

This article was downloaded by:

On: 23 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

CHROMATOGRAPHIC RESOLUTION MECHANISM OF A TRIS(1, 10-PHENANTHROLINE)SILICON(IV) COMPLEX

Yasuharu Ohmori^a; Masaaki Kojima^b; Setsuo Kashino^b; Yuzo Yoshikawa^a

^a Coordination Chemistry Laboratories, Institute for Molecular Science (I. M. S, Okazaki, Japan ^b Department of Chemistry, Faculty of Science, Okayama University, Okayama, Japan

To cite this Article Ohmori, Yasuharu , Kojima, Masaaki , Kashino, Setsuo and Yoshikawa, Yuzo(1996) 'CHROMATOGRAPHIC RESOLUTION MECHANISM OF A TRIS(1, 10-PHENANTHROLINE)SILICON(IV) COMPLEX', *Journal of Coordination Chemistry*, 39: 3, 219 – 230

To link to this Article: DOI: 10.1080/00958979608024330

URL: <http://dx.doi.org/10.1080/00958979608024330>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

CHROMATOGRAPHIC RESOLUTION MECHANISM OF A TRIS(1, 10- PHENANTHROLINE)SILICON(IV) COMPLEX

YASUHARU OHMORI,^a MASA AKI KOJIMA, SETSUO KASHINO
and YUZO YOSHIKAWA^{a,*}

^a*Coordination Chemistry Laboratories, Institute for Molecular Science (I. M. S.),
Myodaiji, Okazaki 444, Japan
Department of Chemistry, Faculty of Science, Okayama University, Tsushima,
Okayama 700, Japan*

(Received 22 August 1995; Revised 13 November 1995; In final form 12 February 1996)

The ion-association constants between the optically active complex cations (Λ - or Δ -[Si(phen)₃]⁴⁺) and the resolving agent anions ([Sb₂{(+)-tart}₂]²⁻, tart = tartrate(4-) ion) were determined spectrophotometrically. Ion-association between the complex cation and the eluent anion occurred in two steps and the stereoselective interaction was observed in the second step. The second-step association constant for the Λ -enantiomer ($K_2 = 1.41 \times 10^3$) is larger than that for the Δ -enantiomer ($K_2 = 1.07 \times 10^3$). The second-step association plays a dominant role in determining the elution order in column chromatographic resolution. The molecular mechanics calculations for the ion-associated species were performed to obtain information about the microscopic interaction between the ions. The total strain energy for the species containing the Λ -enantiomer is smaller than that for the Δ -enantiomer and this can explain the experimental finding that the Λ -enantiomer is eluted faster than the Δ -enantiomer.

Keywords: silicon complex; chromatographic resolution; ion-association; molecular mechanics calculation

INTRODUCTION

Six-coordinate complexes of silicon(IV) are not as common as four-coordinate tetrahedral compounds. Though several six-coordinate Si(IV) complexes have already been synthesized, there are only a few studies of the stereochemistry of them (*e.g.* tris (β -diketonato) silicon(IV),^{1–3, 5} tris (tropolonato) silicon(IV)).⁴

*Author for correspondence.

In the preceding report,⁶ we tried to resolve the $[\text{Si}(\text{phen})_3]^{4+}$ cation by the cation-exchange chromatographic method and succeeded in complete resolution of the complex. We speculated upon the chromatographic elution mechanism from the aspects of the NMR spectra of the complex.

In the present report, we elucidate the resolution mechanism of the complex from the ion-association measurements and molecular force-field calculations.

EXPERIMENTAL

Materials

Silicon tetraiodide (SiI_4) was prepared from silicon and iodine by following the literature method.⁷ Sodium tartratoantimonate(III) ($\text{Na}_2[\text{Sb}_2\{(+)\text{-tart}\}_2]$) was prepared from antimony oxide and sodium hydrogentartrate. All other reagents were purchased commercially as guaranteed reagent chemicals and were used without further purification.

