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Notes

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Biological Analogues. A Planar Quadridentate Ligand with an Axial Thioether Tail

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Planar quadridentate systems with an attached tail containing a donor functionality capable of axial coordination have been the subject of considerable recent interest.[1] Such combinations of planar quadridentate and axial coordination occur frequently in biological systems; examples include the axial imidazole and planar heme in hemoglobin and myoglobin[2] and the axial benzimidazole and quasi-planar corrin in vitamin B_{12}.[3] Cytochrome *c* is a six-coordinate system containing a planar heme with the axial sites occupied by histidine imidazole and methionine thioether.[4]

Prompted by the last, we have synthesized the ligand (*S*)-*N*,*N*′-[(2-(methylthio)ethyl)ethylene]bis(salicylidenimine), salmetH_2, a derivative of *N*,*N*′-ethylenebis(salicylidenimine), salenH_2, containing a thioether tail (Figure 1). The purpose was to determine the coordinating ability of the thioether tail, since, although thioether coordination occurs in the biological system, under normal circumstances thioether ligands coordinate only weakly with the first transition elements in their usual oxidation states.[6] We wished to know whether the chelate effect achieved by tail incorporation would enhance the stability or whether other factors were necessary.

Synthesis and Stereochemical Considerations

The synthesis, originating from (*S*)-methionine, is shown in Figure 1, as is the structure of the sought-after metal complexes. The structural requirement for the tail coordination, namely, that the tail carbon atom emanating from the ethylenediamine backbone be axially disposed, is consistent with observations on substituted salen complexes for which it has been found that the ethylenediamine substituents prefer an axial disposition.[5]

Results

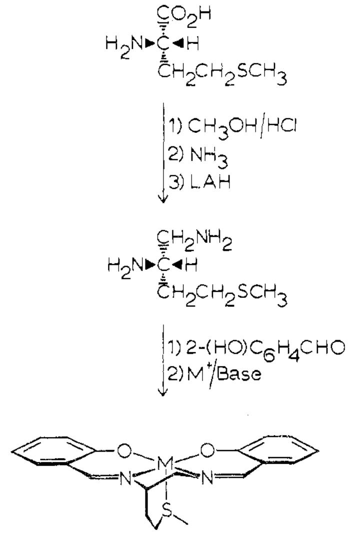

Figure 1. Method of preparation of the salmetH_2 ligand and its complexes.

We have isolated crystalline salmet complexes of copper(II), nickel(II), and iron(III), the latter containing two *N*-methylimidazole (*N*-meim) ligands without which a crystallizable compound could not be obtained. The solid crystalline complexes [Cu(salmet)] and [Ni(salmet)] are dark blue and deep red, respectively, and are quite unlike the colors obtained for the corresponding [Cu(salen)] and [Ni(salen)] complexes. The color of the copper complex is consistent with thioether coordination[6], but new absorption bands could arise in square-planar Cu(II) and Ni(II) salen and salmet complexes because of oxygen–metal interaction between neighboring molecules in the solids. So it is not possible to confidently transfer information from the solid to solution where we show there is no evidence for thioether coordination.

Electronic spectra of [Cu(salmet)] were recorded in chloroform, benzene, methanol, dioxane, dichloromethane, and nitrobenzene. In all cases the visible spectrum (300–800 nm) was identical with that of [Cu(salen)] in the same solvent, indicating lack of coordination of the sulfur in these media. Similarly, electronic spectra of [Ni(salmet)] (diamagnetic)

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were superimposable with those of [Ni(salen)] in dichloromethane and benzene. Moreover, the S–CH_3 ^1H NMR signal of [Ni(salmet)] is unshifted from that of the free ligand (δ = 2.0 in $CDCl_3$).

The iron complex [Fe(salmet)(*N*-meim)$_2$]ClO_4 crystallized as violet needles from ethanol while the previously unreported [Fe(salen)(*N*-meim)$_2$]ClO_4 formed violet blocks. Attempts to isolate complexes containing only a single *N*-meim ligand were unsuccessful. The electronic spectra of [Fe(salmet)(*N*-meim)$_2$]ClO_4 and [Fe(salen)(*N*-meim)$_2$]ClO_4 were identical in ethanol solutions. When either 1 or 2 equiv of $HClO_4$ (1 M) was added to each of these solutions, their spectra behaved identically. The function of the acid is to remove the coordinated *N*-meim ligands through protonation. That this occurs was confirmed by isolating the *N*-meim·$HClO_4$ salt. The observed identity of the spectral behavior of the salmet and salen complexes indicates that even when a vacant coordination site is available, sulfur remains uncoordinated to high-spin iron(III).

