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.

Acknowledgment. T.I.M. wishes to thank Dr. Magini for his illuminating discussions on the problem of iron solution chemistry. Some of the materials incorporated in this work were developed with the financial support of the National Science Foundation (under Contract DMR77-27489, in cooperation with the Department of Energy).

Registry No. Di-μ-hydroxo-octaaquodiiron, 24458-64-8; Fe^{3+}, 20074-52-6.

Contribution from the Department of Chemistry,
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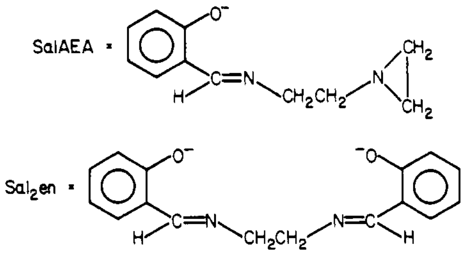
Aziridine Ligand Reaction: Conversion of Bis{*N*-[2-(1-aziridinyl)ethyl]salicylaldimino}nickel(II) to [Bis(salicylidene)ethylenediimino]nickel(II)

Keith R. Levan and Charles A. Root*

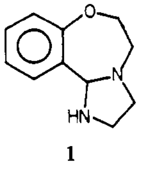
Received October 24, 1980

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.

$$Ni(SalAEA)_2 \xrightarrow{H^+} \text{green intermediate} \rightarrow \text{tan intermediate} \rightarrow Ni(Sal_2en) \quad (1)$$



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 SalAEAH with acid in the absence of nickel(II).



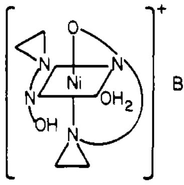
1

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 $CHCl_3$ allows isolation of the ligand. Only one coumpound was found in the $CHCl_3$ extract, and it was positively identified as SalAEAH 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]



2

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 $EDTA^{4-}$ and extraction of the organics into CH_2Cl_2 gives two isolable

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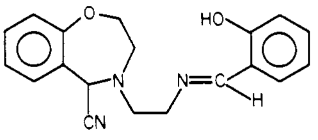
0020-1669/81/1320-3566$01.25/0

compounds. After separation of the mixture on a silica gel column, the two compounds are shown to be SalAEAH and **1**. SalAEAH is identified by its ^1H NMR spectrum which is identical with an authentic sample prepared from salicylaldehyde and *N*-(2-aminoethyl)aziridine. The identity of **1** was deduced from elemental analysis, mass spectrum, IR, and ^1H and ^{13}C NMR results.[2]

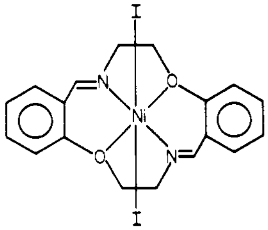
When the tan intermediate is demetalated with aqueous KCN for 1 h, two organic compounds are isolated from the $CHCl_3$ extract of the reaction mixture. They are **1** and a nitrile which is shown to have structure **3**. After separation of the two compounds on a silica gel column, **1** was identified as described above. **3** is characterized by its elemental analysis, mass spectrum, and ^1H NMR spectrum. The mass spectrum shows the parent ion at *m/e* 321 and a peak resulting from the loss of HCN at *m/e* 294. The IR spectrum in $CHCl_3$ has a peak at 2425 cm^{-1} which is assigned to the nitrile group. The ^1H NMR spectrum shows the typical aldimine methine singlet at δ 8.30 while the singlet assigned to the proton on the carbon bearing the nitrile group is at δ 4.95. The broad singlet at δ 12.98 integrates as only one proton in agreement with the second phenol oxygen being part of an ether linkage.



3

It is assumed that **3** is formed by the reaction of **1** with salicylaldehyde which is formed by the hydrolysis of SalAEAH in the basic KCN solution. This is supported by experiments in which the KCN demetalation reactions were run for only 15 min. In these cases, only **1** and SalAEAH were found in the $CHCl_3$ extract.

