$[Cu(tet\ b)(H_2O)(red)^{2+},Y^-]$. Hence

$$k_{obsd} = k_1K_{os}[Y^-] + k_{-1} \qquad (9)$$

This equation is the same as expressed in eq 3, where $k_f = k_1K_{os}$ and $k_{aq} = k_{-1}$.

As shown in Figure 1, the copper(II) of $[Cu(tet\ b)Y(red)]^{2+}$ is in a very slightly distorted square pyramid with the macrocycle equatorial and the oxygen atom of the aqua group axial. All C atoms lie on the lower side of the four-nitrogen plane, while the Cu atom deviates upward from the plane toward the coordinated monodentate ligand. Two bulky axial methyl groups as well as the protons of the macrocyclic ligand lie below the metal ion and hinder the axial position opposite to the coordinated monodentate ligand. Thus the coordination of the sixth ligand to this axial position (trans attack) is inhibited sterically by the "picket fence". On the other hand, $[Cu(tet\ b)Y(red)]^+$ is open to cis attack, in which both the entering group and the leaving group are on the same side of the coordinated macrocyclic ligand in the the transition state.

**Acknowledgment.** The support of the Chemistry Research Center, National Science Council of the Republic of China, under Grants NSC 74-0208-M007-08 and NSC 75-0208-M007-04 is gratefully acknowledged.

**Supplementary Material Available:** Figures 1S–9S, showing plots of $k_{obsd}$ vs. $[Y^-]$ and plots of ln $(k/T)$ vs. $1/T$ (9 pages). Ordering information is given on any current masthead page.

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# Reinvestigation of the Pressure Effect on the Outer-Sphere Electron-Transfer Reaction between Aquapentaamminecobalt(III) and Hexacyanoferrate(II) in Aqueous Solution

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The pressure effect on kinetics of the outer-sphere electron-transfer reaction between $[Co^{III}(NH_3)_5(H_2O)]^{3+}$ and $[Fe^{II}(CN)_6]^{4-}$ was reexamined very carefully under the following conditions: $[Co^{III}] = 5.0 \times 10^{-5}$ M, $[Fe^{II}] = (1.7–9.2) \times 10^{-3}$ M, $I = 0.5$ M ($NaClO_4$), pH 3.8–3.9 (0.05 M acetate buffer), 25 °C. The ion-pair formation constant (194 ± 4 $M^{-1}$ at atmospheric pressure) decreases with increase in pressure at 25–100 MPa, whereas the opposite trend was reported by van Eldik and Kelm. The electron-transfer step within the encounter complex ((9.31 ± 0.13) × $10^{-2}$ $s^{-1}$ at atmospheric pressure) has $\Delta V_e^* = +37.6 \pm 1.2$ $cm^3\ mol^{-1}$ (reported value +26.5 $cm^3\ mol^{-1}$). Other kinetic parameters for the electron-transfer process are $\Delta H_e^* = 115 \pm 2$ kJ $mol^{-1}$ and $\Delta S_e^* = +122 \pm 7$ J $K^{-1}\ mol^{-1}$ (obtained at 25.0–46.3 °C).

## Introduction

Outer-sphere electron-transfer reactions between highly and oppositely charged reactants often give the rate law (1), in which $K_{OS}$ is the formation constant of an outer-sphere encounter complex (ion pair) and $k_e$ the electron-transfer rate constant within it.[2-8] Such reactions enable us to obtain individual values of $K_{OS}$

$$k_{obsd} = k_eK_{OS}[X]/(1 + K_{OS}[X]) \qquad (1)$$

$$X = \text{reactant used in excess}$$

and $k_e$. We have examined the pressure effect on these terms for three outer-sphere electron-transfer reactions[9,10] and found positive $\Delta V_{OS}$ and $\Delta V_e^*$ values. The positive $\Delta V_{OS}$ values were interpreted to be due to a decrease in electrostriction at the outer-sphere solvation sheath by partial charge cancellation. van Eldik and Kelm reported a negative value of $\Delta V_{OS}$ for the outer-sphere electron-transfer reaction (2).[11] Since a negative $\Delta V_{OS}$ value is not in line with our results, we have investigated further details of the pressure effect on reaction 2.

