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Pentaammine Complexes of Chromium(III) with Group V Oxoanionic Ligands. I. Complexes with Ligands PO_4^{3-} and $H_2PO_4^-$

J. CASABO, J. M. CORONAS and M. FERRER
Department of Inorganic Chemistry, Faculty of Chemistry, University of Barcelona, Barcelona, Spain
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The neutral compound $[CrPO_4(NH_3)_5]\cdot 2H_2O$ *and three salts of the complex cation* $[CrH_2PO_4(NH_3)_5]^{2+}$ *–* $[Cr(H_2PO_4)(NH_3)_5](ClO_4)_2\cdot 2H_2O$*,* $[Cr(H_2PO_4)(NH_3)_5]S_2O_6\cdot 2H_2O$ *and* $[Cr(H_2PO_4)(NH_3)]_5Br_2$ *– have been prepared and characterized. Their infrared and electronic absorption spectra are interpreted. Protonation equilibria are studied and the acidity constants corresponding to the first two stages of protonation for* $[CrPO_4(NH_3)_5]$ *are determined.*

Introduction

In earlier works of one of us Cr(III) ammines had been described with the oxoanionic ligands dithionato, chromato[1,2], and μ-oxalato[3]. However, and in contrast to Co(III) ammines[4–8], no Cr(III) ammine with oxoanionic ligands of the group V has apparently been reported. The preparation of such compounds could be interesting in order to study the possible correlations between both series of compounds.

In this work the following Cr(III) pentaammines with ligands phosphato and dihydrogenphosphato have been prepared for the first time: phosphatopentaammine-chromium(III), $[CrPO_4(NH_3)_5]\cdot 2H_2O$, (hereafter referred to as compound I), and three salts of the complex cation dihydrogenphosphatopentaamminechromium(III), $[CrH_2PO_4(NH_3)_5]^{2+}$: $[CrH_2PO_4(NH_3)_5](ClO_4)_2\cdot 2H_2O$, $[Cr(H_2PO_4)(NH_3)_5]S_2O_6\cdot 2H_2O$ and $[CrH_2PO_4(NH_3)_5]Br_2$ (hereafter referred to as compound II, III and IV, respectively). All these new compounds have been characterized by chemical analyses, infrared and visible spectra. Furthermore, titration curves have been obtained for compounds I and II.

All attempts to prepare compound I by heating $[CrH_2O(NH_3)_5](ClO_4)_3$ in aqueous solution with Na_3PO_4, Na_2HPO_4, or mixtures of these, resulted in decomposition of the starting material with precipitation of Cr_2O_3aq in a few minutes. Attempts to prepare compound I in acidic solution (as is usual with Cr(III) ammines) by heating aqueous solutions of $[CrH_2O(NH_3)_5](ClO_4)_3$ with H_3PO_4 or mixtures of H_3PO_4 and NaH_2PO_4 led to red solutions which indeed contained compound I in a protonated form. Addition of excess NH_3 and ethanol to these solutions led to precipitation of compound I along with considerable amounts of ammonium or alkali phosphates. Owing to all this, the method used by Schmidt and Taube for the preparation of the Co(III) analogue[5], $[CoPO_4(NH_3)_5]$, was followed with minor modifications.

Experimental

Preparative Methods

Preparation of compound I.

