that the claimed negative ΔV_{OS}[11] may have been derived from inaccurate observed K_{OS} values. Very recently Krack and van Eldik reported negative ΔV_{OS} values for the reaction between $[Co^{III}(NH_3)_5(Me_2SO)]^{3+}$ (Me_2SO = dimethyl sulfoxide) and $[Fe^{II}(CN)_6]^{4-}$.[19] Close inspection of their data indicates that the linearity of the plots is again rather poor. From our experience on the reaction between $[Co^{III}(NH_3)_5(py)]^{3+}$ and $[Fe^{II}(CN)_6]^{4-}$[21] and the intramolecular electron-transfer reaction of $[(NH)_5Co^{III}(\mu\text{-pyr})Fe^{II}(CN)_5]$[22] (pyr = pyrazine) as well as the present reaction (2), the reaction of $[Co^{III}(NH_3)_5(Me_2SO)]^{3+}$ and $[Fe^{II}(CN)_6]^{4-}$ most likely involves the similar complication reported here. Detailed discussion on the mechanistic significance of the ΔV_{OS} and ΔV_e^* values will be made separately together with other ΔV^* data of related systems.[21,22]

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Supplementary Material Available: A listing of k_{obsd} values at various pressures (Table II), a plot of ln K_{OS} vs. p (Figure 2), and a plot of ln k_e vs. p (Figure 3) (3 pages). Ordering information is given on any current masthead page.

(21) Kanesato, K.; Sasaki, Y.; Saito, K., to be submitted for publication.
(22) Sasaki, Y.; Ninomiya, T.; Nagasawa, A.; Endo, K.; Saito, K., to be submitted for publication.

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Chiral Metal Complexes. 21.[1] Stereochemical Analysis of Ternary Ru(II) Complexes of α-Diimines and Glycine or N-Substituted Glycines, Including the Crystal Structure of *rac*-$[Ru(bpy)_2(gly)]ClO_4 \cdot 2H_2O$

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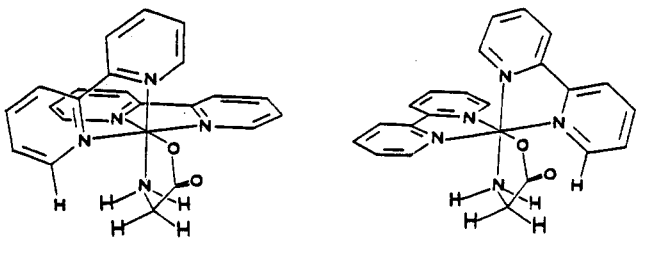
Photolabile complexes of the general form *rac*-$[Ru(diimine)_2(aa)]ClO_4 \cdot nH_2O$ (where *diimine* is either 2,2'-bipyridyl or 1,10-phenanthroline and *aa* is glycine, *N*-methylglycine, or *N*-phenylglycine) have been synthesized and their structures in solution analyzed by using 200-MHz ^1H NMR spectroscopy. The results are compared with the solid-state structure of *rac*-$[Ru(bpy)_2(gly)]ClO_4 \cdot 2H_2O$, which has been determined by X-ray diffraction. This analysis is used to demonstrate the torsional effects of glycine substitution on the structure of the amino acid chelate ring, and on the nature of the diastereomeric ratios in the synthetic product mixtures. Photoequilibration has allowed a quantitative estimate of the discriminatory effects resulting from substitution at the N(*amine*) chiral centres. In the *N*-methylglycine chelates those diastereomers that avoid steric interaction between the CH_3 group and the diimine molecules are selected, whereas the *N*-phenylglycine chelates show stereospecific coordination for the same steric reason. Both the amine and methylene protons of the coordinated amino acids exchange for deuterons at high pD. Crystal data: *rac*-$[Ru(bpy)_2(gly)]ClO_4 \cdot 2H_2O$, $C_{22}H_{24}N_5ClO_8Ru$, triclinic, space group $P\bar{1}$, a = 9.487 (2) Å, b = 12.294 (3) Å, c = 13.041 (3) Å, α = 111.36 (2)°, β = 63.15 (2)°, γ = 113.33 (2)°, U = 1213.77 (10) Å^3, Z = 2. The structure was refined by full-matrix least-squares methods to R = 0.033 and R' = 0.035 for 3752 unique reflections. The molecular structure has Ru–O = 2.105 (3) and Ru–N(amine) = 2.135 (4) Å with the amino acid chelate ring adopting a flattened δ conformation in the Λ enantiomer. The four Ru–N(bpy) bond lengths are not equivalent, the bond trans to Ru–O being significantly shorter (2.008 (4) Å) than the other three (average Ru–N = 2.046 (6) Å).

Introduction

The photolability of complex cations of general form $[Ru^{II}(diimine)_2(aa)]^{n+}$ (where *diimine* is either phen or bpy and *aa* is a bidentate α-amino acidate anion) has allowed their use as versatile quantitative indicators of the intramolecular chiral discriminatory effects that are inherent in such species.[5,6] To date we have reported on the effects that are produced by changes both in the diimine chosen and in the nature of substituents on the α-carbon of the coordinated amino acid. This has shown that higher discriminations in favor of the Λ configuration at the metal center may be obtained by using the more rigid diimine (phen) and (*S*)-amino acids with bulky α-substituents. In such cases a steric interaction involving this side chain and one diimine moiety is seen as the cause.

