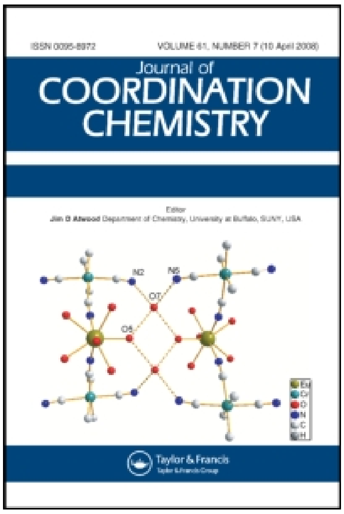

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STEREOCHEMISTRY OF SIX-COORDINATE OCTAHEDRAL SILICON(IV) COMPLEXES CONTAINING 2,2′-BIPYRIDINE

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$[Si(bpy)_3]^{4+}$ (bpy = 2,2′-bipyridine), synthesized from SiI_4 and 2,2′-bipyridine, was optically resolved by a chromatographic method using an SP-Sephadex C-25 column as an adsorbent and a 0.16 M aqueous solution of sodium (2*R*,3*R*)-(−)-*O*,*O*′-dibenzoyltartrate as an eluent. The optical isomers were characterized by measurement of their electronic absorption, circular dichroism, and ^1H NMR spectra. The chromatographic resolution of $[Si(bpy)_3]^{4+}$ was also attempted with an aqueous solution of potassium [(2*R*,3*R*)-(+)-tartrato]antimonate(III), sodium (2*R*,3*R*)-(+)-hydrogentartrate, and sodium (2*R*,3*R*)-(+)-tartrate as eluents. Force-field calculations were used to elucidate the chromatographic elution mechanism. $[Si(OH)_2(bpy)_2]I_2$ was also synthesized from SiI_4 and 2,2′-bipyridine. The optical resolution of this complex was achieved with sodium [(2*R*,3*R*)-(+)-tartrato]antimonate(III).

Keywords: Stereochemistry; six-coordinate silicon(IV) complex; 2,2′-bipyridine; chromatography; force-field calculation

INTRODUCTION

A huge number of six-coordinate complexes of metallic cation centers with didentate ligands have been synthesized. For complexes of the type $[M(L)_3]^{n+}$ (L = 2,2′-bipyridine, 1,10-phenanthroline, M^{II} = Fe, Ru, Os, Ni, Cu, Co, M^{III} = Cr, Fe, Ru, Os, Co, Rh)[1] the stereochemistry and optical resolution have been studied and Λ and Δ enantiomers have been confirmed from circular dichroism (CD) spectra and X-ray analyses. The separation of

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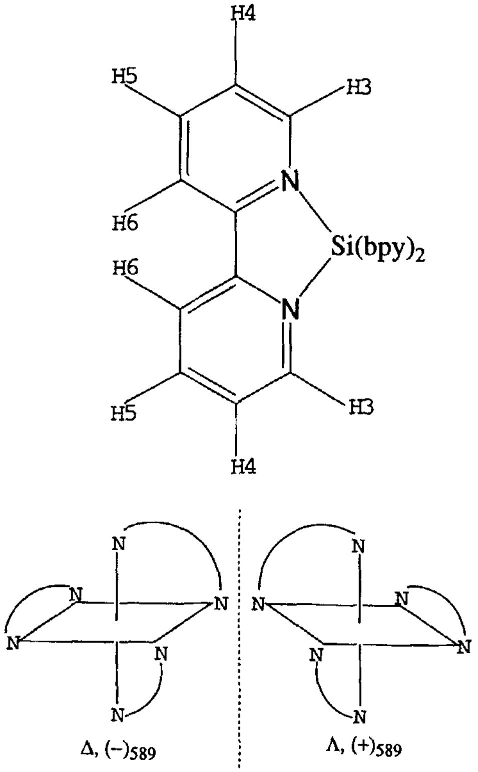
such stereoisomers has been performed by fractional recrystallization of diastereomers with resolving agents for the species $[M(L)_3]^{n+}$ (M^{II} = Fe, Ru, Ni, M^{III} = Rh, Co, Cr).[1] The chemistry of silicon depends on coordination number and valence state.[2] Six-coordinate complexes of silicon(IV) are not as common as four-coordinate tetrahedral compounds. Though several six-coordinate Si(IV) complexes have been synthesized, there are few studies of the isomerism. In previous papers,[3] we reported the complete chromatographic resolution of $[Si(phen)_3]^{4+}$. $[Si(bpy)_3]I_4$ was described by Kummer, *et al.* in 1973,[4] and the ^1H NMR and absorption spectra were measured. The complex $[Si(bpy)_3]I_4$ can exist in two enantiomers, as shown in Figure 1. In a previous paper,[3a] the resolution of $[Si(bpy)_3]^{4+}$ was attempted by column chromatography on SP-Sephadex C-25 using sodium (+)-tartrate as an eluent, but the separation of enantiomers was insufficient. The complete optical resolution of this complex and the characterization are described in the present paper.