10 g of $[Cr(H_2O)(NH_3)_5](ClO_4)_3$ and 19 g of $NaH_2PO_4\cdot 2H_2O$ were dissolved in a mixture of 55 ml of water and 4 ml of 85% phosphoric acid. The mixture was heated on the water bath at 60–70° C for 3 hours. The resulting intense red solution was poured onto a column of Lewatit cation exchange rèsin (18 cm × 2.9 cm i. d.). The resin bed was then washed with water until the effluent gave no test for phosphate. Then compound I was eluted with 0.05*M* NaOH. The most concentrated fractions of the effluent (*ca.* 600 ml) were treated with 60 ml of ammonia and then with 1050 ml of 95% ethanol. The mixture was allowed to stand in the dark at room temperature for 1 hr. The red pink precipitate was filtered, washed with 95% alcohol and ether, and air dried in the dark. Yield 1.67 g (28%). *Anal.* Calcd. for $[CrPO_4(NH_3)_5]\cdot 2H_2O$: Cr, 19.4; PO_4, 35.4; NH_3, 31.8; weight loss at 950°C (assuming $[CrPO_4(NH_3)_5]\cdot 2H_2O \rightarrow CrPO_4 + 5NH_3 + 2H_2O$) 45.2. Found: Cr, 19.1; PO_4, 35.2; NH_3, 31.5; weight loss, 45.4.

Preparation of compound II

A mixture of $[CrH_2O(NH_3)_5](ClO_4)_3$ (5 g), 85% H_3PO_4 (15 ml) and water (35 ml) was heated in an uncovered 250 ml beaker on the water bath at 60–70° C for 3 hours. The mixture was then left in a refrigerator for several hours. The precipitate was filtered and washed and dried as above. Yield 2.8 g (54%). *Anal.* Calcd. for $[CrH_2PO_4(NH_3)_5](ClO_4)_2\cdot 2H_2O$: Cr, 11.1;

PO_4, 20.2; NH_3, 18.1. Found: Cr, 11.0; PO_4, 20.5; NH_3, 18.1.

Preparation of compound III

A solution of $[CrS_2O_6(NH_3)_5]_2S_2O_6 \cdot 5H_2O$ (5 g) in a mixture of 20 ml of water and 5 ml of 85% H_3PO_4 was heated on the water bath at 60–70° C for 3 hours. Then it was cooled and a methanol–ethanol mixture (5:1) was added to incipient precipitation. It was then left in the refrigerator for 24 hours. The precipitate was filtered and washed and dried as above. Yield 2.5 g (50%). *Anal.* Calcd. for $[CrH_2PO_4(NH_3)_5]S_2O_6 \cdot 2H_2O$: Cr, 12.1; PO_4, 22.1; NH_3, 19.8; S_2O_6, 37.2. Found: Cr, 12.1; PO_4, 22.2; NH_3, 19.8; S_2O_6, 37.0.

Compound III may also be obtained by adding aqueous $H_2S_2O_6$ and ethanol to the solution resulting from the heating of $[CrH_2O(NH_3)_5](ClO_4)_3$ with water and H_3PO_4 (see under "Preparation of compound II").

Preparation of compound IV

One gram of $[CrH_2O(NH_3)_5]Br_3$ was dissolved in 7 ml of water and 3 ml of 85% H_3PO_4 was added. The resulting suspension (a small amount of red precipitate usually forms) was heated on the water bath at 60–70° C for 2 hr 30 min and then cooled to room temperature. The small amount of red solid was removed by filtration and the filtered solution was treated with 5 ml of 48% HBr and concentrated on a steam bath at 40–45° C for three hours (a red precipitate usually appears). The solution was filtered, treated with *ca.* 50 ml of 95% ethanol, allowed to stand at room temperature for 0.5–1 hr, and left in the freezing compartment of the refrigerator for several hours. The red–pink solid was filtered and washed and dried as above. Yield 0.59 g (59%). *Anal.* Calcd. for $[CrH_2PO_4(NH_3)_5]Br_2$: Cr, 13.2; PO_4, 24.1; NH_3, 21.6; Br, 40.5. Found: Cr, 13.0; PO_4, 24.0; NH_3, 21.3; Br, 40.4.

Preparation of the starting materials

$[CrH_2O(NH_3)_5](ClO_4)_3$ was prepared from $[CrH_2O(NH_3)_5](NO_3)_3$[9] by precipitation with 60% $HClO_4$.

$[CrH_2O(NH_3)_5]Br_3$ was prepared from $[CrH_2O(NH_3)_5](NO_3)_3$ using Mori's method[10].