The simplest of these systems are those containing coordinated glycine (I) in which this particular discriminatory interaction would not exist. In this form the amine protons and the two methylene hydrogens of the amino acid are each prochiral, but the free



Λ Δ

$[Ru(bpy)_2(gly)]^+$
I

energies of formation of the Λ and Δ isomers are identical since the two forms are enantiomeric. However, an enhanced intramolecular steric effect might be expected if at least one of the amine protons were to be substituted by a bulky alkyl or aryl group. The observed stereospecific coordination of *N*-methylglycine (sarcosine) in the $[Co(en)_2(sar)]^{2+}$ ion exemplifies an analogous effect.[7]

From our own work with these photolabile Ru(II) systems it has become apparent that a marked selection occurs in favor of those diastereomers in which these nonbonded contacts are

(1) Part 20: Cox, M. A.; Griffiths, R. H.; Williams, P. A.; Vagg, R. S. *Inorg. Chim. Acta* **1985**, *103*, 155.
(2) Department of Physics, University College.
(3) Macquarie University.
(4) Department of Chemistry, University College.
(5) Goodwin, T. J.; Williams, P. A.; Stephens, F. S.; Vagg, R. S. *Inorg. Chim. Acta* **1984**, *88*, 165; and references therein.
(6) Vagg, R. S. *J. Proc. R. Soc. N.S.W.* **1984**, *117*, 99.
(7) Buckingham, D. A.; Mason, S. F.; Sargeson, A. M.; Turnbull, K. R. *Inorg. Chem.* **1966**, *5*, 1649.

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minimized.[6] In this paper we report the results of our studies on the Λ,Δ-$[Ru(diimine)_2(aa)]^+$ system, where *aa* is the glycinate, *N*-methylglycinate, or *N*-phenylglycinate anion. The crystal structure of *rac*-$[Ru(bpy)_2(gly)]ClO_4 \cdot 2H_2O$ has been determined by diffraction methods and the molecular structure of the cation analyzed so as to assist with correlation of ^1H NMR features of these glycine-based systems.

Experimental Section

All materials used were of reagent grade. The amino acids glycine (glyH), *N*-methylglycine (*N*-MeglyH), and *N*-phenylglycine (*N*-PhglyH) were used as obtained from Sigma Chemical Co. *cis*-$Ru(bpy)_2Cl_2$ and *cis*-$Ru(phen)_2Cl_2$ were synthesized as described previously.[8]

***rac*-[Ru(bpy)$_2$(gly)]ClO$_4$·H$_2$O.** A suspension of $Ru(bpy)_2Cl_2$ (0.24 g, 0.5 mmol) in water (30 cm^3) was heated until complete dissolution was obtained, then glycine (0.15 g, 2 mmol), 1 M aqueous NaOH (1 cm^3) and $NaClO_4$ (~2 g) were added. The hot, deep red solution was filtered and then allowed to cool and stand for several days. The dark red crystalline product that formed was filtered off, washed with a little cold water, and dried at the pump; yield 0.19 g (63%). Anal. Calcd for $Ru(C_{10}H_8N_2)_2(C_2H_4NO_2)]ClO_4 \cdot H_2O$: C, 43.68; H, 3.67; N, 11.58; H_2O, 3.0. Found: C, 43.37; H, 3.54; N, 11.76; H_2O, 3.0.

The other $[Ru(diimine)_2(aa)]ClO_4 \cdot nH_2O$ complexes were each obtained as dark red or orange-red microcrystalline solids by a method analogous to that given above, with substitution of the appropriate diimine and/or amino acid.

***rac*-[Ru(phen)$_2$(gly)]ClO$_4$·1.5H$_2$O.** Yield: 48%. Anal. Calcd for $[Ru(C_{12}H_8N_2)_2(C_2H_4NO_2)]ClO_4 \cdot 1.5H_2O$: C, 47.17; H, 3.50; N, 10.58; H_2O, 4.1. Found: C, 47.22; H, 3.39; N, 10.51; H_2O, 4.0.

***rac*-[Ru(bpy)$_2$(*N*-Megly)]ClO$_4$·H$_2$O.** Yield: 41%. Anal. Calcd for $[Ru(C_{10}H_8N_2)_2(C_3H_6NO_2)]ClO_4 \cdot H_2O$: C, 44.63; H, 3.91; N, 11.31; H_2O, 2.9. Found: C, 44.95; H, 4.02; N, 11.41; H_2O, 2.3.

***rac*-[Ru(phen)$_2$(*N*-Megly)]ClO$_4$·3.5H$_2$O.** Yield: 45%. Anal. Calcd for $[Ru(C_{12}H_8N_2)(C_3H_6NO_2)]ClO_4 \cdot 3.5H_2O$: C, 45.54; H, 4.10; N, 9.83; H_2O, 8.9. Found: C, 45.77; H, 3.19; N, 9.84; H_2O, 9.4.

