

Pentaammine Complexes of Chromium(III) with Group V Oxoanionic Ligands. II[1]. Complexes with Ligands H_2PO_2^- and Protonated HPO_3^{2-}

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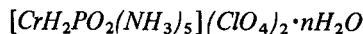
Cr(III) pentaammine complexes containing hypophosphite and hydrogenphosphite, of general formula $[\text{CrH}_2\text{PO}_2(\text{NH}_3)_5]X_2$ and $[\text{CrH}_2\text{PO}_3(\text{NH}_3)_5]X_2$ ($X = \text{ClO}_4, \text{Br}$) are prepared and characterized. The acidity constant for the cation $[\text{CrH}_2\text{PO}_3(\text{NH}_3)_5]^{2+}$ is determined. The IR spectra of coordinated H_2PO_2^- and H_2PO_3^- are discussed.

Introduction

No amine complex of chromium(III) has so far been reported containing hypophosphite or phosphite as ligands, although the corresponding pentaquo complexes are known in solution [2, 3]. In continuation to our studies on chromium(III) amines with oxoanionic ligands, we now report the preparation and characterization of two new acidopentaammine complexes, where the groups H_2PO_2^- and protonated HPO_3^{2-} act as monodentate ligands: $[\text{CrH}_2\text{PO}_2(\text{NH}_3)_5]X_2$ and $[\text{CrH}_2\text{PO}_3(\text{NH}_3)_5]X_2$ (in both cases $X = \text{ClO}_4^-$ and Br^-). In addition, the complex cation $[\text{CrHPO}_3(\text{NH}_3)_5]^+$ is generated in solution by deprotonation of $[\text{CrH}_2\text{PO}_3(\text{NH}_3)_5]^{2+}$.

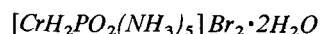
Experimental

Preparation of Compounds

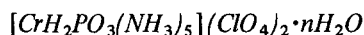


10 g of $[\text{CrH}_2\text{O}(\text{NH}_3)_5](\text{ClO}_4)_3$ was dissolved in 100 ml of water and the solution centrifuged. Then, 40 ml of water, 20 g of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ and 30 ml of 60% HClO_4 were added and the mixture was heated on the water bath at 45 °C for about 19 hr. The mixture was then left in the refrigerator for about 6 h. The crude product was collected, dissolved in water to a total volume of 80 ml and reprecipitated by the addition of 25 ml of 60% HClO_4 with magnetic stirring. The suspension was left in the refrigerator overnight and the red–pink solid was collected, freely washed with 95% ethanol, ether and air-dried in the dark. Yield 5.3 g (55%). *Anal.* Found Cr/ H_2PO_2^- / NH_3

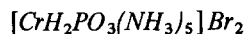
mol ratio for $[\text{CrH}_2\text{PO}_2(\text{NH}_3)_5](\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$:
1/0.97/4.96.



3 g of $[\text{CrH}_2\text{PO}_2(\text{NH}_3)_5](\text{ClO}_4)_2$ (prepared as described above) was dissolved in 20 ml of water and the resulting solution was treated with 15 ml of 48% HBr and 200 ml of ethanol. The mixture was left at room temperature in the dark for 45 min and then in the refrigerator overnight. Yield 2.3 g. The product contains ClO_4^- as evidenced by a weak IR band at 620 cm^{-1} (ν_4 of ClO_4^-). The crude product was recrystallized by dissolving it in 10 ml of water and adding 10 ml of 48% HBr and 100 ml of ethanol. The mixture was allowed to stand at room temperature in the dark for 2 hr and the red product was collected and washed as above. Yield 1.9 g (70%). *Anal.* Calcd. for $[\text{CrH}_2\text{PO}_2(\text{NH}_3)_5]\text{Br}_2 \cdot 2\text{H}_2\text{O}$: Cr, 13.07; H_2PO_2^- , 16.33; NH_3 , 21.39; Br, 40.17. Found: Cr, 13.0; H_2PO_2^- , 16.1; NH_3 , 21.2; Br, 40.5.



10 g of $[\text{CrH}_2\text{O}(\text{NH}_3)_5](\text{ClO}_4)_3$ was dissolved in 70 ml of water and the solution centrifuged. Solid H_3PO_3 (14 g) was added and the solution heated at 60 °C on a water bath for 4 hr after which it was left in the refrigerator for 30 min. The mixture, which was almost completely solidified, was allowed to warm to room temperature and the red product collected and washed as above. Yield 2.3 g (22%). *Anal.* Found Cr/ HPO_3^- / NH_3 mol ratio for $[\text{CrH}_2\text{PO}_3(\text{NH}_3)_5](\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$: 1/1.01/5.03.



