

Figure 3. Molar magnetic susceptibility from 5 to 300 K in a 1.0-T field for **1**. The solid line is a fit to eq 2 plus a Curie-Weiss term, which yields the parameters given in the text.

ions is then estimated to be 13 Å.

Temperature-dependent magnetic susceptibility data for **1** are plotted in Figure 3 and show a broad maximum at about 90 K. This feature is characteristic of intramolecular antiferromagnetic exchange. Intermolecular antiferromagnetic couplings normally result in a phase transition to a long-range ordered state, which gives a sharp maximum at the transition temperature (Neel temperature). Intermolecular exchange has been studied in monomeric Ru(III) complexes with similar ligands, and the effect occurs at much lower temperatures than those observed here.^{19a}

The simplest model for analysis of $S = 1/2$, spin-coupled dimers is the so-called Bleaney-Bowers expression:^{19b}

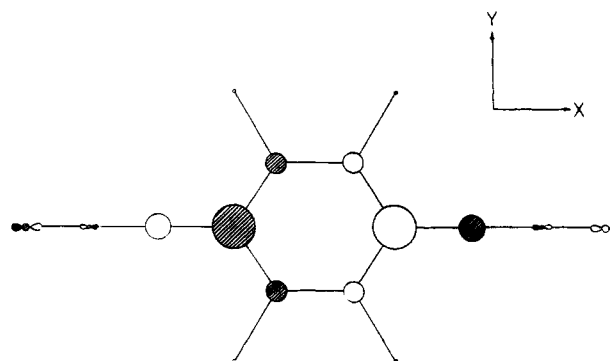
$$\chi_m = (2N\bar{g}^2\beta^2/3kT)[1 - 1/3 \exp(-2J/kT)]^{-1} \quad (2)$$

Here J is the exchange coupling constant, \bar{g} is the powder-averaged g value, and β is the Bohr magneton. This model neglects orbital angular momentum contributions, which are important for Ru(III), t_{2g}^5 . Drillon et al.²⁰ have developed procedures for including the orbital contribution for t_{2g}^n configurations, but analytical expressions are not available. Nonetheless, the use of eq 2 should provide a good first approximation for J . Thus, the data of Figure 3 were analyzed by using eq 2 and included a Curie-Weiss term, $\chi = C/(T - \Theta)$, to model the sharp upturn seen at low temperatures ascribed to a paramagnetic impurity. The fit, the solid line in Figure 3, is excellent, yielding the parameters $J/k = -77$ K, $\bar{g} = 1.76$,²¹ $C = 0.047$ emu cm³ K⁻¹, and $\Theta = -2.2$ K.

It is interesting to contrast the antiferromagnetic behavior found in complex **1** with the absence of significant magnetic interactions ($|J| < 0.2$ cm⁻¹) found in dinuclear ruthenium(III) complexes bridged by pyrazine,²² 4,4'-bipyridine,²³ and *trans*-1,2-bis(4-pyridyl)ethylene.²³ It is probable that the high-energy HOMO of L^{2-} in complex **1** provides a pathway for magnetic interaction that is energetically unavailable to the above complexes.

An extended Huckel calculation²⁴ of the free L^{2-} ligand resulted

in the following schematized drawing of its HOMO:



The 2p orbital contributions are indicated where lobe size is drawn in proportion to the relative contribution of that atomic orbital to the HOMO. Minor atomic orbital contributions are omitted for clarity. It is important to note that the HOMO spans the bridging ligand and can directly interact with the magnetic orbital of each ruthenium(III) ion. Intramolecular magnetic coupling via this HOMO could occur by resonance-exchange and/or spin-polarization mechanisms.^{1,19} Future studies of dinuclear complexes in which the extent of magnetic coupling between Ru(III) ions can be varied depending on the nature of the 1,4-dicyanamidobenzene dianion bridging ligand should reveal the dominant mechanism and together with crystal structures of the complexes provide the experimental background necessary for a quantitative theoretical description.

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Registry No. 1-(ClO₄)₂·²/₃CH₃COCH₃, 134627-11-5; 1²⁺, 134627-12-6; L⁻, 134594-78-8; L, 98507-16-5; L²⁻, 134594-74-4; [AsPh₄]₂[L], 134594-75-5; [(NH₃)₃Ru(OH₂)]₂[PF₆]₂, 34843-18-0; tetraphenylarsonium 2,5-dichloro-1,4-dicyanamidobenzene(2-), 134594-76-6; tetraphenylarsonium 2,3,5,6-tetrachloro-1,4-dicyanamidobenzene(2-), 129239-19-6; tetraphenylarsonium 1,4-dicyanamidobenzene(2-), 134594-77-7.

Supplementary Material Available: Full listings of crystal structure data, atomic parameters, anisotropic thermal parameters, bond lengths, and bond angles (5 pages); a listing of final structure factors (16 pages). Ordering information is given on any current masthead page.