Kluiber and Sasso[5] reported a ligand reaction worthy of comparison here. The reaction of square-planar bis[*N*-(2-bromoethyl)salicylaldiminato]nickel(II) with NaI in acetone gives a macrocyclic complex shown[6] to have structure **4**. Similar cyclization by ether formation did not occur when the corresponding (3-bromopropyl)salicylaldamine complex was reacted in the same way. We point out that reaction of bis{*N*-[3-(1-aziridinyl)propyl]salicylaldimino}nickel(II) with acid, analogous to eq 1, does not give any [bis(salicylidene)-1,3-propanediimino]nickel(II).[1] These observations point to control by the metal ion of the course of these ligand reactions. The reactions of Kluiber and Sasso and the reaction discussed here both involve formation of an aryl alkyl ether by attack of an electrophilic carbon on a phenolate ion. Accessibility of the reactive carbon to the phenolate, within the constraints of the metal template, is apparently reduced by longer hydrocarbon chains.

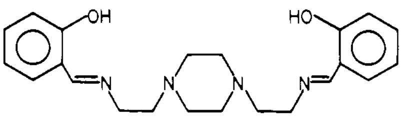


4

It is not possible to say that **1** is actually a ligand in the tan intermediate, but it is clear that there is a secondary amine function in both **1** and the complex. The difference between the N–H stretching frequencies in the complex and in **1**, 125 cm^{-1}, is of the magnitude of the shift seen between coordinated and uncoordinated secondary amines.[7] It is hoped that determination of the crystal structure of the tan intermediate will successfully answer this interesting question. The structure of **1** is not such that it is expected to be a very good donor toward a metal ion. It is presumed that the ligands of the tan intermediate react during the demetalation to give **1**.

1 reacts with salicylaldehyde or with the Schiff base, SalAEAH, to form H_2Sal_2en in the absence of nickel ion. These reactions support the idea that **1** is at least present, if not actually a coordinated ligand, during the course of the overall reaction described in eq 1. The fact that there must be an additional byproduct(s) in these reactions remains as an unsolved problem. The reaction of **1** with salicylaldehyde in an NMR tube as described in the Experimental Section gave some evidence for volatile product(s) containing aliphatic protons.

The significance of the nickel ion in the overall reaction is indicated by the reaction of salicylaldehyde, AEA, and aqueous HBr in ethanol which affords a 34% isolated yield of *N,N'*-bis[2-(salicylidenamino)ethyl]piperazine (**5**). This product is the result of an expected acid-catalyzed ring opening of aziridine.[8] Several piperazines have been synthesized in this manner. It is significant that, in the nickel complex reaction, no trace of the piperazine is observed.



5

Experimental Section

Materials. *N*-(2-Aminoethyl)aziridine was donated by Dow Chemical Co., Midland, MI, and was vacuum distilled prior to use. The fraction boiling at 42–43 °C at 15–17 mm was used. Purity was checked with ^1H NMR, refractive index, and GC. Salicylaldehyde was purchased either from J. T. Baker Chemical Co. or Aldrich Chemical Co. and was distilled prior to use or distilled whenever a yellow color was noticed in the compound. The aziridine and the aldehyde were stored in a refrigerator. All other chemicals used were of reagent grade.

Column chromatography was performed with use of Baker 7G-F silica gel (particle size less than 40 μm) and standard Pyrex columns.

NMR Spectra. Slow-passage ^1H NMR spectra were recorded on a Varian EM-360 spectrometer. ^1H and ^{13}C Fourier transform spectra were obtained with use of a Varian XL-100 spectrometer or a Varian HR-360 spectrometer. Chemical shifts are reported in ppm downfield from Me_4Si.

Infrared Spectra. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer using Nujol or hexachlorobutadiene mulls.

Magnetic Measurements. Magnetic susceptibilities were measured either by the Gouy method or by the ^1H NMR method of Evans as modified by Fritz and Schwarzhans.[9] The Gouy measurements were conducted at three different field strengths with $Hg[Co(SCN)_4]$ as calibrant. ^1H NMR measurements were made with absolute MeOH solutions with $[Fe(acac)_3]$ as calibrant. Ligand corrections were made with use of Pascal's constants.

Electronic Spectra. Electronic spectra of the two intermediate complexes were obtained with use of a Cary 14 recording spectrophotometer.

Elemental Analyses. Microanalyses for C, H, N, and Br were performed by M-H-W Laboratories, Phoenix, AZ.