Δ, $(-)_{589}$ Λ, $(+)_{589}$

FIGURE 1 Two enantiomers of $[Si(bpy)_3]^{4+}$.

EXPERIMENTAL

Measurements

The ^1H NMR studies were performed on a JEOL EX 270 NMR spectrometer in D_2O (DSS) solution. Electronic and circular dichroism spectra were measured using a HITACHI U-3400 spectrophotometer and a JASCO J-720 automatic recording spectropolarimeter, respectively. The elution curves were obtained using a JASCO UV-970 Intelligent UV/Vis detector.

Materials

2,2′-Bipyridine, a product of Tokyo Kasei Kogyo Co. Ltd., was dried at 80–90 °C under reduced pressure for 6 h before use. Silicon tetraiodide was prepared according to the known procedure.[5] Sodium (2*R*,3*R*)-(−)-*O*,*O*′-dibenzoyltartrate was prepared by the reaction of (2*R*,3*R*)-(−)-*O*,*O*′-dibenzoyltartaric acid monohydrate and sodium hydroxide. (2*R*,3*R*)-(−)-*O*,*O*′-dibenzoyltartaric acid monohydrate was obtained from Wako Pure Chemical Industries, Ltd. $[Si(bpy)_3]I_4 \cdot 2H_2O$ and $[Si(OH)_2(bpy)_2]I_2 \cdot 2H_2O$ were synthesized from SiI_4 and 2,2′-bipyridine following the literature method.[6] The ^1H NMR signals were assigned according to the literature.[4]

Anal. Calcd for $C_{30}H_{28}N_6I_4O_2Si$($[Si(bpy)_3]I_4 \cdot 2H_2O$)(%): C, 34.64; H, 2.71; N, 8.08. Found: C, 33.93; H, 2.53; N, 8.00. ^1H NMR: δ H(D_2O) 9.30 (H3, d), 9.04 (H4, t), 8.21 (H5, t), 7.78 (H6, d). UV/VIS: ν_{max}/cm^{-1} (log ε), 24400 (sh), 29400(4.74), 30650(4.77).

Anal. Calcd for $C_{20}H_{18}N_4I_2O_2Si \cdot 2H_2O$($[Si(OH)_2(bpy)_2]I_2 \cdot 2H_2O$)(%): C, 36.17; H, 3.34; N, 8.44. Found: C, 36.78; H, 3.32; N, 8.26. ^1H NMR: δ H(D_2O) 9.62 (d), 8.88 (d), 8.77 (t), 8.69 (d), 8.34 (t), 8.26 (t), 7.54 (t), 7.26 (d), UV/VIS: ν_{max}/cm^{-1} (log ε), 31150(4.43), 32500(4.44).

Optical Resolution

The complex $[Si(bpy)_3]I_4 \cdot 2H_2O$, (2 mg dissolved in a few "mL" of water) was poured on an SP-Sephadex C-25 column (diameter, 4.3 cm; length, 50 cm) and eluted with a 0.16 M sodium (2*R*,3*R*)-(−)-*O*,*O*′-dibenzoyltartrate solution at the rate of 2 mL per minute. The absorbance of effluent at 340 nm (cell thickness, 1 cm) was plotted against the volume of the effluent. The effluents containing two isomers were separately diluted with water and were adsorbed again on a small column of SP-Sephadex. The column was washed with a large amount of 0.01 M HCl, and then the complex was eluted with 1.0 M HCl. Each effluent was evaporated to dryness in a vacuum desiccator over NaOH and P_2O_5 to give the chloride of the complex. The perchlorate salt was precipitated from an aqueous solution of the chloride salt by addition of $NaClO_4$. The resulting orange-red crystals were recrystallized from water.

CD(in water) for Λ-$[Si(bpy)_3](ClO_4)_4$: ν_{max}/cm^{-1} ($\Delta\varepsilon$), 29400(+208.3), 32300(−72.1), 42600(+24.0), 45800(−44.9), 48300(+17.6); Δ: 29400 (−208.5), 32300(+72.0), 42700(−24.2), 45800(+44.6), 48300(−17.4).

