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New Complexes of Pentaamminechromium(III) with Selenate and Dihydrogenarsenate as Ligands

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Several new Cr(III) pentaammine complexes containing the oxoanionic ligands selenate and dihydrogenarsenate, of formula $[CrSeO_4(NH_3)_5]X$ $(X = HSeO_4^-, ClO_4^-, NO_3^-, Cl^-,$ *and* $Br^-)$ *and* $[CrH_2AsO_4(NH_3)_5](ClO_4)_2$ *have been prepared and characterized. The arsenate anion enters and leaves the coordination sphere of Cr(III) very rapidly.*

Introduction

Although ammine complexes of Co(III) containing monodentate selenato [1] or bridging selenato [2] are known, no chromium ammine complex with selenato ligand has been reported. Following our interest in oxoanions coordinated to ammine complexes of Co(III), Cr(III), *etc.* [3–6], we describe in this work the preparation and characterization of five salts of the complex cation selenatopentaamminechromium(III), $[CrSeO_4(NH_3)_5]X$ ($X = HSeO_4$, ClO_4, NO_3, Cl, and Br). Furthermore we have prepared the first ammine complex of chromium(III) containing the labile ligand dihydrogenarsenato, $[CrH_2AsO_4(NH_3)_5](ClO_4)_2$.

Experimental

Preparative Methods

$[CrSeO_4(NH_3)_5]HSeO_4 \cdot 2H_2O$

Selenic acid (B.D.H., 96%) (2.5 g) and $[CrCl(NH_3)_5]Cl_2$ (0.5 g) were warmed at 70 °C until no more evolution of chlorine was observed (*ca.* 6 h). The solution was allowed to cool to room temperature and excess of methanol was added. The red-rose solid was collected and washed with methanol (note: the solid was not allowed to suck dry except on the last washing; then, it was quickly manipulated with a spatula and transferred to a dessicator). Yield 89%. *Anal.* (%). Calcd. for $[CrSeO_4(NH_3)_5]HSeO_4 \cdot 2H_2O$: Cr, 11.30; Se, 34.32; NH_3, 18.51. Found: Cr, 11.3; Se, 33.9; NH_3, 18.4.

$[CrSeO_4(NH_3)_5]ClO_4 \cdot H_2O$

1.0 g of the hydrogenselenate salt was treated with water until complete dissolution. Then 60% perchloric acid was added dropwise and with constant stirring until complete precipitation. The solid was filtered and washed with ethanol and ether. Yield 82%. *Anal.* (%). Calcd. for $[CrSeO_4(NH_3)_5]ClO_4 \cdot H_2O$: Cr, 13.08; Se, 19.86; NH_3, 21.42. Found: Cr, 12.5; Se, 19.6; NH_3, 21.1.

$[CrSeO_4(NH_3)_5]NO_3 \cdot H_2O$

1.0 g of the hydrogenselenate salt was dissolved in the minimum amount of water and an equal volume of concentrated nitric acid was added. Then, excess of ethanol was added and the mixture was allowed to stand in the dark overnight. The precipitate was filtered and washed with ethanol and ether. Yield 77%. *Anal.* (%). Calcd. for $[CrSeO_4(NH_3)_5]NO_3 \cdot H_2O$: Cr, 14.44; Se, 21.92; NH_3, 23.64. Found: Cr, 14.4; Se, 21.8; NH_3, 23.8.

$[CrSeO_4(NH_3)_5]Cl \cdot 2H_2O$

1.0 g of the hydrogenselenate salt was dissolved in the minimum amount of water and the solution treated with an excess of concentrated hydrochloric acid and ethanol. If no precipitate was observed, the solution was placed in the freezing compartment of the refrigerator for *ca.* 5 min and treated with an excess of acetone. The suspension was allowed to stand at room temperature overnight. The solid was filtered and washed with water and ethanol Yield 84%. *Anal.* (%). Calcd. for $[CrSeO_4(NH_3)_5]Cl \cdot 2H_2O$: Cr, 14.79; Se, 22.46; NH_3, 24.22. Found: Cr, 14.7; Se, 22.2; NH_3, 24.2.

$[CrSeO_4(NH_3)_5\text{-}Br \cdot 3H_2O$

1.0 g of the hydrogenselenate salt was dissolved in the minimum amount of ice-cold water. Then an excess of 48% hydrobromic acid was added followed by ethanol. The suspension was allowed to stand in the dark overnight. The solid was collected and

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washed with ethanol. Yield 77%. *Anal.* (%). Calcd. for $[CrSeO_4(NH_3)_5]Br \cdot 3H_2O$: Cr, 12.56; Se, 19.07; NH_3, 20.57. Found: Cr, 12.6; Se, 18.9; NH_3, 21.2.

$[CrH_2AsO_4(NH_3)_5](ClO_4)_2 \cdot 2H_2O$

8 *M* arsenic acid was prepared by stirring 150 g of arsenic oxide (RP Carlo Erba) with 100 ml of water for several hours and filtering the resulting suspension. Aquopentaamminechromium(III) perchlorate (2.0 g), water (1.5 ml), and 8 *M* arsenic acid (45 ml) were mixed and filtered to remove any residue. The cherry-red solution was warmed at 60 °C for 10 min, concentrated to approximately three fourths of the initial volume in a rotary evaporator at 60 °C and left in the freezing compartment of a refrigerator for approximately seven days. The rose solid was collected and washed with ethanol. Yield 48%. (Note: the method used for collecting the hydrogenselenate salt should be used here). *Anal.* (%). Calcd. for $[CrH_2AsO_4(NH_3)_5](ClO_4)_2 \cdot 2H_2O$: Cr, 10.14; As, 14.60, NH_3, 16.60. Found: Cr, 9.95; As, 14.9; NH_3, 16.8.

