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Alkaline Hydrolysis of Hydroxylamine-N-sulfonate

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The kinetics has been investigated for the alkaline decomposition of hydroxylamine-N-sulfonate ion, $HONHSO_3^-$

$$2HONHSO_3^- + 2OH^- \longrightarrow 2SO_3^{2-} + N_2O + 3H_2O$$

Its rate law is

$$-d[HONHSO_3^-]/dt = [\text{stoichiometric } HONHSO_3^-] \left\{\frac{[OH^-]}{1 + K_B[OH^-]}\right\} \times \left\{(1 - \alpha)k_a + \frac{\alpha k_b}{1 + (k_c/k_d)[SO_3^{2-}]}\right\}$$

where k_a, k_b, k_c, and k_d are rate constants, K_B is a composite acid dissociation constant for $HONHSO_3^-$, and α and $1 - \alpha$ are the fractions of the tautomeric forms of the conjugate base $HON^-SO_3^-$ and $^-ONHSO_3^-$, respectively. The form of the kinetic dependence on $[OH^-]$ and the observation that the N_2O does not contain excess O^{18} when the reaction is carried out in water enriched with O^{18} are consistent with a mechanism involving cleavage of the conjugate base rather than nucleophilic attack on nitrogen. The kinetic dependence on $[SO_3^{2-}]$ is consistent with a mechanism having two pathways, one of which involves an intermediate species that can rapidly rereact with sulfite. It is suggested that one or the other tautomers of nitroxyl, HNO or HON, is the intermediate.

Introduction

It has been known since 1889[1] that hydroxylamine-N-sulfonate, upon treatment with hot concentrated alkali, gives hyponitrite in good yield

$$2HONHSO_3^- + 4OH^- \longrightarrow 2SO_3^{2-} + {}^-ON{=}NO^- + 4H_2O \quad (1)$$

Apart from the qualitative demonstration by Nast, *et al.*, that NO^- is an intermediate in the reaction,[2] its mechanism does not appear to have been investigated. We report here its kinetics and an isotopic experiment pertinent to the mechanism.

Experimental Section

Materials.—Potassium hydroxylamine-N-sulfonate was prepared by acid hydrolysis of dipotassium hydroxylamine-N,N-disulfonate according to the method of Degener and Seel.[3] When kept in a vacuum desiccator over magnesium perchlorate in a refrigerator, it did not decompose detectably for 1 year. *Anal.* Calcd for $HONHSO_3K$: S, 21.2; N, 9.3; H, 1.3. Found: S, 20.5; N, 9.4; H, 2.1.

Standard ceric sulfate solution was prepared from G. F. Smith reagent, standardized against dried primary standard arsenic(III) oxide, and diluted to 0.02 *M* for use. Ferroin indicator was prepared by dissolving 0.5 g of 1,10-phenanthroline monohydrate in 100 ml of 0.025 *M* $FeSO_4$ solution. All other chemicals were reagent grade and used without further purification. Water isotopically enriched in O^{18} was purchased from Bio-Rad Laboratories.

Analytical Procedure.—The rate of decomposition of hydroxylamine-N-sulfonate was followed by analysis of aliquots for unreacted material. Each aliquot was acidified to about 0.5 *M* sulfuric acid, boiled for 1 hr, and the resulting hydroxylamine was determined by the ferric salt method of Bray, *et al.*,[4] with the modification that ceric sulfate was used as titrant with ferroin as indicator.

In the stoichiometric studies, the gaseous product was analyzed by gas chromatography on molecular sieve. Sulfite was determined by spectrophotometry, using the 2760-A absorption of SO_2. In the isotopic studies, the relative abundances of N_2O^{16} and N_2O^{18} were determined with a Consolidated Electrodynamics Model 21-103C mass spectrometer.