Discussion

The lack of coordination of the thioether tail to the three metals studied admits to two possible explanations. Either structural features prevent coordination or the sulfur–metal (thioether) bond is very weak with these metals in their present electronic states. We consider it improbable that structural effects prevent coordination since previous work on substituted salen complexes has shown that the substituents attached to the ethylenediamine backbone prefer an axial disposition.[5] If this is so, then the fact that the tail is attached to the quadridentate ligand should enhance coordination and not suppress it.

Both the copper and nickel complexes appear to have coordinated thioether in the solids, but there is no evidence for coordination in solution even with poorly coordinating solvents such as benzene. This, perhaps surprising, observation suggests that axial coordination of thioether to copper and nickel is exceedingly weak and that, in order to get coordination, a much more rigid framework is required to hold the thioether tail in place. Rigidity may partly explain the presence of thioether coordination in horse cytochrome *c* in which the thioether ligand is held in its coordination position by the protein structure. In addition cytochrome *c* is spin paired when *both* the axial ligands are attached, and this will undoubtedly increase the stability of the iron–sulfur bond. Our iron system is spin free even with two axial *N*-meim ligands.

Thus it appears that features more subtle than simply the presence of an attached tail are required for five-coordination. Such factors as the spin state of the metal atom, the rigidity of the tail to hold the thioether group in the axial position, and perhaps the presence of a hydrophobic pocket may all be significant in obtaining thioether tail coordination.

Experimental Section

Electronic spectra were obtained using a Unicam SP-800A spectrophotometer. Proton magnetic resonance spectra (60 MHz) were recorded on a Varian Associates T-60 spectrometer, and all samples were run in $CDCl_3$ with Me_4Si as an internal standard. Magnetic susceptibility measurements were obtained at 20 °C using the Gouy method.

(*S*)-Methionine Methyl Ester Hydrochloride. This was prepared by standard procedures;[7] $[\alpha]_D$ +25.8° (0.18 M in H_2O). Anal. Calcd. for $C_6H_{14}NO_2SCl$: C, 36.1; H, 7.1; N, 7.0; S, 16.1; Cl, 17.8. Found: C, 36.3; H, 7.2; N, 7.1; S, 16.0; Cl, 17.8.

(*S*)-Methionamide Hydrochloride. (*S*)-Methionine methyl ester hydrochloride (45 g) was dissolved in methanol (350 mL). The solution was saturated with ammonia at 0 °C. After 5 h, it was resaturated with ammonia and again after 2.5 days. After the solution was allowed to stand for a total of 5 days, the methanol was removed under vacuum to leave a white solid. This was taken up in hot water (20 mL) and then quickly diluted with ethanol (475 mL). The mixture was allowed to stand at 5 °C for 18 h, and the white needles of the pure product were collected and were washed with ethanol and then with ether (33.5 g); $[\alpha]_D$ +16.3° (1% in H_2O). Anal. Calcd for $C_5H_{13}N_2OSCl$: C, 32.5; H, 7.0; N, 15.2; Cl, 19.2. Found: C, 32.6; H, 6.9; N, 15.0; Cl, 19.1.

(2*S*)-2-Amino-5-thiahexylamine ("(*S*)-Methionamine"). Lithium aluminum hydride (20 g) was suspended in dry tetrahydrofuran (500 mL). Solid (*S*)-methionamide hydrochloride (33.5 g) was added carefully in small portions over a period of 30 min. The mixture was stirred at 55 °C for 16 h. It was then cooled to 5 °C and cautiously quenched by adding, successively and dropwise, water (20 mL), 15% NaOH (20 mL), and finally water (60 mL). The precipitated, granular alumina was filtered, washed with hot THF, and then extracted three times with boiling THF (200-mL portions). The combined filtrates were taken to dryness in vacuo at 50 °C. The remaining liquid was distilled at 10 mm (bp 123–129 °C) and was redistilled at 0.1 mm (bp 60–62 °C) to give 16 g of a colorless liquid. Anal. Calcd for $C_5H_{14}N_2S$: C, 44.7; H, 10.5; N, 20.9; S, 23.9. Found: C, 44.8; H, 10.5; N, 20.8; S, 23.9.