$[CrCl(NH_3)_5]Cl_2$ [7] and $[CrH_2O(NH_3)_5](ClO_4)_3$ [8] were prepared from $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5$ [7]. After washing, all the chromium complexes were kept in the dark in a silica gel dessicator.

Other Techniques

Chromium was determined spectrophotometrically at 372 nm after alkaline oxidation with hydrogen peroxide [9]. Selenium was determined iodometrically [10] after reducing Se(VI) to Se(IV) with potassium bromide [11]. Arsenic was also determined iodometrically [12]. Ammonia was determined by distillation using the boric acid method.

Visible spectra in solution were recorded on a Beckman UV 5230 spectrophotometer. The solid state spectrum of the arsenato complex was recorded on the same apparatus as a KBr disk. IR spectra were recorded on a Beckman IR 20A spectrophotometer purged with dry air. Samples were prepared as KBr disks. Conductivities were measured on a Radiometer CDM 3 conductivity meter.

Results and Discussion

Selenato Complexes

The salts of the selenatopentaamminechromium(III) cation are red-rose solids, stable in the dark, and easily soluble in water. All the salts except the hydrogenselenate salt do not give any precipitate on being treated with aqueous 0.25 *M* $Pb(NO_3)_2$. The hydrogenselenate salt gives an abundant precipitate of $PbSeO_4$ with the same reagent. Molar conductivities for the chloride, bromide, perchlorate, and nitrate salts, in water and at room temperature, gave values (100–160 ohm^{-1} cm^2 mol^{-1}) typical of 1:1 electrolytes. The conductivity of the hydrogenselenate salt was not measured since abnormally high values would have been obtained due to the acidity of the anion. The visible spectra in 0.1 *M* $HClO_4$, which are retained at room temperature for at least 1 h, show the two bands typical of the acidopentaamminechromium(III) complexes at 502 nm (ϵ = 41.6 M^{-1} cm^{-1}) and at 371 nm (ϵ = 36.0 M^{-1} cm^{-1}) with a minimum at 423 nm (ϵ = 14.6 M^{-1} cm^{-1}).

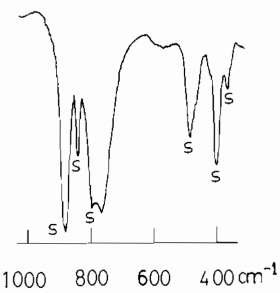

Fig. 1. Infrared spectrum of $[CrSeO_4(NH_3)_5]Cl \cdot 2H_2O$. S indicates bands due to coordinated SeO_4^{2-}.

The infrared spectra of the chloride (Fig. 1) and the bromide salts show bands attributable to the selenate group at 880, 845 (ν_3); 790 (ν_1); 480, 400 (ν_4); and 370 cm^{-1} (ν_2). The occurrence of these bands indicates that the selenate group functions as a monodentate ligand (C_{3v} symmetry) in agreement with an infrared study of the analogous cobalt complexes [13].

Arsenato Complex

Co(III) ammine complexes containing arsenate as a ligand are well known [14] but no chromium analogue has been reported. We have prepared a solid with the formulation $[CrH_2AsO_4(NH_3)_5](ClO_4)_2$. On adding concentrated arsenic acid to an acidic solution of $[CrH_2O(NH_3)_5](ClO_4)_3$, the colour changes instantaneously from orange to cherry-red and the arsenato complex may be isolated from this solution. The solid state spectrum of the arsenato complex (maxima at *ca.* 505 nm and *ca.* 365 nm) is the same as that of the cherry-red solution: maxima at 503 nm (ϵ = 40 M^{-1} cm^{-1}) and 370 nm (ϵ = 33 M^{-1} cm^{-1}), and minimum at 425 nm (ϵ = 12). On the other hand, on dissolving the arsenato complex in 0.1 *M* perchloric acid, the complex aquates very rapidly and a solution of aquopentaamminechromium(III) is obtained as evidenced by the visible spectrum.

Other systems which behave similarly have been reported: $[CrH_2O(NH_3)_5]^{3+}$ with IO_3^- [15], HSO_3^- and $HSeO_3^-$ [16], and $[CoH_2O(NH_3)_5]^{3+}$ with $HSeO_3^-$ [17], HSO_3^- [18], and $H_2AsO_4^-$ [19] *etc.* All these systems involve 'labile oxoanions' (*i.e.* oxoanions which exchange oxygen with solvent water very fast) and the rapidity of the processes is thought to be related to this lability since the reactions can occur not by metal–oxygen bond rupture but by non-metal–oxygen bond rupture. In contrast, the same aquo ions complex very slowly with 'inert oxoanions' like phosphate, sulphate, selenate, *etc.*, and the corresponding acido complexes also aquate very slowly; the reactions occur in this case by metal–oxygen bond rupture.

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