Tris(1,10-phenanthroline)silicon(IV) perchlorate, $[\text{Si}(\text{phen})_3](\text{ClO}_4)_4$, was prepared by following the literature method.⁸ Before the preparation, 1,10-phenanthroline monohydrate was dehydrated by heating at 80–100°C under reduced pressure with a liq. N_2 trap and then used for the following preparation. Silicon tetraiodide (3.2 g, 5.9 mmol) and 1,10-phenanthroline (11.2 g, 62 mmol, 3.5-fold excess) were heated in a 100 cm^3 Kjeldahl flask at 120°C for 12 h with stirring under a nitrogen atmosphere. The reaction mixture was ground and then washed with CHCl_3 (or CH_2Cl_2) to remove the unreacted ligand. The yield of the crude product was 7.6 g. The $[\text{Si}(\text{phen})_3]^{4+}$ cation was purified by a chromatographic method (column: SP-Sephadex C-25 ϕ 2.5 \times 15 cm, eluent: 0.4 M NaCl). The tris-complex perchlorate was obtained by adding a saturated NaClO_4 solution to the concentrated tris-complex solution. The perchlorate was recrystallized twice from water and dried *in vacuo*, yield 1.5 g (26%); Anal. calcd. for $\text{C}_{36}\text{H}_{24}\text{Cl}_4\text{N}_6\text{O}_{16}\cdot 0.5\text{H}_2\text{O}$: C, 44.32; H, 2.58; N, 8.61%. Found: C, 44.37; H, 2.58; N, 8.59%.

Optical Resolution of $[\text{Si}(\text{phen})_3]^{4+}$

The resolution for obtaining the elution curve was performed under the following conditions: column, SP-Sephadex C-25 ϕ 1.1 \times 46 cm; eluent, 0.08 M $\text{Na}_2[\text{Sb}_2\{(+)\text{-tart}\}_2]$; elution rate, 0.8 $\text{cm}^3 \cdot \text{min}^{-1}$. The absorbance of eluate for each 2.8 cm^3 fraction was measured at 34,500 cm^{-1} (290 nm) to obtain the elution curve.

Resolution to obtain larger amounts of enantiomers was performed under slightly different conditions: column, SP-Sephadex C-25 ϕ 4.5 \times 30 cm; eluent, 0.1 M $K_2[Sb_2\{(+)\text{-tart}\}_2]$; elution rate, 0.8 $cm^3 \cdot min^{-1}$.

Absorption spectra, optical rotations, and CD spectra were measured in aqueous solution at room temperature with a JASCO Ubest-30 spectrophotometer, a JASCO DIP-370 polarimeter, and a JASCO J-500A spectropolarimeter, respectively. Absorbance of each eluate was measured with a JASCO Ubest-30 spectrophotometer.

Determination of Association Constants

The ionic strengths of eight sample solutions containing each enantiomer were made 0.1 by the addition of NaCl. The absorbance of a sample solution was measured at 25°C and 345, 340, and 335 nm with a 5 mm light path cell.

The concentrations of the complex enantiomers and the eluting agent, tartratoantimonate(III) in the sample solutions (20 cm^3) were as follows:

Δ -enantiomer; 9.985 $\times 10^{-5}$ M with eluting agent; 0.0, 1.023 $\times 10^{-4}$, 2.046 $\times 10^{-4}$, 4.092 $\times 10^{-4}$, 6.821 $\times 10^{-4}$, 1.023 $\times 10^{-3}$, 1.988 $\times 10^{-3}$ and 2.983 $\times 10^{-3}$ M.

Δ -enantiomer; 9.859 $\times 10^{-5}$ M with eluting agent; 0.0, 1.011 $\times 10^{-4}$, 2.022 $\times 10^{-4}$, 4.043 $\times 10^{-4}$, 6.378 $\times 10^{-4}$, 1.011 $\times 10^{-3}$, 1.953 $\times 10^{-3}$ and 2.930 $\times 10^{-3}$ M.

The calculations for determination of association constants were performed using the program (CALC⁹) on an EPSON PC-286VF computer at this laboratory.

Molecular Mechanics Calculations

The calculations were performed using the program MM2KY on the IBM SP2 computer (I. M. S.). The program MM2KY was modified to be able to treat six-coordinate compounds.¹⁰ Total strain energy of a molecule is expressed as a sum of the bonded terms (bond stretching, angle bending, torsional interaction) and the non-bonded terms (van der Waals and electrostatic interactions) in Allinger's force fields. In the program MM2KY the van der Waals interactions between atoms with the atomic distance longer than 10 Å were neglected.

