it hydrogen bonds to a paramagnetic triphenylphosphine triiodometalate(II).[14] However, it is questionable whether this type of interaction could transmit enough unpaired spin density to the nitrogen atom to give the size of contact shift observed. The third way in which unpaired spin could be transferred to the cation is through direct overlap of the metal orbitals containing unpaired spin with a nitrogen s orbital. This, of course, depends critically on the ion pairing distance. In the ^{17}O work on $Cr(H_2O)_6(ClO_4)_3$ mentioned previously,[16] it was assumed that the downfield ^{17}O shift for ClO_4^- and H_2O in the second coordination sphere was due to σ overlap of oxygen sp hybrid orbitals of H_2O or ClO_4^- with the Cr(III) t_{2g} orbitals. For our system it appears that this means of transferring spin to the cation is unlikely. If one calculates the value of a nickel 3d orbital at a distance 3.8 Å from the nickel and squares this number, the result is on the order of 10^{-8} au^{-3}. This is too small to contribute significantly to $|\Psi(0)|^2$ in eq 3. From eq 2 one would expect a value on the order of 1 au^{-3} for $|\Psi(0)|^2$ for a 1-ppm resonance shift. In addition, if spin were transferred directly to the cation by the metal 3d oribitals one might expect more spin to be transferred for a chloro complex than for an iodo complex because the cation could approach the metal more closely in the chloro complex. However, for both NiX_4^{2-} and CoX_4^{2-} anions the magnitude of the observed downfield shifts vary with X as $MCl_4^{2-} < MBr_4^{2-} < MI_4^{2-}$. This seems to be rather convincing experimental evidence that a nitrogen s orbital does not receive much spin from direct overlap with metal orbital, so that in all likelihood spin is transmitted to the cation through the halogen ligands of the complex. The halide orbitals containing unpaired spin must donate spin directly into a nitrogen s orbital giving the observed spin density at the nitrogen nucleus. The alternative proposed to this, that spin enters the σ framework of the cation through the H_1 proton, would not transfer enough spin to the nitrogen to give the isotropic shifts observed. However, it cannot be disputed that the H_1 proton is interacting with the halide ligands as evidenced by the results seen for the NiX_4^{2-} complexes. In fact it is quite likely that in all cases the H_1 resonance occurs at higher field than might be expected from only pseudocontact interaction.

It should be pointed out that the preceding discussion about the nature of the direct contact mechanism is of necessity very qualitative because of the fact that factors such as the exact manner in which spin is transferred to the cation. In addition to the fact that spin is transferred to the cation in these complexes, it is likely that multiple ion pairs or even micelle formation also occurs. Because of these two factors the simple method previously reported[5,7] for calculating ion pairing distances should not be expected to be particularly reliable. The very short distances calculated for the triphenylphosphine triiodometalates is probably due to a combination of these two effects.

To summarize, it has been shown that in systems with a tetrabutylammonium cation ion paired to a paramagnetic, ^{14}N isotropic resonance shifts have been observed. The only way in which the shifts can be explained is to postulate a Fermi contact interaction between the unpaired electrons on the anion and the cation. This requires some type of weak covalent interaction between the anion and cation in the ion pair.

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The Effect of Coordinated Ligands on the Rate of Replacement of Bound Water by Ammonia in Nickel(II) Complexes. II

J. Paul Jones, E. J. Billo, and Dale W. Margerum[1]

Contribution from the Department of Chemistry,
Purdue University, Lafayette, Indiana 47907. *Received August 30, 1969*

Abstract: As the number of coordinated nitrogens in nickel-polyamine complexes increases, the rate of replacement of the remaining coordinated water increases. Rate constants for the exchange of water by ammonia are larger for nickel-trien than for nickel-dien at 8° by a factor of 5. tren, a branched tetradentate polyamine, gives a more rapid NH_3-H_2O exchange than trien. Six-membered chelate rings in polyamine complexes and alkyl groups on en also increase the rate.

The characteristic rate of replacement[2] of water from the first coordination sphere is affected by the presence of other groups bound to the metal ion. An earlier paper[3] showed that the charge of the complex *per se* is not of much importance in the rate of replacement of water in nickel complexes, but that coordinated nitrogens tend to increase the exchange rate. Thus, the ammonia–water exchange in eq 1 increases as L is

$$[NiL(H_2O)_x]^n + NH_3 \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} [NiL(H_2O)_{x-1}(NH_3)]^n + H_2O \quad (1)$$

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[1] Author to whom correspondence should be addressed.

[2] For a review see (a) M. Eigen and R. G. Wilkins, "Mechanism of Inorganic Reactions," American Chemical Society, Washington, D. C., 1965, pp 55–65; (b) M. Eigen and L. DeMaeyer, "Technique of Organic Chemistry," Vol. VIII, Part II, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1963, pp 895–1054.