$[CrS_2O_6(NH_3)_5]S_2O_6 \cdot 5H_2O$ was obtained as indicated in a previous work[1].

The purity of the starting materials was confirmed by analysis for Cr and NH_3, and by their visible spectra.

Analytical Methods

Chronium was determined volumetrically with standard Fe(II) after oxidation to Cr(VI)[11] and spectrophotometrically by oxidation of the complexes in aqueous solution with NaOH and H_2O_2, making up to a definite volume, and measuring the absorbance at 372 nm against a standard[12]. Ammonia was determined by distillation using the boric acid procedure[11].

Phosphate was determined gravimetrically using Perrin's method[13] after destruction of complexes with NaOH.

Dithionate was determined gravimetrically as $BaSO_4$ after oxidation with HNO_3[11].

Bromide was determined gravimetrically as AgBr (without previous destruction of the sample)[11].

Spectra

Infrared spectra were recorded on a Beckman IR 20A infrared spectrophotometer purged with dry air. Samples were prepared using the KBr disk technique.

Electronic absorption spectra were recorded on a Beckman DB GT spectrophotometer. 4 cm cells were used to obtain spectra of the effluents from the resin.

Acid dissociation constants were determined from the titration curves obtained with a Radiometer Model 4 pH-meter by titration of compounds I and II with $0.1M$ $HClO_4$ or $0.1M$ NaOH, respectively. The concentration of the complex solutions was $0.005M$. The ionic strength of the complex solutions, $HClO_4$, and NaOH was made up to unity with $NaClO_4$.

Conductivity measurements for compound I were obtained with a Philips model GM 4249 conductivity bridge.

Cation exchange techniques were carried out with the strong acid cation exchanger, Lewatit S 100 G1 (H^+ form).

Results and Discussion

Infrared Spectra

The infrared spectrum of compound I (see Figure 1, a), clearly indicates that the phosphate group functions as an unidentate ligand. The following band assignment has been stablished for the free phosphate ion: $\nu_1(A_1) = 938\ cm^{-1}$; $\nu_2(E) = 420\ cm^{-1}$; $\nu_3(T_2) = 1017\ cm^{-1}$; and $\nu_4(T_2) = 567\ cm^{-1}$ [14]. Of all these only the $2T_2$ vibrations are infrared active. Coordination to a metal cation through the oxygen atom lowers the symmetry of the phosphate group from T_d to C_{3v} and the following correlations are found:

$A_1(T_d) \rightarrow A_1(C_{3v})$; $E(T_d) \rightarrow E(C_{3v})$; $T_2(T_d) \rightarrow (A_1 + E)(C_{3v})$. In the C_{3v} group, all the mentioned normal modes are infrared active. Thus, the appearance of bands at 935 and 440 cm^{-1} (corresponding to the inactive modes for free PO_4^{3-}) and the splitting of both $\nu_3(T_2)$ (1020 and 960 cm^{-1}), and $\nu_4(T_2)$ (595 and 565–530 cm^{-1}), confirm the monodentate character of the phosphato ligand for compound I. The additional weak splitting observed in the doubly degenerate component of the ν_4 band is probably due to effects of the crystalline environment.

The infrared spectrum of compound IV (Figure 1, b) is very similar to those of compounds II and III except for the occurrence in the two latter of the bands

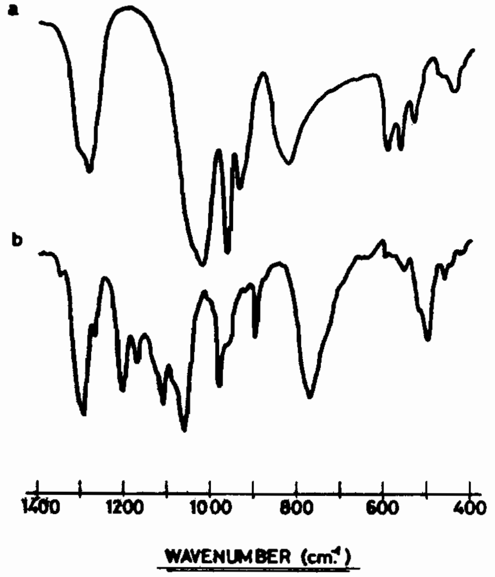

Figure 1. Infrared spectra of compound I (a) and IV (b).