The partial charges on the individual atoms were determined using Pauling's electroneutrality principle.

In the present study, the charge, +1 was given to Si and +0.25 to Sb, and the residual charges of the two complex ions were uniformly distributed on all the H atoms of phen and the coordinating O (*i.e.*, the lone pairs belonging to them) of tartrato(4-) ligands, respectively.

The relative tendency of the calculated results was the same for the changes of the partial charges, 0 — +2 (Si) and 0 — +1.5 (Sb).

The sets of Si(IV)- and Sb(III)-related force constants used in the present calculations were obtained from Co(III)- and Pt(II)-related parameters used in other studies.¹⁰ The strain-free bond distances and angles were adjusted so as to reproduce well the crystallographic data obtained from the literature¹¹ and from the preliminary study of single crystal X-ray analysis of $[\text{Si}(\text{phen})_3](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$. The torsional interactions including a silicon atom or an antimony atom inside were excluded in the present force field because of the mathematical validity in octahedral complexes and the presumed slight contribution. The parameters are given in Table I (for nomenclature, see Chart 1).

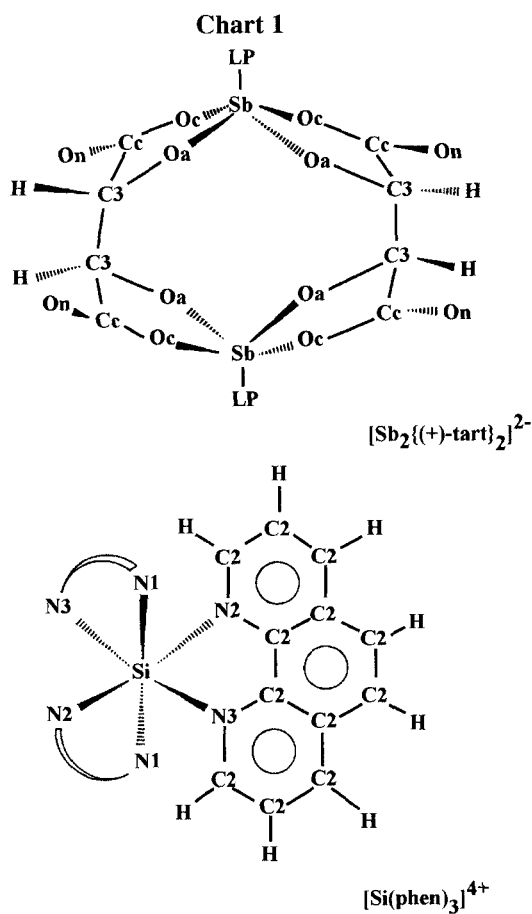


TABLE I Force Field Parameters Used in the Present Calculations. (LP = lone pair, Oa = O (alcoholic), Oc = O (carboxylic), On = O (carbonyl), C2 = C (sp²), C3 = C (sp³), Cc = C (carboxylic), Cn = C (carbonyl))