The resolution of $[Si(OH)_2(bpy)_2]I_2$ was carried out by fractional crystallization of a diastereomeric salt with half-equimolar [(+)-tartrato]-antimonate(III). The less soluble salt contained (+)-$[Si(OH)_2(bpy)_2]^{2+}$. (+)-$[Si(OH)_2(bpy)_2]Cl_2$ was obtained by ion-exchanging the diastereomeric salt.

CD (in 0.001 M HCl) of (+)-$[Si(OH)_2(bpy)_2]Cl_2$: ν_{max}/cm^{-1} (observed $\Delta\varepsilon$), 30900(+18.7), 32900(−15.9).

RESULTS AND DISCUSSION

Figure 2 shows the elution curve in terms of the absorbance and the corresponding curve in terms of the apparent dissymmetry factor ($\Delta\varepsilon_{340}/\varepsilon_{340}$). The dotted lines show the plots of the dissymmetric factors for the two elution bands, deduced from the $\Delta\varepsilon_{340}/\varepsilon_{340}$ values on the assumption that the initial and final constant values of $\Delta\varepsilon_{340}/\varepsilon_{340}$ correspond to the $\Delta\varepsilon_{340}/\varepsilon_{340}$ values of 100% optical purity. The absorption and circular dichroism spectra are shown in Figure 3. According to exciton theory, the absolute configurations of the faster and slower-moving isomers were assigned to Λ and Δ, respectively.

In order to study the chromatographic elution mechanism, the resolution of $[Si(bpy)_3]^{4+}$ on an SP-Saphadex column (φ1.0 cm × 60 cm) was attempted by use of an aqueous solution of 0.08 M potassium [(+)-tartrato]antimonate(III) ($K_2[Sb_2\{(+)\text{-tart}\}_2]$), 0.32 M sodium (+)-hydrogentartrate (NaHtart), 0.2 M sodium (+)-tartrate(Na_2tart), 0.16 M sodium (2*R*,3*R*)-(−)-*O*,*O*′-dibenzoyltartrate($Na_2(benz)_2$tart) under the same conditions (2 mg, 1.0–1.5 mL/min). The complex was separated into the two optical isomers only by sodium (2*R*,3*R*)-(−)-*O*,*O*′-dibenzoyltartrate. For the others, resolutions were partial. The faster-moving isomer by NaHtart and Na_2tart was Λ-$[Si(bpy)_3]^{4+}$, and the elution order agrees with that with $Na_2(benz)_2$tart as the eluent. The faster-moving isomer by $K_2[Sb_2\{(+)\text{-tart}\}_2]$ was Δ-$[Si(bpy)_3]^{4+}$.

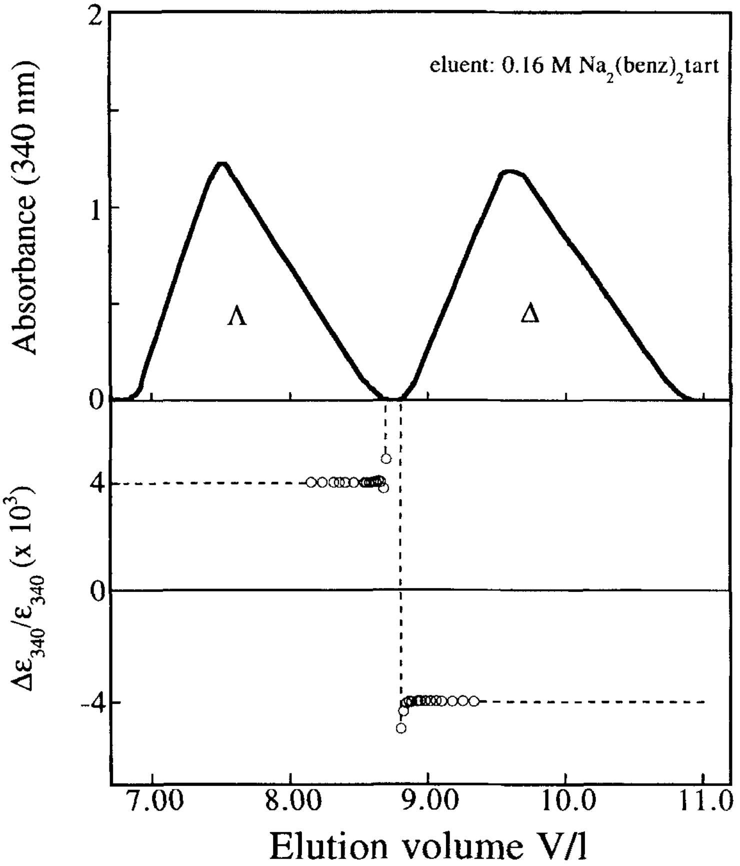


FIGURE 2 The elution curve of $[Si(bpy)_3]^{4+}$ and the corresponding curve in terms of the apparent dissymmetric factor (Δε/ε).