(*S*)-*N*,*N*′-[(2-(Methylthio)ethyl)ethylene]bis(salicylidenimine) (salmetH_2). (2*S*)-2-Amino-5-thiahexylamine (2.0 g) was dissolved in benzene (40 mL), and freshly distilled salicylaldehyde (3.7 g) was added. The mixture immediately turned yellow. It was refluxed for 5 min, cooled, and dried with Na_2SO_4. The benzene was removed giving a yellow oil which was taken up in CCl_4 (4 mL), and cyclohexane (~30 mL) at 60 °C was added. The clear solution was allowed to cool slowly to 25 °C and then was held at 5 °C for 18 h. The lustrous yellow needles were collected and washed with cyclohexane (3.8 g): mp 59–60 °C; ^1H NMR δ 8.30 (1 H, singlet), 8.23 (1 H, singlet), 7.4–6.6 (8 H, complex), 4.0–3.5 (3 H, complex) 2.7–1.8 (4 H, complex), 2.00 (3 H, singlet); $[\alpha]_D$ +144.5° (10^{-2} M in MeOH). Anal. Calcd for $C_{19}H_{22}N_2O_2S$: C, 66.6; H, 6.5; N, 8.2; S, 9.4. Found: C, 66.7; H, 6.4; N, 8.3; S, 9.5.

[Ni(salmet)]. Nickel acetate–4-water (1.24 g) was dissolved in methanol (5 mL) and was added to a solution of salmetH_2 (1.71 g) in methanol (5 mL). The dark amber mixture was warmed on a steam bath for 10 min and then was cooled slowly to 0 °C. The product was collected and was washed with ether. It was recrystallized from methanol by the careful addition of ether. The pure diamagnetic complex formed deep red needles (1.25 g): ^1H NMR δ 7.3–6.2 (10 H, complex), 4.3–2.6 (3 H, complex), 2.6–1.8 (4 H, complex), 2.00 (3 H, singlet). Anal. Calcd for $NiC_{19}H_{20}N_2O_2S$: C, 57.1; H, 5.0; N, 7.0; S, 8.0. Found: C, 57.2; H 5.3; N, 7.2; S, 7.9.

[Cu(salmet)]. Copper acetate–water (0.66 g) in ethanol (20 mL) was added to salmetH_2 (1.14 g) in ethanol (10 mL), and the resultant mixture was heated on a steam bath for 30 min. The ethanol was removed under reduced pressure, the resultant blue solid was dissolved in CH_2Cl_2, and the solution was washed three times with water. The CH_2Cl_2 layer was dried and the solvent was removed in vacuo. The residue was recrystallized from methanol by the addition of ether to yield 1 g of deep blue needles, μ_{eff} = 1.9 μ_B (20 °C). Anal. Calcd for $CuC_{19}H_{20}N_2O_2S$: C, 56.5; H, 5.0; N, 6.9; S, 7.9. Found: C, 56.6; H, 5.3; N, 7.0; S, 7.9.

[Fe(salmet)(*N*-meim)$_2$]ClO_4. Ferrous perchlorate–6-water (7.2 g) was dissolved in ethanol (40 mL), and to it was added a solution of salmet H_2 (6.8 g) in ethanol (50 mL). The mixture was warmed, and *N*-methylimidazole (6.6 g; 3 equiv) was added. The white precipitate which formed (*N*-mein·$HClO_4$) was collected on a sinter and washed with ethanol (100 mL). The filtrate and washings were warmed to 60 °C, and *N*-methylimidazole (1.0 g) was added. The violet solution was filtered while hot, was allowed to cool to 30 °C, and then was filtered again. After the solution was allowed to stand at 25 °C for 18 h, the violet needles which formed were collected and were washed with 50% ethanol–ether and then with ether (7.0 g); μ_{eff} = 6.0 μ_B (20 °C). Anal. Calcd for $FeC_{27}H_{32}N_6O_6SCl$: C, 49.2; H, 4.9; N, 12.8; S, 4.9; Cl, 5.4. Found: C, 49.2; H, 5.0; N, 12.6; S, 4.9; Cl, 5.3.