<i>Bonding interaction</i>			
	<i>force constant (mdyn·Å⁻¹)</i>		<i>equilibrium value (Å)</i>
Si—N1, N2, N3	1.75		1.91
Sb—LP	6.1		0.60
Sb—Oa	1.75		1.99
Sb—Oc	1.75		2.16
<i>Valence angle interaction</i>			
	<i>force constant (mdyn·Å·rad⁻¹)</i>		<i>equilibrium value (deg)</i>
N1—Si—N2	0.68		90.0
N2—Si—N3	0.68		90.0
N1—Si—N3	0.68		90.0
N1—Si—N1	0.68		180.0
N2—Si—N2	0.68		180.0
N3—Si—N3	0.68		180.0
Si—N1—C2	0.30		120.0
Si—N2—C2	0.30		120.0
Si—N3—C2	0.30		120.0
Oa—Sb—Oc	0.45		80.8
Oc—Sb—Oc	0.45		151.0
Oa—Sb—Oa	0.45		99.6
LP—Sb—Oc	0.35		103.0
LP—Sb—Oa	0.35		130.0
Cc—Oc—Sb	0.35		114.15
C3—Oa—Sb	0.35		117.95
LP—Oa—Sb	0.35		97.5
LP—Oc—Sb	0.35		97.5
<i>Out of plane bending parameters</i>			
N1—Si	0.05		0.0
N2—Si	0.05		0.0
N3—Si	0.05		0.0
<i>Torsion angle interaction</i>			
	<i>force constant (kcal mol⁻¹)</i>		
	V1	V2	V3
C2—C2—N1—Si	0.0	10.0	0.0
C2—C2—N2—Si	0.0	10.0	0.0
C2—C2—N3—Si	0.0	10.0	0.0
H—C2—N1—Si	0.0	10.0	0.0
H—C2—N2—Si	0.0	10.0	0.0
H—C2—N3—Si	0.0	10.0	0.0
C3—Cc—Oc—Sb	0.0	0.5	0.0
On—Cc—Oc—Sb	-3.285	5.6	0.0
C3—C3—Oa—Sb	0.8	0.0	0.0
H—C3—Oa—Sb	0.0	0.0	0.2
Cn—C3—Oa—Sb	0.0	0.0	0.09

TABLE I (Continued)

	Van der Waals interaction	
	van der Waals radius (Å)	EPS (kcal·mol ⁻¹)
Si	2.25	0.14
Sb	2.475	0.319

RESULTS AND DISCUSSION

We already reported complete resolution of the [Si(phen)₃]⁴⁺ cation.⁶ There were two eluting bands and resolution was effectively achieved. From each band, the enantiomer was isolated as the perchlorate. The specific rotations for both enantiomers were $[\infty]_{\text{D}}^{25} = \pm 2100$ (deg · g⁻¹ · cm³ · dm⁻¹). Both enantiomers were so stable in aqueous solutions that the absorption spectrum and the optical rotation remain unchanged after a month at room temperature.

The absorption and CD spectra of the complex have been reported.⁶ The numerical data are given in Table II. Both isomers have CD bands at 34,000 and 36,000 cm⁻¹ with the reverse sign. According to the exciton theory, we assigned the absolute configuration of the faster-eluted isomer as Λ and this elution order was the same as in the resolution of the [Co(phen)₃]³⁺ cation.¹²

In general, chromatographic resolution is based on the difference of the adsorption ability to the adsorbent caused by decrease of the electric (positive) charge of the adsorbing species. The ion-association between a cation and an anion acts the important part in the resolution mechanism. In order to obtain information about the interaction between the complex cation and the eluent anion in the process of resolution, we determined the ion-association constants between these ions by the spectrophotometric method.

TABLE II Spectroscopic Data for the Enantiomers of [Si(phen)₃]⁴⁺ in Aqueous Solution at 20°C

complex	absorption		circular dichroism	
	$\bar{\nu}$ cm ⁻¹	ϵ M ⁻¹ · cm ⁻¹	$\bar{\nu}$ cm ⁻¹	$\Delta\epsilon$ M ⁻¹ · cm ⁻¹
$\Lambda - (+)_\text{D} - [\text{Si}(\text{phen})_3]^{4+}$	3.50×10^4	5.94×10^4	3.40×10^4	306.3
	4.81×10^4	9.75×10^4	3.60×10^4	-233.8
$\Delta - (-)_\text{D} - [\text{Si}(\text{phen})_3]^{4+}$			4.31×10^4	37.5
			3.40×10^4	-310.6
			3.60×10^4	241.3
		4.31×10^4	-37.5	

The ion-association absorption band appeared around $30,000\text{ cm}^{-1}$ in the absorption spectra of the sample solutions containing each enantiomer (Figures 1 and 2). The molar ratios between the complex cation and the eluent anion in the sample solutions were set as follows:

$$[\text{Si}(\text{phen})_3]^{4+} : [\text{Sb}_2\{(+)-\text{tart}\}_2]^{2-} = 1 : 0.0, 1.0, 2.0, 4.0, 6.7, 10, 20, 30.$$

We can assume that the association between the complex cation and the eluent anion occurs in two steps because the electric charge of the complex cation was 4+ and the eluent anion 2-.

