

# Notes

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## Some Reactions of Cyanopentaquochromium(III) Ion

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A strong trans-labilizing effect appears to be exerted by cyanide ligands in cyanoaquo chromium(III) complexes, as evidenced by the highly stereospecific nature of the consecutive aquation products of hexacyanochromate(III).<sup>2-6</sup> This suggests that these complexes may prove useful as reactive intermediates for certain stereoselective syntheses. To explore this possibility, a study of the reactions of the simplest member of the series, cyanopentaquochromium(III), with some common anions was undertaken. In addition to possibly discovering new synthetic routes to known complexes, it was hoped that such a study might produce new mixed-ligand complexes and further evidence regarding trans-labilizing effects of cyanide ligands.

The cyanopentaquochromium(III) ion was selected for study as a representative member of the series, because it is relatively simple to prepare in solution and the products of its reactions with various anions should be few, hence easier to separate and identify. As representative nucleophiles, sulfate, thiocyanate, chloride, bromide, and nitrate ions were selected. Their simple chromium(III) complexes have been characterized, so they could be readily identified and measured by spectral and chromatographic properties. To minimize complications due to hydroxy species and polymer formation, studies were limited to reactions in acidic solutions of pH 3 or less. Optimum solution stability for cyanopentaquochromium(III) is provided in the pH range 2-3, as aquation is catalyzed both by acid and base.<sup>7</sup>

Preliminary work in this investigation demonstrated that cyanopentaquochromium(III) undergoes aquation and anation reactions at competitive rates. The aquation and anation products can undergo further reactions with anions at slower but significant rates. Further attempts to make quantitative kinetic measurements were abandoned when these complications were recognized. Subsequent experimental work was directed at determination of identities and relative amounts of products under various conditions in the presence of different anions. Since hexaquo chromium(III) is a major product in every case, its reactions were also studied under similar conditions for the purpose of comparison and to enable estimates to be made of the amounts of

substitution products derived from it rather than from the initial reactant cyanopentaquochromium(III).

Methods of isolating cyanopentaquochromium(III) salts were also explored. It was found that the sulfate salt, although contaminated by potassium sulfate, can be isolated by a technique based on that devised by Moore and Basolo.<sup>8</sup>

## Experimental Section

**Materials.** Potassium hexacyanochromate(III) was prepared and purified as described elsewhere.<sup>9</sup> All other chemicals were reagent grade and used without further treatment, except as noted. Lithium thiocyanate solutions were prepared from a concentrated stock solution and freed of iron impurities by acidification with dilute perchloric acid and exhaustive extraction with ethyl ether. For use in conjunction with thiocyanate, a 0.2 M stock solution of reagent grade hexaquo chromium(III) perchlorate was adjusted to pH 2 with perchloric acid, made 0.01 M in lithium thiocyanate, and exhaustively extracted with ethyl ether to remove traces of iron.

**Preparation of Cyanopentaquochromium(III) Sulfate Monohydrate,  $[\text{Cr}(\text{H}_2\text{O})_5(\text{CN})]\text{SO}_4 \cdot \text{H}_2\text{O}$  (Containing Coprecipitated Potassium Sulfate).** The procedures used for preparing cyanopentaquochromium(III) and isolating it as the sulfate salt were essentially those described respectively by Jimerson<sup>6</sup> and by Moore and Basolo.<sup>5</sup> Modifications were necessary to avoid anions other than sulfate and to minimize hydrolysis by use of potassium sulfate in place of sulfuric acid.

