

with the large close boron hydrides, which are their geometrical duals.⁶

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Stereochemistry of Six-Coordinated Silicon Complexes. 2. Optical Resolution of $[\text{Si}(\alpha\text{-diimine})_3]^{4+}$ ($\alpha\text{-Diimine} = \text{bpy, phen}$)

Six-coordinated complexes of silicon(IV) are not very familiar as compared to four-coordinated tetrahedral compounds. Though several six-coordinated Si(IV) complexes have already been synthesized, there are few studies of the isomerism.

In the present paper, we report the complete optical resolution of $[\text{Si}(\text{phen})_3]^{4+}$. $[\text{Si}(\text{phen})_3]^{4+}$ was synthesized from SiI_4 and 1,10-phenanthroline following the literature method¹ and chromatographically purified. The resolution was performed by a chromatographic method using an SP-Sephadex C-25 column ($\phi = 1.1 \text{ cm} \times 46 \text{ cm}$) as an adsorbent and a 0.08 M aqueous solution of sodium ((+)-tartrato)antimonate(III),² $\text{Na}_2[\text{Sb}_2((+)\text{-tart})_2]$ as an eluent. Figure 1 shows the elution curve. The two elution bands are completely separated, and complete resolution is effectively achieved. Each enantiomer is so stable in aqueous solution that the absorption spectrum and optical rotation were unchanged after a month at room temperature. There are some examples of enantiomeric six-coordinated silicon(IV) complexes,³⁻⁶ but all of them are unstable in aqueous solutions. This is the first example of stable (in water) enantiomers of six-coordinated octahedral silicon(IV) complexes. The absorption and circular dichroism (CD) spectra are shown in Figure 2. According to exciton theory,⁷ the absolute configuration of the faster-moving (+)₅₈₉ isomer can be assigned to Δ . Though we have already attempted the resolution of $[\text{Si}(\text{bpy})_3]^{4+}$ by a chromatographic method, the separation of enantiomers was insufficient under the same conditions. Sodium (+)-tartrate was found to be a less effective eluting agent for both complexes.

The elution order (Δ moves faster than Δ) of the enantiomers for both the bpy and phen complexes is the same as that observed for the corresponding cobalt(III) complexes.²

The ¹H NMR spectra of $[\text{Si}(\text{bpy})_3]^{4+}$ and $[\text{Si}(\text{phen})_3]^{4+}$ were measured in the presence and absence of $[\text{Sb}_2((+)\text{-tart})_2]^{2-}$, in order to elucidate the mechanism of the chromatographic resolution, i.e. the stereoselective interaction between the complex ions and

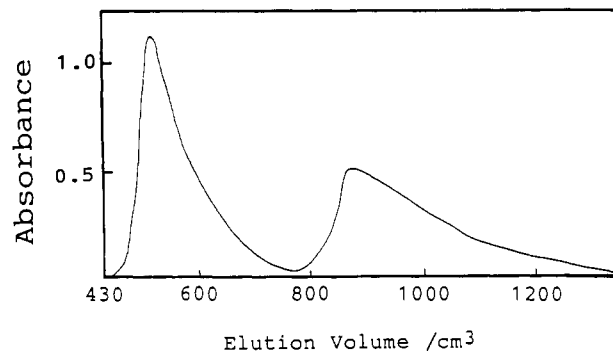


Figure 1. Elution curve of $[\text{Si}(\text{phen})_3]^{4+}$ on an SP-Sephadex column. Chromatographic conditions: column, SP-Sephadex C-25, $\phi = 1.1 \text{ cm} \times 46 \text{ cm}$; eluent, $\text{Na}_2[\text{Sb}_2((+)\text{-tart})_2]$ (0.08 M); flow rate, $0.8 \text{ cm}^3 \text{ min}^{-1}$; UV detection, 290 nm.

