Table IV. Band Maxima for Electronic Absorption Spectra and Associated Circular Dichroism of the First Ligand $\pi - \pi^*$ Transition

Complex	Isotropic absorption spectrum	Circular dichroism
Co[(7-CH_3-sal)$_2$(−)pn]	28,750 (7100)[a]	28,150 (3.4);[b] 31,200 (2.3)
Co[(7-C_6H_5-sal)$_2$(−)pn]	28,300 (10,000)	28,200 (2.9); 29,900 (0.9)
Co[(5-OCH_3,7-CH_3-sal)$_2$(−)pn]	24,500 (9300)	25,300 (1.3); 28,900 (1.5)
Co[(5,6-benzosal)$_2$-(−)pn]	26,500 (15,000); 27,400 (14,800)	25,600 (3.0); 27,900 (2.9)
Co[(sal)$_2$-(−)pn]	27,500 (11,500); 28,600 (12,600)	26,600 (1.5); 28,260 (1.7)

[a] The values of ϵ_{max} are given in parentheses. [b] The values of $(\epsilon_l - \epsilon_r)_{max}$ are given in parentheses.

indicates that the substituents on the aryl ketone ring have a considerable effect on the energy of the empty π orbitals which are involved in the charge transfer absorptions.

Concomitant with this shift in the energy of the charge transfer and ligand bands, the CD associated with the $\pi \rightarrow \pi^*$ band varies in magnitude as a function of the substituent at the 4 or 5 position (Table IV). More detailed studies of the effects of substituents on the positions and magnitudes of the bands are in progress.

Acknowledgments. This work was supported in part by the National Science Foundation under Grants GP-7510 and GP-11776. The authors are also indebted to Dr. M. L. Sage for use of the equipment used to obtain the near-infrared CD spectra and for helpful discussions.

Water Exchange between Solvent and Aquoamminenickel(II) Complexes

Arvind G. Desai, Harold W. Dodgen, and John P. Hunt[1]

Contribution from the Department of Chemistry, Washington State University, Pullman, Washington 99163. *Received July 22, 1969*

Abstract: Water exchange rates with $Ni(H_2O)_5NH_3^{2+}$, $Ni(H_2O)_4(NH_3)_2^{2+}$, and $Ni(H_2O)_3(NH_3)_3^{2+}$ are reported. The k_1 (for a particular water molecule) values at 25° are 2.5 (±0.2) × 10^5, 6.1 (±0.2) × 10^5, and 2.5 (±0.2) × 10^6 sec^{-1}, respectively. The corresponding $\Delta H^{\ddagger}$ values are 10.6 ± 0.5, 7.8 ± 0.3, and 10.2 ± 0.5 kcal/mol. Scalar coupling constants for ^{17}O (A/h) in the same order are 2.5 (±0.2) × 10^7, 1.9 (±0.2) × 10^7, and 2.6 (±0.2) × 10^7 cps. T_{1e} for $Ni(H_2O)_3(NH_3)_3^{2+}$ is estimated to be 1.1 (±0.5) × 10^{-12} sec. Some discussion of ligands which do and do not labilize remaining water molecules is given.

Using ^{17}O nmr measurements, water exchange kinetics in labile aquo and substituted aquo ions can be studied. Such studies are of interest because of their relations to substitution mechanisms in general as well as providing information on effects caused by ligands adjacent to coordinated water molecules. A previous report has given results for several Ni(II) complexes.[2] In general, the remaining water molecules appear to be labilized as the extent of substitution by other ligands increases. A different result has been reported for the terpyridyl complexes.[3] This paper reports a detailed study on the mono-, di-, and triammine complexes which can be compared with previous studies, especially with ethylenediamine as ligand.[2]

Experimental Section

The nmr equipment and conditions used have been described previously.[2,4] A Varian 24.6-kG magnet was employed and the ^{17}O resonance in water observed at *ca.* 14.19 MHz. The water used was enriched to *ca.* 7% in ^{17}O. It was distilled from alkaline permanganate and redistilled *in vacuo* before each use. Other chemicals used were Mallinckrodt A R $Ni(NO_3)_2 \cdot 6H_2O$, NH_4NO_3, and 58% NH_4OH. Solutions were prepared in 2 *M* NH_4NO_3 by addition of known amounts of all reagents. Some pH measurements were made to provide estimates of species concentrations used in a computer program which calculated the equilibrium concentrations.[2] Values used for the acidity constant of NH_4^+ and the nickel-ammine complexes were those of Bjerrum[5] for 2 *M* NH_4NO_3. Enthalpy of formation values were those of Spike, as listed in ref 6. Since the equilibria do shift slightly with temperature, solution compositions were calculated as a function of temperature. Some typical results are shown in Table I for the solutions employed.