[3] D. W. Margerum and H. M. Rosen, *J. Amer. Chem. Soc.*, **89**, 1088 (1967).

Table I. Coordinated Ligands and Experimental Conditions Used in the Study[a]

Ligand	Ligand abbreviation	Range of $[NiL]_T \times 10^3$, M	Range of $[NH_3]_T \times 10^3$, M	pH range
Ethylenediamine	en	20–36	26–51	7.20–7.81
1,2-Diaminopropane	pn	17–50	20–53	7.60–8.15
N-Methylethylenediamine	N-Meen	3.5–33	13–39	7.35–8.06
N,N′-Dimethylethylenediamine	N,N′-diMeen	4.1–30	4.0–43	7.68–8.17
N-Ethylethylenediamine	N-Eten	3.5–33	13–39	7.61–8.02
N,N-Dimethylethylenediamine	N,N-diMeen	3.5–33	13–39	7.90–8.19
1,3-Diaminopropane	tn	4.1–33	13–39	7.86–8.19
N-Methyliminodiacetate	MeIDA	3.7–26	6.6–27	7.90–8.05
N-Hydroxyethyliminodiacetate	HEIDA	3.7–41	6.6–46	7.97–8.08
Ethylenediaminediacetate	EDDA	0.8–3.2	2.7–13	7.90–8.00
cis,cis-1,3,5-Triaminocyclohexane	*cis,cis*-tach	4.0–14	13–26	7.91–7.98
Triethylenetetramine	trien	11–37	66–130	8.02–8.11
Tris(2-aminoethyl)amine	tren	3.5–32	40–130	7.99–8.10

[a] $\mu = 0.40$ M $NaClO_4$ except for pn, where $\mu = 0.30$, and en where $\mu = 0.25$.

changed from water to en to dien. However, the exchange rates for nickel–trien and nickel–tetren appeared to be less than for aquo-nickel. A report by Gordon[4] that the H_2O^{17} exchange with $[Ni(tetren)(H_2O)]^{2+}$ was extremely rapid prompted us to reexamine the relaxation studies of the NH_3 reactions with $[Ni(trien)(H_2O)_2]^{2+}$ and with $[Ni(tetren)(H_2O)]^{2+}$. In the present work we have found a fast relaxation for the nickel–trien system at 8°; this relaxation is too fast for us to observe at 25°. The slow relaxation reported previously[3] for nickel–trien is shown to be due to another reaction. A fast relaxation was not observed with nickel–tetren but it could easily be too fast to measure under our conditions. We conclude that there is a continuous increase in water lability with increase in the number of coordinated nitrogens rather than a maximum at three.

In other aspects of the present study the configuration of the ligand, the chelate ring size, and the presence of N-alkyl groups are shown to significantly affect the NH_3-H_2O exchange rate.

Experimental Section

Reagents. The ligands used and their abbreviations are found in Table I.

Nickel perchlorate was prepared from nickel carbonate and perchloric acid and recrystallized from water. Nickel solutions were standardized by the addition of excess *trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetate followed by back-titration with Ca^{2+} using methyl thymol blue indicator.

Ammonia and pn were purified by distillation. trien was purified by extraction of the sulfate salt followed by distillation under reduced pressure. tetren was prepared and recrystallized as $[H_5(tetren)(SO_4)_{2.5} \cdot 2.5H_2O]$. MeIDA and HEIDA were recrystallized as the free acids. EDDA was boiled in basic solution to remove the cyclic imide form and was crystallized from water at pH 5–6 by adding 2-propanol. The EDDA was recrystallized several times by this procedure. The solution of EDDA was used soon after preparation to avoid the cyclic impurity. The hydrochloride salt of tren was prepared[5] and gave a good analysis of tren · 3HCl.

Solutions of other ligands were prepared from reagent grade chemicals without further purification.

The stock solutions of ammonia, en, N,N′-diMeen, N-Meen, N,N-diMeen, N-Eten, pn, tn, and MeIDA were standardized by acid or base titration. The stock solutions of trien, tetren, EDDA, and HEIDA were standardized by a spectrophotometric mole-ratio method with a standard copper solution. The stock solution of tren was standardized by adding excess zinc and titrating the released acid with NaOH.

A sample of $[Ni(cis,cis\text{-}tach)(H_2O)_3](NO_3)_2$ was obtained from Dr. R. A. D. Wentworth, Indiana University. Freshly prepared solutions were used to avoid possible hydrolysis or disproportionation.