***rac*-[Ru(bpy)$_2$(*N*-Phgly)]ClO$_4$·H$_2$O.** Yield: 61%. Anal. Calcd for $[Ru(C_{10}H_8N_2)_2(C_8H_8NO_2)]ClO_4 \cdot H_2O$: C, 49.38; H, 3.85; N, 10.28; H_2O, 2.7. Found: C, 48.98; H, 3.82; N, 10.32; H_2O 2.9.

***rac*-[Ru(phen)$_2$(*N*-Phgly)]ClO$_4$·4H$_2$O.** Yield: 68%. Anal. Calcd for $[Ru(C_{12}H_8N_2)_2(C_8H_8NO_2)]ClO_4 \cdot 4H_2O$: C, 49.10; H, 4.12; N, 8.94; H_2O, 9.2. Found: C, 49.28; H, 3.39; N, 8.76; H_2O, 10.0.

^1H NMR Measurements. Proton NMR spectra were recorded at 200 MHz on a Varian 200-XL instrument. In the cases of the N-substituted amino acid chelates the same sample solutions were then exposed to sunlight and their NMR spectra recorded at various intervals until constant isomeric ratios were obtained, thus indicating the attainment of thermodynamic equilibrium. Spectral assignments and the determination of coupling constants were assisted by homonuclear resonance decoupling experiments.

X-ray Structural Analysis. *rac*-$[Ru(bpy)_2(gly)]ClO_4 \cdot H_2O$ was recrystallized from aqueous ethanol to yield a dihydrate form as small deep red plates lying on [001]. A crystal 0.2 mm thick of *ab* diagonal dimensions 0.4 × 0.7 mm was selected for the X-ray analysis. Crystal Data: $C_{22}H_{24}N_5Cl_1O_8Ru$, M_r = 623.0, triclinic, a = 9.487 (2) Å, b = 12.294 (3) Å, c = 13.041 (3) Å, α = 111.36 (2)°, β = 63.15 (2)°, γ = 113.33 (2)°, U = 1213.77 (10) Å^3, Z = 2, D_c = 1.70 Mg m^{-3}, $F(000)$ = 632, μ(Mo Kα) = 7.20 mm^{-1}, space group $P\bar{1}$.

Initially unit cell parameters were determined from single-crystal precession photographs produced by using Mo Kα radiation. Accurate cell parameters were obtained from a least-squares fit to diffractometer data. Intensities were collected in a $\omega,2\theta$ scan mode from $5° < 2\theta < 60°$ at 20 °C on a Hilger and Watts Y290 four-circle diffractometer using Mo Kα radiation and a solid-state detector, the latter eliminating the need for beam monochromatization. Of the 4897 reflections recorded in the octants $-7 \leq h \leq +7$, $-12 \leq k \leq +12$, and $0 \leq l \leq +12$, 3752 had $I > 3\sigma(I)$ and these were used for the structural analysis. Intensities were corrected for Lorentz and polarization effects but not for absorption or extinction.

The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedures which minimized the function $\sum w\Delta^2$, the weight given to each reflection being that obtained from counting statistics. After isotropic refinement a difference synthesis was used to locate the H atoms. The positions of those bound to C or N were optimized by assuming the C–H and N–H distances to be 1.0 Å and using idealized bond angles. All H atoms were assigned B = 3.0 Å^2, and their parameters were maintained as invariant, although their positions were recalculated at the final stage of anisotropic refinement. The refinement process was terminated with the maximum parameter shift $<0.15\sigma$, and a final difference map showed no residual electron density greater than |0.5| e Å^{-3}. The final R based on all 3752 reflections was 0.033, and R' $[=(\sum w\Delta^2/\sum w|F_o|^2)^{1/2}]$ was 0.035.

The refinement and structural analysis calculations were carried out on a FACOM M3405 computer using programs written by F.S.S. Neutral scattering factors were taken from ref 9. The coordinates of

Table I. Final Atomic Coordinates (×10^4) for Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses

	x	*y*	*z*
Ru	2124.5 (5)	2493.0 (3)	2111.1 (3)
Cl	7421 (2)	2823 (1)	6264 (1)
O(1)	9084 (4)	2789 (3)	5746 (3)
O(2)	7247 (5)	3567 (3)	5724 (4)
O(3)	6398 (5)	1637 (3)	6023 (4)
O(4)	7052 (6)	3334 (4)	7493 (3)
O(W1)	−1399 (5)	3405 (3)	−565 (3)
O(W2)	−460 (6)	1698 (4)	−2730 (4)
O(11)	1461 (4)	3078 (3)	1105 (3)
O(12)	−33 (5)	4124 (4)	1199 (3)
N	877 (4)	3783 (3)	3443 (3)
N(1)	2844 (4)	2179 (3)	3183 (3)
N(2)	4264 (4)	3868 (3)	2030 (3)
N(3)	3068 (4)	1243 (3)	664 (3)
N(4)	103 (4)	1020 (3)	2210 (3)
C(1)	483 (6)	3730 (4)	1661 (4)
C(2)	−120 (6)	4017 (4)	3019 (4)
C(11)	4151 (6)	3062 (4)	3455 (4)
C(12)	4672 (7)	3000 (5)	4272 (4)
C(13)	3862 (8)	2007 (6)	4797 (5)
C(14)	2615 (7)	1116 (5)	4496 (5)
C(15)	2134 (6)	1217 (4)	3713 (4)
C(21)	4960 (5)	4005 (4)	2781 (4)
C(22)	6335 (6)	4934 (4)	2855 (5)
C(23)	7051 (6)	5741 (4)	2119 (5)
C(24)	6353 (6)	5583 (4)	1335 (5)
C(25)	4986 (6)	4658 (4)	1310 (4)
C(31)	1979 (5)	146 (4)	443 (4)
C(32)	2449 (6)	−750 (4)	−549 (4)
C(33)	4022 (6)	−527 (4)	−1351 (4)
C(34)	5119 (6)	582 (5)	−1139 (4)
C(35)	4612 (6)	1433 (4)	−135 (4)
C(41)	314 (5)	24 (4)	1327 (4)
C(42)	−1002 (6)	−1031 (4)	1288 (4)
C(43)	−2509 (6)	−1067 (4)	2159 (4)
C(44)	−2703 (6)	−56 (4)	3078 (4)
C(45)	−1409 (5)	951 (4)	3078 (4)