$$[Co^{III}(NH_3)_5(H_2O)]^{3+} + [Fe^{II}(CN)_6]^{4-} \overset{K_{OS}}{\rightleftharpoons} \text{encounter complex} \xrightarrow{k_e} \text{products} \qquad (2)$$

## Experimental Section

**Materials.** Aquapentaamminecobalt(III) perchlorate hydrate, $[Co^{III}(NH_3)_5(H_2O)](ClO_4)_3 \cdot H_2O$, was prepared by the known method.[12] All other materials, including $Na_4[Fe^{II}(CN)_6] \cdot 10H_2O$, disodium dihydrogen ethylenediaminetetraacetate (EDTA),[13] diethylenetriaminepentaacetic acid (DTPA),[13] ascorbic acid, sodium perchlorate, and sodium acetate, were obtained commercially and recrystallized once or twice from water. Acetic acid (reagent for microanalytical use) was used as received.

**Kinetic Runs.** All the kinetic studies were carried out by the stopped-flow method with the iron complex in at least 40-fold excess over the cobalt complex. A solution of the cobalt(III) complex containing the appropriate buffer component and DTPA was mixed with a solution of $[Fe^{II}(CN)_6]^{4-}$ to start kinetic runs. Most runs were monitored at 420 nm, where the $[Fe^{III}(CN)_6]^{3-}$ ion has a strong absorption peak ($\epsilon = 1023$ $mol^{-1}$ $dm^3\ cm^{-1}$).[14] The $[Fe^{II}(CN)_6]^{4-}$ ion is oxidized slowly in air, and the rate is greater at lower pH. About 10% of it was oxidized after 2 h ($[Fe^{II}] = 6.0 \times 10^{-3}$ M) at pH 3.6, and hence the kinetic studies (mostly at pH 3.8–3.9) are not disturbed by the air oxidation. Reaction temperature was carefully controlled within ±0.1 °C. The pressure was monitored by a Toyo Baldwin HT-3500 pressure cell connected to a Unipulse AM10 DC amplifier and is subject to uncertainty by ca. 5%.

**Measurements.** Kinetic runs at ambient pressure were carried out by use of a Union-Giken RA-401 stopped-flow spectrophotometer. A Hikari Koatsu FIT-3A high-pressure apparatus[15] was connected to the spec-

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(1) (a) Tohoku University. (b) Institute for Molecular Science.
(2) Gaswick D.; Haim, A. *J. Am. Chem. Soc.* **1971**, *93*, 7347.
(3) Kondo, S.; Sasaki, Y.; Saito, K. *Inorg. Chem.* **1981**, *20*, 429.
(4) Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1939.
(5) Sasaki, Y.; Kawamura, R. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3379.
(6) Kremer, E.; Cha, G.; Morkevicius, M.; Seaman, M.; Haim, A. *Inorg. Chem.* **1984**, *23*, 3028.
(7) Neves, A.; Herrmann, W.; Wieghardt, K. *Inorg. Chem.* **1985**, *23*, 3435.
(8) References cited in ref 5–7.
(9) Sasaki, Y.; Ueno, F. B.; Saito, K. *J. Chem. Soc., Chem. Commun.* **1981**, 1135.
(10) Kanesato, M.; Ebihara, M.; Sasaki, Y.; Saito, K. *J. Am. Chem. Soc.* **1983**, *105*, 5711.
(11) van Eldik, R.; Kelm, H. *Inorg. Chim. Acta* **1983**, *73*, 91.
(12) Rutenberg, A. C.; Taube, H. *J. Chem. Phys.* **1952**, *20*, 823.
(13) The abbreviations EDTA and DTPA are used where the extent of protonation need not be specified.
(14) Miralles, A. J.; Armstrong, R. E.; Haim, A. *J. Am. Chem. Soc.* **1977**, *99*, 1416.
(15) This apparatus is partly modified from that reported previously (Ishihara, T.; Funahashi, S.; Tanaka, M. *Rev. Sci. Instrum.* **1982**, *53*, 1231).

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trophotometer for the measurements at elevated pressures. Absorption spectra were obtained with a Hitachi 330 spectrophotometer. The pH values were measured with a TOA HM-20E pH meter.