Syntheses. Bis{*N*-[2-(1-aziridinyl)ethyl]salicylaldimino}nickel(II), [Ni(SalAEA)$_2$]. To 50 mL of commercial MeOH and 50 mL of Et_2O

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was added 5.64 g (16.8 mmol) of bis(salicylaldehydo)diaquonickel(II),[1] [Ni(Sal)$_2$(H$_2$O)$_2$], and 2.89 g (33.6 mmol) of *N*-(2-aminoethyl)aziridine, AEA, with stirring. The chartreuse-green solution turned olive green immediately upon AEA addition. After 12 h of stirring at room temperature, the solvent was evaporated, and the olive green crystals were filtered and washed with 6 M NaOH and then Et_2O. Recrystallization from CH_2Cl_2 yielded dark green prisms. After the crystals were dried in vacuo at 40 °C for 2 h, the yield was 6.22 g (83.0%). The IR spectrum matched a previous spectrum.[1]

[Bis(salicylidene)ethylenediimino]nickel(II), [Ni(Sal$_2$en)]. To 2.00 g (4.55 mmol) of [Ni(SalAEA)$_2$] in 30 mL of 1-BuOH was added 0.800 g of 48% aqueous HBr 4.74 mmol) with stirring. The solution was magnetically stirred and refluxed 35 h. The flask was allowed to cool overnight, and 1.45 g (4.46 mmol) of red-brown needles of [Ni(Sal$_2$en)] was filtered. The yield was 98.1%. An IR spectrum of these crystals matched a known sample of [Ni(Sal$_2$en)] made with use of salicylaldehyde, ethylenediamine, and $Ni(OAc)_2{\cdot}4H_2O$.[1] [Ni(Sal$_2$en)] may be recrystallized from absolute EtOH yielding long red needles. ^{1}H NMR (Me_2SO): δ 3.42 (s, 4 H), 6.3–7.4 (m, 8 H), 7.9 (s, 2 H).

Green Intermediate. To 0.500 g (1.14 mmol) of [Ni(SalAEA)$_2$] in 10 mL of 1-BuOH was added 0.200 g of 48% aqueous HBr solution (1.19 mmol) with stirring. The solution immediately changed to a lighter green. After a 30-min stirring, the solution was evaporated nearly to dryness at room temperature and light green crystalline flakes were filtered. Care must be taken not to heat this solution as further reaction to form the tan intermediate will occur. The solid was dried in vacuo at 40 °C for 2 h. The yield was 0.570 g (93.1%). Elemental Anal. Calcd for $NiC_{22}H_{29}N_4O_3Br$: C, 49.29; H, 5.45; N, 10.45; Br, 14.90. Found: C, 49.02; H, 5.01; N, 10.34; Br, 15.01. IR (Nujol): 3300 (s, br), 1655 (s), 1610 (s), 1550 (m), 1360 (m), 1300 (m), 1260 (m), 1125 (s), 1065 (m), 1025 (m), 950 (m), 905 (s), 888 (m), 760 cm^{-1} (s, br). An aqueous solution of this light green powder gave an intermediate precipitate of AgBr upon treatment with aqueous 0.5 M $AgNO_3$. Magnetic moment: Gouy, 3.11 μ_B; ^{1}H NMR in MeOH, 2.89 μ_B. Electronic spectrum: 843 (ϵ 22.1 L mol^{-1} cm^{-1}), 543 (ϵ 14.6), 370 (ϵ 7030). A 1:1 ethanol:water solution of the compound gave a positive phenol test when treated with a 1% aqueous solution of $FeCl_3$.