Other complexes were prepared from stoichiometric amounts of nickel and ligand. Large ratios of $[NiL]/[NH_3]$ and $[NH_4^+]/[NH_3]$ were used in order to simplify the relaxation expression and to avoid the hydrolysis of nickel. Low concentrations of NH_3 and $NiLNH_3$ were also necessary to reduce the possibility of appreciable concentrations of $NiL(NH_3)_2$. In every case there was spectrophotometric evidence for mixed complexes.

Ionic strength was controlled with recrystallized $NaClO_4$. The pH was adjusted to the desired value with NaOH or $HClO_4$.

A summary of the experimental conditions for the ligands studied is given in Table I.

Kinetic Measurements. The temperature-jump apparatus used has been described previously.[3] The temperature-jump cell was thermostated to ±0.1° and the magnitude of the jump was 5.7° using a 40-kV discharge. Between jumps 5–7 min were allowed for the solution to attain temperature equilibrium.

The reaction studied is given in eq 1, where L is a multidentate ligand and x is 6 − the number of coordination positions occupied by L. Reaction 1 was coupled to the much faster reactions 2 and

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O \qquad (2)$$

$$In^- + H_2O \rightleftharpoons HIn + OH^- \qquad (3)$$

3 in order to provide a sensitive spectrophotometric method for following the relaxation. Phenol red (at 555 mμ) was used as the indicator.

For each system studied, a solution containing the nickel complex without ammonia was run to determine whether a relaxation was present due to other reactions. In some cases relaxation reactions due to the formation and dissociation of bidentate ligand complexes could be observed, but their τ values were much larger than that for reaction 1 and could be neglected or separated. The N,N-diethylethylenediamine and N-isopropylethylenediamine complexes had τ values of about the same magnitude as that for their reaction with NH_3 and thus were not studied further.

For reactions 1–3, the protolytic reactions reach equilibrium much faster than the metal complex reaction and can be assumed to be at equilibrium at all times. Thus the relaxation expression becomes

$$\frac{1}{\tau} = k_{21} + k_{12}\left([NH_3] + \frac{[NiL]}{1 + \alpha}\right) \qquad (4)$$

where

$$\alpha = \frac{[H^+]}{K_{NH_4^+} + [NH_3]\left(\dfrac{K_I + [H^+]}{K_I + [H^+] + [In]}\right)} \qquad (5)$$

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(4) In the lecture, but not in the abstracts, of his paper at the Xth International Conference on Coordination Chemistry, Nikko, Japan, Sept 1967.

(5) L. J. Wilson and N. J. Rose, *J. Amer. Chem. Soc.*, **90**, 6041 (1968).

Table II. Equilibrium Constants Used to Calculate Species Distribution

Ligand	Log K_{HL}	Log K_{H_2L}	Log K_{NiL}	Log K_{NiL_2}	Log K_{NiL_3}
Ethylenediamine (en)	10.18[a]	7.47	7.60	6.48	5.03
1,2-Diaminopropane (pn)	10.00[b]	7.13	7.43	6.19	4.27
N-Methylenethylenediamine (N-Meen)	10.40[a]	7.56	7.36	5.74	2.01
N,N′-Dimethylethylenediamine (N,N′-diMeen)	10.29[b]	7.47	7.11	4.73	1.50
N-Ethylethylenediamine (N-Eten)	10.56[a]	7.63	6.78	5.30	2.00
N,N-Dimethylethylenediamine (N,N-diMeen)	9.53[c]	6.63	6.67	3.85	2.82
1,3-Diaminopropane (tn)	10.62[d]	9.12	6.39	4.39	1.23
N-Methyliminodiacetate (MeIDA)	9.65	2.12	8.73	7.22	
N-Hydroxyethyliminodiacetate (HEIDA)	8.73[e]	2.20	9.28	4.97	
Ammonia (NH_3)	9.43[f]		2.80[g]	2.00	

[a] F. Basolo and R. K. Murmann, *J. Amer. Chem. Soc.*, **74**, 2373 (1952); **74**, 5243 (1952); 25°, 0.75 μ. [b] F. Basolo, R. K. Murmann, and Y. T. Chen, *ibid.*, **75**, 1478 (1953); 25°, 0.75 μ. [c] S. Chaberek and A. E. Martell, "Organic Sequestering Agents," John Wiley and Sons, Inc., New York, N. Y., 1959; 25°, 0.1 μ. [d] I. Poulsen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 1407 (1955); 25°, 1.0 μ. [e] G. Schwarzenbach, G. Anderegg, W. Schneider, and H. Senn, *Helv. Chim. Acta*, **38**, 1147 (1955); 20°, 0.1 μ. [f] Reference 8; 25°, 0.50 μ. [g] P. F. Derr and W. C. Vosburgh, *J. Amer. Chem. Soc.*, **65**, 2408 (1943); 25°, 0.1 μ.