Force-field calculations were also carried out to elucidate the elution mechanism for all the systems above. For the systems containing the doubly negative charged ions, (+)-tartrate, (−)-dibenzoyltartrate, and [(+)-tartrato]-antimonate(III) which have the same absolute configurations of the tartrate skeletons, the 1 : 2 ion pairs were assumed, and their structures and strain energies were obtained by empirical force-field calculations. For the system containing (+)-hydrogentartrate ions, a 1 : 4 ion pair was assumed. For the charge of Si, +2 was adopted. The other parameters were described previously.[3b]

Table I shows the results of the strain energies calculated for diastereomers containing Λ- or Δ-$[Si(bpy)_3]^{4+}$. The energy differences between

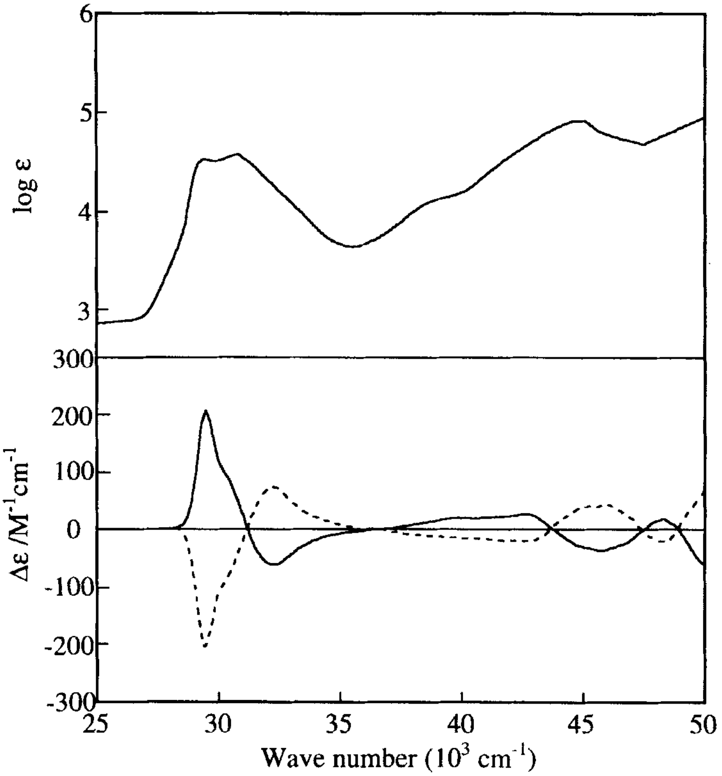


FIGURE 3 Absorption and CD spectra of Λ- (—) and Δ- $[Si(bpy)_3]^{4+}$ (- -).

TABLE I Total strain energies of ion pairs by force field calculations (kcal/mol)

Ion associated species	*Containing* Λ *enantiomer*	*Containing* Δ *enantiomer*	*Energy difference* (Λ – Δ)
$[Si(bpy)_3]$ $[(benz)_2tart]_2$	−114.4	−97.1	−17.3
$[Si(bpy)_3]$ $[Sb_2\{(+)\text{-}tart\}_2]_2$	+749.1	+745.7	+3.4
$[Si(bpy)_3]$ $[(+)\text{-}tart]_2$	−149.9	−148.4	−1.5
$[Si(bpy)_3]$ $[(+)\text{-}Htart]_4$	−258.9	−245.2	−13.6

$[(benz)_2tart]^{2-}$ = (2*R*,3*R*)-(−)-*O*,*O*′-dibenzoyltartrate ion.
$[Sb_2\{(+)\text{-}tart\}_2]^{2-}$ = (2*R*,3*R*)-(+)-tartratoantimonate(III) ion.
$[(+)\text{-}tart]^{2-}$ = (2*R*,3*R*)-(+)-tartrate ion, $[(+)\text{-}Htart]^{-}$ = (2*R*,3*R*)-(+)-hydrogentartrate ion.