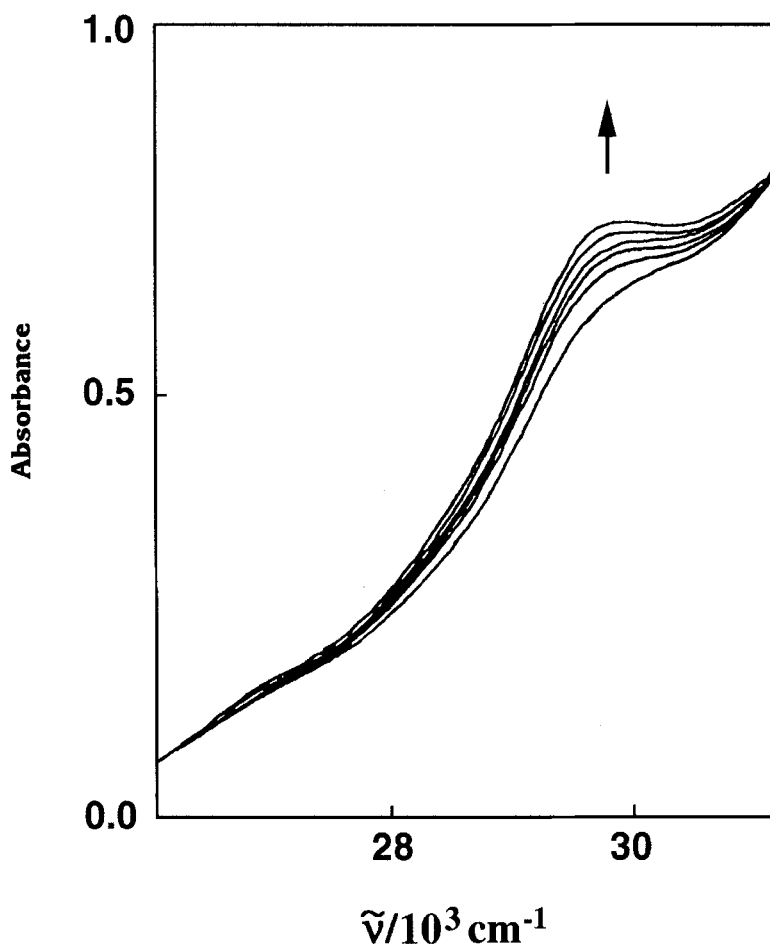


FIGURE 1 Variation of the absorption spectrum of the sample solution (containing the Λ -enantiomer).

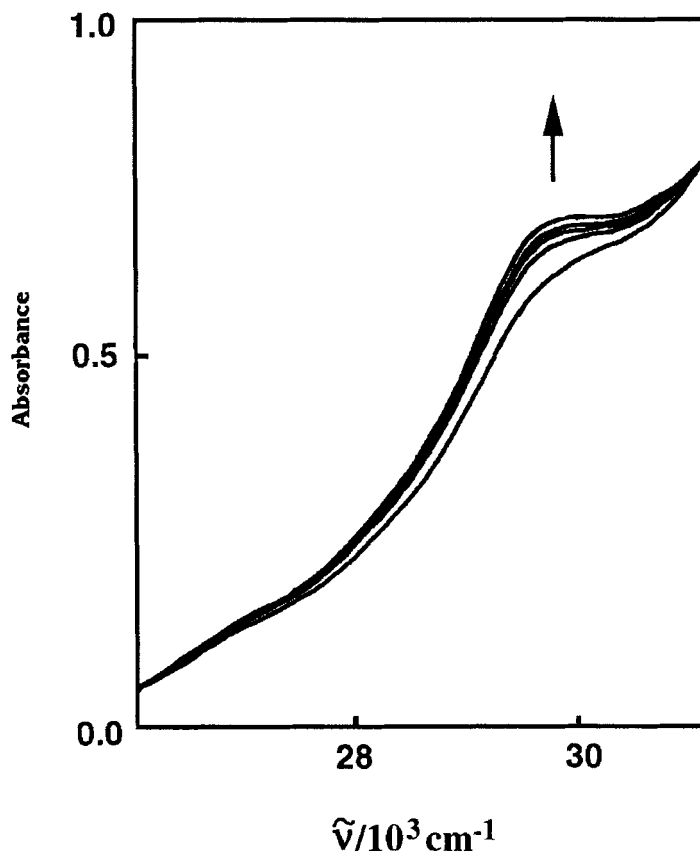
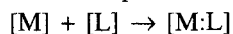