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Stereochemistry of Six-Coordinated Silicon Complexes. 1. Stereoselectivity and CD Spectra of Tris(optically active β-diketonato)silicon(IV) Complexes

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Introduction

There have been very few studies about six-coordinated silicon(IV) complexes compared to four-coordinated ones. Six-coordinated complexes of phthalocyaninate,¹ octaethylporphinate,² heterocyclic amines,³ *N,N*-dimethylformamide,⁴ and Schiff bases⁵

- (18) We have obtained crystal structures of the tetraphenylarsonium salts of the following dianion ligands: 2,5-dichloro-1,4-dicyanamidobenzene, 2,3,5,6-tetrachloro-1,4-dicyanamidobenzene, and unsubstituted 1,4-dicyanamidobenzene. In all structures, each cyanamide group is nearly coplanar with the phenyl ring and in a *trans* configuration. For L^{2-} , it would seem that the weaker π interaction between a cyanamide group and the phenyl ring together with the steric hinderance of ortho-methyl groups is enough to cause the cyanamide groups to move out of plane while still maintaining a *trans* configuration.
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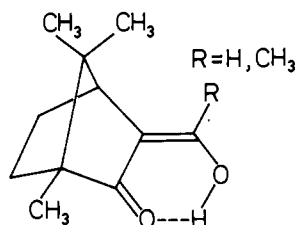


Figure 1. Optically active β -diketonate ligands: R = H, (+)-(hydroxymethylene)camphor, (+)-hmcH; R = CH₃, (+)-acetylcamphor, (+)-atcH.

have thus far been synthesized and characterized.

We have also started a research project on six-coordinated silicon(IV) complexes from the standpoint of their stereochemistry.

Kirschner et al. first succeeded in the optical resolution of a six-coordinated silicon(IV) complex, [Si(acac)₃]⁺.⁶ Larsen et al. assigned the absolute configuration of the optically active isomer, (-)₅₈₉[Si(acac)₃]⁺ to Λ in terms of the exciton theory, on the basis of the CD spectral data.⁷

Inoue et al. have investigated kinetically the racemization of the optically active tris(bidentate)silicon(IV) complexes of acetylacetonate and β -diketonates and proposed an intramolecular mechanism through an intermediate with a unidentate ligand.⁸ Similar studies have been carried out on tris(tropolonato)silicon(IV).⁹

The present study was performed in order to test the theoretical assignment of the absolute configuration of (-)₅₈₉[Si(acac)₃]⁺ by experimental findings. The optically active β -diketonate ligands (Figure 1) have the stereoselective complexation expected.

The tris[(+)-(hydroxymethylene)camphorato]cobalt(III) complex has already been reported, and its high selectivity was ascertained.¹⁰

Experimental Section

Reagents. SiCl₄ was obtained from Kishida Kagaku Co., Ltd. (+)-(Hydroxymethylene)camphor (hmcH)¹¹ and (+)-acetylcamphor (actH)¹² were synthesized according to well-established methods and dried over silica gel under reduced pressure before using. SiCl₄ and all other chemicals commercially available were used without further purification.

[Si((+)-hmc)₃]⁺ was synthesized by mixing SiCl₄ and (+)-hmcH in the molar ratio of 1:3 in dried CHCl₃ (ca. 1 M). The reaction solution has a pale yellow color. Although the addition of Et₂O to the reaction solution gives a white precipitate, the complex is unstable and gradually decomposes in air. Therefore, the following measurements were carried out directly on the reaction solution.

¹H NMR spectra were obtained with a JEOL JNM-PMX60 spectrometer at the probe temperature. Samples in CDCl₃ were run in 5-mm tubes. TMS and dichloroethane were used as internal references. The latter was used as a standard sample for normalization of signal intensities during the continuous-variation-method study, where the following solutions were prepared and mixed in the proportions shown in Figure 3: a, A 5-mL CDCl₃ solution containing 0.810 g of (+)-(hydroxy-

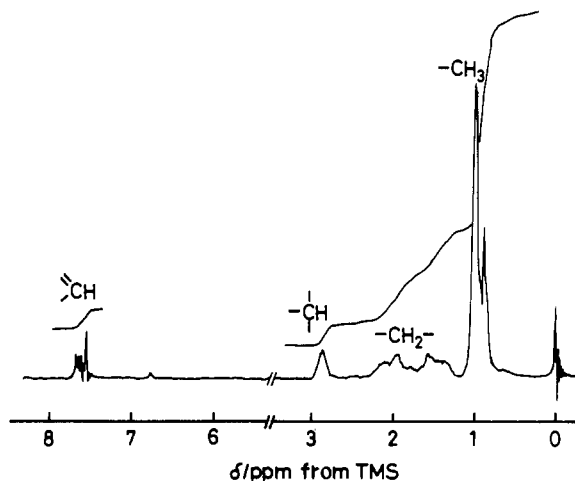


Figure 2. ¹H NMR spectrum of [Si((+)-hmc)₃]Cl·HCl in CDCl₃. The signal for HCl is omitted because of fluctuation in position.