the diastereomeric ion-pairs are given in the last column in the table. The $[Si(bpy)_3]\{(benz)_2tart\}_2$ system, where complete resolution was achieved, gives a larger energy difference (−17.3 kcal/mol) than the other systems. The negative sign of the energy differences suggests that the Λ isomer will be eluted faster than the Δ isomer, since the eluent (resolving agent) interacts

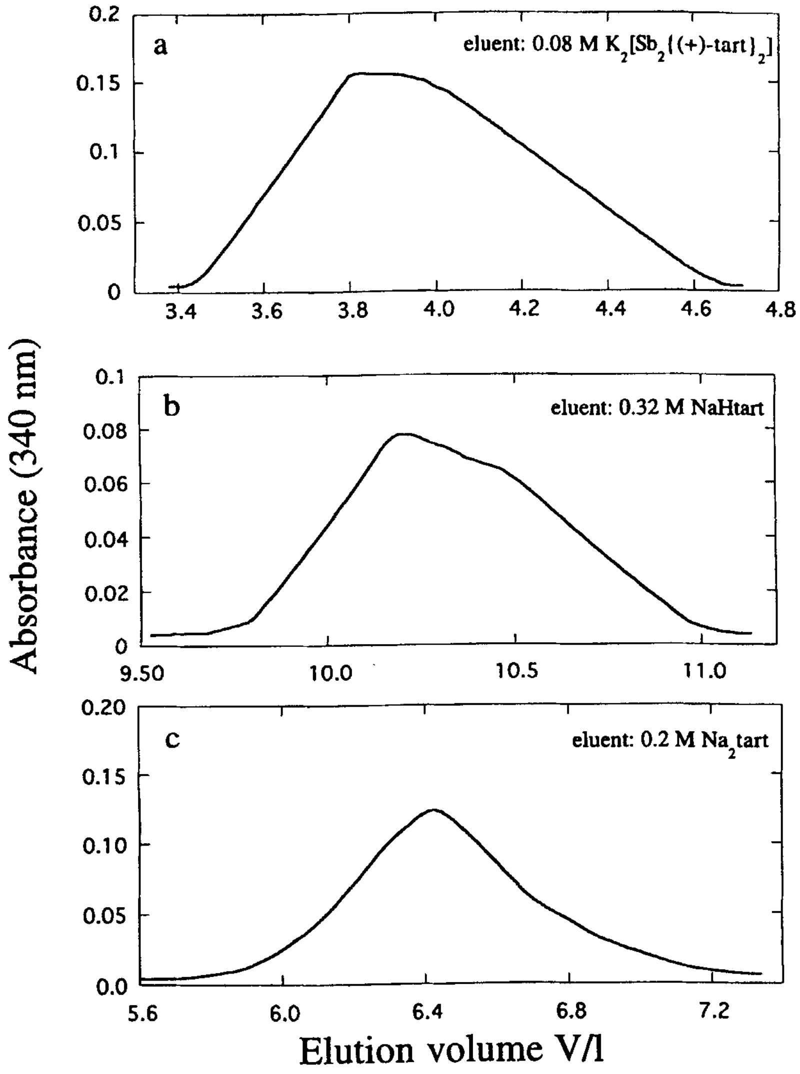


FIGURE 4 The elution curve of $[Si(bpy)_3]^{4+}$. Eluents: a, $K_2[Sb_2\{(+)\text{-tart}\}_2]$; b, NaHtart; c, Na_2tart.

more strongly with the Λ isomer. Only the $[Si(bpy)_3][Sb_2\{(+)\text{-tart}\}_2]_2$ system giving the inverse elution order (the Δ isomer is eluted faster than the Λ isomer), shows the positive sign. Thus, these results correspond to the present experimental ones. Structures of the calculated diastereomers are shown in Figure 6 for the systems with (−)-dibenzoyltartrate. The corresponding stereoscopic figures are also given in Figure 7.

