hibited strong NO stretching frequencies at *ca.* 1775 cm^{-1}, and borohydride reduction of these solutions afforded unstable yellow-green solutions. Neither of these solutions afforded solids when treated with a variety of countercations.

In conclusion, the voltammetric, esr, and infrared spectral results seem to indicate that the initial electron-transfer reaction is relatively fast whereas the subsequent reactions, either electron reexchange or ligand exchange, occurring simultaneously or sequentially, occur relatively slowly. The intermediate in these exchange reactions may be a dimeric species, as has been suggested for the nickel bisdithiolene exchange reactions.

Experimental Section

The nitrosyl complexes employed in this work were prepared as described previously.[4] Voltammetric measurements were made using a Heathkit Model EUW-401 instrument with a platinum electrode rotating at 620 rpm. All results were obtained in dried and redistilled dichloromethane at 25°, which contained the complexes at 10^{-3} M and the base electrolyte $[(C_2H_5)_4]ClO_4$ at 0.1 M concentrations. The results are quoted against a saturated calomel electrode containing 1 M aqueous LiCl solutions. The electron spin resonance spectra were obtained at room temperature using a Varian Model V-4500 spectrometer and the infrared spectra in dichloromethane solution were recorded using Unicam SP100 and Infracord 457 spectrophotometers.

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Water Exchange Rate of the Mono(2,2',2''-terpyridine)nickel(II) Ion by Oxygen-17 Nuclear Magnetic Resonance[1a]

BY DAVID RABLEN AND GILBERT GORDON[1b]

In two recent publications, Wilkins and coworkers[2,3] have reported the substitution kinetics of a number of first-row transition series bivalent metal ions with the ligands phenanthroline (including substituted phenanthrolines), bipyridine, and 2,2',2''-terpyridine (terpyridine). The substitution rates observed for formation of all 1:1 complexes and the higher bipyridine and phenanthroline complexes conformed to the general ligand–metal ion complex formation mech-

anism[4] with no significant effect of previously coordinated ligands on the substitution rate. However, in the case of formation of bis(terpyridine) complexes from the mono complexes for Fe(II), Co(II), and Ni(II) (the only metal ions for which the reaction could be conveniently studied) substitution rates were observed to be respectively 7×10^2, 6×10^2, and 2×10^2 times more rapid than the formation rates of the corresponding mono complexes.[5] Since these results strongly suggested that the coordinated terpyridine had labilized the water in the first coordination sphere of these ions, we considered it of interest to test this hypothesis by directly measuring the water-exchange rate by means of the oxygen-17 nuclear magnetic resonance line-broadening technique.[6,7] Since the mono(terpyridine)-nickel(II) complex is considerably more inert to disproportionation[8] than the corresponding complexes of Fe(II) and Co(II), it was selected for study.

In addition, measurements of the rate of water exchange for the aquonickel ion were made and are compared to those reported by Connick and coworkers.[6,9]

Experimental Section

Bis(terpyridine)nickel(II) bromide was prepared according to the procedure of Morgan and Burstall.[10] Mono(terpyridine)-nickel(II) bromide was prepared by thermal decomposition of the bis complex as described by Hogg and Wilkins.[8] *Anal.* Calcd for $NiC_{15}H_{11}N_3Br_2$: C, 39.6; H, 2.5; N, 9.1. Found: C, 39.8; H, 2.45; N, 9.3.

The terpyridine used in these preparations was obtained from the G. Frederick Smith Chemical Co., Columbus, Ohio. It was purified by sublimation; the melting point (85.5–86.0°) was in good agreement with the literature value.[8] The water employed in the nmr experiments was obtained from Yeda Research and Development Co., Ltd., Rehovoth, Israel, and contained 2.14% O^{17} and 14.2% O^{18}.