Tan Intermediate. To 4.00 g (9.11 mmol) of [Ni(SalAEA)$_2$] in 100 mL of MeCN was added 1.60 g of 48% aqueous HBr (9.49 mmol). The original green solution immediately turned blue-green. After 1.5 h of reflux, the solution was red-brown. Upon rotary evaporation to ca. 10 mL a tan powder precipitated from solution, was filtered, and was dried in vacuo at 30 °C for 2 h. The yield was 3.60 g (73.5%). The tan powder was recrystallized for an analytical sample by heating 1-BuOH to 70 °C, adding the tan powder until no more dissolved, and gravity filtering. After the flask remained untouched for ca. 3 days, small dark brown prisms formed. This intermediate was very soluble in H_2O, CH_2Cl_2, and MeOH but insoluble in EtOAc and Et_2O. Elemental Anal. Calcd for $NiC_{22}H_{29}N_4O_3Br$: C, 49.29; H, 5.45; N, 10.45; Br, 14.90. Found: C, 49.28; H, 5.91; N, 10.35; Br, 14.26. IR (Nujol): 3460 (m, br), 3120 (s), 1655 (s), 1630 (s), 1605 (s), 1530 (m), 1400 (m), 1360 (m), 1208 (s), 1191 (m), 1148 (s), 1130 (m), 1105 (s), 1061 (s), 1028 (m), 999 (s), 913 (m), 900 (s), 862 (m), 793 (s), 759 (s), 743 (m), 732 (m), 645 (w), 600 (w), 551 (w), 499 (w), 484 (w), 467 cm^{-1} (w). Electronic spectrum (MeOH): 830 (ϵ 34.2), 785 (ϵ 32.5), 537 (ϵ 39.9), 370 (ϵ 9540). This complex gave an immediate precipitate of AgBr upon treatment with aqueous 0.5 M $AgNO_3$. Magnetic moment: Gouy, 2.96 μ_B; ^{1}H NMR in MeOH, 3.05 μ_B. A 1:1 ethanol:water solution of the compound gave a positive phenol test when treated with 1% aqueous solution of $FeCl_3$.

Demetalation Reactions. Demetalation of Green Intermediate Using KCN. The ligand from the green intermediate can be isolated as the pure organic compound by treatment of the complex with excess aqueous KCN and extraction into $CHCl_3$. Ni(II) stays in the aqueous phase as the very stable $[Ni(CN)_4]^{2-}$ ion. Thus, 0.500 g of the green intermediate (0.930 mmol) was dissolved in 50 mL water, and 1.00 g (15.3 mmol) of KCN was added with stirring. After 1 h, the solution was extracted with 50 mL of $CHCl_3$. The $CHCl_3$ solution was bright yellow and was shown by TLC to contain a single component. The $CHCl_3$ solution was then dried ($MgSO_4$) and evaporated with a rotary evaporator. ^{1}H NMR showed the resulting yellow oil to be SalAEAH. ^{1}H NMR ($CDCl_3$): δ 1.13 (m, 2 H), 1.76 (m, 2 H), 3.50 (t, 2 H, J = 6 Hz), 3.93 (t, 2 H, J = 6 Hz), 6.62–7.52 (m, 4 H), 8.40 (s, 1 H), 12 (s, br, 1 H). *Caution*: The aqueous CN$^-$ containing layer was treated with excess $KMnO_4$ to destroy the cyanide ion. *Extreme care must be exercised in all procedures involving KCN.*

Demetalation of Tan Intermediate Using EDTA. Five (5.00) grams (9.30 mmol) of tan intermediate, 10.0 g (26.6 mmol) of trisodium ethylenediaminetetraacetic acid, and enough KOH to dissolve the latter were placed in 300 mL water. After being stirred at room temperature for 1 h, the solution was extracted with three portions of CH_2Cl_2 totalling 750 mL. The blue nickel–EDTA complex remained in the aqueous layer. The yellow CH_2Cl_2 solution was dried ($MgSO_4$) and evaporated to a yellow oil which was added to a 1 × 12 in. silica gel column which was packed from a heptane slurry. The column was then eluted with Et_2O which moved a narrow yellow band shown by TLC to contain a single compound. Proton NMR unequivocally showed this compound to be SalAEAH. Following the Et_2O elution, the column was washed with EtOAc and then eluted with absolute EtOH which afforded a second organic compound, **1**, which crystallized from the pale yellow oil formed by evaporation of the ethanol. **1** was recrystallized from dry Et_2O giving nearly white prisms, mp 69–71 °C. IR (Nujol): 3245 (s), 3055 (m), 1610 (m), 1585 (m), 1490 (m), 1325 (s), 1295 (s), 1285 (m), 1220 (s), 1163 (m), 1135 (m), 1045 (s), 1031 (s), 953 (s), 904 (s), 864 (s), 814 (s), 784 (s), 763 (s), 719 (m), 684 (w), 634 (w), 585 (m), 542 (w), 514 cm^{-1} (m). ^{1}H NMR ($CDCl_3$): δ 2.35 (s, 1 H), 2.63 (q, 1 H, J = 8.1 Hz), 2.96 (m, 1 H), 3.12–3.40 (m, 4 H), 3.86 (m, 1 H), 4.34 (dt, J_1 = 13.0 Hz, J_2 = 3 Hz, 1 H), 4.60 (s, 1 H), 7.00 (dd, 1 H, J_1 = 9 Hz, J_2 = 1.5 Hz), 7.08 (td, 1 H, J_1 = 9 Hz, J_2 = 1.5 Hz), 7.20 (td, 1 H, J_1 = 9 Hz, J_2 = 1.5 Hz), 7.52 (dd, 1 H, J_1 = 9 Hz, J_2 = 1.5 Hz). Elemental anal. Calcd for $C_{11}H_{14}N_2O$: C, 69.45; H, 7.42; N, 14.73. Found: C, 69.34; H, 7.47; N, 14.76. Mass spectrum *m/e*: 190 (M$^+$), 1.89 (base), 161, 147, 119, 97, 91. ^{13}C NMR ($CDCl_3$), δ 44.08, 56.03, 56.09, 72.26, 78.89, 121.10, 123.74, 126.11, 128.79, 133.66, 158.71.

