Notes

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Fluoro-Containing Complexes of Chromium(III). 8. Preparation and Characterization of a Dimethoxo-Bridged Dimer of Chromium(III)[1]

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Recently there have been a number of investigations concerning the preparations, crystal structures, and magnetic properties of bridged dimers of chromium(III).[2-5]

Apparently there are, in the diamine system, no reported examples of alkoxo-bridged dimers of chromium(III) which contain a single diamine and two acido ligands bound to each chromium(III) center. The synthesis and characterization of such a dimer are reported in this paper.

Experimental Section

Preparation of Starting Material. *trans*-Difluorobis(trimethylenediamine)chromium(*III*) chloride was prepared as described in the literature.[6] A 9.0-g (33-mmol) sample of crude *trans*-difluorobis(trimethylenediamine)chromium(III) chloride was dissolved in 40–50 mL of water at room temperature and the solution was filtered. The filtrate was treated with 5 mL of concentrated hydriodic acid and the reaction mixture was allowed to stand at room temperature for 15 min. At the end of this time the beaker and its contents were cooled in an ice bath for 30 min. The solid product was collected, washed with acetone, and air-dried; yield 4.52 g (28%). Anal. Calcd for *trans*-$[Cr(C_3N_2H_{10})_2F_2]I\cdot H_2O$: C, 18.7; H, 5.75; N, 14.6. Found: C, 18.5; H, 5.65; N, 14.7. The electronic absorption spectrum in aqueous solution was characterized by λ_{max} 537 nm (ϵ 16.8 M^{-1} cm^{-1}), λ_{max} 465 nm (ϵ 21.4), λ_{max} 395 nm (ϵ 16.3), and λ_{max} 360 nm (ϵ 16.3). Literature values:[7] 538 (16.8), 468 (20.7), 398 (16.5), 360 (16.3).

Preparation of the Bridged Dimer. A 3.0-g (7.85-mmol) sample of *trans*-$[Cr(C_3H_{10}N_2)_2F_2]I\cdot H_2O$ was placed in the thimble of a Soxhlet extractor, and the sample was extracted with methyl alcohol for 48 h. At the end of this time, the blue product which had precipitated in the extraction flask was collected along with some starting material which precipitated during filtration. These solids were placed in the extraction thimble, the filtrate was returned to the extraction flask, and the extraction was continued. At 24-h intervals additional blue solid was collected from the reaction flask and placed in the thimble, the filtrate was returned to the extraction flask, and the extraction was continued. The total reflux time involved was 8 days. At the end of this time the blue solid was collected from the extraction thimble, washed with acetone, and dried at 115 °C for 18 h; yield 0.79 g (52%). An aqueous solution of the blue solid gave a negative test for iodide ion when treated with aqueous silver nitrate. Anal. Calcd for $[F_2(C_3H_{10}N_2)Cr(OCH_3)_2Cr(C_3H_{10}N_2)F_2]$: C, 24.6; H, 6.65; N, 14.4; F, 19.6; Cr, 26.7; O, 8.0. Found: C, 24.6; H, 6.6; N, 14.2; F, 20.0; Cr, 26.6; O (by difference), 7.9.

The molecular weight of the complex was determined by vapor pressure osmometry in water at 65 °C: calcd, 390; found, 386. The infrared spectrum indicated the absence of any water in the complex. A 1 mM aqueous solution of the complex had a molar conductance of 2.4 cm^2 Ω^{-1} M^{-1} at 25 °C. The molar conductance slowly increased reaching 190 cm^2 Ω^{-1} M^{-1} after 100 h.

The electronic spectrum of a freshly prepared aqueous solution of the bridged complex was characterized by λ_{max} 556 nm (ϵ 78.5 M^{-1} cm^{-1}), λ_{min} 467 nm (ϵ 11.7), and λ_{max} 401 (ϵ 36.9).

The bridged complex has a moderate solubility in water, and it is insoluble in methyl alcohol, dichloromethane, and chloroform.

Hydrolysis Studies. A 226-mg (0.58-mmol) sample of the bridged complex was quickly dissolved in 4.5 mL of water at room temperature, the solution was filtered, and the filtrate was frozen solid in a dry ice–2-propanol slush and was lyophilized. The volatile fraction was collected and analyzed by gas chromatography. The volatile fraction was water with only a trace amount of methyl alcohol.