Treatment of Data and Results

A fairly detailed discussion of data treatment has been given.[2] Line broadenings and chemical shifts are observed in the free water species produced by the various nickel species over a wide range of temperature. The line broadenings are reported in terms of the defined quantity $T_{2p}' = 2M(Ni)/\gamma\Delta'$, where M(Ni) refers to the total molarity of all Ni(II) species, γ is 3628 G^{-1} sec^{-1}, and Δ' is $W_{obsd} - W_0$. The quantity W_{obsd} is the full line width for the Ni(II) solutions (in G) mea-

---

[1] To whom inquiries may be addressed. This work supported by U. S. A. E. C. Contract AT(45-1)-2040 and is Report No. RLO-2040-16.

[2] A. G. Desai, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, 91, 5001 (1969).

[3] D. Rablen and G. Gordon, *Inorg. Chem.*, 8, 395 (1969).

[4] R. Murray, H. W. Dodgen, and J. P. Hunt, *ibid.*, 3, 1576 (1964).

[5] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Sons, Copenhagen, 1941.

[6] L. G. Stillen and A. E. Martell, Ed., "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964.

Table I. Solution Composition at 25°[a]

Solution	Total Ni(II), *M*	Total NH_3, *M*	pH_{obsd}	pH_{calcd}	% $Ni(H_2O)_6^{2+}$	% Ni-$(H_2O)_5NH_3^{2+}$	% $Ni(H_2O)_4$-$(NH_3)_2^{2+}$	% $Ni(H_2O)_3$-$(NH_3)_3^{2+}$	% $Ni(H_2O)_2$-$(NH_3)_4^{2+}$
I	0.1	0.021	5.8	5.70	80.6	18.2	1.2		
II	0.1	0.071	6.4	6.32	44.3	42.7	12.0	0.9	
III	0.1	0.208	7.3	7.14	3.9	24.5	44.8	22.6	3.9
IV	0.1–0.4				100				

[a] Medium, 2 *M* NH_4NO_3.

Table II. Line Broadening Data

Solution I			Solution II		
t, °C	Δ', *G*	$T_{2p}' \times 10^5$, *M* sec	*t*, °C	Δ', *G*	$T_{2p}' \times 10^5$, *M* sec
15.1	0.17	31.7	1.4	0.21	26.8
20.1	0.29	18.7	5.5	0.25	22.1
25.0	0.39	14.0	9.6[a]	0.38	14.4
30.5	0.55	10.1	10.7	0.37	14.7
35.6	0.73	7.51	14.8[a]	0.48	11.5
39.9	0.95	5.79	19.9[a]	0.64	8.58
44.6	1.35	4.08	25.0[a]	0.82	6.71
50.2	1.60	3.45	30.5	0.97	5.66
55.2	1.78	3.10	30.6[a]	1.02	5.38
60.7	2.14	2.58	35.0	1.28	4.31
66.5	2.38	2.32	35.6[a]	1.40	3.93
70.6	2.53	2.18	39.9[a]	1.52	3.62
76.2	2.65	2.08	44.6[a]	1.77	3.12
80.6	2.50	2.20	50.2	1.95	2.82
84.4	2.41	2.28	55.2	2.14	2.58
88.6	2.24	2.47	60.7	2.14	2.58
			66.5	2.20	2.50
			70.3	2.05	2.68
			76.2	2.03	2.72
			80.2	1.97	2.80
			84.4	1.79	3.08
			88.6	1.67	3.30