A solution of 6.50 g of potassium hexacyanochromate(III) in 200 ml of 0.50 M perchloric acid was purged with pure nitrogen for 30 min at room temperature and then 30 min at 0° to remove dissolved oxygen and released hydrogen cyanide. Without interruption of nitrogen purging, 2 ml of 0.1 M chromium(II) perchlorate was added to the solution (in ice bath). After approximately 30 min, when the spectrum of an air-oxidized portion of the solution was essentially that of the cyanopentaquochromium(III) cation, the chromium(II) catalyst was oxidized by bubbling air through the ice-cold solution for 5 min. Nitrogen purging was continued for 1 additional hr to remove hydrogen cyanide, and the pH of the cold solution was adjusted to 2.5. Potassium perchlorate was removed by filtration. The filtrate was diluted with an equal volume of ice water and passed through a Bio-Rad AG 50W-X4 (100-200 mesh) cation-exchange column cooled below 1°, previously treated with 0.6 M potassium sulfate (pH 2.5) to convert it to the potassium ion form and rinsed with deionized water. The loaded column was washed with deionized water, and the monocyano complex was eluted with 0.2 M potassium sulfate (pH 2.5). The solution of eluted product was diluted with an equal volume of ethanol precooled to 0° in an ice bath. Using an ice bath to maintain the low temperature, precipitated potassium sulfate was removed by suction filtration, and the filtrate was extracted twice with diethyl ether, each time with a volume equal to that of the aqueous alcohol layer. The retained aqueous layer was diluted with ethanol (half the volume of aqueous phase) and the resulting small amount of precipitated potassium sulfate was removed by suction filtration. The filtrate was then shaken with diethyl ether (5 volumes). After separation from the ether, the aqueous layer was diluted with ethanol (6-8 volumes), causing precipitation of the finely divided, red product. The product was collected by suction filtration, washed generously with ice-cold ethanol followed by ether, and dried under vacuum over anhydrous magnesium perchlorate; yield 4 g. Analysis indicated that the product contained 9.8%  $\text{K}_2\text{SO}_4$ , based on gravimetric determination of potassium as potassium tetraphenylborate. Sulfate ion content was determined gravimetrically as  $\text{BaSO}_4$ , and the cyanopentaquochromium(III) ion content was determined spectrophotometrically, after verification that the spectra of solutions prepared from the solid were indistinguishable from those of freshly prepared and purified solutions of cyanopentaquochromium(III) perchlorate.<sup>4,5,7</sup>

*Anal.* Calcd for a mixture consisting of 90.2%  $[\text{Cr}(\text{H}_2\text{O})_5(\text{CN})]$ -

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**Table I.** Analysis of Products from  $[\text{Cr}(\text{H}_2\text{O})_5(\text{CN})(\text{ClO}_4)]_2$  (and from  $[\text{Cr}(\text{H}_2\text{O})_6](\text{ClO}_4)_3$ )<sup>h</sup> in Solutions of Lithium Salts at Various pH Values (ca. 298°K)

