Table VII. A Comparison of Nucleophilic Reactivity at Divalent Sulfur, sp^3 Carbon, and Platinum(II)

Values of 10^3k_2, M^{-1} sec^{-1} for nucl	Subst at $S_3O_6^{2-}$ (eq 12)[a]	Subst at sp^3 carbon (eq 21)[b]	Subst at Pt-(II) (eq 22)[b]
$C_2H_5S^-$	740		
$C_6H_5S^-$	28	1070	6,000
$(C_6H_5)_3P$	7.1	1.3	249,000
CN^-	0.5	0.65	4,000
SO_3^{2-}	0.02–0.003	44	250
$S_2O_3^{2-}$	<0.003	114	9,000

[a] See footnotes in Table V. [b] Values at 25° in methanol solvent, from ref 27.

That polarizable nucleophiles react with particular advantage at the bridge sulfur in trithionate is readily understood by considering the effect of the two lone pairs and two bond pairs of electrons present on that center.[8] The electrophilic character of the bridge sulfur resembles that of peroxide oxygen[26] and sulfenyl sulfur.[9] Although polarizability is the dominant factor, basicity is also important, more so, it would appear, than at peroxide oxygen or sulfenyl sulfur. This behavior in trithionate may arise from a greater degree of bond breaking in the transition state, resulting in a greater positive charge on the bridge sulfur.

$$^-O_3SS^{\delta+}\cdots SO_3^{(1+\delta)-}$$

Thus, nucleophiles which are good proton bases are likely to be more effective in displacing the rather basic SO_3^{2-} ion.[7]

It is of interest to compare reactivity at the bridge sulfur in trithionate with that found for substitution at sp^3 carbon in methyl iodide (eq 21) and at Pt(II) in *trans*-$Pt(py)_2Cl_2$ (eq 22).[27] Rate data for nucleophiles

$$CH_3I + Nu^- \longrightarrow CH_3Nu + I^- \qquad (21)$$

$$trans\text{-}Pt(py)_2Cl_2 + 2Nu^- \longrightarrow trans\text{-}Pt(py)_2Nu_2 + 2Cl^- \qquad (22)$$

in common are presented in Table VII. The three centers are similar in their general response to polarizability in the nucleophile. However, they clearly do not share any overall order of reactivity. The bridge-sulfur center resembles more closely the medium-soft sp^3 carbon than it does the very soft Pt(II). Reactions at divalent sulfur, like those at sp^3 carbon, are subject to steric hindrance.[2] Thus, the reactivity of triphenylphosphine at these centers may be considerably reduced (*cf.* triphenylphosphine at platinum). It is surprising that the lower rate for $(C_6H_5)_3P$ appears to arise from an entropy effect (Table V). In comparing reactivities at these three centers, account must be taken of the effect of the difference in charge type. The inherent reactivities of negatively charged nucleophiles, especially those of SO_3^{2-} and $S_2O_3^{2-}$, are partially masked in reaction with the $S_3O_6^{2-}$ ion. The large, negative $\Delta S^{\neq}$ values (Table V) indicate the magnitude of this electrostatic effect on the rate.

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Kinetics of Water Exchange between Solvent and Aquobipyridylnickel(II) Complexes

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Abstract: Water exchange rates with $Ni(H_2O)_6^{2+}$, $Ni(H_2O)_4bipy^{2+}$, and $Ni(H_2O)_2(bipy)_2^{2+}$ in 10^{-3} *M* HCl are reported. The k_1 (25°, sec^{-1}) values (per H_2O) are 3.2×10^4, 4.9×10^4, and 6.6×10^4, respectively. The corresponding ΔH^* and ΔS^* values are 12.1 ± 0.5, 2.6 ± 2; 12.6 ± 0.5, 5.1 ± 2; and 13.7 ± 0.5, 9.2 ± 4 kcal mol^{-1}, eu. Scalar coupling constants (A/h) in the same order are 2.1×10^7, 1.6×10^7, and 3.8×10^7 cps. A summary of data on $Ni(H_2O)_6^{2+}$ is given.