Kinetic Procedure.—Preliminary studies having shown that alkaline hydroxylamine-N-sulfonate reacts rapidly with even traces of oxygen, the reaction vessel (Figure 1) was designed to permit reactants to be mixed and aliquots withdrawn in the absence of oxygen. The desired reactants were added as solids to the central flask, along with a magnetic stir bar, and the sodium hydroxide solution was placed in the side flask. After five cycles of freezing, pumping, and thawing, the solution in the side flask was warmed to approximately reaction temperature, nitrogen was admitted to a pressure of slightly more than atmospheric, and the side flask was tipped to permit the reactants to mix. The process of solution required only a few seconds, and the attainment of thermal equilibrium (the central flask being immersed in circulating thermostated water) no more than a few minutes, times short relative to the half-life of the reaction. Aliquots for analysis were withdrawn through the tip-over thief, which was afterward rotated to the upward position so that the solution remaining in it could be forced out, leaving it clean for the next sampling.

Each run was continued for at least 3 half-lives. In those runs containing added sulfite in an amount large compared to that liberated by the reaction, excellent first-order plots were obtained. When no sulfite was initially present, that liberated by the reaction caused the rate progressively to diminish (*cf.* Figure 2), and for these runs the reported rate constant is that for the initial rate. Solutions were adjusted to the desired ionic strength by addition of Na_2CO_3 or Na_2SO_4.

Results and Discussion

Verification of Stoichiometry.—Under the conditions of the kinetic study, namely 0.1 to 1.6 *M* OH^-, the sulfur-containing product within analytical error was SO_3^{2-}, and the nitrogen-containing product within analytical error was N_2O, which is the expected decomposition product of hyponitrite at this temperature and alkalinity,[5] no more than a trace of hyponitrite as such remaining. No ammonia, hydroxylamine, nitrite,

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(1) E. Divers and T. Haga, *J. Chem. Soc.*, **55**, 760 (1889); *cf.* G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," Enke, Stuttgart, 1960, p 442.

(2) R. Nast, K. Nyul, and E. Grziwok, *Z. Anorg. Allgem. Chem.*, **267**, 304 (1952).

(3) E. Degener and F. Seel, *ibid.*, **285**, 129 (1956).

(4) W. C. Bray, M. E. Simpson, and A. A. MacKenzie, *J. Am. Chem. Soc.*, **41**, 1363 (1919).

(5) J. R. Buchholz and R. E. Powell, *ibid.*, **85**, 509 (1963).

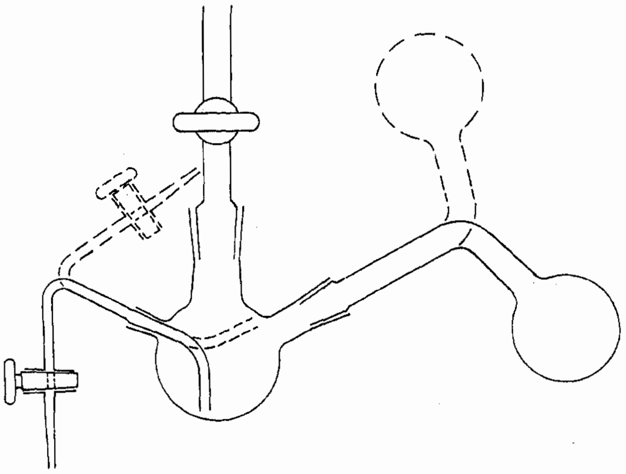


Figure 1.—Reaction vessel.

or nitrate was detectable. The same stoichiometry was observed in the presence of initially added 0.5 *M* sulfite. So we are dealing with reaction 1 within 99+%.

Isotopic Studies.—When the reaction was carried out in water containing 1.58 atom % O^{18}, the N_2O product contained only the natural abundance of O^{18} (in the absence of added sulfite, 0.22 ± 0.02% O^{18}; in the presence of 0.80 *M* sulfite, 0.21 ± 0.02% O^{18}). This observation rules out the otherwise very plausible mechanism of a nucleophilic displacement on nitrogen

$$HONHSO_3^- + OH^- \longrightarrow SO_3^{2-} + HN(OH)_2 \qquad (2)$$

which would lead to at least 50% incorporation of O^{18} into the product and more if the reverse reaction is fast in comparison to the dimerization.

Acceptable mechanisms could involve the decomposition of one or the other, or both, of the tautomers of the conjugate base

$$HON^-SO_3^- \longrightarrow HON + SO_3^{2-} \qquad (3a)$$

$$^-ONHSO_3^- \longrightarrow ONH + SO_3^{2-} \qquad (3b)$$

Kinetics.—At small OH^- concentrations, the rate is proportional to $[OH^-]$, but at higher concentrations it levels off to beome independent thereof (*cf.* Figure 3).

