Optical Resolution of a Six-Coordinate Silicon(IV) Complex with a Tripodal Hexadentate Ligand

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The reaction of silicon tetraacetate with a tripodal hexadentate ligand (H_3L = 1,1,1-tris(*N*-salicylideneaminomethyl)ethane) afforded the colorless $[Si(L)]^+$ complex. The X-ray analysis of the complex revealed that the Si–N bond distance, av. 1.926(2) Å, is much longer than the Si–O bond distance, av. 1.723(2) Å. The complex is stable toward hydrolysis and could be optically resolved by fractional crystallization of the diastereomeric salt with (–)-dibenzoyl-L-tartaric acid.

The formation and structure of silicon(IV) complexes with coordination number greater than four (hypervalent silicon complexes) are areas of lively interest.[1] Few complexes of silicon are stable in aqueous solution. We have been interested in stereoisomerism of water-soluble silicon(IV) complexes and reported the optical resolution and mechanism of resolution of $[Si(bpy)_3]^{4+}$ and $[Si(phen)_3]^{4+}$ by column chromatography.[2] The stability of these complexes toward hydrolysis seems to be related to the hydrophobicity of the ligands. If the central silicon ion is surrounded by a cage-like ligand, it will be protected against attack by a water molecule. Here we report the preparation, resolution, and structure of a silicon(IV) complex with a half-caged tripodal hexadentate ligand (H_3L = 1,1,1-tris(*N*-salicylideneaminomethyl)ethane, Figure 1).

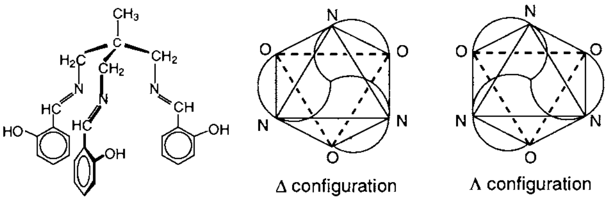

Figure 1. The H_3L ligand and a pair of enantiomers of $[Si(L)]^+$, Δ and Λ.

The ligand, H_3L, was prepared by condensation of tris(aminomethyl)ethane[3] and salicylaldehyde in ethanol in a 1 : 3 molar ratio. Yield: 86%.[4] The acetate of the silicon(IV) complex was prepared by the reaction of silicon tetraacetate with the ligand in benzene. The reaction mixture was heated under reflux, and after the evolution of acetic acid had stopped, the solution was evaporated to yield colorless crystals. The acetate was converted into the perchlorate: an aqueous solution of $NaClO_4$ was added to an aqueous solution of the complex acetate to precipitate the perchlorate of the complex, $[Si(L)]ClO_4 \cdot H_2O$.[5]

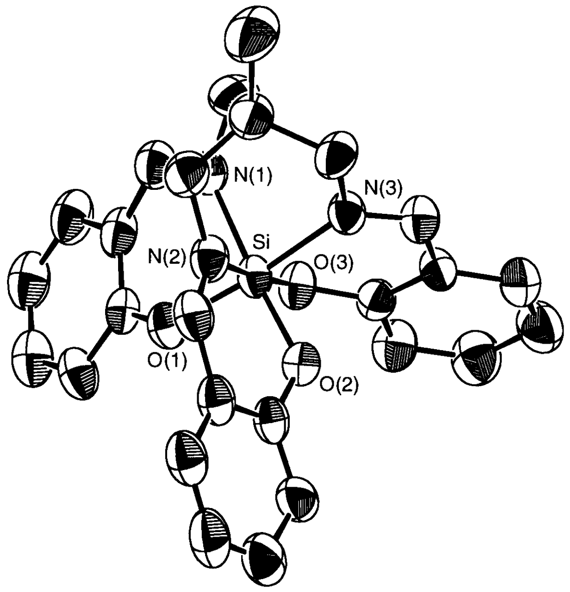

Figure 2. ORTEP view for the complex cation, $[Si(L)]^+$ with 50% probability ellipsoids. Selected bond lengths (Å) and bond angles (deg): Si–O(1), 1.731(3); Si–O(2), 1.725(3); Si–O(3), 1.714(3); Si–N(1), 1.919(4); Si–N(2), 1.926(4); Si–N(3), 1.933(4); O(1)–Si–N(1), 90.2(2); O(2)–Si–N(2), 90.5(2); O(3)–Si–N(3), 90.8(2); N(1)–Si–N(2), 87.0(2); N(1)–Si–N(3), 85.7(2); N(2)–Si–N(3), 86.3(2).