## Results and Discussion

**1. Survey of Previous Studies.** Gaswick and Haim added EDTA to prevent precipitation, which otherwise occurs during the reaction.[2] They indicated that the redox reaction between $[Co^{II}(edta)]^{2-}$ and $[Fe^{III}(CN)_6]^{3-}$ had no significant influence on the reaction of interest. The first-order rate constant, $k_{obsd}$, was obtained at [EDTA] = $2 \times 10^{-4}$ M since it tended to decrease with increase in [EDTA] at $>5 \times 10^{-4}$ M. $k_{obsd}$ was found to be independent of pH in the range 3.4–4.9. They obtained $K_{OS}$ = 1500 ± 100 $M^{-1}$ and $k_e = 0.19 \pm 0.01$ $s^{-1}$ under the conditions $[Co^{III}] = (0.195\text{–}2.20) \times 10^{-4}$ M, $[Fe^{II}] = (0.19\text{–}3.01) \times 10^{-3}$ M, $I = 0.1$ M ($NaClO_4$), pH 4.7–4.9 (0.005 M acetate buffer), and 25 °C.

van Eldik and Kelm studied this reaction under the conditions $[Co^{III}] = 5 \times 10^{-4}$ M, $[Fe^{II}] = (3\text{–}30) \times 10^{-3}$ M, $I = 0.5$ M ($NaClO_4$), pH 4.7 (0.05 M acetate buffer), and 25 °C and obtained $K_{OS} = 483 \pm 112$ $M^{-1}$ and $k_e = 0.112 \pm 0.007$ $s^{-1}$ at 2.5 MPa.[11] From the data in the pressure range 2.5–100 MPa, $\Delta V_{OS} = -15.4 \pm 7.9$ $cm^3$ $mol^{-1}$ and $\Delta V_e^\ddagger = +26.5 \pm 2.4$ $cm^3$ $mol^{-1}$ were reported.

**2. Preliminary Studies at Ambient Pressure.** We have carefully reexamined the reaction with special reference to the following points: first, the accuracy of determination of the infinity absorbance; second, the linearity of the first-order plots, ln ($D_\infty - D_t$) vs. $t$, where $D_\infty$ and $D_t$ are the absorbances at infinite time and time $t$, respectively; third, the goodness of fit of $k_{obsd}$ on the rate law (3).

$$k_{obsd} = k_e K_{OS}[Fe^{II}]/(1 + K_{OS}[Fe^{II}]) \qquad (3)$$

**a. Stoichiometry of the Reaction.** This was studied under the conditions $[Co^{III}] = 5.0 \times 10^{-4}$ M, $[Fe^{II}] = 3.0 \times 10^{-3}$ M, pH 3.90 (0.05 M acetate buffer), [DTPA] = $1.0 \times 10^{-3}$ M, and $I$ = 0.5 M ($NaClO_4$). The amount of the produced $[Fe^{III}(CN)_6]^{3-}$ was estimated from the absorbance at 420 nm (measured ca. 20 min after the mixing) to be $4.7 \times 10^{-4}$ M. Thus, the 1:1 stoichiometry was confirmed.

**b. Scavenger of the Produced Cobalt(II).** The exact infinity value of absorbance at 420 nm has been determined with difficulty in the presence of $1.0 \times 10^{-3}$ M EDTA because of a slow decrease in absorbance after the maximum value is reached under various reactant concentrations. By the use of DTPA, however, the infinity absorbance value has been accurately determined. The concentration of DTPA in the range $2.0 \times 10^{-4}$–$1.0 \times 10^{-3}$ M has given no significant influence on the rate constant, $k_{obsd}$.

**c. Reaction pH.** The observation that the reaction rate is independent of pH in the pH range 3.4–4.9[2] has been confirmed by use of DTPA as a scavenger of $Co^{II}$. The pH was set to 3.8 in detailed kinetic studies to avoid possible influence from deprotonation of the cobalt(III) complex (p$K_a$ = 6.2 at $I$ = 0.3 M ($NaClO_4$), 25 °C).[16]

**d. Reactant Concentration.** The first-order plot, ln ($D_\infty - D_t$) vs. $t$, gives good straight lines at a low cobalt concentration ($<5 \times 10^{-4}$ M) but deviates appreciably at higher concentrations.[17]

**e. Other Kinetic Conditions.** Attempts have been made to follow the reaction by measuring the decrease of the cobalt complex concentration at 490 nm by adding various amounts of ascorbic acid, which rapidly reduces the produced $[Fe^{III}(CN)_6]^{3-}$. Also, excess amounts of cobalt complex ($6.0 \times 10^{-3}$ M) in relation to the amount of $[Fe^{II}(CN)_6]^{4-}$ ($3.0 \times 10^{-4}$ M) have been used for the runs at 420 nm. All these have failed to give sufficiently good linear first-order plots.