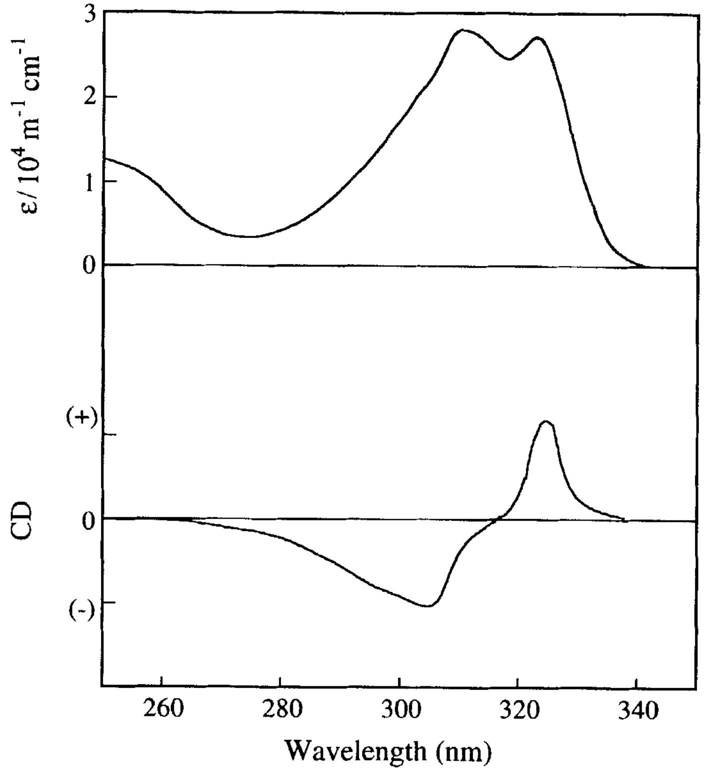


FIGURE 5 Absorption and CD spectra of (+)-$[Si(OH)_2(bpy)_2]^{2+}$ which forms the less-soluble $[Sb_2\{(+)\text{-tart}\}_2]^{2-}$ salt (0.001 M HCl).

The optical isomer, (+)-$[Si(OH)_2(bpy)_2]^{2+}$ obtained from the less-soluble part of the diastereomer with $[Sb_2\{(+)\text{-tart}\}_2]^{2-}$, exhibits the same CD pattern as Λ-(+)-$[Si(bpy)_3]^{4+}$: a major positive CD band at lower frequency and a negative CD band at higher frequency in the region of the lowest-energy ligand $\pi - \pi^*$ transition with long-axis polarization (Figure 5). On the basis of exciton theory, the isomer (+)-$[Si(OH)_2(bpy)_2]^{2+}$ was assigned to the Λ-configuration. The CD intensity (in 0.001 M HCl) of (+)-$[Si(OH)_2(bpy)_2]^{2+}$ decreased to one-half its initial value after 10 h at 5 °C during which time the absorption spectrum of the complex remained unchanged. Thus the optically active bis complex slowly racemizes.

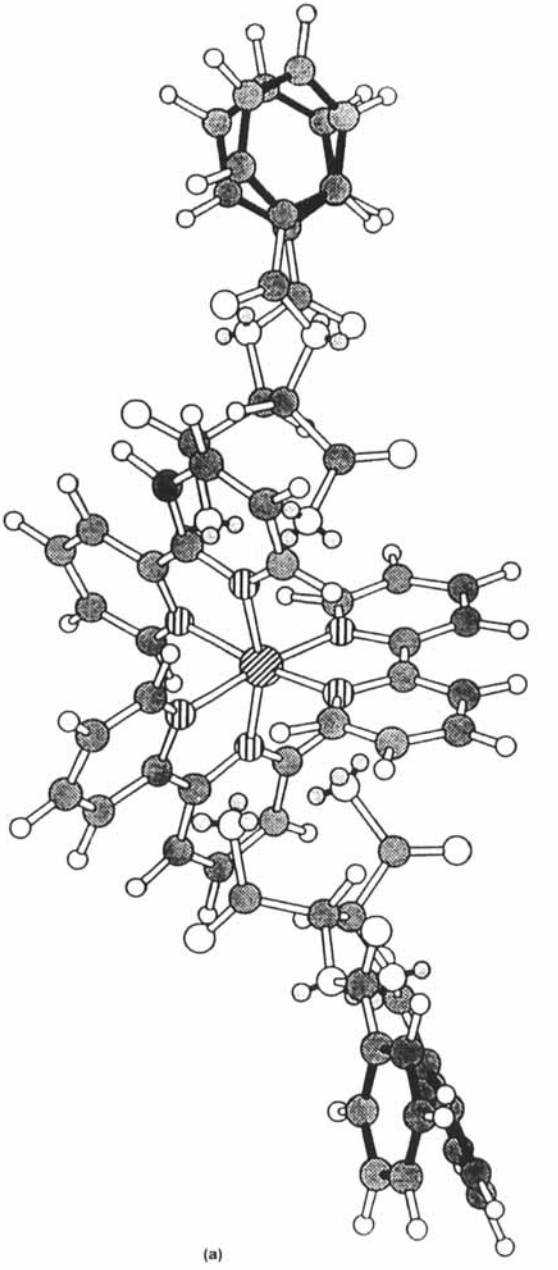


FIGURE 6(a)

