(3)
O(*n*1)–Ru(*n*)–N(*n*1)	173.6(4)	172.6(3)
O(*n*1)–Ru(*n*)–N(*n*2)	96.6(3)	95.2(3)
O(*n*1)–Ru(*n*)–N(*n*3)	92.3(3)	88.1(4)
O(*n*1)–Ru(*n*)–N(*n*4)	88.7(3)	90.4(3)
N(*n*)–Ru(*n*)–N(*n*1)	96.0(4)	98.8(3)
N(*n*)–Ru(*n*)–N(*n*2)	87.9(4)	88.3(3)
N(*n*)–Ru(*n*)–N(*n*3)	170.8(3)	166.9(3)
N(*n*)–Ru(*n*)–N(*n*4)	98.0(4)	97.4(3)
N(*n*1)–Ru(*n*)–N(*n*2)	78.5(3)	77.7(3)
N(*n*1)–Ru(*n*)–N(*n*3)	92.4(4)	94.4(4)
N(*n*1)–Ru(*n*)–N(*n*4)	96.6(3)	96.8(3)
N(*n*2)–Ru(*n*)–N(*n*3)	97.5(3)	94.6(4)
N(*n*2)–Ru(*n*)–N(*n*4)	172.8(4)	172.7(4)
N(*n*3)–Ru(*n*)–N(*n*4)	77.2(4)	80.9(4)
Ru(*n*)–O(*n*1)–C(*n*1)	119(1)	118(1)
Ru(*n*)–N(*n*)–C(*n*2)	112(1)	108(1)
Ru(*n*)–N(*n*1)–C(*n*11)	118(1)	117(1)
Ru(*n*)–N(*n*1)–C(*n*15)	129(1)	123(1)
Ru(*n*)–N(*n*2)–C(*n*21)	116(1)	117(1)
Ru(*n*)–N(*n*2)–C(*n*25)	123(1)	128(1)
Ru(*n*)–N(*n*3)–C(*n*31)	117(1)	115(1)
Ru(*n*)–N(*n*3)–C(*n*35)	122(1)	131(1)
Ru(*n*)–N(*n*4)–C(*n*41)	116(1)	112(1)
Ru(*n*)–N(*n*4)–C(*n*45)	126(1)	126(1)
O(*n*1)–C(*n*1)–O(*n*2)	125(1)	125(1)
O(*n*1)–C(*n*1)–C(*n*2)	117(1)	114(1)
N(*n*)–C(*n*2)–C(*n*1)	109(1)	108(1)
N(*n*)–C(*n*2)–C(*n*3)	111(1)	114(1)
O(*n*2)–C(*n*1)–C(*n*2)	117(1)	120(1)
C(n1)–C(*n*2)–C(*n*3)	113(1)	110(1)
N(*n*1)–C(*n*11)–C(*n*12)	128(1)	120(1)
N(*n*1)–C(*n*11)–C(*n*21)	113(1)	114(1)
C(*n*12)–C(*n*11)–C(*n*21)	119(1)	126(1)
C(*n*11)–C(*n*12)–C(*n*13)	117(1)	118(9)
C(*n*12)–C(*n*13)–C(*n*14)	117(1)	121(1)
C(*n*13)–C(*n*14)–C(*n*15)	119(1)	120(1)
C(*n*14)–C(*n*15)–N(*n*1)	125(1)	120(1)
C(*n*11)–N(*n*1)–C(*n*15)	113(1)	121(1)
N(*n*2)–C(*n*21)–C(*n*22)	123(1)	122(1)
N(*n*2)–C(*n*21)–C(*n*11)	114(1)	115(1)
C(*n*22)–C(*n*21)–C(*n*11)	123(1)	123(1)
C(*n*21)–C(*n*22)–C(*n*23)	119(1)	120(1)
C(*n*22)–C(*n*23)–C(*n*24)	115(1)	121(1)
C(*n*23)–C(*n*24)–C(*n*25)	123(1)	118(1)
C(*n*24)–C(*n*25)–N(*n*2)	120(1)	124(1)
C(*n*21)–N(*n*2)–C(*n*25)	121(1)	115(1)
N(*n*3)–C(*n*31)–C(*n*32)	119(1)	126(1)
N(*n*3)–C(*n*31)–C(*n*41)	110(1)	118(1)
C(*n*32)–C(*n*31)–C(*n*41)	132(1)	116(1)
C(*n*31)–C(*n*32)–C(*n*33)	117(1)	120(1)
C(*n*32)–C(*n*33)–C(*n*34)	122(1)	115(1)
C(*n*33)–C(*n*34)–C(*n*35)	118(1)	120(1)
C(*n*34)–C(*n*35)–N(*n*3)	124(1)	125(1)
C(*n*31)–N(*n*3)–C(*n*35)	120(1)	113(1)
N(*n*4)–C(*n*41)–C(*n*42)	123(1)	120(1)
N(*n*4)–C(*n*41)–C(*n*31)	119(1)	114(1)
C(*n*42)–C(*n*41)–C(*n*31)	118(1)	126(1)
C(*n*41)–C(*n*42)–C(*n*43)	117(1)	121(1)
C(*n*42)–C(*n*43)–C(*n*44)	119(1)	118(1)
C(*n*43)–C(*n*44)–C(*n*45)	118(1)	122(1)
C(*n*44)–C(*n*45)–N(*n*4)	125(1)	116(1)
C(*n*41)–N(*n*4)–C(*n*45)	117(1)	122(1)
O(*n*A)–Cl(*n*)–O(*n*B)	114(1)	110(2)
O(*n*A)–Cl(*n*)–O(*n*C)	103(1)	120(1)
O(*n*A)–Cl(*n*)–O(*n*D)	112(1)	101(2)
O(*n*B)–Cl(*n*)–O(*n*C)	117(2)	108(2)
O(*n*B)–Cl(*n*)–O(*n*D)	105(1)	122(2)
O(*n*C)–Cl(*n*)–O(*n*D)	107(1)	97(2)

