Experimental Section

Selenacyclopentane and selenacyclohexane were prepared and purified by the method of McCullough and Lefohn.[4] The sources and methods of purification for iodine and carbon tetrachloride were the same as those given in ref 1.

Absorbance data[5] were measured on a Cary recording spectrophotometer, Model 11, with a thermostated cell compartment. Matched sets of absorption cells with lengths of 1.000, 9.998, 25.03, and 100.1 mm were used. Several recordings were made of each sample and the results were averaged. Absorbances were measured at wavelengths near the visible absorption maximum at 428 mμ for both complexes at each of three temperatures. An additional set of 20 measurements was made on the selenacyclopentane complex at 25.5° in the region of the ultraviolet absorption maximum at 322 mμ. The ultraviolet measurements showed considerably more scatter than those made at the visible maximum, especially for 10 points where iodine was in excess. For this reason, only data with the selenide concentration equal to or greater than that for iodine were used in the ultraviolet-band calculations. This behavior in the ultraviolet region was similar to that noted for another very stable complex, that of 1,4-diselenane.[6]

The equilibrium constants and molar absorptivities were computed from the absorbance data by the cyclic least-squares procedure described earlier.[7] Values of $\Delta H_c°$ for the complexes were computed from the change in K with temperature on the assumption that ϵ remains constant. Actually, the observed variation of ϵ with T was small; in no case did a value differ by more than 1.1 standard deviations from the appropriate mean value given in Table I.

TABLE I

VALUES OF MOLAR ABSORPTIVITY (ϵ) AND DISSOCIATION CONSTANT (K_c) FOR $D \cdot I_2$ AT VARIOUS WAVELENGTHS AND TEMPERATURES IN CARBON TETRACHLORIDE (ESTIMATED STANDARD DEVIATIONS IN PARENTHESES)

λ, mμ	ϵ	10^4K_c, M		
		15.0°	25.5°	40.0°
(a) D = Selenacyclopentane, C_4H_8Se				
Concentration Ranges: Selenide, 1.0×10^{-4} to 1.6×10^{-3} M; Iodine, 8.0×10^{-3} to 1.5×10^{-3} M				
415	3,070 (60)	2.44	4.85	11.5
420	3,230	2.45	4.83	11.4
425	3,330	2.45	4.81	11.4
430	3,350	2.49	4.81	11.3
Av		2.46 (0.05)	4.82 (0.07)	11.4 (0.2)
316	37,700 (700)		4.85	
320	39,600		4.89	
324	39,600		4.96	
328	38,100		4.91	
Av			4.90 (0.12)	
(b) D = Selenacyclohexane, $C_5H_{10}Se$				
Concentration Ranges: Selenide and Iodine, 1.6×10^{-4} to 2.0×10^{-3} M				
415	3,030 (100)	4.05	7.49	16.0
420	3,160	4.09	7.47	15.7
425	3,210	4.11	7.44	15.7
430	3,200	4.15	7.47	15.9
Av		4.10 (0.08)	7.47 (0.06)	15.8 (0.4)

Results and Discussion

The equilibrium constants and molar absorptivities are given in Table I and the derived thermodynamic quantities in Table II. The small dissociation constants show that the iodine complexes of selenacyclopentane and selenacyclohexane are among the most stable compounds of this type. In keeping with this is the fact that both complexes are obtained as crystalline solids with melting points of 99 and 114°, respectively.[8,9] In contrast, attempts to isolate solid iodine complexes of the corresponding sulfides have been unsuccessful.

TABLE II

VALUES FOR THE DISSOCIATION CONSTANT (K_c), MOLAR FREE ENERGY ($\Delta G_c°$), MOLAR ENTHALPY ($\Delta H_c°$), AND MOLAR ENTROPY ($\Delta S_c°$) FOR THE DISSOCIATIONS IN CARBON TETRACHLORIDE AT 25°[a]

Complex[b]	10^4K_c, M	$\Delta G°$, kcal mole^{-1}	$\Delta H_c°$, kcal mole^{-1}	$\Delta S_c°$, cal deg^{-1} mole^{-1}
$C_4H_8SeI_2$	4.54	4.58	11.1	22
$C_5H_{10}SeI_2$	7.16	4.32	9.8	18
$C_4H_8SI_2$	55.0	3.10	8.7	19
$C_5H_{10}SI_2$	74.0	2.92	7.1	14

[a] Estimated standard deviations: $\Delta G_c°$, 0.03; $\Delta H_c°$, 0.3; $\Delta S_c°$, 1. [b] Values for sulfur compounds are from ref 3 and are included for comparison.

