

Figure 2. Radial distribution functions of the previously investigated solutions.² The compositions of the solutions are given under Figure 1.

lution¹ nor ours² seem to contain appreciable amounts of hydrolysis products whatever is the equilibrium situation of these solutions. In Morrison's solution, only about 8% of the total iron concentration is present as dimer (2,2 in the notation of Figure 1) while about 90% is present as nonhydrolyzed ion (1,0 in Figure 1).

X-ray results on three acidic aqueous solutions² confirmed the situation shown in Figure 1; Figure 2 shows their radial distribution functions. They do have a peak around 2.8 Å, i.e., where Fe-Fe contacts would occur in the iron(III) dimer; nevertheless, this peak must be ascribed to the typical solvent-solvent interactions since its size decreases with increasing iron concentration (i.e., with decreasing water content). Furthermore our least-squares analysis² of the $i(s)$ curves, through direct comparison of the experimental $i(s)$ data with $i(s)$ calculated for various models of the solutions, is consistent with $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ complexes, in octahedral configuration, and ClO_4^- anions, in tetrahedral configuration being the only important diffracting species present in these solutions.

This behavior of iron(III) with respect to hydrolysis is not restricted to the perchlorate solutions which have been just considered. In all acidic solutions at $\text{pH} \leq 1.0$, detectable amounts of hydrolyzed complexes are hardly formed. In fact by X-ray similar results to those reported here, i.e., absence of hydrolysis complexes, have been also obtained in solutions of iron(III) sulfate,⁹ nitrate,¹⁰ and chloride.¹¹

- (9) M. Magini, *J. Chem. Phys.*, **70**, 317 (1979), and references therein.
 (10) M. Magini and R. Caminiti, *J. Inorg. Nucl. Chem.*, **39**, 91 (1977).
 (11) M. Magini and T. Radnai, *J. Chem. Phys.*, **71**, 4255 (1979).

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Structural Characterization of Iron(III) Solutions by EXAFS

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Recently, Magini et al. have performed X-ray scattering experiments on iron(III) aqueous solutions,¹ and the results

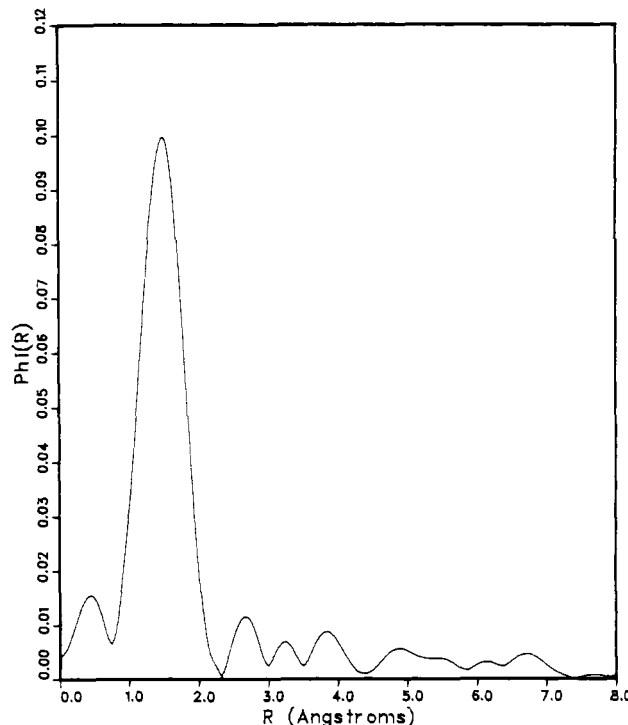


Figure 1. Absolute value of Fourier transform of k -weighted EXAFS data obtained on 1 M Fe^{3+} solution at Stanford Synchrotron Radiation Laboratory.

of these experiments contradict earlier conclusions reached by Morrison, Reis, et al. in EXAFS experiments.² Magini claims that there is no significant amount of di- μ -hydroxo-octa-aquodiron(III) in the solution studied. We believe this claim to be true. We have recently begun to reinvestigate iron(III) solutions by EXAFS techniques, and preliminary results from data obtained at the Stanford Synchrotron Radiation Laboratory⁴ are consistent with the conclusions of Magini et al.¹ in that they show no evidence of substantial amounts of dimers of higher multimers in the solutions. (See Figure 1.)

The discrepancies between the early EXAFS conclusions and those reached by Magini et al. (and by us) arise from several factors. First, the early EXAFS experiments were performed on a "in-house" EXAFS spectrometer,^{2,3} and the raw data can be seen to have a poor signal-to-noise ratio. The effects of high noise levels have been shown to cause spurious features in the Fourier transform of the EXAFS,⁴ and this is undoubtedly a major contribution to the erroneous results obtained. Further, the iron-iron distance was inferred by "eyeballing" the position of the second peak in the Fourier transform of the early EXAFS data and making some questionable approximations concerning the linearity of phase shifts in R space.² Finally, that there are two frequency components under the first peak in the Fourier transform is indisputable; that these two frequencies represent two real distances is questionable.

We are forced to conclude that the early EXAFS study is in error due primarily to the poor quality of data and to a lack of understanding of the effect of high noise levels and problems of solution chemistry. We shall present the results of new EXAFS experiments performed at SSRL under more optimal

- (1) M. Magini, *J. Inorg. Nucl. Chem.*, **40**, 43-48 (1978).
 (2) T. I. Morrison, A. H. Reis, Jr., G. S. Knapp, F. Y. Fradin, H. Chen, and T. E. Klippert, *J. Am. Chem. Soc.*, **100**, 3262-3264 (1978).
 (3) G. S. Knapp, H. Chen, and T. E. Klippert, *Rev. Sci. Instrum.*, **49**, 1658 (1978).
 (4) T. I. Morrison, Ph.D. Thesis, University of Illinois at Urbana-Champaign, 1980.

conditions that will support, in general, the conclusions of Magini et al. and demonstrate the need for careful, precise work in EXAFS and the dangers of the "show-and-tell" experiments that all too often appear in the literature.