TABLE V. Selected Interatomic Distances (Å).

Intramolecular	$n = 1$	$n = 2$
C(*n*2)····H(*n*25)	3.33	3.97
(C*n*2)····H(*n*45)	3.31	2.87
C(*n*3)····H(*n*45)	3.32	3.98
H(*n*2)····H(*n*25)	3.06	4.26
H(*n*2)····H(*n*45)	4.82	2.16
H(N*n*1)····H(*n*45)	1.96	2.46
H(N*n*2)····H(*n*25)	3.39	3.20
H(*n*12)····H(*n*22)	1.99	2.24
H(*n*32)····H(*n*42)	2.30	1.96
Intermolecular		
	acceptor at	
O(W1)····O(12)	x, y, z	2.82(1)
O(W2)····O(22)	x, y, z	2.97(2)
N(1)····O(1D)	$\frac{1}{2} - x, y - \frac{1}{2}, 2 - z$	3.05(2)
N(2)····O(2D)	$\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$	3.03(3)
N(1)····O(2A)	$\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$	3.36(2)
N(2)····O(1A)	$\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$	3.25(2)

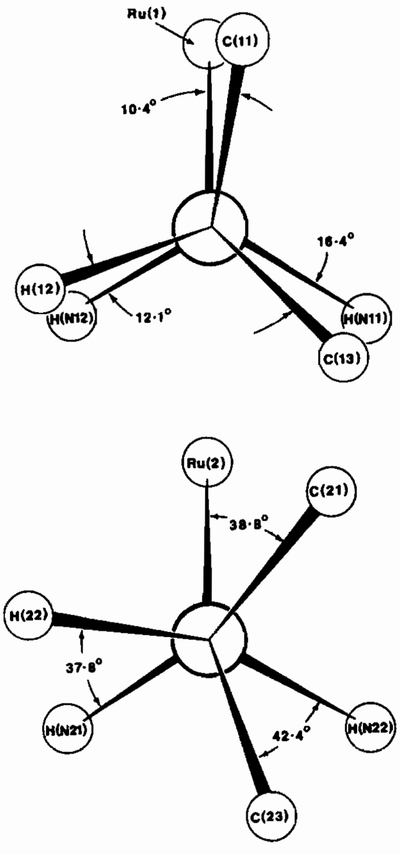

Fig. 4. Projections down the C_α–$N_{(amine)}$ bonds of the coordinated amino acids showing torsion angles.

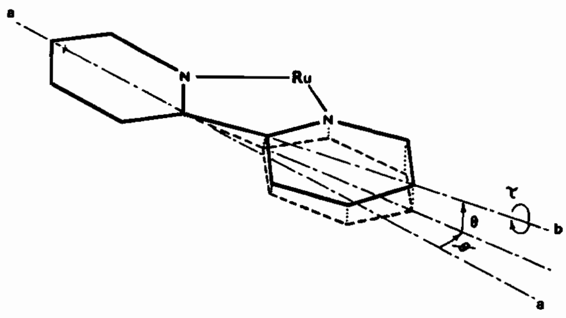

Fig. 5. Angular distortions in the coordinated 2,2′-bipyridine groups. The rotation axis ((a) or (b)) of each ring is defined as the least-squares line of best fit for the five points derived from the centroid of the ring, the mid-points between the pairs of atoms N(*nm*) & C(*nm*2) and C(*nm*3) & C(*nm*5), and the positions of the atoms C(*nm*1) and C(*nm*4). A positive value for τ represents a clockwise rotation of that ring around the central C–C bond.