An X-ray diffraction study of the crystalline complex of selenacyclopentane[10] has shown a short Se–I bonded distance of 2.762 A which is only 0.26 A longer than the sum of the normal, single, covalent bond radii, 2.50 A. As a result of this relatively short bond that one iodine atom makes with selenium, the I–I distance is lengthened from the uncomplexed value of 2.66 to 2.914 A. These observed bond distances are in line with the high degree of stability found for the complex in solution.

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[5] The absorbance data have been deposited as Document No. 9379 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

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Acetonitrile Exchange Rates in Solutions of Nickel(II) Ions by Nuclear Magnetic Resonance

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In a number of recent studies the rates of solvent exchange between the bulk solution and the ligand sphere of paramagnetic ions as determined by the effect

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of the exchange process on the nuclear magnetic resonance spectrum of the solvent have been reported. Notable examples include the exchange rates of water which were derived from ^{17}O data by Swift and Connick,[2] ammonia determined from ^{14}N data by Hunt, Dodgen, *et al.*,[3] methanol determined from proton data by Luz and Meiboom[4] and Sheppard and Burdett,[5] and dimethylformamide, which was worked out from proton data by Matwiyoff[6] and from ^{17}O data by Babiec, Langford, and Stengle.[7] In this report the results of a set of measurements of proton spectra obtained in solutions of $Ni(CH_3CN)_6(ClO_4)_2$ in acetonitrile are described.

Experimental Section

Materials.—Hexakis(acetonitrile)nickel(II) perchlorate was prepared by the inert atmosphere methods of Wickenden and Krause.[8] Solutions of this material (0.091 and 0.204 *M*) were made up in acetonitrile. This operation was carried out in an atmosphere of dry nitrogen. The acetonitrile was freshly distilled from phosphorus pentoxide through an efficient fractionating column.

Nmr Measurements.—The nmr spectra were obtained with a Varian Dual Purpose spectrometer operating at 56.4 Mc. The sample temperature was controlled to ±1° using a Varian variable-temperature unit. Calibration of the spectra was effected by the usual side-band technique. A minimum of three spectra were taken at each temperature, with the average line width reproducible to 0.5 to 5% depending on the width of the line. The chemical shifts were measured with respect to a dioxane internal standard.

Results and Discussion

The experimental results of the line-width measurements are given in Figure 1. The quantity $(1/P_M)\cdot(1/T_2 - 1/T_{2A}{}^0)$ is plotted as a function of reciprocal temperature, where P_M is the mole fraction of acetonitrile in the solution which is coordinated to nickel (calculated assuming a coordination number of six), T_2 is the experimental relaxation time of the solution (obtained from the observed line width by $\Delta\nu = 1/\pi T_2$), and $T_{2A}{}^0$ is the relaxation time of pure acetonitrile. The curve clearly breaks down into several linear regions. At the lowest temperatures studied ($1/T > 0.00380$) the exchange process is too slow to affect the solvent spectrum. The small effect present here is due to solvent exchange with the second and further removed spheres of the complex ion. Since this effect exists at all temperatures, a correction for it is made to all of the data. The slope of the line corresponds to an activation energy of 1.7 kcal/mole, which is similar to the value obtained by Luz and Meiboom for the same region in methanol solutions of Ni(II).[4]