Demetalation of Tan Intermediate with KCN. Fifty milliliters of $CHCl_3$ containing 0.500 g (0.930 mmol) of tan intermediate was mixed and stirred rapidly with 50 mL of H_2O containing 0.302 g (4.64 mmol) of KCN. After 1 h the yellow $CHCl_3$ layer was separated from the aqueous layer and evaporated to a yellow oil. Two components were indicated by TLC on silica gel with MeOH. The compounds were separated by dissolving the oil in 2 mL of $CHCl_3$ and placing it on a 1 × 12 in. silica gel column packed with heptane slurry. Elution with dry Et_2O gave a narrow yellow band. Evaporation of the ether eluate gave a yellow oil that was shown by TLC to be a single compound, **3**, which could not be crystallized. IR ($CHCl_3$, 0.0269-mm pathlength): 2425 (w), 1645 (s), 1600 (m), 1505 (s), 1475 (m), 1295 (s), 1170 (m), 680 cm^{-1} (s). ^{1}H NMR ($CDCl_3$): δ 2.7–4.5 (m, 8 H), 4.95 (s, 1 H), 6.8–7.8 (m, 8 H), 8.30 (s, 1 H), 12.98 (s, br, 1 H). The broad singlet at δ 12.98 exchanges with D_2O. Mass spectrum *m/e*: 321 (M$^+$), 294, 263, 225, 187, 167, 149 (base).

The second product was eluted with absolute EtOH after the column was washed with EtOAc. The light yellow eluate was evaporated to an oil which crystallized upon standing. After recrystallization from Et_2O, the ^{1}H NMR was identical with that of **1** described previously.

Reactions without Metal Present. Synthesis of *N*,*N'*-Bis[2-(salicylidenamino)ethyl]piperazine. To 20 mL of absolute EtOH containing 1.22 g (10.0 mmol) of salicylaldehyde and 0.86 g (10.0 mmol) of *N*-(2-aminoethyl)aziridine was added 0.405 g (2.40 mmol) of 48% aqueous HBr dropwise with stirring. The mixture was refluxed for 1 h to give an orange-yellow solution. Twenty milliliters of Et_2O was added with cooling to afford 0.65 g (34%) of yellow needles. Crystals for an analytical sample were obtained by recrystallization two times from absolute EtOH and drying in vacuo at 40 °C; mp 151–153 °C. Elemental Anal. Calcd for $C_{22}H_{28}N_4O_2$: C, 69.45; H, 7.42; N, 14.72. Found: C, 69.42; H, 7.25; N, 14.60. IR (Nujol): 1640 (s), 1625 (m), 1585 (s), 1500 (m), 1320 (m), 1292 (s), 1167 (s), 1149 (m), 1121 (w), 1104 (w), 1043 (m), 1024 (m), 1008 (m), 970 (m), 887 (m), 860 (m), 778 (w), 760 (s), 753 (s), 739 (s), 667 (w), 645 cm^{-1} (w). ^{1}H NMR ($CDCl_3$): δ 2.60 (s, 8 H), 2.69 (t, 4 H, J = 6 Hz), 3.73 (t, 4 H, J = 6 Hz), 6.7–7.5 (m, 8 H), 8.35 (s, 2 H), 13.45 (s, br, 2 H). The broad singlet at δ 13.45 exchanged with D_2O. Mass spectrum *m/e*: 380 (M$^+$), 259, 246, 244, 177, 139 (base), 111, 100, 97.