C(α)-N(amine) bonds shown in Fig. 4. In the Λ,*L* isomer the torsion angles of *ca.* 40° demonstrate a large degree of 'puckering' in that ring, indicative of a lack of steric strain. The Δ,*L* isomer, however, shows a closely eclipsed conformation due to the enforced bond rotations and as a result the ring is considerably flattened. These marked differences in the amino acid structures are demonstrated by their least-squares planes (Table VI, planes 1 and 2), and in particular by the deviations of the α-C atoms from the planes defined by the other four atoms in each chelate ring (Table VI, planes 3 and 4). The two carboxylic groups are closely planar (planes 5 and 6) but in the Δ isomer the metal atom is significantly out of that plane as a result of the bonding requirements of the α-carbon atom in a flattened ring.

This latter effect is observed also for the pyridine rings (Table VI, planes 7–14), with the higher deviations of the Ru atoms from the ring planes being observed for the bipyridine group (defined by N(13) and N(14)) which shows the close contact with the alanine-CH_3 group in the Δ diastereoisomer.

An analysis of angular distortions in the bipyridine groups is presented in Table VII and these distortions are defined in Fig. 5. Each group shows only a small degree of out-of-plane bending (θ) which is far less than was observed for the 'bowed' conformations of some related *trans*-$[Ru(bipy)_2L_2]^{2+}$ species [8]. An in-plane bending is evidenced by the values of φ shown in Table VII. This is a common effect resulting from the ligand's bidentate function [9], and is reflected also in the low internal bond angles at the 2- and 2′-carbon atoms (Table IV). Variations in the contact distances between H atoms on the 3- and 3′-carbon atoms of each diimine [Table V, H(*n*12)···

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 (Å) derived with respect to the orthogonal axes a' b, c. Deviations (Å) of relevant atoms from the planes are given in square brackets.

	l	m	n	p
Plane (1): C(11), C(12), N(1), O(11)	−0.5708	−0.1414	0.8088	6.4670
[C(11) 0.095, C(12) −0.081, N(1) 0.043, O(11) −0.057, Ru(1) 0.051]				
Plane (2): C(21), C(22), N(2), O(21)	−0.4393	−0.1895	0.8781	1.1164
[C(21) −0.169, C(22) 0.150, N(2) −0.083, O(21) 0.103, Ru(2) 0.610]				
Plane (3): Ru(1), O(11), C(11), N(1)	−0.5760	−0.1117	0.8098	6.4097
[Ru(1) 0.040, O(11) −0.066, C(11) 0.055, N(1) −0.029, C(12) −0.160]				
Plane (4): Ru(2), O(21), C(21), N(2)	−0.5957	0.0822	0.7990	1.2712
[Ru(2) 0.047, O(21) −0.076, C(21) 0.064, N(2) −0.035, C(22) 0.539]				
Plane (5): O(11), O(12), C(12)	−0.4621	−0.1291	0.8774	7.2511
[C(11) 0.073, Ru(1) 0.372]				
Plane (6): O(21), O(22), C(22)	−0.6735	−0.1572	0.7222	0.3069
[C(21) −0.079, Ru(2) −0.081]				
Plane (7): N(11), C(111)–C(115)	0.1056	−0.9901	−0.0929	1.4101
[N(11) −0.004, C(111) 0.010, C(112) −0.016, C(113) 0.016, C(114) −0.011, C(115) 0.005, Ru(1) −0.051, C(121) 0.031, C(122) 0.038, N(12) 0.057]				
Plane (8): N(12), C(121)–C(125)	0.1271	−0.9910	−0.0431	2.0397
[N(12) −0.011, C(121) 0.011, C(122) −0.001, C(123) −0.008, C(124) 0.009, C(125) 0.001, Ru(1) −0.077, C(111) 0.070, C(112) 0.098, N(11) 0.062]				
Plane (9): N(13), C(131)–C(135)	0.6878	0.1393	0.7124	10.0531
[N(13) −0.011, C(131) 0.018, C(132) 0.003, C(133) −0.032, C(134) 0.039, C(135) −0.017, Ru(1) −0.273, C(141) 0.095, C(142) 0.334, N(14) −0.068]				
Plane (10): N(14), C(141)–C(145)	0.7977	0.0650	0.5996	9.0432
[N(14) 0.010, C(141) −0.007, C(142) −0.013, C(143) 0.028, C(144) −0.024, C(145) 0.005, Ru(1) 0.126, C(131) −0.043, C(132) −0.204, N(13) 0.169]				
Plane (11): N(21), C(211)–C(215)	0.0796	0.9931	−0.0866	1.8607
[N(21) −0.006, C(211) −0.010, C(212) 0.021, C(213) −0.016, C(214) −0.001, C(215) 0.012, Ru(2) 0.0002, C(2221) 0.039, C(222) 0.014, N(22) 0.098]				
Plane (12): N(22), C(221)–C(225)	0.1221	0.9918	−0.0382	2.3206
[N(22) −0.002, C(221) 0.013, C(222) −0.010, C(223) −0.005, C(224) 0.016, C(225) −0.013, Ru(2) −0.093, C(211) 0.039, C(212) 0.156, N(21) 0.026]				
Plane (13): N(23), C(231)–C(235)	0.7206	−0.1134	0.6840	5.5608
[N(23) −0.018, C(231) 0.020, C(232) −0.012, C(233) 0.001, C(234) −0.0004, C(235) 0.008, Ru(2) −0.096, C(241) −0.099, C(242) 0.291, N(24) 0.040]				
Plane (14): N(24), C(241)–C(245)	0.7946	−0.0897	0.6005	5.3246
[N(24) 0.008, C(241) −0.019, C(242) 0.024, C(243) −0.017, C(244) 0.007, C(245) −0.002, Ru(2) 0.110, C(231) −0.004, C(232) 0.119, N(23) 0.108]				