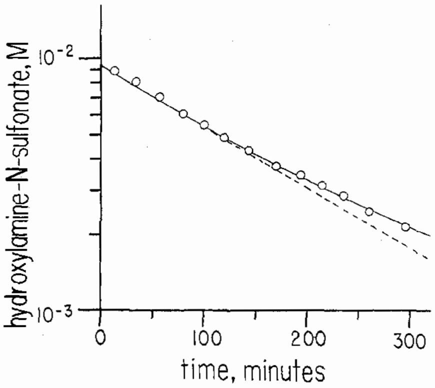


Figure 2.—A run without added sulfite, showing diminishing rate on a first-order plot, at 73.8°, $[OH^-]$ = 0.980 *M*, $[Na_2CO_3]$ = 0.20 *M*, initial $[HONHSO_3^-]$ = 9.28 × 10^{-3} *M*. Solid curve, calculated from the integrated form of the rate law (6); dashed line, extrapolated initial slope.

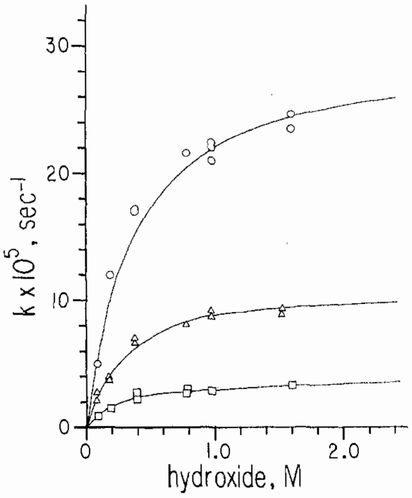


Figure 3.—Dependence of the pseudo-first-order rate constant on hydroxide concentration: circles, 83.5°; triangles, 73.8°; squares, 64.2°.

This behavior is consistent with the rapid, reversible formation of the conjugate base of hydroxylamine-N-sulfonate, followed by its relatively slow decomposition

$$OH^- + HONHSO_3^- \underset{}{\overset{K_B}{\rightleftharpoons}} \left\{ \begin{matrix} HON^-SO_3^- \\ ^-ONHSO_3^- \end{matrix} \right\} \begin{matrix} \longrightarrow HON + SO_3^{2-} & (3a) \\ \longrightarrow ONH + SO_3^{2-} & (3b) \end{matrix}$$

The corresponding rate law takes the form

$$\text{rate} = \text{constant}\,\frac{[OH^-][\text{stoichiometric } HONHSO_3^-]}{1 + K_B[OH^-]} \qquad (4)$$

and the smooth curves in Figure 3 have been computed from this expression, with the K_B values assembled in Table I. The corresponding dissociation constant of $HONHSO_3^-$ as a weak acid, K_A, has been calculated by multiplying K_B by the literature value of K_w. From these data, the corresponding thermodynamic quantities for the acid dissociation at 75 ± 10° and ionic strength 1.6 are ΔH = 7.4 kcal mole^{-1} and $\Delta S°$ = -34.5 cal deg^{-1} mole^{-1}. If these values apply at room temperature, the expected pK_A of hydroxylamine-N-sulfonate is approximately 13.0. As a rough check of this prediction, to a 0.01 *M* KOH solution (containing K_2SO_4 to bring the ionic strength up to 1.5) solid $HONHSO_3K$ was added to make its concentration 0.10 or 0.05 *M*, and any change in pH was observed with a glass-electrode pH meter. If the substance had no acidic property, there would be no change in pH. In fact, there was a change to lower pH of an amount consistent with a pK_A of 12.5 ± 0.2. This observation, while not of the refinement necessary for a full

TABLE I

ACID DISSOCIATION OF HYDROXYLAMINE-N-SULFONATE (AT IONIC STRENGTH 1.6)

Temp, °C	K_B	$10^{13}K_w$[a]	$10^{13}K_A \equiv 10^{13}K_BK_w$
64.2	3.54 ± 0.37	1.19	4.21 ± 0.44
73.8	3.39 ± 0.35	1.91	6.38 ± 0.66
83.5	2.73 ± 0.29	2.94	8.03 ± 0.85

[a] Data of H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940).