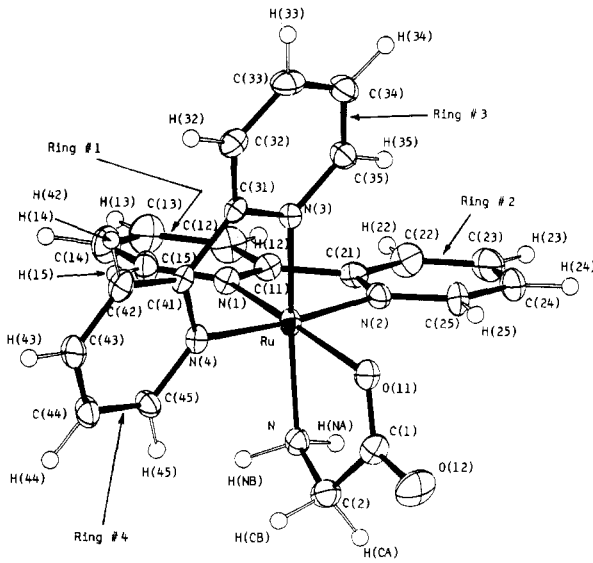

Figure 1. Molecular structure of Λ-$[Ru(bpy)_2(gly)]^+$ showing the atomic labeling. Thermal ellipsoids for non-hydrogen atoms are scaled to include 35% probability. H atoms have B = 1.0 Å^2.

(8) Vagg, R. S.; Williams, P. A. *Inorg. Chim. Acta* **1981**, *51*, 61.

(9) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England 1974; Vol. IV, pp 72–83.

Table II. Selected Bonding Parameters and Interatomic Distances in $[Ru(bpy)_2(gly)]ClO_4 \cdot 2H_2O$[a]

(a) Bond Lengths (Å)

Ru–N	2.135 (4)	C(1)–O(11)	1.260 (6)
Ru–O(11)	2.105 (3)	C(1)–O(12)	1.225 (5)
Ru–N(1)	2.008 (4)	C(1)–C(2)	1.542 (7)
Ru–N(2)	2.052 (4)	C(2)–N	1.443 (6)
Ru–N(3)	2.043 (4)		
Ru–N(4)	2.042 (3)		

(b) Bond Angles (deg)

O(11)–Ru–N	79.1 (1)	Ru–N–C(2)	109.6 (3)
N(1)–Ru–N(2)	78.7 (2)	Ru–O(11)–C(1)	117.1 (3)
N(3)–Ru–N(4)	78.8 (1)	N–C(2)–C(1)	113.0 (4)
		O(11)–C(1)–C(2)	116.6 (5)

(c) H··H Interatomic Distances (Å)[b]

H(25)··H(NA)	3.5	H(12)··H(22)	2.2
H(25)··H(CA)	4.2	H(32)··H(42)	2.2
H(45)··H(NB)	2.2		
H(45)··H(CB)	2.4		

(d) Proposed Hydrogen Bonds (Å)

O(W1)–H(W11)···O(12)	2.839 (5)	N–H(NA)···O(1^{II})	3.134 (5)
O(W1)–H(W12)···O(12^{I})	3.051 (5)	N–H(NB)···O(2^{III})	3.088 (6)
O(W2)–H(W21)···O(1)	3.020 (6)		
O(W2)–H(W22)···O(W1)	2.839 (6)		

[a] Estimated standard deviations are given in parentheses. Roman numeral superscripts refer to the following equivalent positions relative to x, y, z: (I) $-x, 1-y, 1-z$; (II) $x-1, y, z$; (III) $1-x, 1-y, 1-z$. [b] H atoms were placed in calculated positions that were not allowed to vary. Hence no esd values derive from the least-squares refinement.

non-hydrogen atoms are given in Table I, and selected interatomic parameters are presented in Table II.