The nuclear magnetic resonance line width measurements were carried out on two independently prepared solutions for both the aquonickel and mono(terpyridine)nickel(II) ions. The solutions were prepared by weight and molarities were calculated from densities which were measured by weighing solutions in a calibrated polyethylene pipet. Solution A of mono(terpyridine)-nickel(II) bromide was prepared from a sample of this salt generously provided by R. G. Wilkins. In all cases, solutions were sufficiently acidic to avoid any possibility of errors caused by the strong pH dependence of the line width of water in the vicinity of the neutral point.[11] Solutions were acidified with small portions of nitric acid which were added to the enriched water samples with a microliter syringe and the pH values were checked with a Beckman Model G pH meter. In order to detect any possible disproportionation of the mono(terpyridine)nickel(II) complex, the optical absorption spectra of solutions were recorded before and after the nmr line width measurements by means of a Cary 14 spectrophotometer. At 900 mμ, these measurements

(1) (a) Part of a Ph.D. Thesis submitted by D. Rablen to the University of Maryland, Jan 1968. (b) Address enquiries to this author at the Department of Chemistry, University of Iowa, Iowa City, Iowa 52240.

(2) R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **4**, 929 (1965).

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(11) S. Meiboom, *J. Chem. Phys.*, **34**, 375 (1961).

would have revealed a change of 1% in the concentration of the mono(terpyridine)nickel(II) species.[12] No changes in the optical spectra were observed.

The line widths of acidified oxygen-17 water[13] were measured as a function of temperature in the range 0–100°. All solution line widths were corrected for the natural line width of water at that particular temperature and pH. No additional corrections for second-sphere broadening were made.[7] The line width measurements were performed with a Varian DP-60 nuclear magnetic resonance spectrometer in the wide-line configuration at 8.00 MHz by using a variable-frequency oscillator. The side-band method of detection[14] was employed with 395-Hz modulation. The solutions were contained in a two-piece dewar cell which was equipped with a heat-exchange coil and thermocouple well. A similar cell has been described by Swift and Connick.[6] The sample temperature was controlled to ±0.3° with a gas flow cryostat. Temperatures were measured with a copper-constantan thermocouple. The variable-frequency oscillator was continuously monitored with a Hewlett-Packard Model 524 D frequency counter during line width scans. The precession field scanning unit was calibrated by introducing known increments in the frequency and measuring the distance in length of chart paper between resonances of a sample of O^{17}-enriched water as the magnetic field was continuously scanned. Calibration factors were reproducible to ±0.5%. A minimum of three line width scans were made at each temperature.

Results and Discussion

The experimental results of the line width measurements for both the aquonickel ion and mono(terpyridine nickel(II) are shown in Figure 1. The quantity $(2\pi T_{2p})^{-1}$ has been calculated by subtracting the water
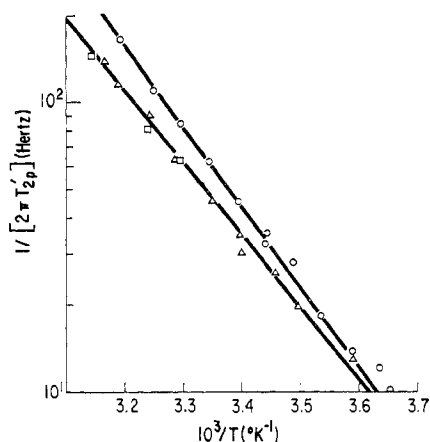

Figure 1.—Log $[1/2\pi T_{2p}']$ for O^{17} as a function of reciprocal absolute temperature. The data points represent original $[2\pi T_{2p}']^{-1}$ data which have been normalized to 0.10 M paramagnetic species: O, measurements made on 0.136 and 0.368 M solutions of nickel nitrate; □, measurements made on a 0.0595 M sample of mono(terpyridine)nickel(II) bromide supplied by R. G. Wilkins; △, measurements made on a 0.0981 M sample of mono(terpyridine)nickel(II) bromide from this work.