due to the anions ClO_4^- and $S_2O_6^{2-}$ respectively. The bands at 1205, 1170, 1110, 1060, 980(960), 895, 555(520) and 500 cm^{-1}, are attributed to coordinated $H_2PO_4^-$.

Electronic Absorption Spectra

The electronic absorption spectra of the compounds studied in this work may be interpreted in terms of an exactly octahedral symmetry for the Cr(III) ion. No distortion attributable to the asymmetry of the ligand field is observed, which agrees with the results for other pentaammine complexes of the same cation.

Absorption maxima and minima, and molar extinction coefficients corresponding to the species isolated as solid compounds (nonprotonated and diprotonated species) along with those of species occurring in solution (mono- and triprotonated species) are listed in Table I. Proposed assignments for the observed bands and calculated crystal field parameters are also given in Table I. The values of both the interelectronic repulsion parameter, B, and the third spin-allowed transition have been calculated by interpolation in the Tanabe–Sugano energy diagram for a d^3 ion[15]. The value for the parameter x (energy difference between the terms ^4F and ^4P of the central ion in the limit when the crystal fiels tends to zero) and that for the parameter x/β (β being the same energy difference for the free central ion) have been calculated from the corresponding weak field equations for a d^3 ion[16].

From the results given in Table I and by comparison with the results for the ligands Cl^-, Br^-, H_2O, and $S_2O_6^{2-}$ in related complexes[2,16], the ligands studied here can be arranged in the spectrochemical series for Cr(III) pentaammine complexes in the following order:

$$Br^- < PO_4^{3-} < Cl^- < HPO_4^{2-} < H_2PO_4^- < H_3PO_4 < H_2O \cong S_2O_6^{2-}$$

Finally and from the value x/β, the ligands can be arranged in the nephelauxetic series in the following order:

$$PO_4^{3-} < HPO_4^{2-} < H_2O \cong S_2O_6^{2-} < H_2PO_4^- < Cl^- \cong H_3PO_4$$

Properties

Compound I is a red-pink solid which decomposes slowly even in the dark, with ammonia being evolved. It is very soluble in water giving a somewhat alkaline solution. Compound I is a nonelectrolyte as shown by conductivity measurements in aqueous solution ($\Lambda_{1024} = 13$ ohm^{-1} cm^2 mol^{-1} at 19° C) and by its behaviour on the cation exchange column in the course of its preparation (the compound, which is adsorbed in the column as the diprotonated species, is easily eluted from the resin with 0,05*M* NaOH prior to its separation as a solid phase). Both the infrared spectrum

TABLE I. Electronic Absorption Spectra.

Species	ν_1(nm)	ν_2(nm)	Minimum (nm)	ν_3 (calculated, nm)	Δ_o(cm^{-1})	B(cm^{-1})	x(cm^{-1})	β(cm^{-1})	x/β
$[CrPO_4(NH_3)_5]$	517 ($\varepsilon = 58.5$)[a]	397 ($\varepsilon = 33.0$)	442 ($\varepsilon = 18.9$)	248	19432	516	8195	13800	0.60
$[CrHPO_4(NH_3)_5]^+$	508 ($\varepsilon = 54.6$)	379 ($\varepsilon = 28.8$)	430 ($\varepsilon = 14.2$)	240	19685	606	9615	13800	0.70
$[CrH_2PO_4(NH_3)_5]^{2+}$	502 ($\varepsilon = 48.5$)	370 ($\varepsilon = 29.2$)	423 ($\varepsilon = 10.6$)	235	20000	640	10160	13800	0.73
$[CrH_3PO_4(NH_3)_5]^{3+}$	499 ($\varepsilon = 44.2$)	367 ($\varepsilon = 29.0$)	418 ($\varepsilon = 9.2$)	233	20120	654	10324	13800	0.75

[a] Units of ε are M^{-1} cm^{-1}.