In previous studies[2] on nickel complexes we have reported labilizing effects on water molecules in aquo complexes as a result of substitution of water by various ligands. Rablen and Gordon[3] found that terpyridine substitution, on the contrary, caused only a small change in water exchange rates. We wish to report here studies on 2,2′-bipyridyl complexes of nickel where similarly only a slight change in water exchange behavior occurs.

Experimental Section

The nmr equipment and techniques used have been described.[4] A Varian 24.6-kG magnet was employed and the ^{17}O resonance ordinarily observed at 14.19 MHz.

The water used was obtained from YEDA R and D Co. Ltd., Rehovoth, Israel, and contained *ca.* 7 atom % ^{17}O (normal H content). It was distilled *in vacuo* for reuse. Other reagents were Mallinckrodt AR $Ni(NO_3)_2 \cdot 6H_2O$, HCl, and 2,2′-bipyridyl purified by sublimation or recrystallization from water.

Solutions were prepared from measured amounts of all reagents. Hydrochloric acid was used to give a pH of 2.9 to reduce possible

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(1) This work supported by USAEC contract No. AT(45-1)-2040 and is report No. RLO-2040-17.

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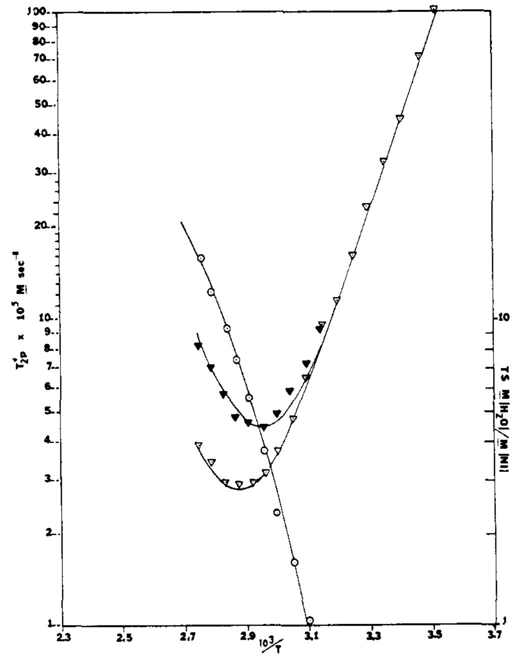

Figure 1. Semilogarithmic plot of T_{2p}^* *vs.* $10^3/T$ and $TSM(H_2O)/M(Ni)$ *vs.* $10^3/T$ for solution B. The right-hand scale refers to the shift data. ⊙, shift function; ▽, 14.19 MHz; ▼, 8.53 MHz.

complications due to hydrolysis. Nickel concentration was 0.1 or 0.4 *M*. No attempt to keep ionic strength constant was made as the K_{eq} values are not known over the necessary range. Data in the literature suggest that ionic strength effects are small. The measured values of Anderegg[5] (μ = 0.1, $NaNO_3$) were used to calculate equilibrium concentrations of species as a function of temperature. Competition of H^+ for the ligand could be neglected and solution composition varied only slightly with temperature so that mean values were used over the temperature range studied (*ca.* 0–90°). The calculated constitutions of the solutions used are given in Table I.

Table I. Solution Composition[a]

Soln	Ni(II), *M*	ΣL, *M*	% Ni-$(H_2O)_6^{2+}$	% Ni-$(H_2O)_4$-bipy^{2+}	% Ni-$(H_2O)_2$-$(bipy)_2^{2+}$	% Ni-$(bipy)_3^{2+}$
A	0.40	0.28	49.3	34.3	13.7	2.7
	0.10	0.070				
B	0.40	0.40	34.6	36.9	22.2	6.3
	0.10	0.10				
C	0.40	0.60	17.3	31.7	33.7	17.3
	0.10	0.15				

[a] Parameters used in calculations are $Ni(H_2O)_4bipy^{2+}$: log β_1 = 7.1, ΔH = −9.6 (kcal mol^{-1}); $Ni(H_2O)_2(bipy)_2^{2+}$: log β_2 = 14.01, ΔH = −19.0 (overall); $Ni(bipy)_3^{2+}$: log β_3 = 20.54, ΔH = −28.2 (overall).