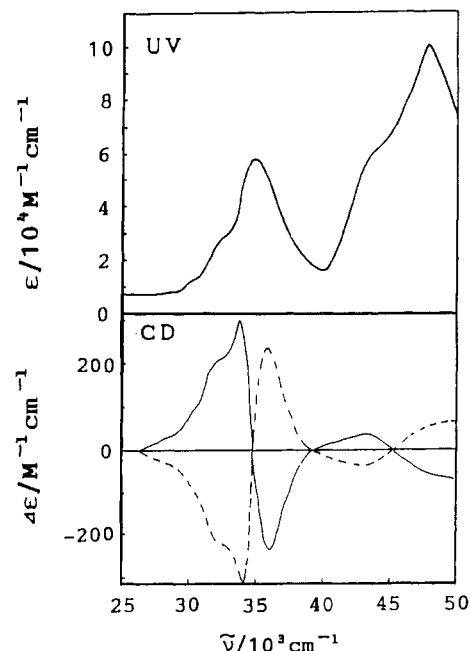


Figure 2. Absorption and CD spectra of (+)₅₈₉ (—) and (-)₅₈₉ (---) $[\text{Si}(\text{phen})_3]^{4+}$.

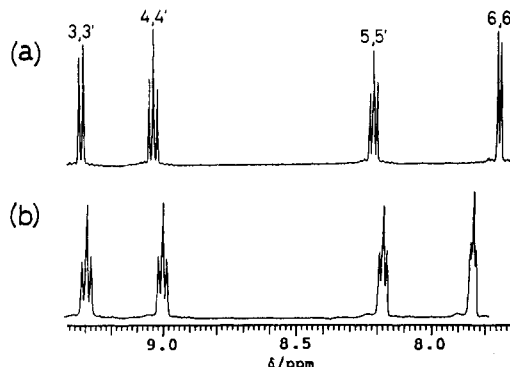
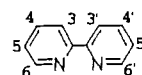


Figure 3. ¹H NMR spectra (500 MHz) of $[\text{Si}(\text{bpy})_3]^{4+}$ (ca. 0.02 M) in D_2O , (a) in the absence and (b) in the presence of $\text{Na}_2[\text{Sb}_2((+)\text{-tart})_2]$ (0.4 M).

(tartrato)antimonate(III) ions. Figures 3 and 4 show the ¹H NMR spectra of an ca. 0.02 M D_2O solution of $[\text{Si}(\text{bpy})_3]^{4+}$ and an ca. 0.004 M D_2O solution of $[\text{Si}(\text{phen})_3]^{4+}$, respectively. The largest

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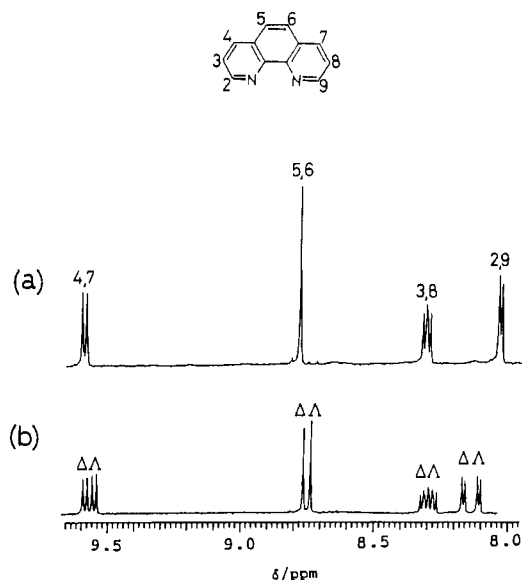


Figure 4. ^1H NMR spectra (500 MHz) of $[\text{Si}(\text{phen})_3]^{4+}$ (ca. 0.004 M) in D_2O , (a) in the absence and (b) in the presence of $\text{Na}_2[\text{Sb}_2(+)\text{-tart}]_2$ (0.08 M).