Results and Discussion

A diagram of the Λ form of the molecular cation is shown in Figure 1, and bonding details of the metal coordination sphere and the glycine chelate ring, together with a proposed hydrogen-bonding system in the crystal, are given in Table II. The Ru atom adopts the expected six-coordination with its bonding parameters very similar to those of the (*S*)-alanine,[11] (*S*)-threonine,[12] and (*S*)-allothreonine[12] analogues. The bond distance Ru–N(1), which is trans to the coordinated amino acid carboxyl group, again is significantly less than those of the other three Ru–N bonds to the diimine ligands. This effect has been observed in analogous chelates, and an explanation in terms of Ru→N(bpy) π backbonding has been offered.[13]

The two bipyridyl groups are closely planar, with the dihedral angles between the least-squares planes of best fit for pairs of pyridine rings 1 and 2 and 3 and 4 being 7.4 and 1.4°, respectively. These small angular distortions largely represent out-of-plane bending (defined as θ in ref 11) rather than twists around the central C–C bonds. This planarity enforces close contacts (Table II) between the 3- and 3′-hydrogen atoms of the bpy groups (i.e. atom pairs H(12) and H(22) and H(32) and H(42)), a factor that has been shown to result in relatively pronounced acidity for such protons.[14]

The salient difference in the steric environments of the alternate sides of the amino acid chelate ring is manifested by the H··H contacts listed in Table II. The close proximity of H(45) to the α-methylene proton H(CB) and the amine proton H(NB) is not mirrored in the disposition of H(25) relative to the other side (i.e.

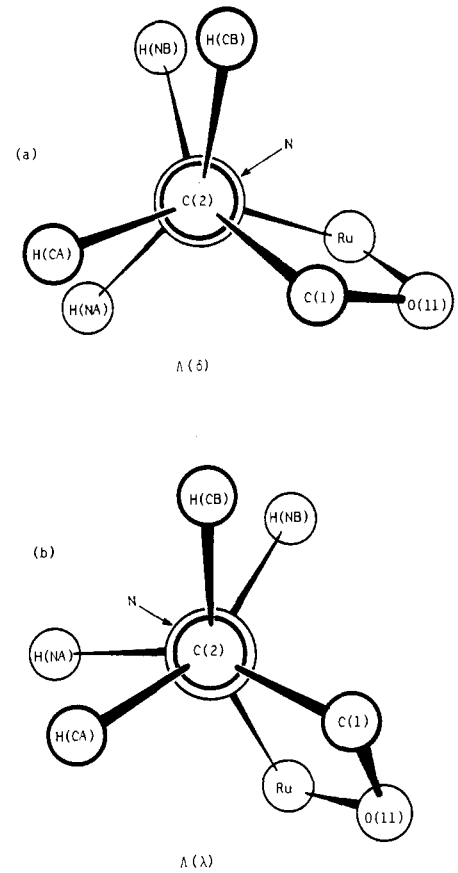

Figure 2. Projection down the C(2)–N bond of the various diastereomers: (a) all Λ isomers except Λ-[Ru(diimine)$_2$((*S*)-*N*-Megly)]$^+$; (b) Λ-[Ru(diimine)$_2$((*S*)-*N*-Megly)]$^+$. Atoms H(NB) and H(CB) are those protons proximal to the interacting H(45) of an adjacent pyridyl ring in these Λ diastereomers. For the *N*-substituted amino acidates either H(NA) or H(NB) is replaced by a CH_3 or C_6H_5 group.

atoms H(CA) and H(NA)) of the chelate ring. It is this difference in the environments of these protons that has been proposed as the source of chiral discrimination in analogous complexes with chiral amino acids.[5,6] This glycine structure thus may be seen as representing the least strained or energetically most favorable conformation for such $[Ru(bpy)_2(aa)]^+$ chelates. This being the case, an analysis of the geometry of the coordinated amino acid would be of value, and in particular would allow a detailed comparison with the structure indicated by the proton NMR spectrum of the chelate.

The bond lengths and angles involving the amino acid are given in Table II. Each of these parameters is consistent with those of the six analogous diastereomers investigated previously.[11,12] One important factor of the glycine structure is its conformation as defined by the torsion angle along the C_α–N bond. This was observed to be a measure of significant structural differences between the two diastereomeric forms of $[Ru(bpy)_2(S\text{-ala})]^+$,[11] but not between the four 2(*S*)-amino-3-hydroxybutanoic acid diastereomeric analogues.[12] The relevant Ru–N–C(2)–C(1) torsion angle in these glycine enantiomers is 23.2° and is represented in Figure 2a. The consequent puckering of the chelate rings then could be described as a flattened δ conformation in the Λ isomer, its antipode being the Δ(λ) form.

This point is of some interest, for in each of the previously described *S*-ala, *S*-thr, and *S*-allothr diastereomers[11,12] the δ conformation exists in both Λ and Δ isomers. If the Δ(λ) conformation in the glycine structure represents the most energetically favorable conformation, this being the one corresponding to the best fit of H(45) between H(NB) and H(CB), then strain must arise in the Δ(δ) conformations observed for the (*S*)-amino acid chelates. The δ conformation in those chelates arises from the α-substituent adopting an equatorial disposition relative to the chelate ring. This is further accentuated in the Δ diastereomer

(10) Johnson, C. K. "ORTEP"; Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965; revised 1971.
(11) Stephens, F. S.; Vagg, R. S.; Williams, P. A. *Inorg. Chim. Acta* **1983**, *72*, 253.
(12) Goodwin, T. J.; Williams, P. A.; Stephens, F. S.; Vagg, R. S. *Inorg. Chim. Acta* **1984**, *88*, 165.
(13) Eggleston, D. S.; Goldsby, K. A.; Hodgson, D. J.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 4573.
(14) Constable, E. C.; Seddon, K. R. *J. Chem. Soc., Chem. Commun.* **1982**, 34.