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Registry No. Di- μ -hydroxo-octaaquodiiron, 24458-64-8; Fe³⁺, 20074-52-6.

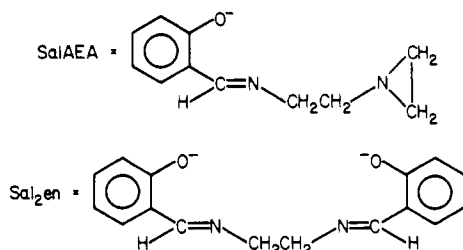
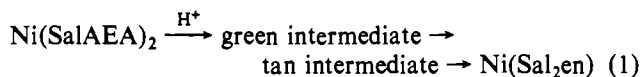
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**Aziridine Ligand Reaction: Conversion of
Bis[N-(2-(1-aziridinyl)ethyl)salicylaldimino]nickel(II) to
[Bis(salicylidene)ethylenediimino]nickel(II)**

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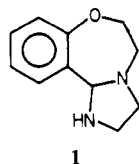
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Since our report of an unexpected reaction of bis[N-(2-(1-aziridinyl)ethyl)salicylaldimino]nickel(II), [Ni(SalAEA)₂], with acid,¹ we have been engaged in attempts to understand the course of this reaction. We now report that two intermediate complexes from the reaction have been isolated and partially characterized as shown in eq 1. Both intermediates



are paramagnetic and do not have NMR spectra which are useful for assigning structures to the ligands; however, we have characterized the organic compounds derived from demetalation of the intermediates and, from this information, gained new evidence concerning the structure of the intermediates.

One of the compounds derived from the tan intermediate represents a new heterocyclic ring system **1**.² Metal ion



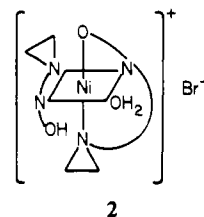
control of the reaction sequence shown in eq 1 is implied since different products are obtained from the reaction of SalAEA with acid in the absence of nickel(II).

This study is an example of how the reactivity of the strained aziridine ring can be altered by utilization of a metal template. Derivatives of the new heterocyclic ring system, **1**, could presumably be prepared from the appropriately substituted reagents with use of the techniques described here.

Results and Discussion

Isolation and Characterization of the Intermediates. The green intermediate forms rapidly after addition of aqueous HBr to an alcoholic solution of [Ni(SalAEA)₂]. If the solution is heated above room temperature, the green intermediate rapidly converts to the tan intermediate. The composition of the green intermediate corresponds to that of [Ni(SalAEA)₂] plus HBr and one water molecule. An intense broad band at 3300 cm⁻¹ is compatible with a phenolic O-H stretch, but coordinated or lattice water may also contribute to this band. Bands at 1655, 1610, and 1550 cm⁻¹ are characteristic of the salicylaldimine moiety. The absence of a sharp secondary amine stretch implies that the aziridine ring has not been opened. The electronic absorption spectrum as well as the solution and solid-state magnetic moments of 2.89 and 3.11 μ_B , respectively, support assignment of a six-coordinate environment for the nickel ion.

Demetalation of the green intermediate with aqueous KCN and extraction of the organics into CHCl₃ allows isolation of the ligand. Only one compound was found in the CHCl₃ extract, and it was positively identified as SalAEA by ¹H NMR. It is proposed that one of the ligands in Ni(SalAEA)₂ is protonated at the phenolate oxygen and the oxygen-nickel bond breaks. The vacated coordination site is then taken by water to give a complex such as **2**. The possibility of a



coordinated bromide and lattice water cannot be ruled out. O-Protonation of coordinated salicylaldimines has been proposed recently in a kinetic study of Cu(II) complexes.³ The geometric arrangement of ligands shown in structure **2** follows from the assignment of a meridional structure for Ni(SalAEA)₂.¹

By elemental analysis of a recrystallized sample, the tan intermediate is shown to be isomeric with the green intermediate. The IR and electronic spectra make it clear that the two intermediates are considerably different, however, both in the structure of the ligands and in the coordination of the metal ion. The electronic spectrum and magnetic moment (2.96 and 3.05 μ_B in solid state and solution, respectively) are in agreement with a six-coordinate structure. The IR spectrum has peaks at 1655, 1630, and 1605 cm⁻¹ consistent with the salicylaldimine double-bond stretches. A broad peak at 3460 cm⁻¹ is assigned to O-H stretching, and a strong, sharp peak at 3120 cm⁻¹ is assigned to a coordinated secondary amine. The presence of an N-H stretch is evidence that at least one of the aziridine rings of Ni(SalAEA)₂ has opened in the tan intermediate. Intense bands at 1208 and 999 cm⁻¹ are diagnostic for the C-O-C stretches of an aryl alkyl ether.⁴

Demetalation of the tan intermediate with aqueous EDTA⁴⁻ and extraction of the organics into CH₂Cl₂ gives two isolable

(1) Root, C. A.; Rising, B. A.; VanDerveer, M. C.; Hellmuth, C. F. *Inorg. Chem.* **1972**, *11*, 1489.
(2) Levan, K. R.; Root, C. A. *J. Org. Chem.* **1981**, *46*, 2404.

(3) Elias, H.; Fröhn, U.; von Irmer, A.; Wannowius, K. *J. Inorg. Chem.* **1980**, *19*, 869.
(4) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 3rd ed.; Wiley: New York, 1974; p 94.