line width from the observed line width and gives the broadening due to the paramagnetic species in hertz. In Figure 1, the data have been normalized[6] to that of a 0.10 M solution $(2\pi T_{2p}')$. For both the aquonickel ion and the mono(terpyridine)nickel(II) ion, good linearity of the log $(2\pi T_{2p}')^{-1}$–reciprocal temperature plot is observed. This behavior is taken as evidence that the line broadening is limited by the lifetime of water molecules in the first coordination sphere of the ion in question. Under these conditions, regardless of relaxation mechanism,[6] $T_{2p}^{-1} = P_M \tau_M^{-1}$, where T_{2p}^{-1} is the relaxation rate due to the presence of the paramagnetic ion, τ_M is the mean lifetime of a water molecule in the first coordination sphere, and $P_M = n[M]/[H_2O]$, where n is the hydration number of the paramagnetic species, $[M]$ is its molar concentration, and $[H_2O]$ is the molar concentration of water. The pseudo-first-order rate constant for water exchange is then given by $(T_{2p}')^{-1}[H_2O]/n[M] = \tau_M^{-1}$ or k_e. The data in Figure 1 were fitted to the equation

$$\ln (\tau_M^{-1}) = \ln k_e = \ln (kT/h) -$$
$$[\Delta H^{\ddagger}/RT] + [\Delta S^{\ddagger}/R] \quad (1)$$

by using a nonlinear least-squares treatment.[15] This yielded the following activation parameters at 25°: aquonickel(II) nitrate, $k_e = (3.4 \pm 0.1) \times 10^4$ sec^{-1}, $\Delta H^{\ddagger} = (12.1 \pm 0.3)$ kcal mol^{-1}, $\Delta S^{\ddagger} = (2.9 \pm 0.9)$ eu; mono(terpyridine)nickel(II) bromide, $k_e = (5.2 \pm 0.4) \times 10^4$ sec^{-1}, $\Delta H^{\ddagger} = (10.7 \pm 0.4)$ kcal mol^{-1}, $\Delta S^{\ddagger} = (-1.0 \pm 1)$ eu.

The indicated uncertainties correspond to standard deviations and are calculated directly by the program.[15] The above parameters were calculated by assuming that the coordination sphere of the aquonickel ion contains six kinetically equivalent water molecules and that the mono(terpyridine)nickel(II) ion contains three. These hydration numbers are only estimated but nonetheless with any reasonable hydration number for these two ions, one must conclude that the water-exchange rates for the two ions are very similar. By using the above values of 6 and 3, the water-exchange rate of the mono(terpyridine)nickel(II) ion is calculated to be only 1.5 times faster than the rate of water exchange for the aquonickel at room temperature.

Our results for the aquonickel ion are in good agreement with the values reported by Swift and Connick[6] and Connick and Fiat.[9,16] In the former study, it was reported that at 25°, $k_e = 2.7 \times 10^4$ sec^{-1}, $\Delta H^{\ddagger} = 11.6$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 0.6$ eu, and in the latter study $k_e = 3.4 \times 10^4$ sec^{-1}, $\Delta H^{\ddagger} = (10.8 \pm 0.5)$ kcal mol^{-1}.

A considerable body of evidence has been accumu-

(12) At 900 mμ the extinction coefficients of the aquonickel ion, the mono-(terpyridine)nickel(II) ion, and bis(terpyridine)nickel(II) ion are, respectively, 0, 18, and 20 M^{-1} cm^{-1}. These values are such that any disproportionation of the mono(terpyridine)nickel(II) ion according to the stoichiometry 2Ni(terpy)$^{2+}$ ⇌ Ni^{2+} + Ni(terpy)$_2^{2+}$ can readily be detected.

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(14) J. V. Acrivos, *J. Chem. Phys.*, **36**, 1097 (1962).

(15) The nonlinear least-squares computer program was obtained from T. W. Newton and R. Moore and is described in Los Alamos Scientific Report LA-2367 plus addenda.

(16) D. Fiat, XIVth Colloque Ampere, Ljubljana, Yugoslavia, "Magnetic and Electric Resonance and Relaxation," L. Blinc, Ed., North-Holland Publishing Co., Amsterdam, 1967.

lated supporting the view that substitution reactions of a large number of aquometal ions conform to a two-step mechanism first formulated by Eigen

$$L + M(H_2O)_6 \xrightarrow{K_{os}} M(H_2O)_6 \cdots L \xrightarrow{k_e} L-M(H_2O)_5 + H_2O \quad (2)$$
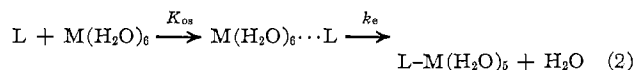
In the first step, the aquometal ion and ligand diffuse together to form an outer-sphere complex with an association constant K_{os}. This process is followed by the rate-determining step, which corresponds to the loss of a coordinated water molecule from the metal ion. According to this mechanism, the second-order formation rate constant k_{M-L} is given by the equation

$$k_{M-L} = K_{os}k_e \quad (3)$$

where K_{os} is the outer-sphere formation constant and k_e is the rate constant for water exchange of the outer-sphere complex.