7 g of $[\text{CrH}_2\text{O}(\text{NH}_3)_5](\text{ClO}_4)_3$ was dissolved in 50 ml of water and the solution centrifuged. Solid H_3PO_3 (13 g) was added and the resulting solution was heated at 60 °C on the water bath for 5–6 hr after which it was left in the refrigerator overnight. The mixture which was completely solidified was allowed to warm somewhat and water was added to a total volume of ca. 35 ml. The mixture was centrifuged, treated with 14 ml of 48% HBr and 550 ml of ethanol and left in the freezing compartment of the

refrigerator for 9 hr. The product (2.8 g) was filtered, washed with ethanol and dissolved in 12 ml of water. The resulting solution was treated with 10 ml of 48% HBr and 300 ml of ethanol and left in the freezing compartment of the refrigerator overnight. The red solid was collected and washed as above. Yield 2.1 g (36%). *Anal.* Calcd. for $[\text{CrH}_2\text{PO}_3(\text{NH}_3)_5]\text{Br}_2$: Cr, 13.76; HPO_3 , 21.17; NH_3 , 22.52; Br, 42.30. Found: Cr, 13.8; HPO_3 , 21.0; NH_3 , 22.2; Br, 42.1.

Starting Materials

$[\text{CrH}_2\text{O}(\text{NH}_3)_5](\text{ClO}_4)_3$ was prepared in 50–60% yield from 10 g of $[\text{CrH}_2\text{O}(\text{NH}_3)_5](\text{NO}_3)_3$ [4] in 120 ml of water, filtering or centrifuging to remove any charcoal and adding 70 ml of 60% HClO_4 with magnetic stirring (usually a double precipitation is necessary to free the product from NO_3^-).

WARNING! Although we have experienced no difficulties with the perchlorate salts of the new complexes prepared here in the course of this research, these compounds must be treated as potentially explosive and handled with care. In a deliberate experiment a small amount of solid $[\text{CrH}_2\text{PO}_2(\text{NH}_3)_5](\text{ClO}_4)_2$ detonated violently when heated in a crucible with a Bunsen burner.

Analyses

Chromium was determined spectrophotometrically after oxidation of the complexes with NaOH and H_2O_2 by measuring the absorbance at 372 nm against a standard [5]. Ammonia was determined by distillation using the boric acid procedure. Both hypophosphite and phosphite were determined by two different methods. In the first method the complexes (*ca.* 0.04 g) were destroyed with boiling concentrated HClO_4 (*ca.* 6 ml) in a 100 ml Kjeldahl flask until oxidation of Cr(III) to Cr(VI). The phosphate thus formed was determined gravimetrically by Perrin's method [6]. In the second method, HPO_3^{2-} and H_2PO_2^- were determined volumetrically with Ce(IV) [7]. Both methods were in good agreement. Bromides which interfered in the second method were removed by passing the bromide salts through an anion exchanger (Amberlite IR 400) in the ClO_4^- form. Bromides were determined gravimetrically as AgBr after removing the complex cations with a cation exchanger in the H^+ form.

The perchlorate salts were found to contain a variable amount of water of crystallization so that mol ratios were used to report analytical results.

Spectra

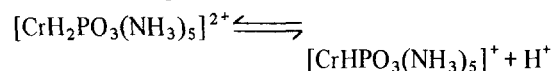
IR spectra were recorded on a Beckman IR 20A spectrophotometer purged with dry air. Samples were prepared using the KBr pellet technique. Visible spectra were recorded on a Beckman DB-GT spectrophotometer. Determinations of ϵ were carried out with a Beckman DU 2 spectrophotometer.

Equivalent weights and acid dissociation constants were determined by potentiometric titration (with a Radiometer model 4 pH-meter) of 0.005M solutions of the hydrogenphosphito complexes with 0.1M NaOH. The ionic strength of all solutions was adjusted to 1.0 with NaClO_4 . Cation exchange techniques were carried out with the strong acid cation exchanger Lewatit S 100 G1.

Results and Discussion

The new red–pink compounds are easily soluble in water and fairly stable in the solid state if kept in the dark. None of them gives immediate precipitate on being treated in aqueous solution with 0.1M HgCl_2 –2M HClO_4 at 50–60 °C, which proves the ligand character of HPO_3^{2-} and H_2PO_2^- (aqueous solutions of NaH_2PO_2 and H_3PO_3 of similar concentration give immediate precipitates on being treated in the same manner).