(see above) which is very similar to that of the Co(III) analogue, and the fact that its aqueous solution does not give precipitate with $AgNO_3$ confirm the assumption that the PO_4^{3-} ion is indeed coordinated to the residue $Cr(NH_3)_5$. The identity of the visible spectrum carried out in water or in 0.1*M* NaOH, and its reversible change when carried out in 0.1*M* $HClO_4$ indicate its non-protonated character. The two inflection points observed in the titration of compound I with $HClO_4$ (see below) also agree with its non-protonated character.

Compounds II, III, and IV are red-pink solids somewhat more stable than compound I. They are very soluble in water giving acidic solutions. Compounds II and III do not give precipitate with $AgNO_3$ in a NaAcO–HAcO buffer (pH = 5.2). The visible spectra of compounds II, III, and IV are practically the same whether they are carried out in water or in 0.1*M* $HClO_4$. In 0.1*M* NaOH, the spectrum changes reversibly to that of compound I. The behaviour of compounds II, III, and IV on a cation exchanger is that expected for a dispositive cation. In a typical experiment, 0.0970 g of compound II was loaded onto a cation exchange column (6.5 × 0.78 cm). The compound was easily eluted with 0.10*M* NaOH and the spectrum of the eluted solution was identical with that of compound I. In another run 0.0970 g of compound II dissolved in 0.1*M* $HClO_4$ was loaded onto the column and $HClO_4$ of different concentrations was tried as eluent. Elution was not attained with 0.1, 0.5, or 1.0*M* $HClO_4$, but easily with 2.0*M* $HClO_4$, which is typical of a dipositive cation[17–19]. The visible spectrum of the eluted solution was identical with those of compounds II, III, and IV.

Titration of compound II with standard NaOH also shows two inflections which further support its two-protonated character.

From the analysis of the titration curves for both compounds I and II, the following acidity constants have been determined.

$$[CrHPO_4(NH_3)_5]^+ \rightleftharpoons [CrPO_4(NH_3)_5] + H^+ \qquad pK_1 = 7.8$$

$$[CrH_2PO_4(NH_3)_5]^{2+} \rightleftharpoons [CrHPO_4(NH_3)_5]^+ + H^+ \qquad pK_2 = 3.0$$

($\mu = 1.0$ with $NaClO_4$; temp. 17.1 °C)

A comparison of these acidity constants with those of the Co(III) analogue[5,20] indicates somewhat higher acidity constants for the Cr(III) derivative. A greater electron withdrawing effect can be attributed to the $Cr(NH_3)_5$ residue compared with $Co(NH_3)_5$. This is also in agreement with the fact that $[Cr(H_2O)(NH_3)_5]^{3+}$ is a somewhat stronger acid than $[CoH_2O(NH_3)_5]^{3+}$ [21].

In order to measure the absorption maxima and molar extinction coefficients for the species present in solution at different pH values, the following conditions were selected: 0.1*M* NaOH for $[CrPO_4(NH_3)_5]$; NaAcO–HAcO buffer (pH = 5.2) for $[CrHPO_4(NH_3)_5]^+$; 0.1*M* $HClO_4$ for $[CrH_2PO_4(NH_3)_5]^{2+}$; and 5*M* $HClO_4$ for $[CrH_3PO_4(NH_3)_5]^{3+}$. Conditions for the first three species were selected on the basis of the titration curves for both compound I and II. Conditions for the latter species were selected by analogy with the corresponding Co(III) species[5,6]. The results are given in Table I.

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