Table III. Selected ^{1}H NMR Data for the Complexes[a]

	complex[b]							
	1[c]	**2**[d]	**3**[c]	**4**[c]	**5**[d]	**6**[d]	**7**[e]	**8**[e]
$\delta_{H(NA)}$	3.86	4.22		4.58		5.12	7.59	7.93
$\delta_{H(NB)}$	4.52	4.98	5.12		5.77			
$\delta_{H(CA)}$	3.34	3.48	3.04	3.47	3.18	3.65	3.58	3.86
$\delta_{H(CB)}$	3.55	3.76	3.66	3.64	3.89	3.81	4.06	4.47
$\delta_{N(CH3)}$			1.51	2.12	1.47	2.26		
$J_{NA,NB}$	12.0	10.0						
$J_{CA,NB}$	1.0	2.8	8.0		8.0		2.0	2.0
$J_{CA,NA}$	8.0	8.4		7.0		7.0		
$J_{CB,NA}$	12.0	12.0		10.0		10.0		
$J_{CB,NB}$	8.0	8.0	7.0		7.0		7.0	8.0
$J_{CA,CB}$	18.0	16.8	16.0	17.0	17.0	17.0	16.0	17.0
$J_{CH3,NA}$				6.0		6.0		
$J_{CH3,NB}$			6.0		6.0			
$\delta_{H(45)}$	9.18	9.84	9.10	9.22	9.89	9.94	9.99	10.29
$\delta_{H(25)}$	8.86	9.44	8.88	8.82	9.53	9.44	9.00	9.36
$J_{44,45}$	7.0	5.0	6.0	6.0	4.0	5.0	6.0	6.0
$J_{24,25}$	7.0	4.5	6.0	6.0	4.0	5.0	6.0	5.0

[a] Chemical shifts (δ) are reported in ppm (±0.005) relative to acetone-d_6 (δ 2.04) or dmso-d_6 (δ 2.62) peaks used for internal reference; coupling constants (J) are in Hz (±0.5). [b] Key: **1**, Λ-[Ru(bpy)$_2$(gly)]$^+$; **2**, Λ-[Ru(phen)$_2$(gly)]$^+$; **3**, Λ-[Ru(bpy)$_2$((*S*)-*N*-Megly)]$^+$; **4**, Λ-[Ru(bpy)$_2$((*R*)-*N*-Megly)]$^+$; **5**, Λ-[Ru(phen)$_2$((*S*)-*N*-Megly)]$^+$; **6**, Λ-[Ru(phen)$_2$((*R*)-*N*-Megly)]$^+$; **7**, Λ-[Ru(bpy)$_2$((*R*)-*N*-Phgly)]$^+$; **8**, Λ-[Ru(phen)$_2$((*R*)-*N*-Phgly)]$^+$. [c] D_2O:acetone-d_6 = 4:1. [d] D_2O:acetone-d_6 = 1:4. [e] 100% acetone-d_6.

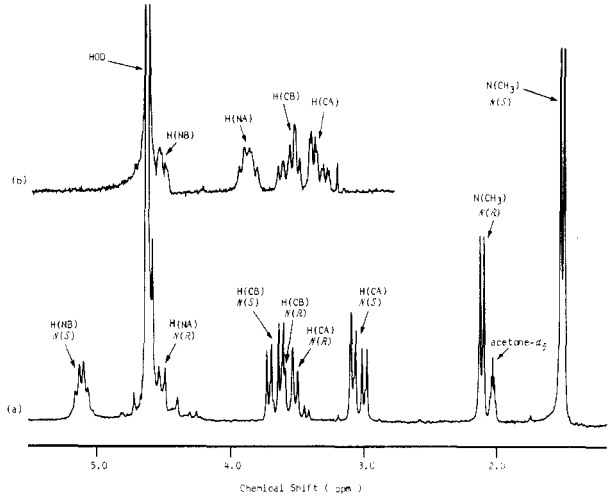

Figure 3. ^{1}H NMR spectra in the 1–5 ppm range for (a) [Ru(bpy)$_2$(*N*-Megly)]$^+$ and (b) [Ru(bpy)$_2$(gly)]$^+$. Details of solvents used are given in Table III. Proton assignments are for Λ enantiomers only.

by steric interaction between that substituent and the diimine α-proton, H(45).

Analogies may be drawn from this structural analysis to solution NMR results concerning the several glycine chelates in solution. A list of significant ^{1}H NMR data for these glycine and N-substituted glycine chelates is given in Table III, and sections of the spectra arising from the amino acid are shown in Figure 3. In each case the α-methylene protons H(CA) and H(CB), split in turn by coupling to the amine protons (H(NA) and/or H(NB)), give rise to a typical ABMX spectrum. The latter signal elaboration is lost upon proton–deuteron exchange to give easily interpreted AB spectra. The two protons of the glycine molecule H(CB) and H(NB), which are close to the bpy proton H(45), are each observed further downfield, a fact which may be attributed to both contact deshielding and electronic deshielding by the pyridyl ring containing N(4). Atoms H(CA) and H(NA) may, in turn, feel an electronic shielding effect from the pyridyl ring containing N(2).