Treatment of Data and Results

A rather complete discussion of the treatment of data has appeared.[2] Some points pertinent to the present system are as follows. A detailed study of the $Ni(H_2O)_6^{2+}$ system in 10^{-3} *M* HCl was carried out. Both line-broadening and shift measurements were made at 24.6 and 14.8 kG. These results are given in Table IV. Our values are very similar to those of Connick and Fiat[6] (ΔH^* may be slightly higher) in 0.1 *M* $HClO_4$. Our numbers were used to help sort the contributions of the various species. It was found that $Ni(bipy)_3^{2+}$ solutions showed no line broadenings at the concentrations used in this work. The line-broadening data were treated in terms of $T_{2p}^* \equiv 2M(Ni)/\gamma\Delta'$, where *M*(Ni) refers to total concentration of *water-containing nickel species*, γ is 3628 G^{-1} sec^{-1}, and Δ' is the line broadening $W - W_0$. Here *W* is the full line width at one-half maximum in the absorption curve for the paramagnetic solution and W_0 the same for the blank. The blank used was 0.1 *M* $Zn(ClO_4)_2$ in 10^{-3} *M* HCl. The observed width of the blank varied from *ca.* 0.22 to 0.13 G over the temperature range involved. Chemical shifts were used in the form $Q = TSM(H_2O)/M(Ni)$ where *T* is the absolute temperature, *S* is the shift in ppm relative to the blank, and the molarities refer to free water and total nickel concentrations.

Typical data at 24.6 kG are given for solution B in Table II. These data are plotted in Figure 1. The Arrhenius regions for solutions A, B, and C were very similar with a slight increase in slope as more bisbipyridyl complex was present. As previously found,[2] the results are mainly controlled by a $\Delta\omega$ mechanism, but a small contribution from T_{2M} is needed for the higher complexed species. Line broadenings were measured at 24.6 and 14.8 kG, $\Delta\omega$ was assumed to be proportional to magnetic field strength, and the relevant parameters were chosen to be consistent with the line broadening and the shift data. The data obtained by curve fitting are given in Table III. The scalar cou-

Table II. Typical Data for Solution B, 24.6 kG

A. Line-broadening data			B. Shift data		
Temp, °C	Δ′, G	T_{2p}^* × 10^5 *M* sec	Temp, °C	*S*, ppm	*TSM*-(H_2O)/*M*(Ni)
11.0[a]	0.20	102	49.2[b]	4.3	1.04
15.4	0.29	72	55.0	8.8	1.60
21.0	0.47	44	60.0	12.8	2.37
25.6	0.63	33	65.0	20.2	3.78
30.5	0.90	23	70.0	29.3	5.57
35.0	1.29	16.1	75.3	38.3	7.40
39.9	1.80	11.5	79.7	47.9	9.40
45.0[b]	0.54	9.6	85.3	55.3	12.2
50.0	0.80	6.4	91.1	61.8	15.8
55.0	1.09	4.7			
60.4	1.38	3.7			
65.0	1.64	3.2			
69.5	1.75	2.95			
74.6	1.77	2.92			
80.1	1.75	2.95			
86.0	1.51	3.4			
91.2	1.33	3.9			

[a] Solutions 0.4 *M* in Ni to 45.0°. [b] Solutions 0.1 *M* in Ni above 45°.

Table III. Kinetic and Nmr Parameters

	$Ni(H_2O)_6^{2+}$	$Ni(H_2O)_4$-$(bipy)^{2+}$	$Ni(H_2O)_2$-$(bipy)_2^{2+}$
Exchange rate (25°), *M* sec^{-1}	1.92 × 10^6	1.99 × 10^6	1.32 × 10^6
k_1, sec^{-1} (25°)	3.2 × 10^4	4.9 × 10^4	6.6 × 10^4
ΔH^*, kcal mol^{-1}	12.1 ± 0.5	12.6 ± 0.5	13.7 ± 0.5
ΔS^*, cal mol^{-1} deg^{-1}	2.6 ± 2	5.1 ± 2	9.2 ± 4
A/*h*, cps	2.1 × 10^7	1.6 × 10^7	3.8 × 10^7
T_{1e}, sec			*Ca.* 1 × 10^{-12}
E_a for T_{1e}, kcal mol^{-1}			*Ca.* 2

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(5) G. Anderegg, *Helv. Chim. Acta*, **46**, 2397, 2813 (1963).