The outer-sphere formation constant is given by the equation

$$K_{os} = 4\pi Na^3/3000$$

where N is Avogadro's number and a is the distance of closest approach of the two partners of the outer-sphere complex. For a large number of metal-substitution reactions, K_{os} values of 0.1 have been calculated and the corresponding water-exchange rates account nicely for the magnitude of the second-order substitution rate constant. For the mono(terpyridine)nickel(II) reaction,[3] a K_{os} value of approximately 4 would be required to be consistent with the rate of water exchange reported here for the mono(terpyridine)nickel-(II) ion.

If the theoretical equations used to calculate K_{os} values are strictly applicable for outer-sphere formation between mono(terpyridine)nickel(II) and terpyridine, then the unusually large values of K_{os} required to accommodate the water-exchange rate and mono(terpyridine)nickel(II)–terpyridine substitution rate serve as evidence of the breakdown of the general metal ion–ligand complex formation mechanism in this instance. The reaction could then be classified as S_N2. However, one cannot rule out the possibility that at least a weak interaction between the two terpyridine molecules in the mono(terpyridine)nickel-(II)–terpyridine outer-sphere complex gives rise to an enhanced K_{os}.

It will be of considerable interest to extend substitution studies of the mono(terpyridine)nickel(II) ion to other ligands, particularly monodentates and bidentates, to determine if rapid substitution is general or just characteristic of certain ligands.

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Potassium Calcium Paramolybdate and Cryoscopy of Paramolybdates

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Paramolybdates react, in solution, with various metal cations, especially those of most transition metals, to form heteropoly complexes.[2] It was found that a reproducible new salt forms when a solution containing potassium paramolybdate is treated with calcium ions. Since it has sometimes been contended[3] that spherically symmetrical ions such as Ca^{2+} and Mg^{2+} might also form heteropoly anions with molybdates, it was desirable to subject the new salt to more detailed investigation as a contribution toward settling that point. As expected, this investigation has shown that the new compound is a double salt, $K_4Ca[Mo_7O_{24}] \cdot 7H_2O$, wherein the calcium is not in the anionic complex in solution. This work led to potentiometric, spectrophotometric, and cryoscopic investigations of paramolybdate. The crystallographic unit cell and space group for the new double salt were determined by single-crystal X-ray studies. The combined results add confirmation, by a sensitive independent method, to the formula for paramolybdate which has been proposed in recent years by Lindqvist[4] and Sillén and coworkers.[5]

Experimental Section

Preparation of Potassium Calcium Paramolybdate.—A sample of $K_2CO_3 \cdot 1.5H_2O$ weighing 11.48 g (0.0695 mol) was dissolved in water and the solution was heated to boiling, whereupon 10.0 g (0.0695 mol) of MoO_3 was added slowly in small portions. After the evolution of carbon dioxide had ceased, heating was discontinued and concentrated nitric acid was added to the hot solution until methyl red turned orange (pH 5). The solution was diluted to about 200 ml and allowed to cool to 40° or less, and a solution of $Ca(NO_3)_2 \cdot 4H_2O$ in about 20 ml of water was added with stirring. The amounts of calcium nitrate used for different preparations were 5.0 g (0.0212 mol), 7.0 g (0.0297 mol), and 8.0 g (0.0339 mol). The pH's of the final solutions were in the range 4.7–5.3. Potassium nitrate was added to each solution to increase the rate of crystallization and the yield. The amount of KNO_3 added was not constant and varied from a few milliliters of a nearly saturated solution to 28 g (0.277 mol) of the salt. Thus, the total amount of K^+ ions used in the preparations was varied from 0.14 to 0.42 mol. The white, crystalline new double salt was filtered onto sintered glass, washed well with cold water followed by ace-

(1) Addressee for reprints, at Georgetown University

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