Table III. Kinetic Parameters Obtained from Relaxation Data for Polyamine Ligands for the Exchange of NH_3, $\mu = 0.40\ M$

Ligand	k_{12}, M^{-1} sec^{-1}	Temp, °C	Coordinated H_2O	k^{-H_2O}, sec^{-1}	k_{21}, sec^{-1}	K_{NiLNH_3} M^{-1}
H_2O[a]	2.8×10^3	25	6	2.8×10^4	2.6	1×10^3
	9.6×10^2	7	6	9.6×10^3	1.2	8×10^2
en	1.2×10^4	25	4	1.8×10^5	80	160
tn	2.9×10^4	25	4	4.4×10^5	420	70
dien[a,b]	4.3×10^4	25	3	8.6×10^5	7.7×10^2	56
	1.8×10^4	7	3	3.6×10^5	1.5×10^2	120
cis,cis-tach	1.9×10^5	25	3	3.8×10^6	3.1×10^3	61
	8.0×10^4	7	3	1.6×10^6	8.6×10^2	93
trien	1.2×10^5	8	2	3.6×10^6	7.6×10^2	154
tren	2.6×10^5	6	2	7.8×10^6	4.9×10^3	53
$(en)_2$[c]	7×10^6	25	2	2.1×10^8		
$(NH_3)_5$	7.2×10^4 [d]	25	1	4.3×10^6	6.0×10^4	1.2[e]
	3.0×10^4	7	1	1.8×10^6	1.6×10^4	1.9[e]

[a] Values taken from ref 3. [b] dien = diethylenetriamine. [c] The k_{12} value is for the reaction of en with $Ni(en)_2(H_2O)_2^{2+}$ to form the monodentate en intermediate. [d] Values calculated from k_{21} values given in ref 12–14. [e] L. G. Sillén and A. E. Martell, "Stabilty Constants of Metal-Ion Complexes," The Chemical Society, London, 1964. Values were taken from J. L. Schultz, Thesis, 1959, University of Minnesota, Microfilms 59–2370.

For the experimental conditions the indicator concentration was $10^{-5}\ M$ and the free ammonia was always less than $5 \times 10^{-3}\ M$ and greater than $7.6 \times 10^{-5}\ M$ in the pH range 7.8–8.1. Therefore α was less than 0.01 and could be neglected.

Each τ value was obtained from an average of three or more individual relaxation experiments; 4–11 different concentrations of nickel complex and NH_3 were used for each system. Appropriate protonation constants for ammonia were used for each temperature.[6] Good straight line plots were obtained for eq 4. For the stronger complexes, where disproportionation or partial dissociation of the 1:1 complex was negligible, the stoichiometric concentration of NiL was used for the kinetic calculations. A computer program[3] was used which first assumed that ([NiL] + [NH_3]) = $[NiL]_T$ and gave a least-squares fit of k_{21} and k_{12} for eq 4. It then solved for k_{12}/k_{21} (= K_{NiLNH_3}) and for the corrected concentrations of NiL and NH_3. The process was repeated until K_{NiLNH_3} was constant to ±2%.

For the bidentate ligands and some of the tridentate ligands, a similar program was written in which the concentrations of all species were calculated by means of a subroutine COGS (concentration of generalized species) written by Perrin and Sayce.[7] The species considered were Ni^{2+}, NiL, NiL_2, NiL_3 (where appropriate), $NiNH_3^{2+}$, $Ni(NH_3)_2^{2+}$, NH_3, NH_4^+, L, HL, H_2L, and $NiLNH_3$. The equilibrium constants used in the calculations are given in Table II. The initial assumption was that mixed complex formation was negligible. The value of k_{12}/k_{21} (= K_{NiLNH_3}) in eq 4 was iterated to a convergence limit of ±1%. Solutions for which [$NiLNH_3$] was greater than 10% of [NiL] were omitted from the calculations, because it was observed that, for solutions having [$NiLNH_3$] much greater than this limit, the relaxation times were too fast and did not give a linear fit to eq 4. These small τ values are probably the result of the contribution of a faster reaction (involving $NiLNH_3$ and NH_3) to the observed relaxation time. The iterative calculation tends to detect appreciable error of this type because it causes k_{12}/k_{21} to become unreasonably large or causes lack of convergence. The experimental conditions permitted only small amounts of NiL_2 and even smaller amounts of any possible NiL_2NH_3 complexes in order to avoid contributions from these species to the observed relaxation.

Results and Discussion

The forward rate constant, k_{12}, determined for reaction 1 is a second-order constant which can be considered to be the product of an outer-sphere association constant, K_{os}, and the rate constant for the exchange of water in the inner coordination sphere, k^{-H_2O}. The rate of formation of the outer-sphere complex is a diffusion-controlled process and is fast compared to the exchange of water bound to nickel. As before, the K_{os} value for ammonia is approximately 0.1 M^{-1} for all complexes.[3,8] In order to compare complexes which have different numbers of water molecules available

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(6) R. G. Bates and G. D. Pinching, *J. Res. Natl. Bur. Stand.*, **42**, 419 (1949).