[Fe(salen)(*N*-meim)$_2$]ClO_4. This compound was prepared by a method similar to that just described for the salmet complex; μ_{eff} = 6.0 μ_B (20 °C). Anal. Calcd for $FeC_{24}H_{26}N_6O_6Cl$: C, 49.2; H, 4.5; N, 14.3; Cl, 6.0. Found: C, 49.2; H, 4.5; N, 14.2; Cl, 6.0.

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Registry No. [Ni(salmet)], 68013-58-1; [Cu(salmet)], 68013-57-0; [Fe(salmet)(*N*-meim)$_2$]ClO_4, 68013-56-9; [Fe(salen)(*N*-meim)$_2$]ClO_4, 68013-54-7; salmetH$_2$, 68013-50-3; (*S*)-methionamine, 68013-51-4; (*S*)-methionamide hydrochloride, 16120-92-6; (*S*)-methionine methyl ester hydrochloride, 2491-18-1; salicylaldehyde, 90-02-8.

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The Chemistry of Trivalent Uranium. 2. Synthesis of UCl$_3$(18-crown-6) and U(BH$_4$)$_3$(18-crown-6)[1,2]

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A variety of crown ether complexes of uranium have been studied, but little evidence existed until recently to support the idea that direct coordination of uranium to the oxygens of the crown cavity had been achieved. Although a lanthanum nitrate crown ether complex had been found to possess the lanthanum coordinated in this manner,[3] only recently has a uranium(IV) complex been shown to exhibit this type of coordination.[4] The factors influencing the binding of uranium to the crown cavity still remain somewhat uncertain, however. Similarly, the extent that such coordination is oxidation state specific remains unknown. For these reasons, as well as the close similarity of La(III) and U(III) ionic radii and the limited information on chemical properties of U(III) compounds, we have undertaken the study of uranium(III)–crown ether complexes.

In this paper we wish to report the synthesis of UCl$_3$(18-crown-6) and its reaction with sodium borohydride yielding U(BH$_4$)$_3$(18-crown-6).

Experimental Section

All manipulations were performed under a dry nitrogen atmosphere by using standard Schlenk techniques or by using standard vacuum techniques. All solvents used in this study were reagent grade and were dried prior to use. UCl$_4$ was prepared by literature procedures.[5] 18-Crown-6 was obtained from Parish Chemical Co. and was recrystallized from acetonitrile and sublimed prior to use. NMR spectra were recorded on Varian Associates EM-360 and EM-390 spectrometers. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

UCl$_3$(THF)$_x$ + 18-Crown-6. As previously reported, 0.38 g (1 mmol) of UCl$_4$ and 0.24 g (10 mmol) of NaH were reacted in tetrahydrofuran (THF) solution to yield ~0.8 mmol of UCl$_3$(THF)$_x$ in 50–60 mL of THF.[2] This solution was filtered onto a stirred solution of 0.3 g (1.1 mmol) of 18-crown-6 in 30 mL of THF. An immediate reaction occurred yielding a finely divided red precipitate. The reaction was allowed to continue for 6–12 h to ensure complete reaction. The red precipitate was collected on a fine glass frit and was vacuum-dried overnight. The reaction yielded 0.45 g (0.74 mmol) of UCl$_3$(18-crown-6). Anal. Calcd for C$_{12}$H$_{24}$O$_6$UCl$_3$: C, 23.68; H, 3.97; U, 39.10; Cl, 17.47. Found: C, 22.65; H, 3.93; U, 39.11; Cl, 20.92.

Thermogravimetric analyses of UCl$_3$(18-crown-6) revealed no decomposition below 200 °C. Above 200 °C a weight loss of 43% was observed, which suggested loss of the crown ether (calcd 44%).