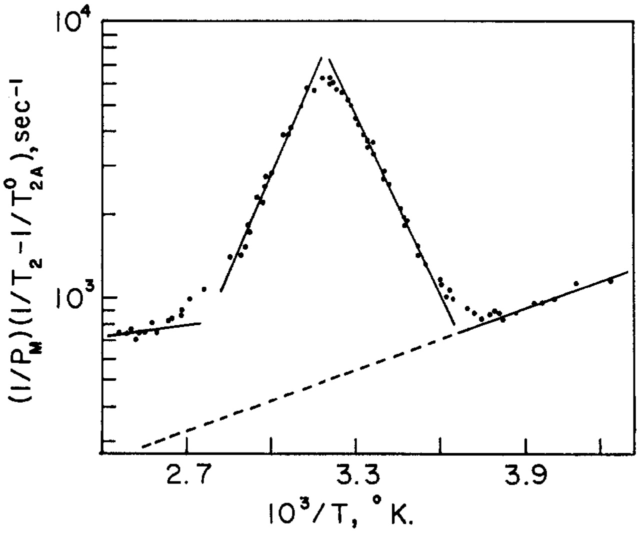

Figure 1.—Temperature dependence of $(1/P_M)(1/T_2 - 1/T_{2A}{}^0)$ for the protons in acetonitrile solutions of $Ni(CH_3CN)_6(ClO_4)_2$ at 56.4 Mc.

The two regions of steep slope must be connected with processes dependent on τ_M, the average residence time of an acetonitrile molecule in the ligand coordination sphere of the Ni(II) ion. The temperature dependence of the line width in these regions is described by the relationship[2]

$$\frac{1}{T_2} - \frac{1}{T_{2A}} = P_M \frac{1/T_{2M}(1/T_{2M} + 1/\tau_M) + (\Delta\omega_M)^2}{\tau_M(1/T_{2M} + 1/\tau_M)^2 + \tau_M(\Delta\omega_M)^2} \quad (1)$$

where $1/T_{2A}$ is made up of a contribution due to interactions beyond the ligand sphere (evaluated from the low-temperature region) and a contribution due to relaxation mechanisms which operate in the absence of paramagnetic ions (*i.e.*, processes contributing to $T_{2A}{}^0$), T_{2M} is the relaxation time of a nucleus in the ligand sphere of the Ni(II) ion, and $\Delta\omega_M$ is the chemical shift between acetonitrile bound to the metal ion and acetonitrile in the bulk solvent. At temperatures where the rate of exchange of solvent with Ni(II) is not too great (specifically where either $\Delta\omega_M{}^2 \gg 1/T_{2M}{}^2$, $1/\tau_M{}^2$ or $1/T_{2M}{}^2 \gg \Delta\omega_M{}^2$, $1/\tau_M{}^2$) eq 1 reduces to

$$\frac{1}{T_2} - \frac{1}{T_{2A}} = \frac{P_M}{\tau_M} \quad (2)$$

Under these conditions the temperature dependence of the quantity $(1/T_2 - 1/T_{2A})(1/P_M)$ should be that of a reaction rate constant, *viz.*

$$\frac{1}{\tau_M} = \frac{kT}{h}\exp(-\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R) \quad (3)$$

where $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the activation parameters corresponding to the first-order rate constant. Fitting the parameters of eq 2 and 3 to that part of the line-width curve between $1/T = 0.0032$ and 0.0035 yielded the quantities listed in Table I.

In the high-temperature region ($1/T < 0.0032$) the line width is determined by

$$\frac{1}{T_2} - \frac{1}{T_{2A}} = \frac{P_M}{T_{2M}} + P_M(\Delta\omega_M)^2\tau_M \quad (4)$$

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Table I

Rate Data for the Ni(II)–Acetonitrile Exchange Reaction

Quantity	Value
$1/\tau_M$, sec^{-1} at 25°	$(2.8 \pm 0.5) \times 10^3$
$\Delta H^{\ddagger}$, kcal/mole	11.7 ± 1.0
$\Delta S^{\ddagger}$, cal/deg	-3.6 ± 1.0
A/h, cps[a]	$-(8.1 \pm 0.5) \times 10^5$

[a] Calculated assuming $\mu_{eff} = 3.15$ BM.[8]