(7) D. D. Perrin and I. G. Sayce, *Talanta*, 14, 833 (1967).

(8) D. B. Rorabacher, *Inorg. Chem.*, **5**, 1891 (1966).

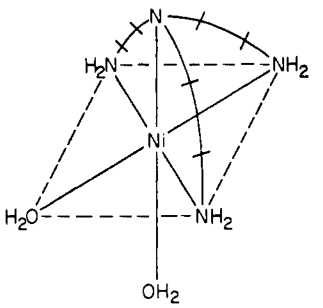

Figure 1.

for exchange, a statistical correction is made and the $k^{-\mathrm{H_2O}}$ values are calculated using

$$k^{-\mathrm{H_2O}} = \frac{k_{12}}{K_{\mathrm{os}}}\left(\frac{6}{\text{no. of H}_2\text{O}}\right) \tag{6}$$

Effect of Amine-Nitrogen Coordination. The values of k_{12} and k_{21} increase with an increase in the number of amine nitrogens coordinated to nickel as shown in Table III.

In the nickel trien-ammonia system the previously reported[3] relaxations (τ 6-10 msec) were once again the only observable ones at 25°. However, these relaxations are caused by as little as 0.5% excess trien in equilibrium with nickel-trien as $\mathrm{Ni(trien)_2}^{2+}$. This complex has not been previously reported and its stability and kinetic behavior are under investigation.[9] Therefore a search was made for the true nickel-trien-ammonia relaxation. At 8° a fast relaxation was found with τ values in the range of 200-400 μsec. It is difficult to observe τ values of less than 100 μsec due to reactions 2 and 3 which have a large displacement. No fast relaxation was present at 8° in the absence of NH_3.

In the nickel-tetren-ammonia system the previously reported relaxations (τ = 200-400 msec) are the only ones observed from 5 to 25°: $[\mathrm{Ni(tetren)}^{2+}] = 1.8 \times 10^{-2}$ M, $[\mathrm{NH_3} + \mathrm{NH_4}^+] = 6.6\text{-}13 \times 10^{-2}$ M and pH 8.0 to 8.8. However, these relaxations also are present in the absence of NH_3. They are not dependent on excess tetren. The magnitude of the relaxation is small but it increases slightly in going from pH 8 to 7. The relaxation may be due to $\mathrm{Ni(tetren)H}^{3+}$. A second reason to doubt the initial assignment is due to the disagreement between the relaxation data and the spectrophotometrically determined stability constant[10] for $\mathrm{Ni(tetren)(NH_3)}^{2+}$. This constant has a value of 6.7 ± 1.1 M^{-1} rather than 53 M^{-1} as estimated from the relaxation data. No fast relaxation could be found for nickel-tetren-ammonia, but the absence of a relaxation does not mean that there cannot be a fast exchange reaction with ammonia. The low stability of the mixed complex requires higher ammonia concentrations and if the exchange with nickel-tetren is faster than with nickel-trien, the relaxation would be too fast to be observed.

Effect of the Structure of the Amines. tren, which is the branched isomer of trien, also was tested. tren is restricted to one structure about the metal ion as shown in Figure 1. The ammonia exchange is rapid and the k_{12} value is 2.2 times greater than for trien.

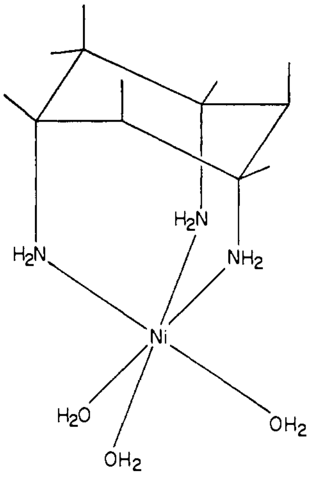

Figure 2.

The ligand *cis,cis*-tach is tridentate, forms six-member chelate rings, and is forced to coordinate to a face of the nickel octahedron as shown in Figure 2.[11] Its k_{12} value is larger than is the case for the linear tridentate polyamine; k_{12} for *cis,cis*-tach is larger than the value for dien at 7° by a factor of 4.4. Another polyamine, tn, which forms a six-membered chelate ring with nickel, has a faster rate of exchange than that for en which forms a five-membered chelate ring; k_{12} for tn is larger than the value for en at 25° by a factor of 2.4. The six-membered chelate ring in $\mathrm{Nitn(H_2O)_4}^{2+}$ would allow this complex to form a trigonal bipyramidal intermediate upon the loss of one group more readily than the five-membered chelate ring ligand.