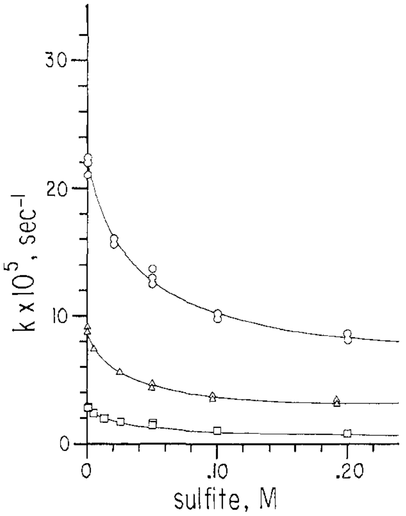
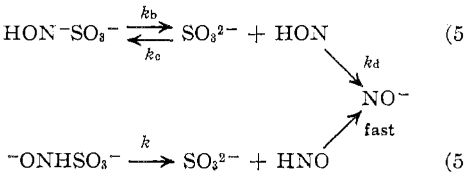


Figure 4.—Dependence of the pseudo-first-order rate constant on sulfite concentration: circles, 83.5°; triangles, 73.8°; squares, 64.2°.

thermodynamic study, does verify that hydroxylamine-N-sulfonate is a weak acid, of about the dissociation constant indicated by the kinetic evidence. That the sulfonate group imparts acidity to the N proton or the O proton of hydroxylamine, or both, is no surprise. Aminedisulfonate ion, $HN(SO_3^-)_2$, is known to be an acid of $pK_A = 8.50$ at ionic strength 1.0 and 25°.[6] Hydroxylamine-N,N-disulfonate ion, $HON(SO_3^-)_2$, is known to be weakly acidic, but we cannot find in the literature a value for its dissociation constant; our measurements on it, using a glass-electrode pH meter, indicate its $pK_A = 11.85 \pm 0.03$ at ionic strength 1.6 and 25°. Our data on hydroxylamine-N-sulfonate give us no information concerning the relative population of the N-deprotonated and the O-deprotonated conjugate bases, and we arbitrarily denote their fractions by α and $1 - \alpha$, respectively.

The addition of SO_3^{2-} to the reaction mixture markedly diminishes the rate, but as the concentration of SO_3^{2-} becomes large, the rate approaches asymptotically a finite value rather than zero (Figure 4). The most general reaction mechanism consistent with this observation has two parallel pathways from $ONHSO_3^{2-}$ to NO^-, one passing through an intermediate which can react with SO_3^{2-} to re-form the $ONHSO_3^{2-}$ at a rate comparable to its further decomposition, the other not passing through such an intermediate and therefore not susceptible to suppression by SO_3^{2-}. The chemical nature of the suggested intermediate is fairly closely circumscribed, inasmuch as it must be formed from $ONHSO_3^{2-}$ by loss of SO_3^{2-}, must be capable of reaction with SO_3^{2-} in the reverse sense, and must ultimately yield NO^-. The only species that seems to satisfy this prescription is one or the other tautomer of nitroxyl, namely, HNO or NOH.

We propose the following as a detailed mechanism consistent with the data. Both tautomers of the conjugate base can lose SO_3^{2-} to yield the corresponding tautomers of nitroxyl; one, but not both, of the tautomers of nitroxyl can react rapidly with SO_3^{2-}



$$HON^-SO_3^- \underset{k_c}{\overset{k_b}{\rightleftarrows}} SO_3^{2-} + HON \xrightarrow{k_d} NO^- \tag{5a}$$

$$^-ONHSO_3^- \xrightarrow{k} SO_3^{2-} + HNO \xrightarrow{\text{fast}} NO^- \tag{5b}$$

The rate law corresponding to this mechanism is

$$\text{rate} = [ONHSO_3^{2-}]\left\{(1-\alpha)k_a + \frac{\alpha k_b}{1 + \frac{k_c}{k_d}[SO_3^{2-}]}\right\} \tag{6}$$

The smooth curves of Figure 4 have been drawn with this rate law, using the parameters given in Table II.