The salts of the complex cation hydrogenphosphitopentaamminechromium(III) contain the ligand phosphite in a protonated form as can be seen from the following pieces of evidence: i) the titration curves of both $[\text{CrH}_2\text{PO}_3(\text{NH}_3)_5](\text{ClO}_4)_2$ and $[\text{CrH}_2\text{PO}_3(\text{NH}_3)_5]\text{Br}_2$ show only one equivalence point when the compounds are titrated with standard NaOH. The equivalent weights thus found (485 and 390 respectively) agree well with the formula weights calculated from chromium analyses (476 and 377). ii) Absorption maxima and minima and ϵ are different in acid and basic conditions (Table I) and change reversibly upon changing the pH, and iii) the elution characteristics of $[\text{CrH}_2\text{PO}_3(\text{NH}_3)_5]^{2+}$ are in agreement with the proposed formulation (see below). From the analysis of the titration curves a value of $K_a = 3 \times 10^{-4}$ (27.5 °C, $\mu = 1.0$) can be established for the equilibrium



The corresponding value for free H_2PO_3^- is $K_a = 1.8 \times 10^{-7}$ (18 °C). An enhancement of the acidity of H_2PO_3^- upon coordination by a factor of 10^3 is observed, a fact which has been reported for some other protonated oxoanions [1, 8].

The acidity constant [3] of $[\text{CrH}_2\text{PO}_3(\text{H}_2\text{O})_5]^{2+}$ ($K_a = 2.3 \times 10^{-3}$) is higher than that of $[\text{CrH}_2\text{PO}_3(\text{NH}_3)_5]^{2+}$ by a factor of 10 approximately. This may be due to a greater electron-attracting power of $\text{Cr}(\text{H}_2\text{O})_5^{3+}$ as compared to $\text{Cr}(\text{NH}_3)_5^{3+}$, which in turn may be attributed to the higher electronegativity of oxygen as compared to nitrogen.

The elution behavior of $[\text{CrH}_2\text{PO}_2(\text{NH}_3)_5]^{2+}$ and $[\text{CrH}_2\text{PO}_3(\text{NH}_3)_5]^{2+}$ on cation exchange columns, was studied in order to further characterize the compounds. The experiments with acid eluant (HClO_4) were carried out as follows: a solution of $[\text{CrH}_2\text{PO}_2-$

TABLE I. Visible Absorption Spectra.

Salt dissolved	Conditions	Species Actually Present	L ₁	L ₂	Min.
[CrH ₂ PO ₂ (NH ₃) ₅]X ₂ (X = ClO ₄ , Br)	0.1M HClO ₄ 0.1M NaOH	[CrH ₂ PO ₂ (NH ₃) ₅] ²⁺ [CrH ₂ PO ₂ (NH ₃) ₅] ²⁺	503 ^a (ε ^b = 46.4) 503 (ε = 46.8)	369 (ε = 30.8) 369 (ε = 31.0)	420 (ε = 10.8) 421 (ε = 11.0)
[CrH ₂ PO ₃ (NH ₃) ₅]X ₂ (X = ClO ₄ , Br)	0.1M HClO ₄ 0.1M NaOH	[CrH ₂ PO ₃ (NH ₃) ₅] ²⁺ [CrHPO ₃ (NH ₃) ₅] ⁺	503 (ε = 47.6) 509 (ε = 52.7)	369 (ε = 30.1) 381 (ε = 29.0)	420 (ε = 10.8) 432 (ε = 15.2)

^aWavelength is given in nm.^bUnits of ε are M⁻¹ cm⁻¹.

(NH₃)₅](ClO₄)₂ or [CrH₂PO₃(NH₃)₅](ClO₄)₂ (ca. 1.5 × 10⁻⁴ mol) in dilute HClO₄ was charged on a 1 cm (i.d.) column of cation exchanger (ca. 7 meq) in the acid form. Then the column was washed with water until the effluent was neutral, and HClO₄ of increasing concentration was tried as eluant. Elution was achieved with 2.5M HClO₄ for [CrH₂PO₃(NH₃)₅]²⁺ and with 2.0M HClO₄ for [CrH₂PO₂(NH₃)₅]²⁺, typical in both cases of a di- or tripotivite cation [9]. The experiments with NaOH as eluant were carried out similarly but using the cation exchanger in the Na⁺ form. NaOH of increasing concentration was used as eluant. Elution was achieved with 1.5M NaOH for [CrH₂PO₂(NH₃)₅]²⁺ (typical of a dipositive cation) and with 0.3M NaOH for [CrH₂PO₃(NH₃)₅]²⁺; during the elution with NaOH, the cation [CrH₂PO₃(NH₃)₅]²⁺ is deprotonated to monopositive [CrHPO₃(NH₃)₅]⁺ which according to its charge is more easily eluted. The identity of the eluted solutions was established spectrophotometrically in all cases.