**3. Kinetic Studies. a. Measurements at Ambient Pressure.** These were carried out under the conditions $[Co^{III}] = 5.0 \times 10^{-5}$ M, $[Fe^{II}] = (2.0\text{–}30.0) \times 10^{-3}$ M, [DTPA] = $2.0 \times 10^{-4}$ M, pH 3.8–3.9 (0.05 M acetate buffer), and $I$ = 0.5 M ($NaClO_4$) at 25.0, 33.5, and 46.3 °C. At higher temperatures, a slow increase in absorbance continued after the redox reaction was practically completed and the infinite value of absorbance was often difficult to determine. In such cases the rate constant was obtained from the initial part of the absorbance change. The $k_{obsd}^{-1}$ vs. $[Fe^{II}]^{-1}$ plots at the three temperatures gave good straight lines to give accurate values of $K_{OS}$ and $k_e$ (Table I). Activation parameters were determined from the $k_e$ values to be $\Delta H_e^\ddagger = 115 \pm 2$ kJ $mol^{-1}$ and $\Delta S_e^\ddagger = +122 \pm 7$ J $K^{-1}$ $mol^{-1}$.[18]

**Table I.** Outer-Sphere Encounter Complex Formation Constant ($K_{OS}$) and First-Order Electron-Transfer Rate Constant ($k_e$) for the Reaction of $[Co^{III}(NH_3)_5(H_2O)]^{3+}$ and $[Fe^{II}(CN)_6]^{4-}$ in Aqueous Solution[a]

| temp/°C | pressure/MPa[b] | $K_{OS}/M^{-1}$ | $k_e/10^{-2}$ $s^{-1}$ |
|---|---|---|---|
| 25.0 | 0.1 | 194 ± 4 | 9.31 ± 0.13 |
| 33.5 | 0.1 | 210 ± 8 | 33.8 ± 0.7 |
| 46.3 | 0.1 | 189 ± 10 | 221 ± 7 |
| 25.0 | 2.5 | 188 ± 7 | 9.39 ± 0.23 |
| 25.0 | 25 | 182 ± 6 | 6.49 ± 0.13 |
| 25.0 | 50 | 178 ± 7 | 4.45 ± 0.12 |
| 25.0 | 75 | 169 ± 7 | 3.12 ± 0.09 |

[a] Conditions: $[Co^{III}] = 5.0 \times 10^{-5}$ M; $[Fe^{II}] = (2.0\text{–}30.0) \times 10^{-3}$ M (at 0.1 MPa) and $(1.7\text{–}9.2) \times 10^{-3}$ M (at 2.5–100 MPa); [DTPA] = $2.0 \times 10^{-4}$ M; pH 3.8–3.9 (0.05 M acetate buffer); $I$ = 0.5 M ($NaClO_4$). [b] At 101 MPa, $K_{OS} = 137 \pm 8$ $M^{-1}$ and $k_e = 2.47 \pm 0.10$ $s^{-1}$ were obtained from less accurate $k_{obsd}$ values (see text). These values were excluded for the calculations of $\Delta V_{OS}$ and $\Delta V_e^\ddagger$.

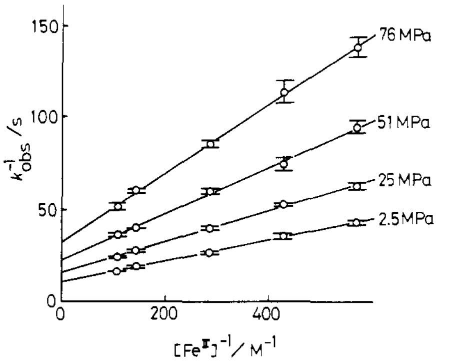

**Figure 1.** Plots of $k_{obsd}^{-1}$ vs. $[Fe^{II}]^{-1}$ for the reaction of $[Co^{III}(NH_3)_5(H_2O)]^{3+}$ with $[Fe^{II}(CN)_6]^{4-}$ at various pressures ($[Co^{III}] = 5.0 \times 10^{-5}$ M; [DTPA] = $2.0 \times 10^{-4}$ M; pH 3.8–3.9 (0.5 M acetate buffer); $I$ = 0.5 M ($NaClO_4$); 25.0 °C).