The conformation observed in the solid state and represented by Figure 2 is consistent with the ^{1}H NMR spectrum of [Ru(bpy)$_2$(gly)]$^+$. The vicinal coupling constants $J_{CA,NA}$ and $J_{CB,NB}$, both ~8 Hz, correlate with the small gauche torsion angle relating each respective proton pair in the crystal structure. The low value for $J_{CA,NB}$, in turn, reflects the corresponding large anti torsion angle of ~97° relating the N–H(NB) and C(2)–H(CA) bonds, a classic Karplus relationship.[15]

This structural correlation of the NMR and X-ray diffraction results for [Ru(bpy)$_2$(gly)]$^+$ suggests that the solution structures of the phen and *N*-substituted glycine analogues may be similarly analyzed. The complex cation [Ru(bpy)$_2$(*N*-Megly)]$^+$ contains two chiral centers (Ru and N(amine)) and hence exists as four diastereomers in two enantiomeric pairs. Details of the NMR spectra of these isomers are given in Table III and are shown in Figure 3. If the two Λ forms only are considered for the purposes of the analysis, then it may be seen that the predominant isomer in the synthetic product mixture has an absolute configuration of *S* at N(amine), equivalent to H(NA) of Figures 1 and 2 being replaced by the CH_3 group. The less abundant Λ(*R*) form, with H(NB) replaced by CH_3, would contain an inherent steric interaction between that methyl group and diimine proton H(45). This energetic preference for the Λ(*S*) form is confirmed by the photoequilibration experiments, an isomeric ratio in D_2O of 3.25 (6) being obtained from the NMR spectrum of the equilibrated solution (Figure 3). This value represents a free energy difference of 2.95 (5) kJ mol^{-1} between the solvated *S* and *R* forms. The corresponding values obtained for the [Ru(phen)$_2$(*N*-Megly)]$^+$ system are 2.51 (7) and 2.28 (6), respectively. These quantities are of some interest, since *N*-methylglycine has been shown to coordinate stereospecifically in its Co(en)$_2^{3+}$ chelate.[7]

The assignment of these configurations, made on a steric basis, is fully consistent with the NMR spectra. The major isomer, Λ(*S*) (and its antipode), would have the CH_3 group shielded by the noninteracting bpy pyridyl ring (N(2),C(21–25) in Figure 1) and thus its signal occurs at high field (δ 1.51). By comparison, in the Λ(*R*) form the methyl group protons would be deshielded by the close proximity of the pyridyl ring N(4),C(41–45), and therefore its resonance is observed at lower field (δ 2.12). A similar steric deshielding also is felt by the diimine proton H(45) in the Λ(*R*) isomer, resulting in its lower field position (9.22 ppm) compared with that of the Λ(*S*) form (9.10 ppm) (Figure 4). An additional distinction may be made between H(45) and H(25) in each of these forms due to the different electronic effects of the two amino acid donor groups. The carboxylic group would shield proton H(25), leading to its higher field position relative to that of H(45). An analogous effect has been observed in related amino acid complexes of tetradentates that contain pyridyl terminal groups.[16]

The coupling constants $J_{CA,NB}$ (8.0 Hz) and $J_{CB,NB}$ (7.0 Hz) of the Λ-[Ru(bpy)$_2$((*S*)-*N*-Megly)]$^+$ isomer are not consistent with the torsional structure shown in Figure 2a, however. A Karplus analysis of these vicinal constants suggests the Λ(λ) conformation shown in Figure 2b, with a torsion angle H(CB)–C(2)–N–H(NB) of ca. 30°. This same structure would be assignable to the analogous Λ(δ) cation (**5** of Table III), which shows similar vicinal coupling. The less abundant Λ-[Ru(phen)$_2$((*R*)-*N*-Megly)]$^+$ cation (**6** of Table III) shows proton coupling consistent with the more common Λ(δ) conformation, however (Figure 2a).

This difference in structural behavior for the Λ-[Ru(diimine)$_2$((*S*)-*N*-Megly)]$^+$ forms might be attributed to a repulsion between the *N*-methyl group and the proximal aromatic ring (that containing N(2)). The direction of the rotation around C(2)–N that would result from this repulsion is consistent with the chelate ring adopting the λ conformation and so too are the changes in chemical shift observed for protons H(NB) and H(CA) relative to those for the unsubstituted glycine analogue (Figure 3).

The *N*-phenylglycine chelates show stereospecific coordination, resulting only in the *R* configuration[17] for the Λ isomers. This

(15) Karplus, M. *J. Am. Chem. Soc.* **1963**, *85*, 2870.
(16) Goodwin, T. J.; Vagg, R. S.; Williams, P. A. *J. Proc. R. Soc. N.S.W.* **1984**, *117*, 1.
(17) In these (*R*)-*N*-Phgly species the proton H(NA) of Figure 1 is replaced by a phenyl ring, and hence they are structurally analogous to the (*S*)-*N*-Megly chelates.