b) Dihedral angles (°) between relevant planes

1–5	7.4	7–8	3.1
3–5	7.7	9–10	10.0
2–6	16.3	11–12	3.7
4–6	15.1	13–14	6.5

TABLE VII. Angular Distortions (°) in Bipyridine Groups.[a]

n[b]	m	$\phi_{(nm,nm+1)}$	$\theta_{(nm,nm+1)}$	$\tau_{(nm,nm+1)}$
1	1	7.4	2.8	+0.9
1	3	10.8	2.8	+9.4
2	1	9.4	3.0	−2.0
2	3	3.9	3.6	−5.7

[a] The parameters ϕ, θ, and τ represent respectively the degree of in-plane bending, out-of-plane bending and relative twist angles in the bipyridine groups as defined in Figure 5. [b] The parameter $\phi_{(11,12)}$ (*i.e.* $n = 1$, $m = 1$) represents the in-plane bending in the bipyridine group containing the atoms N(11) and N(12).

H(n22) and H(n32)···H(n42)] also correlate well with this bending parameter.

The bipyridine group of each cation which does not show a close contact to the amino acid α-C substituent (*i.e.* rings containing N(n1) and N(n2)) have only small twist angles (τ). The higher values observed for τ in the sterically crowded bipyridine groups (rings defined by N(n3) and N(n4)) demonstrates that some relief of steric strain would be allowed by the rotational flexibility of bipy compared with the inflexible *o*-phen ligand. This could account for the higher Λ-selectivities observed for Ru complexes of the latter bidentate with *L*-amino acids [1, 2, 4, 5]. Again the largest bipy twist angle (9.4°) is observed in the Δ diastereoisomer in this structure.

There are small structural differences in the coordination spheres of the two metal atoms (Table IV). The significance of the differences between corresponding bond parameters in the two isomers and the variations within each isomer is not obvious. The average Ru–N_{bipy} distance [2.05(4) Å], and the average N_{bipy}–Ru–N_{bipy} bite angle [78.6(7)°], are each closely comparable with the corresponding parameters in the structures of $[Ru(bipy)_3][PF_6]_2$ (2.06 Å, 78.7°) [10], and *cis*-$[Ru(bipy)_2CO_3]$ (2.03 Å, 79.3°) [11].

The two water molecules defined by O(W1) and O(W2) each lie on crystallographic two-fold axes and hydrogen-bond symmetry related uncoordinated carboxylic O atoms (Table V). The amino acid N–H protons appear to form weak hydrogen bonds with the perchlorate groups (Table V). This is of some interest considering the stereoselective deuterium exchange effects reported earlier for the complexes [4]. In particular it suggests that in solution the amine hydrogen atoms are each capable of forming hydrogen bonds with the solvent molecules.

Some disordering is obvious in the O atoms of the perchlorate groups (Fig. 1 and Table II), and the apparently short Cl(2)–O(2D) bond length of 1.24(2) Å is no doubt a result of positional averaging.

In general, the rare crystallization of both diastereoisomeric forms of the complex cation in the one crystal has allowed a direct comparison of their molecular structures. The Δ,*L* diastereoisomer demonstrates internally derived steric strain which is not apparent in the Λ,*L* form. This is evidenced by rotational distortions in the interacting bipyridine and amino acid molecules of the former isomer. This analysis is consistent with the Λ,*L* isomer being the more energetically favoured, which would result in a preference for that diastereoisomer at equilibrium under conditions of photo-lability [1, 4], and may account for the relative kinetic stabilities of some Co(III) analogues [12].

Acknowledgement

We wish to thank the SERC for financial support.

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