X-Ray analysis was performed for the complex acetate, $[Si(L)]OAc \cdot 2HOAc \cdot H_2O$.[6] The coordination geometry around the silicon atom is approximately octahedral (Figure 2). The Si–N bond distance, av. 1.926(2) Å, is much longer than the Si–O bond distance, av. 1.723(2) Å. These distances should be compared with those of the corresponding cobalt(III) complex, $[Co(L)] \cdot H_2O$, the Co–N and Co–O bond distances being av. 1.911(3) and av. 1.901(2) Å, respectively.[7] The data demonstrate a weak affinity of silicon toward nitrogen when the van der Waals radii of N (1.55 Å) and O (1.52 Å) and ionic radii for octahedral Si^{4+} (0.54 Å) and Co^{3+} (0.69 Å) are taken into consideration.

The silicon complex was resolved by fractional crystallization of the diastereomeric salt with (–)-dibenzoyl-L-tartaric acid (H_2DBT): To an ethanol solution (10 cm^3) of $[Si(L)]OAc \cdot 2HOAc \cdot H_2O$ (0.30 g, 0.46 mmol) was added an ethanol solution (5 cm^3) of $H_2DBT \cdot H_2O$ (0.046 g, 0.13 mmol) with stirring. Water was added dropwise until the solution became slightly turbid. The mixture was left at room tempera-

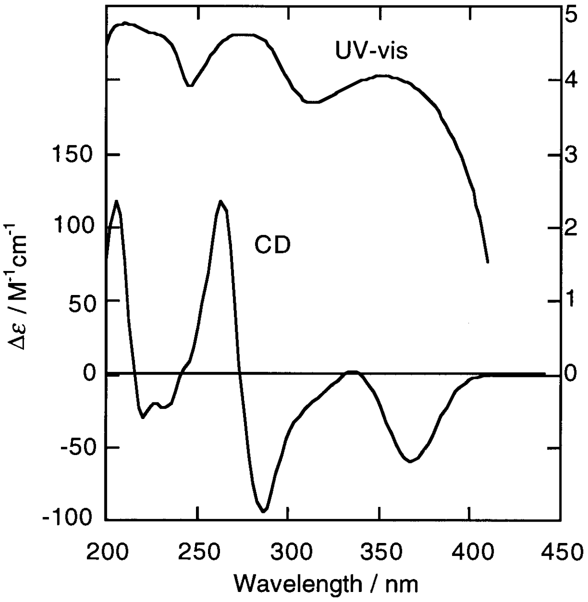

Figure 3. UV-vis and CD spectra of Δ-$[Si(L)]^+$ in ethanol.

ture and the colorless precipitate ($[Si(L)]_2DBT$) was collected by filtration. The optically pure isomer of $[Si(L)]^+$ was obtained by repeated crystallization (*ca.* four times) from ethanol by adding water until the dissymmetry factor ($g = \Delta\varepsilon/\varepsilon$) became constant. The resolving agent was removed by adding $NaClO_4$ to an ethanol solution of the diastereoisomeric salt. The perchlorate salt of the complex was collected by filtration.

Figure 3 shows the UV-vis and CD spectra of the complex in ethanol obtained from the less soluble part of the diastereomeric salt. The CD spectrum shows two negative-positive couplets around 350 and 270 nm, and these couplets can be assigned to the azomethine π–π* and benzene ring π–π* transitions, respectively.[8] Exciton theory predicts that when an octahedral tris(chelate) complex takes the Δ configuration, the negative component will be at lower energy, and at higher energy when the chirality is Λ.[9] Thus, the absolute configuration of the present isomer can be assigned to Δ (Figure 1). This complex perchlorate was converted into the water-soluble acetate by the use of an anion exchanger (Dowex 1 X8, acetate form), and the stability toward hydrolysis was examined by monitoring the change in CD. The CD strength of the complex in water remained unchanged even after one week at 25 °C. The stability may be related to the half-caged structure of the tripodal ligand; the central silicon ion will be protected against attack by a water molecule.

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References and Notes

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4 Anal. Found: C, 72.41; H, 6.23; N, 9.88%. Calcd for $C_{26}H_{27}N_3O_3$: C, 72.71; H, 6.34; N, 9.78%.

5 Anal. Found: C, 54.22; H, 4.68; N, 7.53%. Calcd for $C_{26}H_{26}ClN_3O_8Si$ = $[Si(L)]ClO_4 \cdot H_2O$: C, 54.59; H, 4.58; N, 7.35%.

6 The colorless crystals were obtained by recrystallization from chloroform–hexane. Crystallographic data for $[Si(L)]OAc \cdot 2HOAc \cdot H_2O$: formula weight 651.75, monoclinic, space group $P2_1/n$ (No. 14), a = 11.275(5), b = 15.985(3), c = 18.303(4) Å, β = 104.11(3)°, V = 3199(2) Å^3, Z = 4, D_C = 1.35 g cm^{-3}, μ(Mo Kα) = 1.29 cm^{-1}, 7546 unique reflections ($2\theta_{max}$ = 55°), 3562 ($|F_0| > 3\sigma(|F_0|)$) used in the refinement, R = 0.066, R_w = 0.077.

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