A 303-mg (0.78-mmol) sample of the complex was dissolved in 6.0 mL of water at room temperature, and the solution was kept in a closed flask for 72 h at room temperature. After 72 h the solution was lyophilized. Gas chromatographic analysis of the volatile fraction indicated a methyl alcohol concentration of 0.23 M, and for complete hydrolysis of the complex the methyl alcohol concentration should have been 0.26 M.

A weighed sample of the nonvolatile residue from the freeze-drying was dissolved in cold water and passed through a cation-exchange column in the sodium form. Fraction I, unreacted starting material, moved through the column during the loading process. Successive elution of the column with 200-mL portions of 0.3, 0.6, and 0.90 M aqueous sodium sulfate indicated the presence of species of both charges +1 and +2.

Acid Hydrolysis Studies. A weighed sample of the complex was dissolved in 10.00 mL of 0.11 M perchloric acid and allowed to hydrolyze for 10 min at 24 °C. The reaction mixture was diluted to 50 mL with ice water and charged onto a cation-exchange column (Dowex 50W-X4, 50–100 mesh, H^+, column 12 cm × 1 cm). The experimental conditions have been described previously.[8]

A blue fraction, I, moved through the column during the loading. Fraction I was identified by its electronic absorption spectrum as unreacted starting complex. Fraction II (λ_{max} 545 nm (ϵ 27.2 M^{-1} cm^{-1}), λ_{min} 464 nm (ϵ 5.4), λ_{max} 397 nm (ϵ 13.6); Cr:N:F = 1.0:2.06 ± 0.08:1.95 ± 0.04) was eluted from the resin with 200 mL of 0.15 M sulfuric acid. Fraction III (λ_{max} 534 nm, λ_{min} 453 nm, and λ_{max} 392 nm; Cr:N:F = 1.0:1.96 ± 0.05:0.94 ± 0.03) was eluted from the column with 200 mL of 0.75 M sulfuric acid. Fraction IV which contained complexes of charge +3 was eluted with 200 mL of 3.0 M sulfuric acid.

Several repetitions of the above experiment gave the following product distributions: fraction I, 13.2 ± 0.6% of the total chromium; fraction II, 38.1 ± 2.5%; fraction III, 42.8 ± 3.8%; fraction IV, 6.8 ± 2.8%. In all cases the total chromium recovery was greater than 96%.

The electronic spectra of fractions I and II did not change appreciably after 12 h at 8 °C.

In another experiment, fraction II was collected and the acid concentration was raised to 0.75 M by the addition of cold 10 M sulfuric acid. This fraction was kept at 8 °C for 2 h, diluted to 1 L with cold water, and charged onto the resin. The column was eluted as described previously. Fraction II, which was eluted with 0.75 M sulfuric acid, contained 12.8% of the available chromium.

Analytical Methods and Instrumentation. The analytical methods and instrumentation were the same as those described previously.[1,8] Carbon, hydrogen, nitrogen, and fluorine analyses were carried out by the Huffman Laboratories, Wheatridge, Colo. Molecular weights were determined by Galbraith Laboratories, Knoxville, Tenn. The gas chromatography studies were made using a Varian Aerograph Model 2700 dual-column gas chromatograph coupled to a Sargent Welch SRG recorder. The column was $^1/_4$ in. × 15 ft and loaded with 15% FFAP on 50/80 Chromosorb W. The column was operated at 130 °C at a helium flow rate of 1 mL/s. The detector was operating at 250 °C, and the sample injector temperature was 200 °C.

Results and Discussion

The reaction of *trans*-difluorobis(trimethylenediamine)chromium(III) iodide hydrate with refluxing methyl alcohol has been utilized to prepare the previously unknown dimer di-μ-methoxo-bis(difluoro(trimethylenediamine)chromium(III)).

The experimental data are easily interpreted in terms of a dimeric structure for the new complex. The elemental analysis and molecular weight are in good agreement with the proposed dimer. The proposed structure for the new complex requires that the material behave as a nonelectrolyte. The molar conductance of an aqueous solution of the complex supports the structural assignment. The gradual decrease in the resistance of an aqueous solution of the complex with time is interpreted as being due to slow hydrolysis of the complex to produce methyl alcohol and charged chromium(III) complexes. When the dimer was quickly dissolved in water and lypholized, very little methyl alcohol was detected in the volatile fraction. The lack of methyl alcohol effectively excludes the possibility of the alcohol's being occluded in the solid or being present as an alcoholate.