Solution III			Solution IV		
			[Ni^{2+}], 0.428 *M*		
−5.4	0.58	9.44	8.8	0.21	110.2
1.4	0.74	7.26	13.7	0.40	58.5
5.7	0.92	6.00	18.0	0.55	42.6
9.6	1.17	4.71	22.5	0.79	29.7
14.8	1.37	4.01	26.2	1.02	23.2
19.9	1.54	3.57	[Ni^{2+}], 0.1 *M*		
25.0	1.59	3.47	30.8	0.28	19.7
31.6	1.63	3.38	35.4	0.40	13.8
35.6	1.69	3.25	40.0	0.55	9.97
39.9	1.76	3.13	45.2	0.81	6.82
44.6	1.65	3.34	[Ni^{2+}], 0.05 *M*		
50.2	1.60	3.45	50.2	0.62	4.42
55.2	1.54	3.57	55.4	0.79	3.47
60.7	1.43	3.86	60.4	0.96	2.86
66.5	1.28	4.30	68.4	1.28	2.15
70.3	0.99	5.56	72.7	1.49	1.85
76.2	0.91	6.05	78.4	1.43	1.92
80.2	0.82	6.75	82.3	1.38	2.00
84.4	0.77	7.16	88.3	1.32	2.09
88.6	0.72	7.62			

[a] Measurements made on independently prepared solution.

Table III. Chemical Shift Data for Solution III

t, °C	Shift, ppm	*TSM*(H_2O)/*M*(Ni^{2+})
20.5	25.0	4.08
25.6	29.9	4.95
31.0	40.5	6.83
35.8	45.8	7.85
42.2	52.0	9.11
47.8	59.7	10.64
52.7	65.1	11.76
58.6	71.3	13.13
65.1	74.2	13.55
72.1	76.6	14.68
80.3	79.0	15.50

sured at half-maximum in the absorption curve and W_0 is the same quantity for the blank or reference solution. For these studies the blank was 2 *M* NH_4NO_3. The line widths for this blank differ slightly from those for pure water especially at the lower temperatures. Additions of Zn^{2+} ions had no additional effect. The values of W_0 varied from 0.16 to 0.34 G over the temperatures used. They include *ca.* 0.06 G instrumental broadening. The data are listed in Table II and plotted as log T_{2p}' *vs.* $10^3/T$ in Figure 1. Measured chemical shifts are treated in terms of $Q_{obsd} = TSM(H_2O)/M(Ni)$ where *T* is in °K, *S* is the chemical shift in ppm relative to the blank, and *M*(H_2O) and *M*(Ni) refer to free water and total metal concentrations. Values for solution III only were useful. These are given in Table III and plotted as log *Q* *vs.* $10^3/T$ in Figure 2. In order to obtain T_{2p}' and shift parameters for the individual species we have assumed that an additive two-site situation exists. We can represent this as follows

$$1/T_{2p}'{}_{obsd} = \sum_{i=0}^{3} X_i/T_{2p}'(i)$$

$$S_{obsd} = \sum_{i=0}^{3} X_iS(i)$$

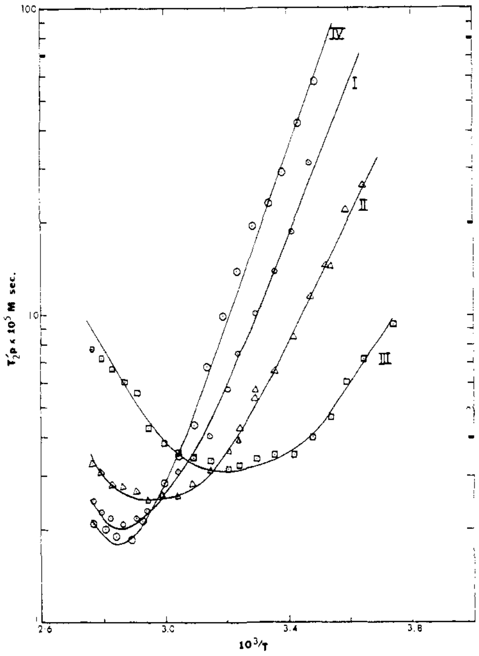

Figure 1. Semilogarithmic plot of T_{2p}' *vs.* $10^3/T$ for data of Table II.