FIGURE 2 Variation of the absorption spectrum of the sample solution (containing the Δ -enantiomer).

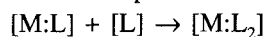
The chemical species in the sample solution might be described as follows:

the first-step association;



$$K_1 = [M:L] / [M] \cdot [L]$$

the second-step association;



$$K_2 = [M:L_2] / [M:L] \cdot [L]$$

$$A = \epsilon_0[M] + \epsilon_1 K_1[M][L] + \epsilon_2 K_1 K_2[M][L]^2 \quad (1)$$

$$C_M = [M] + K_1[M][L] + K_1 K_2[M][L]^2 \quad (2)$$

$$C_L = [L] + K_1[M][L] + 2K_1 K_2[M][L]^2 \quad (3)$$

[M], [L]: Concentration of free complex cation and free eluent anion, respectively

K_1, K_2 : Successive association constants of complex cation and eluent anion

C_M, C_L : Total concentration of the complex cation and the eluent anion, respectively

A: Absorbance of a sample solution (at 1.0 cm light path)

ϵ_0 : Molar absorption coefficient of free complex cation

ϵ_1, ϵ_2 : Molar absorption coefficients of ion-associated species

Values of $K_1, K_2, \epsilon_1, \epsilon_2$ were obtained through the calculation using the computational program CALC (using the least-squares method) and the experimental values of C_M, C_L , and A. The variations of absorbance of the sample solutions are listed in Tables III and IV.

As a result, the first-step association constant for both 1:1 ion-associated species was so large that this step does not affect the resolution. The stereoselective interaction was observed in the second-step association. The second-step association constant for the Λ -enantiomer ($K_2 = 1.41 \times 10^3$) was larger than that for the Δ -enantiomer ($K_2 = 1.07 \times 10^3$).

In general, the elution order of the enantiomers in the liquid column chromatography is governed by the relative order of the association constants. An isomer with a larger association constant is eluted faster. The elution order of the $[\text{Si}(\text{phen})_3]^{4+}$ cation is consistent with the present experimental finding.

TABLE III The Variation of the Absorbance of Sample Solutions. The Concentration of the Λ -enantiomer is 9.99×10^{-5} M in All Sample Solutions

wavelength (nm)	the concentration of eluting reagent in sample solutions ($\times 10^{-4}$ M)							
	0.0	1.02	2.05	4.09	6.82	10.23	19.88	29.83
335	0.692	0.694	0.695	0.703	0.715	0.720	0.728	0.738
340	0.592	0.630	0.638	0.648	0.660	0.666	0.678	0.691
345	0.469	0.497	0.502	0.511	0.521	0.526	0.536	0.548

TABLE IV The Variation of the Absorbance of Sample Solutions. The Concentration of the Δ -enantiomer is 9.86×10^{-5} M in All Sample Solutions

wavelength (nm)	the concentration of eluting reagent in sample solutions ($\times 10^{-4}$ M)							
	0.0	1.01	2.02	4.04	6.74	10.11	19.53	29.30
335	0.642	0.678	0.682	0.689	0.698	0.701	0.707	0.715
340	0.577	0.621	0.626	0.634	0.646	0.650	0.657	0.668
345	0.455	0.490	0.493	0.500	0.511	0.515	0.519	0.529