The UCl$_3$(18-crown-6) is insoluble in THF or acetone but reacts with water to yield a green solution. Because of this insolubility, solution NMR spectra were not obtainable. The broad-line ^{1}H NMR spectrum of a solid sample revealed a broad singlet which appeared to be unshifted from an external tetramethylsilane (Me$_4$Si) reference. However, due to the width of the peak, a shift ±10 ppm would have been undetectable.

UCl$_3$(18-crown-6) + NaBH$_4$. Approximately 0.45 g (0.75 mmol) of UCl$_3$(18-crown-6) and 0.2 g (5.3 mmol) of NaBH$_4$ were loaded into a 100-mL vessel equipped with a greaseless stopcock. The vessel was evacuated and 50 mL of THF was condensed onto the solids. After warming of the mixture to room temperature, the reaction proceeded slowly and the mixture was stirred overnight to ensure complete reaction. The orange-red slurry was filtered to remove NaCl and excess NaBH$_4$. An orange-red filtrate was obtained. The volume of this solution was reduced under vacuum to 10 mL, and 50 mL of diethyl ether was added. This precipitated an orange solid which was then filtered and dried in vacuo. The reaction yielded 0.2 g of product. The product proved to be very air sensitive so extreme caution was exercised in all manipulations. Although good analytical data were difficult to obtain due to the reactivity, elemental analyses generally support the formulation U(BH$_4$)$_3$(18-crown-6).

Anal. Calcd for C$_{12}$H$_{36}$O$_6$B$_3$U: C, 26.35; H, 6.64; B, 5.93 (C$_4$H$_{12}$B). Found: C, 21.68; H, 5.85; B, 4.75 (C$_4$H$_{13}$B). The ^{1}H NMR spectra in THF-d_8 also support this formulation with a broad BH$_4$ singlet at 103 ppm downfield from Me$_4$Si and a sharp singlet due to 18-crown-6 at 2.9 ppm relative to Me$_4$Si = 0 (uncomplexed 18-crown-6 is observed at 3.3 ppm). The relative intensities of these peaks are as expected 1:2.

Results and Discussion

We have found that UCl$_3$(THF)$_x$ readily reacts with 18-crown-6 resulting in displacement of the THF's by the crown ether and formation of UCl$_3$(18-crown-6). Coordination numbers greater than nine are quite common for U(III), and coordination numbers in excess of 12 have been observed. This, coupled with the extreme insolubility of UCl$_3$(18-crown-6), leads us to believe that a chloride-bridged structure is probably present, but a monomeric nine-coordinate structure cannot be discounted with the present data. The high thermal stability suggests that the uranium atom is actually coordinated to the oxygens of the crown cavity. If such coordination were present, one would expect a rather large paramagnetic shift of the crown ether protons in the ^{1}H NMR spectrum. Such shifts of 20–30 ppm have been observed for U(IV) complexes,[4] but we cannot be certain as to what magnitude of shift would be expected for similar coordination of uranium(III). The solid-state ^{1}H NMR spectrum of UCl$_3$(18-crown-6) shows little, if any, shift of the crown proton resonance from that of uncomplexed 18-crown-6. The peak is, however, very broad, and a shift of ±10 ppm could easily go undetected. More studies are currently under way in hopes of establishing the coordination about the uranium in this complex.

Although UCl$_3$(18-crown-6) is insoluble in THF, a slurry has been found to react with NaBH$_4$ to yield a soluble product, U(BH$_3$)$_3$(18-crown-6). Because of the extreme sensitivity to air and water, analytical data for this complex are consistently low in C, H, and B; however, the ratios obtained suggest that the above stoichiometry is probably correct. Similarly, the ^{1}H NMR spectrum supports the formulation as a 1:1 adduct with an integration of BH$_4^-$ to crown ether protons of 1:2. The 12 BH$_4^-$ protons are equivalent on the NMR time scale and are shifted downfield due to the paramagnetic U(III) center. The 24 crown ether protons are also equivalent yielding a single, sharp peak and are barely shifted from the position of free 18-crown-6. This small shift of the crown protons suggests either that little interaction exists between the paramagnetic U(III) center or that the crown ether is exchanging in solution.

Red crystals have been obtained from THF/diethyl ether solutions of U(BH$_4$)$_3$(18-crown-6), but some dissociation of the crown ether is observed during the crystallization process.

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