Absorption maxima, minima and ε for the complex cations are given in Table I. The spectrum of [CrH₂PO₂(NH₃)₅]²⁺ is not altered upon changing the pH of the medium whereas this is not the case for [CrH₂PO₃(NH₃)₅]²⁺ where a reversible protonation equilibrium exists (see above).

The values of L₁ (10Dq) for the new complexes indicate that H₂PO₂⁻ and H₂PO₃⁻ fall very near F⁻ in the spectrochemical series, in agreement with the results [2, 3] found for the same ligands in complexes of the type [CrX(H₂O)₅]²⁺.

The IR spectra of [CrH₂PO₂(NH₃)₅]Br₂ and [CrH₂PO₃(NH₃)₅]Br₂ (Fig. 1) offer the possibility of studying the vibration bands of coordinated H₂PO₂⁻ and H₂PO₃⁻. Band assignment of these anions in metal phosphites and hypophosphites has been made [10-12] but no study apparently exists of the mentioned groups coordinated to a metal atom.

The IR spectrum of [CrH₂PO₂(NH₃)₅]Br₂ exhibits all the bands reported [11] for hypophosphite salts plus a weak band at 920 cm⁻¹ which is inactive in the IR spectrum of uncoordinated H₂PO₂⁻. Similarly the IR spectrum of [CrH₂PO₃(NH₃)₅]Br₂ shows all the bands reported [10] for phosphite salts plus the splitting of the degenerate mode E at 1160 and 1090 cm⁻¹ and a band at 940 cm⁻¹ which we assign to νP-OH in analogy with a similar band found in the spectrum [1] of [CrH₂PO₄(NH₃)₅]Br₂.

The bands (cm⁻¹) due to coordinated H₂PO₂⁻ and H₂PO₃⁻ as observed in the IR spectra of [CrH₂PO₂(NH₃)₅]Br₂ and [CrH₂PO₃(NH₃)₅]Br₂ along with the assignments based on earlier studies [10, 11] are given below:

H₂PO₂⁻: 2350, 2330(s) [ν_s(A₁) P-H], [ν_{as}(B₁) P-H] or [ν_{as}(B₁) P-H, split]; 1175(s) [ν_{as}(B₂) P-O]; 1135(s) [δ(A₁) H-P-H]; 1100(s) [ρ_w(B₂) H-P-H]; 1060(s) [ν_s(A₁) P-O]; 920(w) [ρ_t(A₂) H-P-H];

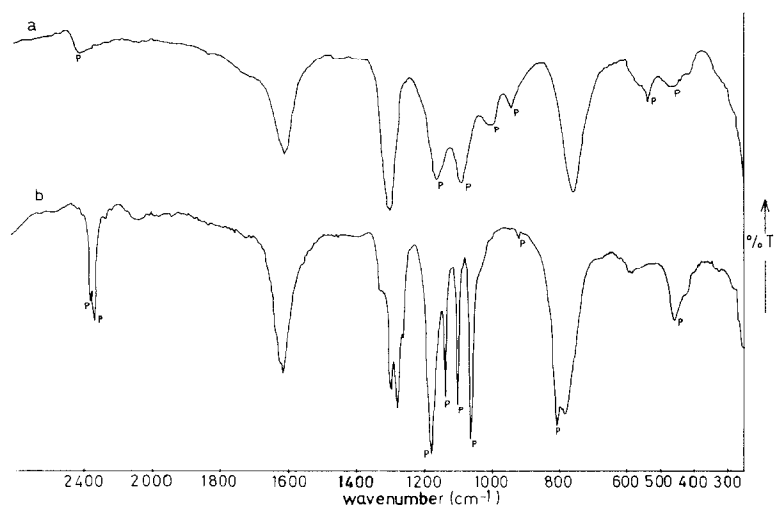


Figure 1. Infrared spectra of $[\text{CrH}_2\text{PO}_3(\text{NH}_3)_5]\text{Br}_2$ (a), and $[\text{CrH}_2\text{PO}_2(\text{NH}_3)_5]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ (b). P indicates bands due to coordinated H_2PO_3^- and H_2PO_2^- .

805(s) [ρ_r (B_1) H–P–H] and 455(m) [$\delta(A_1)$ O–P–O].

H_2PO_3^- : 2420(w) [$\nu(A_1)$ P–H]; 1160, 1090(s) [$\nu_d(E)$ - PO_3]; 1000(m) [$\nu_s(A_1)$ P–O]; 940(m) [ν P–OH]; 535(w) [$\delta_s(A_1)\text{PO}_3$] and 465 cm^{-1} (w) [$\delta_d(E)$ PO_3] (w, weak; m, medium; s, strong).

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