The ammonia exchange data of Hunt[12,13] and VanGeet[14] can be used to calculate the k_{12} values in Table III for five ammonia molecules coordinated to nickel. The rate of addition of the sixth ammonia to the nickel-pentaammine complex is slower than the addition of ammonia to the nickel complexes of trien, tren, or *cis,cis*-tach. Thus the effect of chelate ring nitrogens in linear polyamines seems to be to increase the k_{12} values at least as much as expected from an additional NH_3 group.

A comparison can also be made for the trien, N,N′-bis(2-aminoethyl)-1,3-propanediamine (2,3,2-tet), and bis-en complexes. The reaction of NH_3 with $\mathrm{Ni(en)_2}^{2+}$ would be expected to be at least as fast as the reaction of en with $\mathrm{Ni(en)_2}^{2+}$. The $\mathrm{NH_3} + \mathrm{Ni(en)_2}^{2+}$ system was not worked out in detail because of the interference of en. However, a relaxation was observed which was dependent on the NH_3 concentration and had a τ value similar to that for the $\mathrm{Ni(en)_2}^{2+}$ + en system. The latter system is described in detail elsewhere.[15] Although the rate constants were not obtained at the same temperature (25 and 7°), it is obvious that the $\mathrm{Ni(en)_2}^{2+}$ complex reacts with en considerably faster than the $\mathrm{Ni(trien)}^{2+}$ complex reacts with NH_3.

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[9] D. W. Margerum and D. C. Weatherburn, in preparation.

[10] N. E. Jackobs and D. W. Margerum, *Inorg. Chem.*, **6**, 2038 (1967).

[11] R. A. D. Wentworth and J. J. Felton, *J. Amer. Chem. Soc.*, **90**, 621 (1968).

[12] J. P. Hunt, H. W. Dodgen, and F. Klanberg, *Inorg. Chem.*, **2**, 478 (1963).

[13] H. H. Glaeser, G. A. Lo, H. W. Dodgen, and J. P. Hunt, *ibid.*, 4, 206 (1965).

[14] A. L. VanGeet, *ibid.*, 7, 2026 (1968).

[15] J. P. Jones and D. W. Margerum, *J. Amer. Chem. Soc.*, **92**, 470 (1970).

No relaxation could be detected for the reaction of ammonia with the Ni(2,3,2-tet) complex for [Ni(2,3,2-tet)] = 1.1–2.6 $\times$ 10^{-2} M, [NH_3 + NH_4^+] = 4.0–6.6 $\times$ 10^{-2} M, and pH 7.9–8.8, although there was spectral evidence for mixed complex formation. Like the nickel–tetren system the reaction with ammonia may be too fast to be observed.

The number of coordinated nitrogens is important in labilizing the water exchange but the geometry of the ligand and the configuration around the metal can be equally important.

Aminocarboxylate Complexes. Three additional complexes have been investigated, methyliminodiacetate (MeIDA), hydroxyethyliminodiacetate (HEIDA), and ethylenediaminediacetate (EDDA), and are shown in Table IV with the previously determined values for other aminocarboxylate complexes. The EDDA results are interesting in that the k_{12}, k_{21}, and K values are larger than those for EDTA and HEEDTA. A study of the stability constant of the mixed complex formed from Ni(EDDA) and NH_3 concluded that the addition of carboxylate groups to en had no effect on the stability constant.[10] The measured value of K was 100 ± 10 M^{-1} compared to our value of 114 M^{-1}, which is excellent agreement between the two values. On the other hand, an N-ethyl group and N,N-dimethyl groups on en increase the rate of exchange. In light of this, the coordinated carboxylate groups appear to decrease the k_{12} values when they replace alkyl groups.

Table IV. Kinetic Parameters Obtained from Relaxation Data for Aminocarboxylate Ligands for the Exchange of NH_3 at 25°

Ligand	μ	k_{12}, M^{-1} sec^{-1}	k_{21}, sec^{-1}	K, M^{-1}
IDA^{a,b}	0.25	3.2 $\times$ 10^3	65	49
MeIDA	0.40	5.1 $\times$ 10^3	45	114
HEIDA	0.40	3.0 $\times$ 10^3	18	169
NTA^{b,c}	0.25	5.4 $\times$ 10^3	20	277
EDDA	0.40	6.1 $\times$ 10^3	53	114
HEEDTA^{b,c}	0.25	0.29 $\times$ 10^3	8.3	35
EDTA^{b,c}	0.40	0.44 $\times$ 10^3	20	22

^{a} Recalculated from data of ref 3 using the generalized species concentration program. ^{b} IDA = iminodiacetate, NTA = nitrilotriacetate, HEEDTA = hydroxyethylethylenediaminetriacetate, EDTA = ethylenediaminetetraacetate. ^{c} Values obtained from ref 3.