(6) R. E. Connick and D. Fiat, *J. Chem. Phys.*, **44**, 4103 (1966).

pling constants were calculated from $A/h = (T\Delta\omega_M/\omega_0)(3k/2\pi)(\gamma_N/S(S+1)g_{eff}\beta)$ using g_{eff} values consistent with $\mu_{eff} = 3.2$ BM. Values of k_1 are calculated from $R = nk_1$[Ni species] where n is the number of water molecules present in the species.

Discussion

It may be useful at this stage to summarize the results on $Ni(H_2O)_6^{2+}$ obtained by various investigators under differing conditions. Pertinent quantities are listed in Table IV. The values at low μ and pH are in fair agreement except for the corrected A/h value of Swift, which is out of line. High ionic strength and pH does appear to produce small effects outside of experimental error.

Table IV. Kinetic and Nmr Data on $Ni(H_2O)_6^{2+}$

Conditions	k_1, sec^{-1} (25°)	ΔH^*, kcal mol^{-1}	A/h, cps	Ref
0.1 M $HClO_4$ μ *ca.* 0.4	2.7×10^4	11.6	4.3×10^7	*a*
0.1 M $HClO_4$ $\mu = 0.2 \rightarrow 0.7$	3.0×10^4	10.8	1.9×10^7	6
6.5 M $LiClO_4$	4.1×10^4	9.6	2.8×10^7	*b*
$\mu = 0.5$, pH 6	4.4×10^4	10.3	2.2×10^7	2a
$\mu = 0.4$–1.0, pH 3	3.4×10^4	12.1		3
2 M NH_4NO_3 pH $\simeq 5$	3.6×10^4	12.3	2.3×10^7	2b
10^{-3} M HCl $\mu = 0.3 \rightarrow 1.4$	3.2×10^4	12.1	2.1×10^7	This work

[a] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).
[b] S. F. Lincoln, F. Aprile, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **7**, 929 (1968).

From Table III one can see that bipyridyl produces a relatively small increase in k_1 as it substitutes for water. The slight increase in ΔH^* seems to be real. For the terpyridyl complex similar effects were found,[3] k_1 being intermediate between those for mono- and bisbipyridyl, although ΔH^* seems to be somewhat lower (10.7 ± 0.4). On the other hand, ethylenediamine (en) shows k_1 increasing by factors of *ca.* 10 and 100 for mono and bis species.[2] Other ligands whose effects are consistent with en behavior are Cl^-, NCS^-, and NH_3. Contact-shift studies[7] have suggested some π interaction between nickel and bipyridyl-type ligands. Compensating electron donation effects between σ and back-π bonding could be involved. Solvation changes are probably important also and entropy effects are clearly involved when one looks at all the data.

The so-called "Eigen mechanism" for substitution in labile aquo complexes relates net substitution rates to outer-sphere complex constants (K_{os}) and water exchange rates in the aquo ion. Wilkins,[8] *et al.*, have reported a formation rate constant, k_f (25°), for addition of bipyridyl to $Ni(H_2O)_2(bipy)_2^{2+}$ as 2.0×10^{-3}. Using our water-exchange *rate* for this species one calculates $K_{os} = 0.015$, rather lower than the "usual" value of 0.1 used for neutral ligands. Were the diaquo species *trans*, a possible factor for the effect could be envisioned. Relations between water-exchange and substitution rates can, of course, be rationalized by appropriate changes in estimates of K_{os} as these constants are not generally measurable or even defined uniquely. That such a procedure is not very reasonable is strongly suggested by the recent communication by Caldin[9] in which solvent effects are reported. As more data become available on water exchange in substituted aquo ions and more values of ΔH^* and ΔS^* for net substitution reactions are measured, one can expect a number of subtler effects to be exposed. Certainly solvation effects must be important and mechanisms can change.

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