It was possible to obtain an 88% yield of methyl alcohol upon prolonged hydrolysis of the complex. This slow release of methyl alcohol from the complex is consistent with the conductance experiments.

Further support for the dimeric structure comes from the acid hydrolysis studies. Cleavage of the methoxo bridge by acid could be reasonably expected to produce $[Cr(C_3H_{10}N_2)F_2(OH_2)_2]^+$ as a hydrolysis product. Fraction II obtained from the acid hydrolysis studies exhibited a Cr:N:F ratio consistent with this ion; further, the elution behavior of this fraction is consistent with a species of charge +1.

Fraction III from the ion-exchange studies is assigned to the $[Cr(C_3H_{10}N_2)F(OH_2)_3]^{2+}$ ion on the basis of its elution behavior and the Cr:N:F ratio. Further, the electronic absorption spectrum for fraction III is in good agreement with that reported by DeJovine,[8] who prepared $[Cr(C_3H_{10}N_2)F(OH_2)_3]^{2+}$ by another route.

Fraction III could possibly arise in the following fashion. When the complex hydrolyzes in acid, two complete reactions may be visualized, one of these involving acid-catalyzed fluoride ion release and the other, the cleavage of the bridge. It is possible that the fluoro groups in the bridged complex are fairly reactive, and one is quickly replaced while the bridge is opening. Once the bridge is cleaved, the fluoro ligands become relatively inert. Support for the supposition that the $[Cr(C_3H_{10}N_2)F_2(OH_2)_2]^+$ ion is relatively inert comes from the observation that solutions of this ion in 0.75 M sulfuric acid are only slowly converted to ions of charge +2 at 8 °C. Thus most, if not all, of the $[Cr(C_3H_{10}N_2)F(OH_2)_3]^{2+}$ ion is formed initially along with $[Cr(C_3H_{10}N_2)F_2(OH_2)_2]^+$ and is not formed by acid hydrolysis of $[Cr(C_3H_{10}N_2)F_2(OH_2)_2]^+$.

The possibility of both trimethylenediamine ligands being bound to the same Cr(III) center in the bridged complex can be excluded since only small amounts of chromium complexes of charge +3 were found during the hydrolysis studies.

Other workers[2,9,10] have established the nature of the methoxo bridging group by infrared studies in the 1000–1050 cm^{-1} region. Unfortunately the dimer prepared in this study was not amenable to that technique since both the dimer and the starting material, *trans*-$[Cr(C_3H_{10}N_2)_2F_2]I\cdot H_2O$, had strong infrared absorptions at 1038 cm^{-1}.

The low-energy absorption band in the electronic spectrum of the dimer is at a longer wavelength than the corresponding absorption band in the starting material. This shift is probably due to the differences in the ligand field which result when a trimethylenediamine ligand is replaced by two bridging methoxo ligands.

In all other reported cases of methoxo-bridged dimers of chromium(III), the bidentate ligands have been substituted acetylacetone groups, and the dimers did not form when the simple acetylacetone ligand was the bidentate group. In the case of trimethylenediamine, however, the Cr–N bond can be broken by refluxing with methyl alcohol to form the dimer. In both cases a chelate ring was replaced by two alkoxo bridging groups. It is of interest to note that the same size rings were opened and that the Cr–F bond is sufficiently strong to remain intact when the six-membered trimethylenediamine ring was replaced.

Currently the authors are investigating the general reactions of a number of different fluoro-containing bis(diamine) complexes and mixed-ligand complexes of chromium(III) with various alcohols. In addition, mechanistic studies are in progress.

Registry No. $F_2(C_3H_{10}N_2)Cr(OCH_3)_2Cr(C_3H_{10}N_2)F_2$, 63231-40-3; *trans*-$[Cr(C_3H_{10}N_2)_2F_2]I$, 63231-41-4; *trans*-$[Cr(C_3H_{10}N_2)_2F_2]Cl$, 63231-42-5; $[Cr(C_3H_{10}N_2)F_2(OH_2)_2]^+$, 63231-43-6; $[Cr(C_3H_{10}N_2)F(OH_2)_3]^{2+}$, 42476-41-5.

References and Notes

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