If the chemical shift between bound and free acetonitrile is not too small ($\Delta\omega_M{}^2 \gg 1/T_{2M}\tau_M$) the term in T_{2M} can be neglected and the value of τ_M can be derived if $\Delta\omega_M$ is known from independent measurements. In Figure 2 a plot of $\Delta\omega_M$ *vs.* $1/T$ is given. At the lowest temperatures, the exchange is quite slow and has little effect on the spectrum. In this region (which is not shown on the graph) there is zero chemical shift between the Ni(II) solutions and pure acetonitrile. The shift increases steeply at temperatures where the exchange rate becomes important, and in the limit of very fast chemical exchange it becomes linear with reciprocal temperature. In the latter region the part of the shift due to "contact" interaction is given by[9]

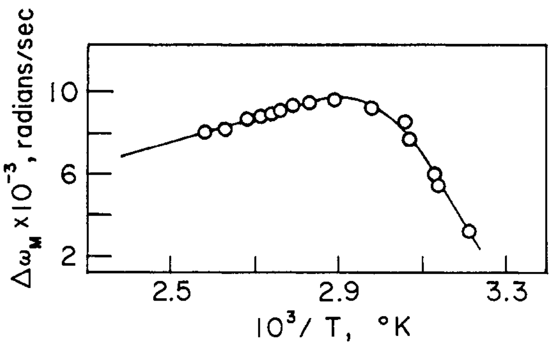

Figure 2.—Temperature dependence of $\Delta\omega_M$ for the protons in acetonitrile solutions of $Ni(CH_3CN)_6(ClO_4)_2$ at 56.4 Mc.

$$\frac{\Delta\omega_M}{\omega} = -\frac{A}{h}\,\frac{[S(S+1)]^{1/2}\mu_{eff}}{3kT\gamma_I} \qquad (5)$$

where k is Boltzmann's constant, ω is the resonance frequency, γ_I is the magnetogyric ratio of the proton, and μ_{eff} and S refer to the Ni(II) ion. A value of the constant A/h calculated from the slope of the high-temperature region of Figure 2 is given in Table I. It is evident that additional terms contribute to the chemical shift; although $\Delta\omega_M$ is linear with $1/T$ in the high-temperature region, the extrapolated line does not pass through the origin as eq 5 would predict.

It is possible to compare the results of chemical-shift and line-width measurements at the higher temperatures. A value of $\Delta\omega_M$ can be calculated from the line-width data if the term in T_{2M} is neglected and τ_M is obtained by extrapolation from lower temperature. The chemical shift derived from this analysis at $1/T = 0.0029$ is 7.8×10^3 radians/sec, as compared with the value of 9.8×10^3 from direct measurement. Due to the long extrapolation involved, it is not clear whether the discrepancy between these numbers is a real effect. It is possible that this point will be cleared up by line-width studies on the ^{14}N nucleus.

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Aminolysis of α,ω-Dichlorosiloxanes[1]

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Recently, we reported the synthesis and properties of N-methylsiloxazanes, which were obtained in mixtures with α,ω-bis(methylamino)siloxanes when α,ω-dichlorosiloxanes in petroleum ether at 5–10° were treated with methylamine and the mixtures were refluxed.[2] In the absence of catalysts, the α,ω-bis(methylamino)siloxanes were thermally stable and could readily be purified by distillation, but in the presence of ammonium sulfate they could be condensed to cyclic N-methylsiloxazanes at 150–180°. It had been reported by others[3] that the α,ω-bis(methylamino)siloxanes were the sole product of the aminolysis reaction.

The differences in the nature of the products reported in these two publications can now be explained on the basis of a temperature effect. In subsequent studies of the synthesis of cyclic siloxazanes, we find that the linear bis(methylamino)siloxanes are the predominant products when the reaction mixtures are maintained below −15°, but cyclic N-methylsiloxazanes are the chief products when the reactions are carried out at 50° or above. Intermediate temperatures such as those reported in our earlier publication afford nearly equal amounts of the two products. A summary of typical experiments which illustrate this temperature effect is given in Table I.

Since the products of treating methylamine with α,ω-dichlorosiloxanes at low temperatures were refluxed before the mixtures were purified, the formation of substantial quantities of cyclic compounds at higher reaction temperature cannot be attributed to thermal condensation or to condensation catalyzed by the presence of the methylamine hydrochloride by-product. A more plausible explanation for cyclic compound

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