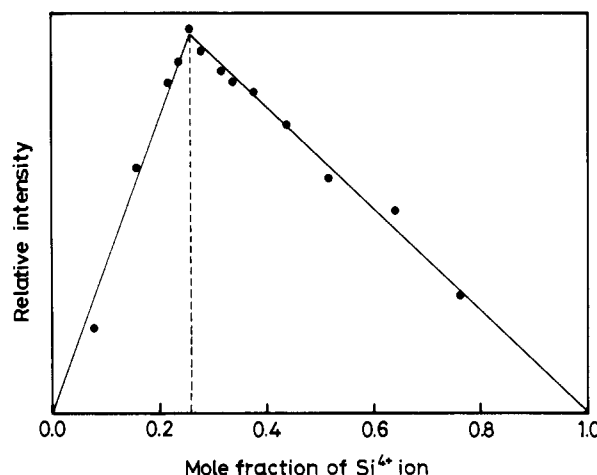


Figure 3. Continuous-variation-method plot for complex formation in the (+)-(hydroxymethylene)camphorato-Si⁴⁺ system using the ¹H NMR data.

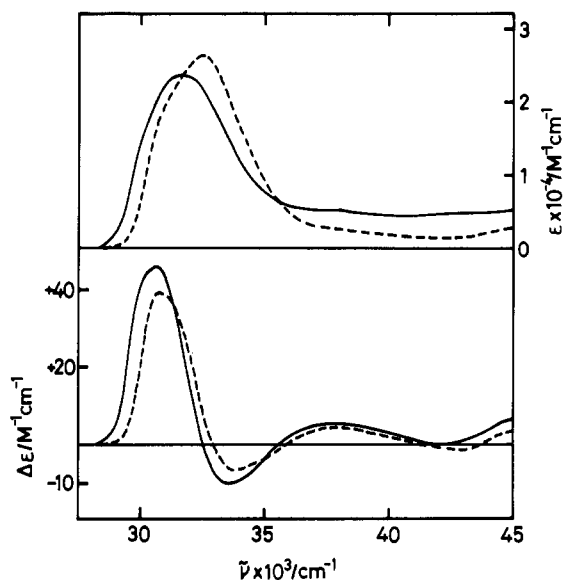


Figure 4. Absorption (upper curves) and CD (lower curves) spectra of [Si((+)-hmc)₃]⁺ (full lines) and [Si((+)-atc)₃]⁺ (broken lines) in acetonitrile.

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methylene)camphor and 0.367 mL of CHCl₂CHCl₂; b, A 3-mL CDCl₃ solution containing 0.765 g of SiCl₄ and 0.220 mL of CHCl₂CHCl₂.

Electronic absorption spectra were recorded on a Hitachi 228 spectrometer, and CD spectra, on a JASCO J-500A spectropolarimeter.

Since electronic absorption in the UV region, as in the present case, is much more sensitive than ^1H NMR absorption, it is necessary to dilute the solutions. However, in a dilute CHCl_3 solution, the complex was unstable and decomposed in 0.5 h. Trace amounts of contaminated water might be responsible for the decomposition. Therefore, the absorption and CD measurements were made on 3×10^{-4} to 2×10^{-5} M (dried) acetonitrile solutions containing HCl. HCl contained in the solution appears to stabilize the complex.

Results and Discussion

Figure 2 shows the ^1H NMR spectrum of a 1.5 M CDCl_3 solution of $[\text{Si}((+)\text{-hmc})_3]\text{Cl}\cdot\text{HCl}$. Each signal was assigned as depicted in the figure. The signal of an enolic hydrogen observed in the ligand disappears in the complex, and thus the signal of the aldehyde hydrogen shifts from 6.7 to 7.6 ppm. Since $[\text{Si}((+)\text{-hmc})_3]^+$ can exist as geometrical isomers, the signal shape of the aldehyde hydrogen is complicated, as can be expected. We assign the sharp band in the higher magnetic field region to a *fac* isomer and the others in the lower magnetic field region to *mer* isomers. Their intensity ratio is also close to the ratio of 1:3 derived

statistically. In addition, the signal for HCl of the hydrochloride was observed around 8.7 ppm, but it fluctuated in position for each run. In order to confirm the formation of the tris complex ion in the solution, the continuous-variation method was performed by using the total signal (at around 7.6 ppm) for the aldehyde hydrogen of the ligand (Figure 3). The maximum occurs at Si^{4+} mole fraction of 0.26, indicating that the tris complex exists predominantly in the reaction solution.

Figure 4 shows the absorption and CD spectra of $[\text{Si}((+)\text{-hmc})_3]^+$. The spectra for $[\text{Si}((+)\text{-atac})_3]^+$, prepared by a similar method, are also shown in the figure. It can be easily seen that the absolute configurations of the two complexes are Δ from the analogy to the results for the corresponding cobalt(III) complexes mentioned above. Both give a positive E band around 33000 cm^{-1} in the $\pi \rightarrow \pi^*$ transition region.

Larsen et al. assigned an absolute configuration of Δ to the catoptromer with the corresponding E band of a negative sign. Thus the assignment based on the exciton theory is supported experimentally by the present results.