**b. Measurements at Elevated Pressures.** The pressure dependence was studied in the pressure range 25–100 MPa under reagent concentrations similar to those at atmospheric pressure. Infinite absorbance was difficult to obtain at higher pressures owing to a slow continuous increase in absorbance. Such a trend became more marked at higher iron(II) complex concentration. Consequently, $k_{obsd}$ was obtained at $[Fe^{II}] < 9 \times 10^{-3}$ M and at less than 100 MPa (Table II).[20] The $k_{obsd}^{-1}$ vs. $[Fe^{II}]^{-1}$ plots gave good straight lines (Figure 1). The $K_{OS}$ values (Table I) clearly decrease with increasing pressure (Figure 2),[20] and the result is not in accord with the claimed observation.[11] Least-squares treatment of the data at ≤76 MPa gave $\Delta V_{OS(0)} = +3.5 \pm 0.6$ $cm^3$ $mol^{-1}$. The ln $k_e$ vs. $p$ plot is a good straight line (Figure 3),[20] and the estimated $\Delta V_e^\ddagger$ value is $+37.6 \pm 1.2$ $cm^3$ $mol^{-1}$.

**4. Conclusion.** It turned out that the reaction (2) gave a self-consistent kinetic behavior under limited conditions only. The conditions employed in the reported work on pressure effect[11] do not seem to be appropriate for obtaining accurate rate constants. The quality of our data is guaranteed by the excellent straight lines of $k_{obsd}^{-1}$ vs. $[Fe^{II}]^{-1}$ plots and ln $k_e$ vs. $p$ plot. Thus we think

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(16) Splinter, R. C.; Harris, S. J.; Tobias, R. S. *Inorg. Chem.* **1968**, *7*, 897.

(17) Rate constants estimated from either the initial or the latter part of the absorbance change did not fit sufficiently to the rate law (3): e.g. the plot of $k_{obsd}^{-1}$ vs. $[Fe^{II}]^{-1}$ did not give a straight line and curved upward.

(18) The values may be compared with those reported in ref 19: $\Delta H_e^\ddagger = 89.9 \pm 2.9$ kJ $mol^{-1}$, $\Delta S_e^\ddagger = +37.8 \pm 8.4$ J $K^{-1}$ $mol^{-1}$.

(19) Krack, I.; van Eldik, R. *Inorg. Chem.* **1986** *25*, 1743.

(20) Supplementary material.

that the claimed negative $\Delta V_{OS}$[11] may have been derived from inaccurate observed $K_{OS}$ values. Very recently Krack and van Eldik reported negative $\Delta V_{OS}$ 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 $\Delta V_{OS}$ and $\Delta V_e^{\neq}$ values will be made separately together with other $\Delta V^{\neq}$ data of related systems.[21,22]

**Acknowledgment.** We are grateful to Dr. Yoshinori Hasegawa, College of General Education, Tohoku University, for the use of the stopped-flow spectrophotometer. Valuable discussions by T. Ninomiya are also acknowledged.

**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.

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(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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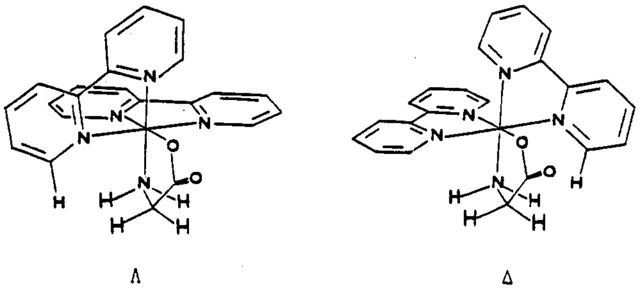
Photolabile complexes of the general form *rac*-$[Ru(diimine)_2(aa)]ClO_4{\cdot}nH_2O$ (where *diimine* is either 2,2′-bipyridyl or 1,10-phenanthroline and *aa* is glycine, *N*-methylglycine, or *N*-phenylglycine) have been synthesized and their structures in solution analyzed by using 200-MHz $^1H$ 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, $\alpha = 111.36$ (2)°, $\beta = 63.15$ (2)°, $\gamma = 113.33$ (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 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]



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

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

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(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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