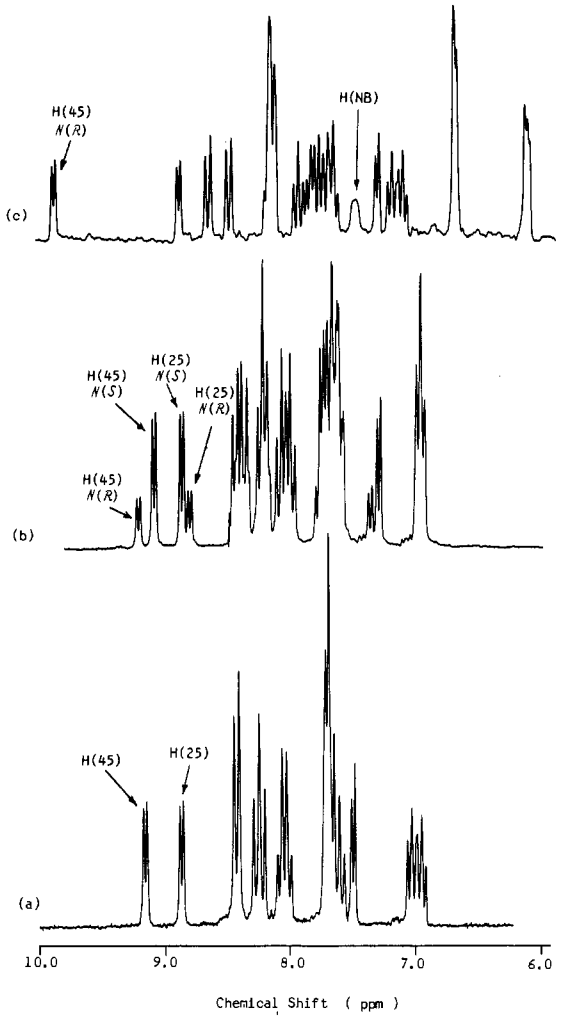

Figure 4. ^{1}H NMR spectra in the aromatic region for the bpy chelates: (a) $[Ru(bpy)_2(gly)]^+$; (b) $[Ru(bpy)_2(N\text{-Megly})]^+$; (c) $[Ru(bpy)_2(N\text{-Phgly})]^+$. Details of solvents used are given in Table III. Proton assignments are for Λ enantiomers only.

selection may be attributed to the prohibitive steric repulsion of H(45) that would result if H(NB) were to be substituted by the bulky aryl group. It is interesting that, unlike the Megly chelates, the ^{1}H NMR spectra of the selected Λ-$[Ru(diimine)_2((R)\text{-}N\text{-}Phgly)]^+$ forms (Table III) indicate the Λ(δ) conformation of Figure 2a. This implies that there is not a repulsive interaction between the bulky phenyl group and the pyridyl ring containing N(4), as is suggested for the Λ(*S*) forms but rather than an attractive π–π interaction between the planar aromatic groups may exist. The mutual shielding of the ring protons that would result from such an interaction is supported by the NMR spectra of the chelates, which show several resonances at relatively high field (Table III and Figure 4). Irradiation of aqueous solutions of these *N*-Phgly chelates with light does not result in the production of any NMR signals attributable to the Λ(*S*) forms, thus confirming the stereospecific formation of the *R* isomers.

In any mixed solvent containing D_2O the single amine proton H(NA) of each *N*-Phgly chelate rapidly exchanges for a deuteron, and its acidic nature is manifested in its low-field resonance in anhydrous acetone-d_6 (Table III). The acidity of these protons may be partly ascribed to the electron-withdrawing character of the phenyl substituent. In addition, the interaction of this amine proton with H(45) would also serve to increase its acidic nature, as has been observed for all chelates of this type.[6] The addition of NaOD to the gly and *N*-Megly chelates leads to the immediate exchange of the amine protons of the coordinated amino acids. Moreover, over several days the methylene protons also are seen to exchange, a phenomenon observed previously in other coordinated glycine systems.[18] Unlike the exchange process for prochiral amine protons of the gly chelates, however, this latter exchange process does not appear to be stereoselective.

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Registry No. **1**, 104639-84-1; **2**, 104639-85-2; **3**, 104549-70-4; **4**, 104639-86-3; **5**, 104549-71-5; **6**, 104639-87-4; **7**, 104549-72-6; **8**, 104549-73-7; $[Ru(bpy)_2(gly)]ClO_4 \cdot 2H_2O$, 104574-58-5; $[Ru(phen)_2(gly)]ClO_4$, 15362-93-3; $[Ru(bpy)_2(N\text{-Megly})]ClO_4$, 104639-89-6; $[Rh(phen)_2(N\text{-Megly})]ClO_4$, 104639-91-0; $[Ru(bpy)_2(N\text{-Phgly})]ClO_4$, 104639-92-1; $[Ru(phen)_2(N\text{-Phgly})]ClO_4$, 104639-94-3; $Ru(bpy)_2Cl_2$, 19542-80-4; *cis*-$Ru(phen)_2Cl_2$, 15453-59-5; D_2, 7782-39-0.

Supplementary Material Available: Tables of coordinates for H atoms, anisotropic thermal parameters, complete bond parameters, and least-squares planes data (6 pages); a table of structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

(18) Golding, B. T.; Gainsford, G. J.; Herlt, A. J.; Sargeson, A. M. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 495 and references therein.