Reaction of 1,2,3,5,6,11b-Hexahydroimidazo[1,2-*d*][1,4]benzoxazepine with Salicylaldehyde. To 0.108 g (0.569 mmol) of the benzoxazepine, **1**, and 0.0695 g of salicylaldehyde (0.569 mmol) was added 1.0 mL of $CDCl_3$ in a standard 5-mm ^{1}H NMR tube. A tight-fitting cap was employed to trap any volatile products. The ^{1}H NMR spectrum was recorded immediately, after heating in an oil bath at 70 °C for 1 h, 2 h, and finally overnight. The cap was at no time removed, and the NMR tube was stored in a freezer until the spectrum was run. The final ^{1}H NMR spectrum was that of H_2Sal_2en. ^{1}H NMR ($CDCl_3$): δ 3.80 (s, 4 H), 6.5–7.7 (m, 8 H), 8.3 (s, 2 H), 13.19 (s, br, 2 H). ^{13}C NMR ($CDCl_3$): δ 59.66, 116.89, 118.60, 131.41, 132.32, 160.96, 166.41. IR (Nujol): 1630 (s), 1050 (s), 1030 (s), 990 (s), 980 (s), 950 (m), 870 (s), 780 (s), 779–750 (s), 660 cm^{-1} (s). The ^{1}H NMR spectrum matched that of a known sample of H_2Sal_2en made from salicylaldehyde and ethylenediamine. When the reaction tube was cooled in a dry-ice bath and the ^{1}H NMR spectrum was recorded within ca. 30 s, some additional peaks in the aliphatic region were observed. These peaks disappeared after ca. 1 min at room temperature and were not investigated further.

Reaction of 1,2,3,5,6,11b-Hexahydroimidazo[1,2-*d*][1,4]benzoxazepine with *N*-[2-(1-Aziridinyl)ethyl]salicylaldimine. A mixture of 0.107 g (0.566 mmol) of the benzoxazepine, 0.0487 g (0.566 mmol) of *N*-(2-aminoethyl)aziridine, 0.0700 g (0.573 mmol) of salicylaldehyde, and 0.0955 g (0.556 mmol) of 48% aqueous HBr and 8.0 mL of 1-BuOH were heated at reflux for 34 h. The original yellow solution began turning orange after ca. 0.5 h of heating. At the end of the reaction, the solution was orange and slightly basic to pH test paper. After cooling in ice afforded no crystals, a TLC (MeOH) showed one yellow component and one spot which did not move at all. The solvent was then evaporated to 2 mL and added dropwise to the top of a 1 × 12 in. silica gel column and eluted with dry Et_2O and then MeOH. Both solvents were completely evaporated, leaving a yellow semisolid. The ^{1}H NMR spectrum was identical with that of H_2Sal_2en except for an additional multiplet at δ 0.6–2.0.

Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society for the support of this research. K.R.L. also acknowledges support from the Gulf Oil Foundation and the Henry and Camille Dreyfus Foundation. We are also indebted to Fred L. Urbach, William DeW. Horrocks, William, J. A. VandenHeuvel, and Amos B. Smith for valuable assistance in obtaining NMR and mass spectral results. We are grateful to John M. Zachara who performed some essential preliminary experiments.

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Kinetics of Reduction of $Co(NH_3)_4C_2O_4^+$ by Oxalato Complexes of Titanium(III)

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Received September 16, 1980

Oxalate ion is an efficient bridging ligand for electron transfer (ET) between transition-metal ions, but the detailed mechanism of the ET step depends on which metal ions are involved. The rate law for reaction of $Ru(NH_3)_4C_2O_4^+$ with Ti(III)[1] differs from the rate law for reaction of $Co(NH_3)_4C_2O_4^+$ with the same reductant.[2] The difference is such as to indicate that cross-bridge electronic interaction, through bridging oxalate ion, is more efficient in the Ru(III)–Ti(III) case than it is in the Co(III)–Ti(III) case.[1] Rate and equilibrium constants have been measured[3] for the formation of oxalato complexes of Ti^{3+}. We now report results of a study of the influence of oxalate ion as a nonbridging ligand on the rate of Co(III)–Ti(III) ET reactions which also involve oxalate as a bridging ligand.