TABLE II
RATE CONSTANTS FOR DECOMPOSITION OF THE CONJUGATE BASE OF HYDROXYLAMINE-N-SULFONATE[a]

Temp, °C	$(1-\alpha)k_a \times 10^5$, sec^{-1}	$\alpha k_b \times 10^5$, sec^{-1}	k_c/k_d, M^{-1}
64.2	2.97 ± 0.37	10.75 ± 0.90	51.3 ± 4.2
73.8	10.7 ± 1.0	26.5 ± 2.2	38.8 ± 3.5
83.5	20.8 ± 4.0	61.2 ± 3.8	23.9 ± 4.0

[a] Ionic strength 1.6, $[OH^-] = 1.0\ M$.

The heats and entropies of activation corresponding to the values in Table II are: for $(1-\alpha)k_a$, $\Delta H_a^* = 24.8 \pm 0.2$ kcal, $\Delta S_a^* = -5.7 \pm 0.6$ cal deg^{-1}; for αk_b, $\Delta H_b^* = 20.9 \pm 0.2$ kcal, $\Delta S_b^* = -15.1 \pm 0.5$ cal deg^{-1}; for k_c/k_d, $\Delta H_c^* - \Delta H_d^* = -9.4 \pm 1$ kcal, $\Delta S_c^* - \Delta S_d^* = -20 \pm 1$ cal deg^{-1}. These values seem to us not implausible for the proposed elementary steps.

It might be asked whether the second deprotonation (our reaction d) is unimolecular or results from attack by OH^-. As a test of this point, a run was made at 0.1 *M* sulfite and 0.5 *M* hydroxide. If there were no hydroxide dependence of reaction d, the rate constant predicted on the basis of the previous data at 1 *M* OH^- would be 8.10 ± 0.56, while, if reaction d were proportional to hydroxide concentration, the predicted rate constant would be 6.51 ± 0.43. The value observed was 8.43 ± 0.40. Within our experimental error, there is no dependence of reaction d on hydroxide.

In formulating the mechanistic sequence (5a–5b), we have arbitrarily chosen the tautomer HON rather than HNO as the one to react preferentially with SO_3^{2-}. This has been done purely on speculative grounds: NOH, being a nitrene, should be expected to react rapidly in comparison with HNO, a nitroso compound. However, it is not impossible that the roles of the two tautomers could be reversed.

Although the nitroxyl species, either as HON or HNO, has often been postulated as an intermediate in the oxidations or reductions of various nitrogen compounds, the present investigation is, so far as we are aware, the first to obtain kinetic evidence for it in aqueous solution.

Candlin and Wilkins,[7] in their study of the acid hy-

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(6) G. J. Doyle and N. Davidson, *J. Am. Chem. Soc.*, **71**, 3491 (1949).

(7) J. P. Candlin and R. G. Wilkins, *ibid.*, **87**, 1490 (1965).

drolysis of hydroxylamine-N-sulfonate to hydroxylamine and sulfate, attributed a deviation from the acid stoichiometry at pH greater than 2 to the reaction reported here. They did not, however, identify the products. At pH 3.5 and 75°, for example, they reported only a 6% yield of hydroxylamine; and, if the remaining material were to decompose to hyponitrite, the corresponding rate of the side reaction would have to be 9.5×10^{-7} sec^{-1}. The rate law we have reported here would only provide a reaction some eight powers of ten slower than that. Consequently, the mechanism proposed here cannot account for their side reaction.

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Equilibrium Ultracentrifugation of Hydrolyzed Thorium(IV) Solutions[1]