In order to obtain more information about the interaction between the complex cation and the eluent anion, we performed molecular mechanics calculations for 1:2 ion-associated species. The distance between the complex cation and the two eluent anions was set about 15 Å at the start of the calculations. Three ions approached each other for the calculations. The final energy-minimized structures for 1:2 ion-associated species are shown in Figures 3 and 5, where the lone pairs are omitted for simplicity. The eluent anions have approached the complex cation along the C_3 axis of the cation. In order to understand the orientational relationship of the three ions, the stereoviews from the C_3 axis of the cation are given in Figures 4 and 6. The individual calculated strain-energy values are listed in Table V. The total strain energy for Λ -[Si(phen)₃] · [Sb₂{(+)-tart}₂]₂ is smaller than that for Δ -[Si(phen)₃] · [Sb₂{(+)-tart}₂]₂ by approximately 20 kcal · mol⁻¹. This result agrees with the finding of the determination of ion-association constants.

TABLE V The Result of Strain Energy Calculations of 1:2 Ion-associated Species (kcal · mol⁻¹)

	$\{\Lambda\text{-[Si(phen)}_3\text{]}\cdot\text{[Sb}_2\text{}\{(+)\text{-tart}\}_2\}_2\}$	$\{\Delta\text{-[Si(phen)}_3\text{]}\cdot\text{[Sb}_2\text{}\{(+)\text{-tart}\}_2\}_2\}$
Compression	5.20	5.97
Bending	40.12	39.64
van der Waals	0.58	4.02
Torsional	-16.35	-15.21
Charge	126.67	144.01
Total	156.23	178.44

Thus, it could be elucidated that the Λ -[Si(phen)₃]⁴⁺ cation which forms a more stable ion-pair with eluent anions is eluted faster than the Δ .

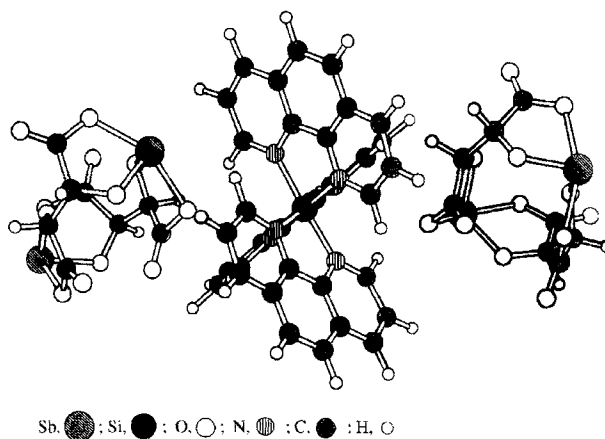


FIGURE 3 The most stable structure for the ion pair (containing the Δ -enantiomer) from the MM2 calculations. Views from the C_2 axis of the complex cation.

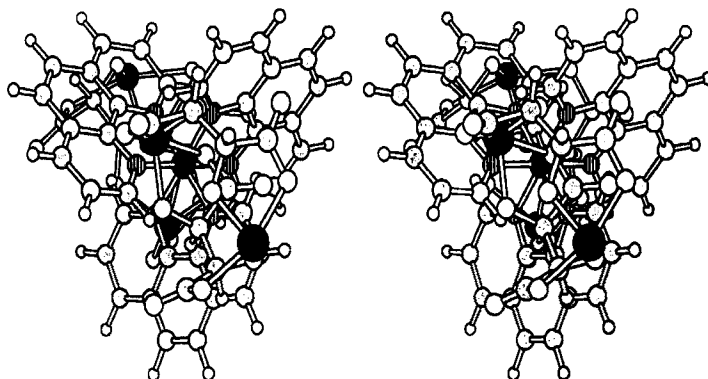


FIGURE 4 The most stable structure for the ion pair (containing the Δ -enantiomer) from the MM2 calculations. Stereoviews from the C_3 axis of the complex cation.

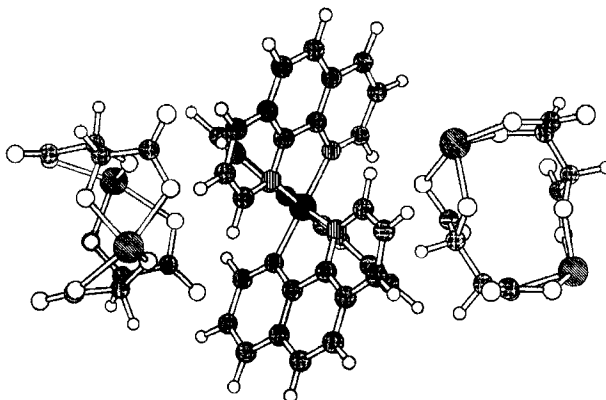


FIGURE 5 The most stable structure for the ion pair (containing the Δ -enantiomer) from the MM2 calculations. View from the C_2 axis of the complex cation.