Additional carboxylate groups in HEEDTA and in EDTA appear to suppress the k_{12} value even more. For $Ni(EDTA)(NH_3)^{2-}$ the K value determined by relaxation (22 M^{-1}) is in excellent agreement with the K value (25 M^{-1}) determined spectrophotometrically.[10] For $Ni(HEEDTA)(NH_3)^-$ at 0.50 M KCl the K value was 100 M^{-1} compared to the relaxation value of 35 M^{-1} at 0.25 M $NaClO_4$, which is fair agreement. There were no relaxations in the absence of ammonia. Strong relaxations were observed in the 25–100-msec range and there were no detectable relaxations at shorter times. Therefore the possibility of a k_{12} value in the range of 10^3 to 10^5 M^{-1} sec^{-1} can be ruled out.

Replacing an acetate group in EDTA by a hydroxyethyl group to give HEEDTA reduces the k_{12} value. The same effect may be present for IDA and HEIDA. The addition of an N-methyl group to IDA to give MeIDA increases the k_{12} value.

Table V. Kinetic Parameters Obtained from Relaxation Data for Alkyl-Substituted Diamines for the Exchange of NH_3 at 25° and 0.40 μ

Ligand	10^3 k_{12}, M^{-1} sec^{-1}	k_{21}, sec^{-1}	K, M^{-1}
en	12 ± 2	80 ± 30	160 ± 60
N-Meen	13 ± 2	150 ± 20	90 ± 20
N,N′-diMeen	8 ± 2	50 ± 20	170 ± 90
pn	15 ± 1	150 ± 20	100 ± 20
N-Eten	31 ± 3	130 ± 30	250 ± 70
N,N-diMeen	36 ± 5	530 ± 70	70 ± 10
tn	29 ± 5	420 ± 80	70 ± 20

Effect of Alkyl-Substituted Diamines. Addition of N-ethyl or N,N-dimethyl groups to en increases the rate of ammonia exchange as shown in Table V. An increase in chelate ring size from 5 to 6 (en to tn) also increases the exchange rate. The increase in H_2O–NH_3 exchange rates for the alkyl-substituted en complexes somewhat parallels the decrease in K_{NiL} values for the 1:1 nickel complexes in Table II.

Similar rate increases were observed for the acid hydrolysis of *trans*-$Co(AA)_2Cl_2^+$, eq 7, for carbon- and nitrogen-substituted diamines.[16] The increases for these rates were also parallel to the number and size of the groups substituted on en. An exception to this trend for the cobalt reaction is the N-Meen which is one-half as fast as the en complex, whereas with the nickel complex N-Meen reacts as fast as en.

$$Co(AA)_2Cl_2^+ + H_2O \rightleftharpoons Co(AA)_2(H_2O)Cl^{2+} + Cl^- \quad (7)$$

The rate increases observed for the ammonia reaction with Ni(II) and for the Co(III) hydrolysis reactions cannot be explained on the basis of inductive effects.[16] Two studies[17,18] involving ligands with substituents too remote to cause steric interaction but with larger changes in base strengths than for the alkyl-substituted diamines gave much smaller changes in rates of water exchange with Ni(II) and Co(III) hydrolysis. As in the Co(III) hydrolysis rates, the observed rate increases for the nickel complex reactions may be explained by a relative increase in stability of the five-coordinated activated complex, formed by the loss of one group, as the size of the coordinated ligand increases.

When diamines with bulkier substituents such as N-isopropylethylenediamine and N,N-diethylethylenediamine were investigated, the rates of the formation and dissociation of these ligands with nickel became as rapid as the ammonia reaction and interfered with the study. The 2,2-dimethyl-1,2-diaminoethane complex formed only a yellow bis complex with nickel and a relaxation with NH_3 was not observed.

In conclusion, the water replacement by ammonia in nickel complexes is enhanced by coordinated amine nitrogens. The exchange rates become faster as the number of coordinated nitrogens is increased.[19] With

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(19) The assumption that larger values of k_{12} are due to increased rates of exchange of coordinated water is confirmed by recently published values for H_2O exchange by ^{17}O nmr: A. G. Desai, H. W. Dod-

ethylenediamine the addition of N-alkyl groups can significantly increase the exchange rate. The configuration of the ligand (tren *vs.* trien) and an increase to six-membered chelate rings (tn *vs.* en and *cis,cis*-tach *vs.* dien) also have significant effects. The presence of carboxylate groups in general does not lead to an increased exchange rate and in some cases appears to decrease the exchange rate.