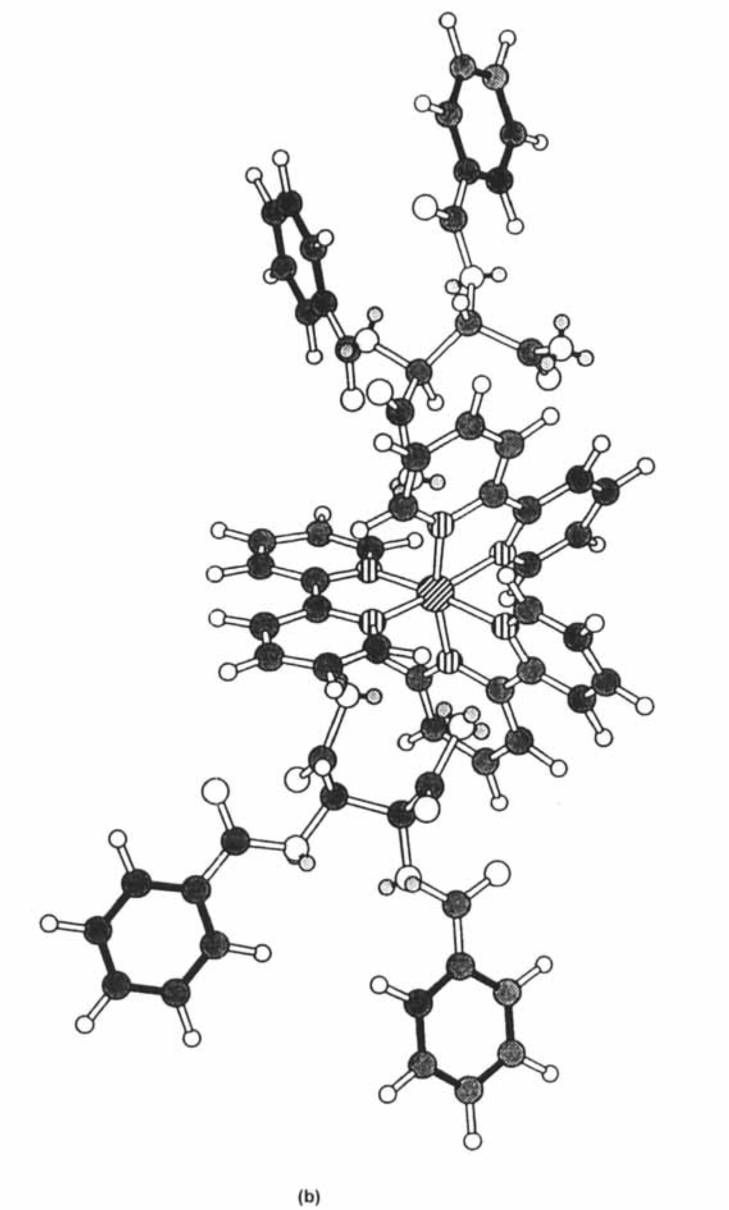


FIGURE 6(b)

FIGURE 6 (a) The structure of the ion pair between Λ-$[Si(bpy)_3]^{4+}$ and (−)-dibenzoyltartrates, (b) The structure of the ion pair between Δ-$[Si(bpy)_3]^{4+}$ and (−)-dibenzoyltartrates.