chemical shift difference between the enantiomers due to the addition of the eluting agent is observed for the 6,6'-protons (0.1 ppm) of $[\text{Si}(\text{bpy})_3]^{4+}$ and for the 2,9-protons (0.1 ppm) of $[\text{Si}(\text{phen})_3]^{4+}$. This suggests that ((+)-tartrato)antimonate(III) ions are near these protons; that is, they approach along the direction of the C_3 axis of the complex ions. The shifts of the 2,9-proton

signals upon the addition of the eluting agent are larger than those of the 6,6'-proton signals. This finding is in accordance with the more effective resolution of $[\text{Si}(\text{phen})_3]^{4+}$ as compared to $[\text{Si}(\text{bpy})_3]^{4+}$. The symbols Δ and Δ in Figure 4b indicate that the signals are attributable to Δ - and Δ - $[\text{Si}(\text{phen})_3]^{4+}$, respectively. The assignments are based on the measurements for the individual enantiomers in the presence of the eluting agent. Upon the addition of $\text{Na}_2[\text{Sb}_2(+)\text{-tart}]_2$, the 2,9-proton signals of the Δ isomer shift to the lower magnetic field side more than those of the Δ one. It appears that the eluent anion interacts more strongly with the Δ cation than with the Δ one. If only a 1:1 ionic interaction is taken into account, it is difficult to explain the chromatographic elution order, for an isomer with a stronger interaction with the eluting agent usually has a larger elution rate.

In general, the chromatographic elution of ionic species largely depends on the degree of electric neutralization, such as the formation of ion pairs. In the present case, it is considered that the formation of the higher ion pairs may play a dominant role in the electric neutralization. In future work, we will carry out ion association measurements and elucidate the chromatographic elution mechanism.

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Articles

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Complexes of Platinum(II) with the Polymeric Amine Ligand Polyaziridine

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$\text{K}_2[\text{PtCl}_4]$, *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, $\text{Pt}(\text{en})\text{Cl}_2$, and $\text{Pt}(\text{bpy})\text{Cl}_2$ form complexes in aqueous solution with polyaziridine, the polymeric amine ligand $-\text{CH}_2\text{-CH}_2\text{-NH}-$ (PEI), as investigated by UV/Vis and ^{195}Pt NMR spectroscopy. The interaction of $\text{K}_2[\text{PtCl}_4]$ and $\text{Pt}(\text{bpy})\text{Cl}_2$ with PEI yields unambiguously "single species" $\text{Pt}(\text{PEI})_4^{2+}$ and $\text{Pt}(\text{bpy})(\text{PEI})_2^{2+}$, respectively. For *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ and $\text{Pt}(\text{en})\text{Cl}_2$, interaction with PEI leads to release of ammonia and ethylenediamine, as detected by ^{14}N NMR spectroscopy. Several products are obtained in these cases. The kinetics of the formation of $\text{Pt}(\text{PEI})_4^{2+}$ follows a rate law $r = k_{\text{obs}}[\text{PtCl}_4^{2-}]$, where k_{obs} increases with increasing PEI concentration and decreases with decreasing pH. $\text{Pt}(\text{II})$ -PEI complexes containing "free" amine donor groups form mixed $\text{Pt}(\text{II})$ - $\text{Cu}(\text{II})$ complexes, in which the magnetic interactions are altered, as compared with the $\text{Cu}(\text{II})$ -PEI complexes.

Introduction

Complexes of platinum(II) were instrumental for the establishment of the coordination theory;¹ they played an important role in the development of coordination chemistry ever since,² and they found an unexpected and important application as anticancer agents.³

Much effort has been devoted to elucidate the mechanism of the cytotoxic reactions in the latter application.⁴ It has been found

that the *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ complex interacts with the biomacromolecule DNA, in a way which blocks the further reproduction of the cells. Many details of this mechanism are known today, which makes the design of new drugs possible.

In our systematic investigation of complex formation with synthetic polymeric amine ligands,⁵ we studied the interaction of various platinum(II) complexes with branched poly(ethyleneimine) (polyaziridine) (I) with two aims: (i) to establish the mechanisms of the interaction of simple platinum complexes with a simple polymer and (ii) to modify the properties of the latter through this complexation.

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