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gen, and J. P. Hunt, *J. Amer. Chem. Soc.*, **91**, 5001 (1969). The $k^{-\mathrm{H_2O}}$ value of 1.8×10^5 sec^{-1} (25°, 0.25 *M* $NaClO_4$) estimated from eq 6 for $Nien(H_2O)_4^{2+}$ is in reasonable agreement with the value of 4.4×10^5 sec^{-1} (25°, 0.52 *M* KNO_3) calculated from the nmr data. The latter data also show an increase in the water exchange rate as one, two, and four amine nitrogens are coordinated to nickel.

Rate Studies on the Primary Step of the Reduction of Chromium(VI) by Iron(II)[1a]

James H. Espenson[1b]

Contribution from the Department of Chemistry
and the Institute for Atomic Research, Iowa State University, Ames, Iowa 50010.

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Abstract: The oxidation of iron(II) to iron(III) in perchloric acid solution by chromium(VI) occurs in a sequence of three one-electron steps. The rate of the first of these has been studied by appropriate choice of concentration conditions and is first order with respect to the concentrations of Fe^{2+} and $HCrO_4^-$. The rate shows close to a second-order dependence upon $[H^+]$, although a more accurate description is given by the equation $-d[HCrO_4^-]/dt = (a[H^+] + b[H^+]^2)[Fe^{2+}][HCrO_4^-]$. Values of *a* and *b* are 4.4×10^3 M^{-2} sec^{-1} and 3.0×10^5 M^{-3} sec^{-1} at 25.0° and 0.084 *M* ionic strength in an $HClO_4$-$LiClO_4$ medium. The rate is essentially independent of temperature. At higher Fe^{2+} concentrations the absorbance change occurs in two steps, the second and slower stage corresponding to dissociation of an iron-chromium complex formed during the reaction. The rate of dissociation of the complex is proportional to $[H^+]$. Mechanisms consistent with these observations are proposed.

The oxidation of iron(II) by chromium(VI) in perchloric acid solution occurs as given in reaction

$$3Fe(H_2O)_6^{2+} + HCrO_4^- + 7H^+ + 2H_2O = 3Fe(H_2O)_6^{3+} + Cr(H_2O)_6^{3+} \qquad (I)$$

I. This reaction has played an important part in the understanding of Cr(VI) oxidation mechanisms. Benson[2] carried out the first studies on the reaction rate; Westheimer[3] has reviewed her results. More recently, the rate behavior was studied under carefully controlled concentration conditions in a perchloric acid–lithium perchlorate medium.[4] The rate expression at low Cr(VI) concentrations[5] under the other conditions in that study was

$$\frac{-d[HCrO_4^-]}{dt} = k\frac{[Fe^{2+}]^2[HCrO_4^-][H^+]^3}{[Fe^{3+}]} \qquad (1)$$

where *k* had the value 2.1×10^8 M^{-4} sec^{-1} at 0° and $\mu = 0.084$ *M*.

Among the important conditions of that study was the addition of high concentrations of Fe^{3+} to all reactant solutions to bring the rate into the region accessible to the conventional measurement techniques employed. The restriction to high Fe(III) concentrations limited the information obtained about the reaction in two important respects. First, the rate constant *k* of eq 1 represents a composite of values belonging to at least two reaction steps so that no rate constant for an elementary reaction in the mechanisms was evaluated. Second, the number of protons involved at different steps in the mechanism is not resolved by eq 1. The steps prior to and including the rate-determining step require three protons, but more detailed information is not available.

The mechanism suggested in accord with eq 1 can be represented *at constant* $[H^+]$ as follows

$$Fe^{2+} + HCrO_4^- \rightleftharpoons Fe^{3+} + Cr(V) \qquad (k_1', k_2') \qquad (II)$$

$$Fe^{2+} + Cr(V) \longrightarrow Fe^{3+} + Cr(IV) \qquad (k_3') \qquad (III)$$

$$Fe^{2+} + Cr(IV) = Fe^{3+} + Cr^{3+} \qquad \text{fast} \qquad (IV)$$

The primed rate constants refer to pseudo-second-order values that may depend upon $[H^+]$. According to this scheme the empirical rate parameter *k* is identified as $k_1'k_3'[H^+]^3/k_2'$, with the usual steady-state approximations made for Cr(V) and Cr(IV). The intermediacy of Cr(V) in the rate-determining step is supported by the scavenging effect toward iodide ion in which a limiting induction factor of 2.0 is achieved.[2,6]

A previous attempt[7] was made to learn the actual species involved in reaction steps II–IV. That attempt involved correlations of three independent results: rate studies on the oxidation of VO^{2+} by $HCrO_4^-$,[7]

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[1] (a) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2626; (b) Fellow of the Alfred P. Sloan Foundation, 1968–1970.

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[5] A second rate term proportional to $[HCrO_4^-]^2$ is completely negligible under the lower Cr(VI) concentrations employed here and can be safely ignored in the present study.

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