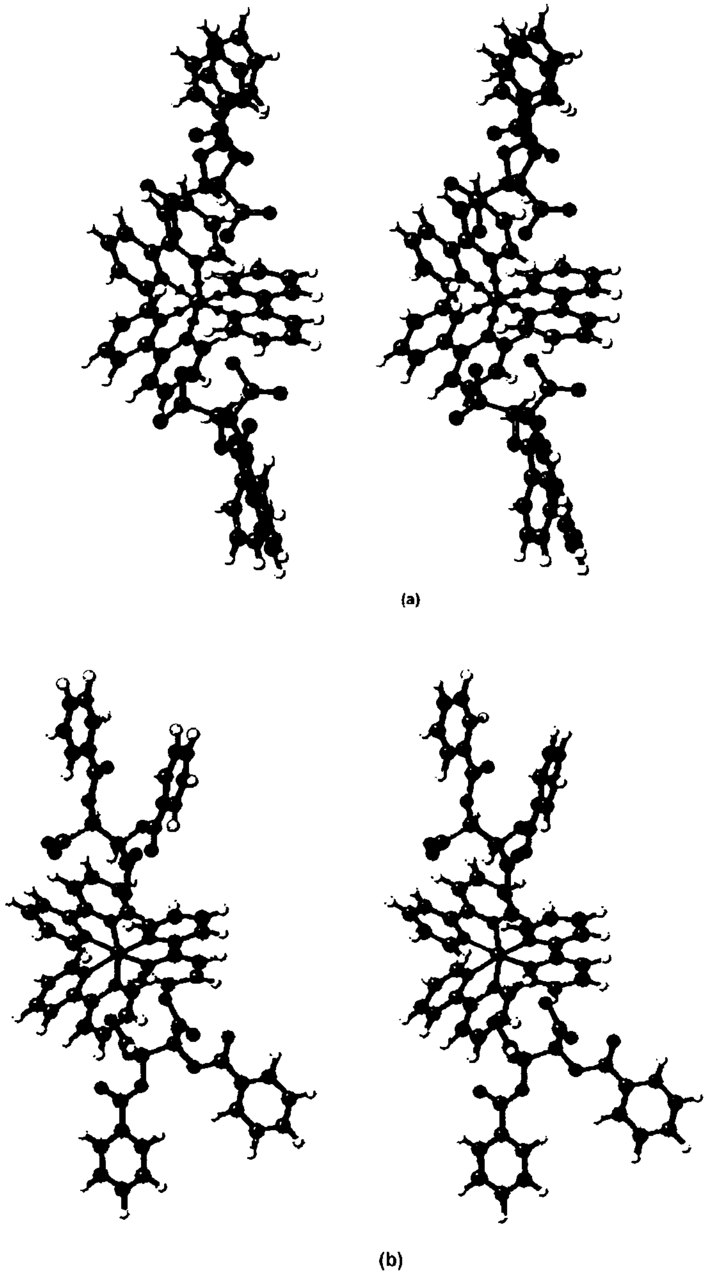


FIGURE 7 (a) The stereoscopic figure of the ion pair between Λ-$[Si(bpy)_3]^{4+}$ and (−)-dibenzoyltartrates, (b) The stereoscopic figure of the ion pair between Δ-$[Si(bpy)_3]^{4+}$ and (−)-dibenzoyltartrates.

The NMR spectrum of the racemic $[Si(OH)_2(bpy)_2]^{2+}$ complex was also measured and the observed eight proton signals are consistent with this *cis* (C_2) structure.

References

[1] (a) Hidaka, J. and Douglas, B.E. (1964) *Inorg. Chem.*, **3**, 8. (b) McCaffery, A.J., Mason, S.F. and Norman, B.J. (1969) *J. Chem. Soc.* (A), 1428. (c) Mason, S.F., Peart, B.J. and Waddell, R.E. (1973) *J. Chem. Soc. Dalton Trans.*, 944. (d) Gillard, R.D., Hill, R.E.E. and Maskill, R. (1970) *J. Chem. Soc.* (A), 1447. (e) Mason, S.F. and Peart, B.J. (1973) *J. Chem. Soc. Dalton Trans.*, 949. (f) Mason, S.F., Peart, B.J. and Waddell, R.E. (1973) *J. Chem. Soc. Dalton Trans.*, 944.

[2] Chuit, C., Corriu, R.J.P., Reye, C. and Young, J.C. (1993) *Chem. Rev.*, **93**, 1371.

[3] (a) Ohmori, Y., Namba, M., Kuroda, Y., Kojima, M. and Yoshikawa, Y. (1992) *Inorg. Chem.*, **31**, 2299. (b) Ohmori, Y., Kojima, M., Kashino, S. and Yoshikawa, Y. (1996) *J. Coord. Chem.*, **39**, 219.

[4] Kummer, D. and Koster, H. (1973) *Z. Anorg. Allg. Chem.*, **402**, 297.

[5] Szekely, G. (1957) *J. Electrochem. Soc.*, **104**, 663.

[6] Kummer, D., Gaisser, K.E., Seifert, J. and Wagner, R. (1979) *Z. Anorg. Allg. Chem.*, **459**, 145.