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The hydrolytic aggregation of Th(IV) in 1 *M* total perchlorate media has been investigated by equilibrium ultracentrifugation (interference optics) from hydroxyl number $\mathbf{n}$ (hydroxyls bound per thorium) of 0–3. Concentrations of Th(IV) were 0.025–0.1 *M* over most of the range. The solutions appeared essentially to reach chemical equilibrium up through $\mathbf{n} = 2.5$. All hydrolyzed solutions contained polymeric species, and the weight-average degree of polymerization, N_w, increased with degree of hydrolysis. Comparison of centrifugations at the same $\mathbf{n}$ but different thorium(IV) concentrations indicated that the charge per monomer unit z' on the polymeric species was not the maximum, $4 - \mathbf{n}$, *i.e.*, that there was some complexing of perchlorate ions by the polymers. At $\mathbf{n} = 2$, for example, N_w was about 3.6 and z' appeared to be about 1.3, instead of the maximum 2. For $\mathbf{n} = 3$, chemical equilibrium was not attained, and molecular weights were much higher and increased with time. Hydrolyzed thorium(IV) chloride solutions did not reach chemical equilibrium and, if aged for a few weeks, contained much more highly aggregated species than perchlorate solutions of the same degree of hydrolysis. Volumes and refractive index increments of hydrolyzed thorium(IV) perchlorate solutes are presented. Approximate molecular weight determinations of some highly aggregated Th(IV) dispersions are described.

For over a decade,[3,4] people in the field have realized that polymeric species are formed when Th(IV) hydrolyzes. Probably the most cited evidence has been the dependence of the acidity of solutions having a given hydroxyl number on thorium concentration. (The hydroxyl number $\mathbf{n}$ is defined as the average number of hydroxides bound per thorium and is determined by the stoichiometric moles of base per mole of Th(IV) in the solution, with a correction for the free acid.) Number-[4] and weight-average[5] molecular weight determinations have also indicated aggregation, however. (Some results of ultracentrifugation studies preliminary to the present have been quoted previously.[6,7])

There has been widespread disagreement concerning the species formed. Since the literature was reviewed not long ago,[5] we shall stress only work from two laboratories which have published on the subject recently. The Stockholm group, on the basis of emf measurements,[8] postulated a continuous series of "core-link" species, $\mathrm{Th[Th(OH)_3]}_l{}^{(4+l)+}$; in a recent publication,[9] they appear to have abandoned this interpretation and now postulate a series $\mathrm{Th}_N\mathrm{(OH)}_{nN}{}^{(4N-nN)+}$ having (N,nN) of (1,2), (2,1), (2,2), (2,3), (6,14), and (6,15). Their earlier measurements were in perchlorate media, and their more recent study in chloride. Baes, Meyer, and Roberts[10] report emf measurements of thorium(IV) perchlorate hydrolysis at 0 and 95° and an interpretation of their data, as well as a reinterpretation of 25° measurements of Kraus and Holmberg.[7] Several schemes were tried; the best two both involved (1,1), (1,2), (2,2), and (6,15) and one other species, (4,8) being slightly preferred over (3,6).

Kraus and Holmberg[7] were able to fit acidity data for the early stages of hydrolysis ($\mathbf{n} < 0.2$) by postulating (1,2) and (2,2) species; these species appear in the other schemes mentioned, along with some others, *e.g.*, (1,1) and (2,1), which should have their greatest importance at the same Th(IV) concentrations and acidities. We report here results of an ultracentrifugation study of Th(IV) hydrolysis in perchlorate media for $\mathbf{n} = 1$ and above, a range overlapped by the Kraus and Holmberg measurements, though outside the range of their interpretation. The degrees of polymerization obtained are similar to those reported on the basis

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[2] Oak Ridge Institute of Nuclear Studies Summer Participant, 1965.

[3] R. Schaal and J. Faucherre, *Bull. Soc. Chim. France*, **14**, 927 (1947).

[4] P. Souchay, *ibid.*, **15**, 143 (1948).

[5] F. C. Hentz, Jr., and S. Y. Tyree, Jr., *Inorg. Chem.*, **4**, 873 (1965).

[6] K. A. Kraus, *Proc. Intern. Conf. Peaceful Uses At. Energy, Geneva, 1955*, 7, 245 (1956).

[7] K. A. Kraus and R. W. Holmberg, *J. Phys. Chem.*, **58**, 325 (1954).

[8] S. Hietanen, *Acta Chem. Scand.*, **8**, 1626 (1954).

[9] S. Hietanen and L. G. Sillén, *ibid.*, **18**, 1018 (1964). See also L. G. Sillén, *ibid.*, **16**, 1051 (1962).

[10] C. F. Baes, N. J. Meyer, and C. E. Roberts, *Inorg. Chem.*, **4**, 518 (1965).