Ti(III) solutions were prepared as described elsewhere.[1] $[Co(NH_3)_4C_2O_4]Cl$ was prepared by the method of Jørgensen.[4] Absorbances (*A*) were measured at 288 nm with use of a Gilford 2400 spectrophotometer and nitrogen-purged solutions of ionic strength 1.0 M (LiCl supporting electrolyte), at 25.0 ± 0.2 °C. For a determination of the effect of additional oxalate, LiCl, Ti(III), and oxalate solutions were mixed with sufficient HCl to give a final [H$^+$] near 0.15 M and allowed to stand for sufficient time for complex-formation reactions to reach equilibrium. The redox reaction was then initiated by injecting oxidant solution (through platinum needles). Concentrations were chosen such that the injection caused only a small perturbation to the preestablished equilibria.

Table I. Kinetics of Reduction of $Co(NH_3)_4(C_2O_4)^+$ by Ti^{3+} at 25.0 °C in 1 M LiCl

$10^3 \times$ [H$^+$], M	$10^3 \times$ [Co(III)], M	$10^3 \times$ [Ti(III)], M	10^3k_1, s^{-1}	k_2,[a] M^{-1} s^{-1}	10^2k,[b] s^{-1}
10.2	0.257	2.68	11.8	4.4	4.5
29.7	0.286	4.02	5.9	1.48	4.4
49.8	0.286	3.35	2.88	0.86	4.3
74.3	0.286	4.02	2.37	0.59	4.4
100.2	0.286	3.35	1.41	0.42	4.2
100.2	0.286	4.69	2.02	0.43	4.3
99.8	0.465	4.69	2.06	0.44	4.4
123.7	0.469	5.36	1.88	0.35	4.3
152.7	0.286	5.36	1.47	0.28	4.2
177.7	0.269	5.36	1.29	0.24	4.3
211.4	0.469	5.36	1.07	0.20	4.2
				av	4.3 ± 0.1

[a] $k_2 = k_1/[Ti(III)]$. [b] $k = k_2[H^+]$.

Experiments carried out under second-order conditions demonstrated that 1.0 mol of Co(III) was reduced for each mole of Ti(III) reacted, both in the presence of added oxalate and in its absence. Normally, kinetic runs were carried out with Ti(III) in large excess over Co(III). Plots of log ($A - A_0$) were linear for at least 85% reaction. Rate constants (k_1) were calculated with use of data taken over 2 half-times. Rate constants for replicate runs generally agreed within 5%.

Equilibria that need to be considered to discuss the influence of added oxalate on the rate of the reaction of interest are given by eq 1–4. The symbols (H), (HL), (M), (ML), and so on

$$H_2C_2O_4 \rightleftarrows HC_2O_4^- + H^+ \qquad K_1 = \frac{(H)(HL)}{(H_2L)} \tag{1}$$

$$HC_2O_4^- \rightleftarrows C_2O_4^{2-} + H^+ \qquad K_2 = \frac{(H)(L)}{(HL)} \tag{2}$$

$$Ti^{3+} + C_2O_4^{2-} \rightleftarrows TiC_2O_4^+ \qquad K_3 = \frac{(ML)}{(M)(L)} \tag{3}$$

$$TiC_2O_4^+ + C_2O_4^{2-} \rightleftarrows Ti(C_2O_4)_2^- \qquad K_4 = \frac{(ML_2)}{(ML)(L)} \tag{4}$$

refer to the activities of the corresponding chemical species H^+, $HC_2O_4^-$, Ti^{3+}, $TiC_2O_4^+$, etc. Values of K_1 and K_2 have been determined[5] to be 0.09 and 4 × 10^{-4} M under conditions of our experiments. Chaudhuri and Diebler[3] have measured K_3 and K_4 (in 1 M NaCl) as 3 × 10^6 and 1 × 10^6 M^{-1}, but at 10 °C rather than 25 °C.

In the absence of added oxalate, the reaction of interest is

$$Co(NH_3)_4C_2O_4^+ + Ti^{3+} \rightarrow \text{products} \tag{5}$$

In agreement with the prior report,[2] we find (Table I) that

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0020-1669/81/1320-3569$01.25/0