Table IV. Kinetic and Nmr Parameters

	Exchange rate, 25°, M sec^{-1}	k_1, 25°, sec^{-1}	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, cal mol^{-1} deg^{-1}	A/h, cps	T_{1e}, sec	E_a for T_{1e}, kcal mol^{-1}
$Ni(H_2O)_6^{2+}$	2.16×10^5	$(3.6 \pm 0.2) \times 10^4$	12.3 ± 0.5	3.6 ± 1.5	$(2.3 \pm 0.2) \times 10^7$		
$Ni(H_2O)_5NH_3^{2+}$	1.25×10^6	$(2.5 \pm 0.2) \times 10^5$	10.6 ± 0.5	1.8 ± 1.5	$(2.5 \pm 0.2) \times 10^7$		
$Ni(H_2O)_4(NH_3)_2^{2+}$	2.44×10^6	$(6.1 \pm 0.2) \times 10^5$	7.8 ± 0.3	-6.0 ± 2.0	$(1.9 \pm 0.2) \times 10^7$		
$Ni(H_2O)_3(NH_3)_3^{2+}$	7.5×10^6	$(2.5 \pm 0.2) \times 10^6$	10.2 ± 0.5	5.0 ± 1.5	$(2.6 \pm 0.2) \times 10^7$	$(1.08 \pm 0.5) \times 10^{-12}$	$+3.2 \pm 0.5$

where X_i is the mole fraction of the ith complex. The simultaneous equations for $T_{2p}'(i)$ were solved by successive approximations using the directly measured values for $Ni(H_2O)_6^{2+}$ (solution IV). For the mono- and diammine species the equations[2] $T_{2p}'(i) = [(H_2O)/n]\cdot[\tau_M(i) + 1/\Delta\omega_M^2(i)\tau_M(i)]$ were used. The triammine required the more complex equation[2] $T_{2p}'(3) = [(H_2O)/3]\cdot[\tau_M(3) + 1/\Delta\omega_M^2(3)\tau_M(3)]/[1 + 1/T_{2M}(3)\tau_M(3)\Delta\omega_M^2(3)]$. Here n is the number of coordinated water molecules, τ_M is the mean lifetime for exchange of a coordinated water molecule, $\Delta\omega_M$ is the shift of the coordinated water nmr line from the blank water, and $T_{2M}(3)$ is the transverse relaxation time for a water molecule in $Ni(H_2O)_3(NH_3)_3^{2+}$. There are no data which permit consideration of isomers in these calculations. Taking $1/\tau_M = (kT/h)e^{-\Delta H^\ddagger/RT}e^{\Delta S^\ddagger/R}$ the temperature dependence is introduced. The variables $\Delta H^\ddagger$, $\Delta S^\ddagger$, $\Delta\omega_M$, and T_{2M} were adjusted using a computer calculation to give the best visual fit to the data. In Figure 3 are shown the results of the fitting. The solid lines in Figure 1 are calculated from the chosen parameters. The fit is as good as can be expected in a complex system. As a check on the fit the shift expected for solution III was calculated using the relation $Q_i = [nT\Delta\omega_M\cdot(i)/\omega_0][1/(1 + \Delta\omega_M^2(i)\tau_M^2(i))]$. The results are shown in Figure 2. The agreement is considered to be satisfactory.

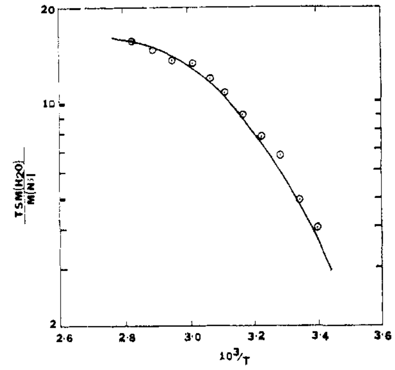

Figure 2. Shift data for solution III.