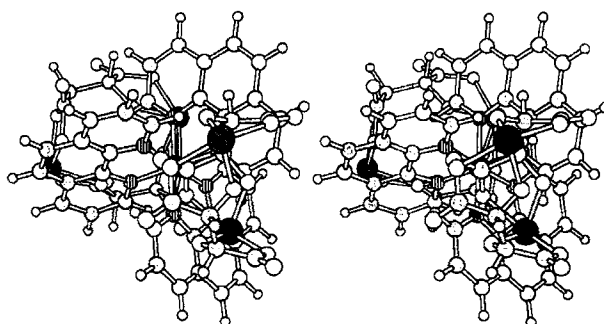


FIGURE 6 The most stable structure for the ion pair (containing the Δ -enantiomer) from the MM2 calculations. Stereoviews from the C_3 axis of the complex cation.

Acknowledgments

We thank the Ministry of Education, Science and Culture of Japan (Scientific Research No. 05403009) for financial support, the X-ray Laboratory of Okayama University for the crystal structure determination, the I. M. S. Computer Center for the use of the IBM SP2 computer, and Prof. K. Sawada and Dr. K. Sato (Niigata Univ.) for their permission to use their program (CALC).

References

- [1] E. Larsen, S.F. Mason and G.H. Searle, *Acta Chem. Scand.*, **20**, 191 (1966).
- [2] T. Inoue and K. Saito, *Bull. Chem. Soc. Jpn.*, **46**, 2417 (1973).
- [3] T. Inoue, J. Fujita and K. Saito, *Bull. Chem. Soc. Jpn.*, **48**, 1228 (1975).
- [4] T. Ito, T. Inoue and K. Saito, *Inorg. Nucl. Chem. Lett.*, **5**, 781 (1969).
- [5] T. Shimizutani and Y. Yoshikawa, *Inorg. Chem.*, **30**, 3237 (1991).
- [6] Y. Ohmori, M. Namba, Y. Kuroda, M. Kojima and Y. Yoshikawa, *Inorg. Chem.*, **31**, 2299 (1992).
- [7] G. Szekely, *J. Electrochem. Soc.*, **104**, 663 (1957).
- [8] D. Kummr, K.E. Gaisser, J. Seifert and R. Wagner, *Z. Anorg. Allg. Chem.*, **459**, 145 (1979).
- [9] K. Sawada and K. Sato, personal communication.
- [10] Y. Yoshikawa, *J. Comput. Chem.*, **11**, 326 (1990).
- [11] L. Bohatý and R. Fröhlich, *Z. Kristallogr.*, **163**, 261 (1983).
- [12] Y. Yoshikawa and K. Yamasaki, *Coord. Chem. Rev.*, **28**, 205 (1979), and the references cited therein.
- [13] (a) E.C. Niederhoffer, A.E. Martell, P. Rudolf and A. Clearfield, *Cryst. Struct. Comm.*, **11**, 1951 (1982). (b) J. Baker, L.M. Engelhardt, B.N. Figgis and A.H. White, *J. Chem., Soc., Dalton Trans.*, 530 (1975). (c) A. Zalkin, D.H. Templeton and T. Ueki, *Inorg. Chem.*, **12**, 1641 (1973). (d) H.A. Goodwin, D.L. Kepert, J.M. Patrick, B.W. Skelton and A.H. White, *Aust. J. Chem.*, **37**, 1817 (1984). (e) D. Boys, C. Escobar and O. Wittke, *Acta Cryst.*, **C40**, 1359 (1984). (f) G.B. Deacon, C.L. Raston, D. Tunaley and A.H. White, *Aust. J. Chem.*, **32**, 2195 (1979).