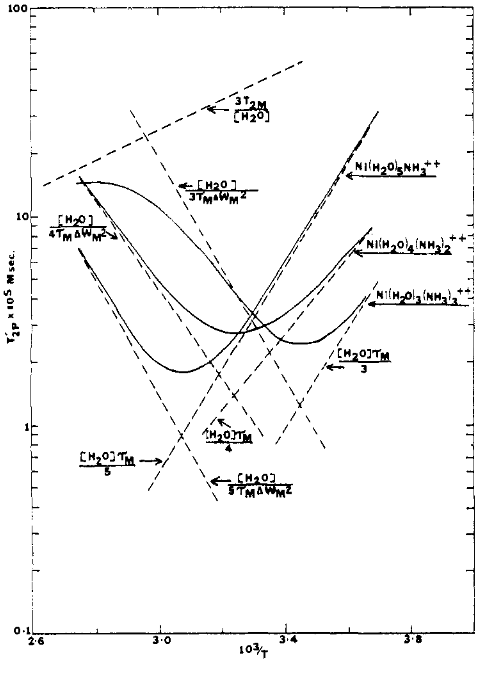

Figure 3. Semilogarithmic plot of T_{2p}' *vs.* $10^3/T$ for individual species from curve fitting.

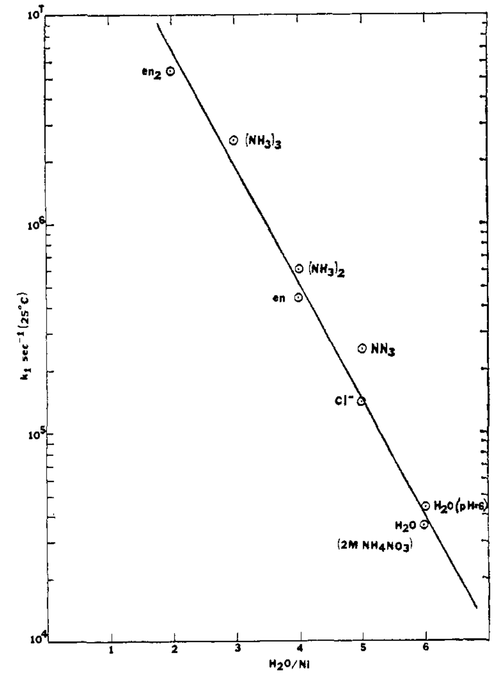

Figure 4. Effects of substitution on water lability at 25°.

In Table IV a summary of pertinent results is given. The errors shown are based on the precision of fitting. The maximum uncertainties are believed to be no greater than twice the listed errors. The scalar coupling constants are calculated from the equation $A/h = (T\Delta\omega_M/\omega_0)(3k/2\pi)(\gamma_N/S(S + 1)g_{eff}\beta)$ using a g_{eff} value consistent with $\mu_{eff} = 3.10$ for the ammines and 3.24 for $Ni(H_2O)_6^{2+}$. The quantity T_{1e} for $Ni(H_2O)_3(NH_3)_3^{2+}$ was calculated from $1/T_{2M} = (^2/_3)S(S + 1)\cdot$

$(A/\hbar)^2T_{1e}$ and E_a from the apparent temperature variation of T_{2M}. The k_1 values are per water molecule assuming them all to be equivalent in a species.

Discussion

In Figure 4 are plotted water exchange results for a variety of species measured by our group using ^{17}O nmr techniques. The data for NCS$^-$ complexes of Ni(II) would fit the line at 25° were the Ni(NCS)$_3$(H$_2$O)$_3$$^-$ species the correct one. The activation enthalpies are lower in general for Cl$^-$ and NCS$^-$ species[7,8] (8 and 6 kcal/mol, respectively). For the others the values are near 10 kcal/mol. There appears to be a general, somewhat regular, labilization of the remaining water molecules upon successive substitution in the aquo ion. The activation parameters appear to vary somewhat nonsystematically. Part of the increased rate does seem to involve the entropy factor. Scalar coupling constants (^{17}O) are quite similar for all species. No doubt both electronic and solvation effects are involved in the observed results, but it is difficult to see a clear explanation at this time.

It is most interesting to note that Rablen and Gordon[3] have found that terpyridyl does not produce the effects mentioned above and in fact causes only a small change in the water lability. Dr. M. Grant in this laboratory has completed a study of the aquo Ni(dipyridyl)$^{2+}$ and Ni(dipyridyl)$_2$$^{2+}$ systems and finds results similar to those of Rablen. It is tempting to ascribe these results to possible back π bonding effects where aromatic rings are involved.

Some comments on the validity and meaning of the nmr studies may be in order. When one replaces all of the water by using excess ligand, no line broadening effects or shifts are observed in the concentration ranges employed. This fact rules out possible contributions to the observed rates from outer-sphere complexes or by water substitution on the fully formed complex. Earlier work in this laboratory on Cl$^-$ and NCS$^-$ showed, indeed, that the results could not be accounted for by processes in which each ligand always replaced the other ("coupled" processes).

The observed activation parameters are somewhat dependent on the absolute values of ΔH for formation of the complexes and these may not always be reliable. The effects observed so far are fairly small and basically hard to account for.

Acknowledgments. We wish to thank the Washington State University Research Committee for funds enabling purchase of the ^{17}O.

---

(7) S. F. Lincoln, F. Aprile, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, 7, 929 (1968).

(8) R. B. Jordan, H. W. Dodgen, and J. P. Hunt, *ibid.*, 5, 1906 (1966).

Structural Studies of Pentacoordinate Silicon. VI. Cyclobis(benzamidodimethylsilane)

F. P. Boer and F. P. van Remoortere

Contribution from the Dow Chemical Company,
Eastern Research Laboratory, Wayland, Massachusetts 01778.

Received July 10, 1969

Abstract: The crystal and molecular structure of 2,2,4,4-tetramethyl-3-benzoyl-6-phenyl-2,4-disila-1,3,5-oxadiazine, $C_{18}H_{22}N_2O_2Si_2$, has been determined by a single-crystal three-dimensional X-ray diffraction study. This compound crystallizes in the centrosymmetric space group Pbca with lattice parameters $a = 10.543 \pm 0.005$, $b = 8.281 \pm 0.003$, and $c = 43.443 \pm 0.020$ Å ($Z = 8$). The intensity data were collected on a Picker automatic diffractometer (Cu Kα radiation) and the structure was solved by iterative application of Sayre's equation. All but methyl hydrogens were located by difference synthesis. Full matrix least-squares refinement of atom positions, hydrogen isotropic thermal parameters, and anisotropic thermal parameters for all other atoms converged at a final $R_1 = 6.1\%$ for 2376 reflections above background. The structure suggests that the Si atom bonded to oxygen is incipiently pentacoordinate *via* an interaction with the exocyclic carbonyl group. The Si···O distance is 2.613 ± 0.003 Å, substantially less than the sum of the Si and O van der Waals radii, 3.35 Å. Distortion of the bond angles provides additional evidence for this interaction. The heterocyclic ring is essentially planar, with a maximum deviation from the least-squares plane of 0.13 Å. The structural features are discussed in relation to the tautomerizations observed for disilaoxadiazines.

A recent series of X-ray diffraction studies[1-5] has demonstrated the presence of expanded-octet bonding in stable organosilicon compounds and thus provided support for the extracoordinate intermediates believed to form during displacement reactions at silicon.[6] Pentacoordinate silicon has been directly established in dimethylsilylamine pentamer,[7] in bis(*o*-phenylenedioxy)phenylsiliconate,[3] and in several triptych compounds,[1,2,4,5] all of which assume essentially a trigonal bipyramid geometry.

Valence shell expansion of silicon has also been pro-

---

(1) J. W. Turley and F. P. Boer, *J. Amer. Chem. Soc.*, 90, 4026 (1968).

(2) F. P. Boer, J. W. Turley, and J. J. Flynn, *ibid.*, 90, 5102 (1968).

(3) F. P. Boer, J. J. Flynn, and J. W. Turley, *ibid.*, 90, 6973 (1968).

(4) J. W. Turley and F. P. Boer, *ibid.*, 91, 4129 (1969).

(5) F. P. Boer and J. W. Turley, *ibid.*, 91, 4134 (1969).

(6) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

(7) R. Rudman, W. C. Hamilton, S. Novick, and T. D. Goldfarb, *J. Amer. Chem. Soc.*, 89, 5157 (1967).