$\text{X}^{n-}$	Initial molarity			Reaction time, hr	Rel yields, % <sup>h</sup>					
	$\text{Li}_n\text{X}$	$\text{H}_n\text{X}$	$\text{Cr}(\text{CN})^{2+}$		$\text{Cr}^{3+}$	$\text{Cr}(\text{CN})^{2+}$	$\text{CrX}_2^{3+-n}$	$\text{Cr}(\text{CN})\text{X}^{2+-n}$	$\text{CrX}_2^{3+-n}$	$\text{Cr}(?)$
$\text{ClO}_4^-$	1.5	0.5	0.030	5	100 (100)	0	0	0	0	0
$\text{NO}_3^-$	1.5	0.5	0.031	5	97 (99)	0	3 (0.7)	0	0	0
$\text{NO}_3^-$	1.0	(pH 2)	0.031	40	95	0	5	0	0	0
$\text{Cl}^-$	1.5	0.5	0.030	5	99 (100)	0	0.7 (0)	0	0	0
$\text{Cl}^-$	1.0	(pH 2)	0.030	40	89 (99)	8	3 (0.7)	0	0	0
$\text{Br}^-$	1.5	0.5	0.032	5	99 (100)	0	0.9 (0)	0	0	0
$\text{Br}^-$	1.0	(pH 2)	0.031	40	94	6	0	0	0	0
$\text{NCS}^-$	1.5	0.5 <sup>a</sup>	0.030	5	86 (94)	0	8 (7)			4, b 2 <sup>d</sup>
$\text{NCS}^-$	1.5 <sup>e</sup>	0.5 <sup>a</sup>	0.030	5	82 (91)	0	10 (9)			8 <sup>b,d</sup>
				19	82	0	13			5 <sup>b,d</sup>
$\text{NCS}^-$	1.0	0.5 <sup>a</sup>	0.031	5	90 (95)	4	6 (5)			4 <sup>b</sup>
$\text{NCS}^-$	1.0	0.1 <sup>a</sup>	0.030	15	86 (95)	0	12 (4)			2, d 2 <sup>b</sup>
				30	82 (93)	0	13 (4)		(4)	2, d 2 <sup>b</sup>
$\text{NCS}^-$	1.0	0.1 <sup>a</sup>	0.052	24	85	0	12		0.5	2, d 3 <sup>b</sup>
$\text{NCS}^-$	2.0	(pH 2)	0.114	17	62	3	18			14 <sup>e</sup>
$\text{NCS}^-$	1.0	(pH 2)	0.032	15	67 (95)	8	16 (4)	4 (3 <sup>d</sup> )	4	0
$\text{NCS}^-$	1.0	(pH 2)	0.031	30	52 (91)	0	24 (7)	2 (3 <sup>d</sup> )	6	17 <sup>f</sup>
$\text{NCS}^-$	0.2	(pH 2)	0.032	30	79 (91)	9	9 (7)	1	2 (2)	0
$\text{NCS}^-$	0.2	(pH 2)	0.053	30	81	7	10	0.7	0.7	0.4 <sup>f</sup>
$\text{NCS}^-$	0.2	(pH 3)	0.052	30	69 (91)	7	13 (6)	3.5	3.8 (2)	3 <sup>f</sup> (1) <sup>f</sup>
$\text{SO}_4^{2-}$	1.5	0.5	0.030	5	92 (96)	0	10 <sup>g</sup> (4) <sup>g</sup>			0
$\text{SO}_4^{2-}$	0.1	0.1	0.032	15	81 (95)	2	15 (4)	0	3 (2)	0
$\text{SO}_4^{2-}$	1.0	(pH 2)	0.102	15	52 (91)	18	38 <sup>g</sup> (10) <sup>g</sup>			0
$\text{SO}_4^{2-}$	1.0	(pH 2)	0.030	30	58 (87)	0	43 <sup>g</sup> (11) <sup>g</sup>			0
$\text{SO}_4^{2-}$	0.2	(pH 2)	0.031	15	56 (93)	15	26 (5)	0	4 (1)	0
				30	60 (91)	1	35 (8)	0	5 (1)	0
$\text{SO}_4^{2-}$	1.0	(pH 3)	0.102	13	40 (85)	17	48 <sup>g</sup> (14) <sup>g</sup>			0

<sup>a</sup>  $\text{HX}$  is  $\text{HClO}_4$ . <sup>b</sup> Chromium species with elution properties of a 3+ ion,  $\lambda_{\text{max}}$  528 and  $\epsilon$  ca. 70. <sup>c</sup>  $\text{NaNCS}$  in place of  $\text{LiNCS}$ . <sup>d</sup> Chromium species with elution properties of a 1+ or 2+ ion,  $\lambda_{\text{max}}$  534 and  $\epsilon$  ca. 80. <sup>e</sup> Mixture of chromium ions of charge less than 2+, not resolved due to high electrolyte concentration. <sup>f</sup> Identified by spectrum and elution properties as  $[\text{Cr}(\text{NCS})_3(\text{H}_2\text{O})_3]$ . <sup>g</sup> May contain some  $[\text{Cr}(\text{SO}_4)_2(\text{H}_2\text{O})_4]^-$ , not resolved due to high electrolyte concentration. <sup>h</sup> Yields from  $[\text{Cr}(\text{H}_2\text{O})_6](\text{ClO}_4)_3$  given in parentheses.

$\text{SO}_4 \cdot \text{H}_2\text{O}$  and 9.8%  $\text{K}_2\text{SO}_4$ :  $\text{K}$ , 4.4;  $\text{Cr}(\text{H}_2\text{O})_5(\text{CN})$ , 53.7;  $\text{SO}_4$ , 36.1. Found:  $\text{K}$ , 4.4;  $\text{Cr}(\text{H}_2\text{O})_5(\text{CN})$ , 53.0;  $\text{SO}_4$ , 36.8.

#### Preparation of Solutions of Cyanopentaaquochromium(III) Ion.

The sulfate salt of the complex, isolated as described above, was used to prepare reaction mixtures containing sulfate ion. For preparing other reaction mixtures, fresh stock solutions of the perchlorate salt of the complex (stored at 0° in the dark no longer than 4 days) were used. These were prepared following the same procedure described above for preparing the sulfate salt, except that cyanopentaaquochromium(III) was eluted (displaced) from the column using 0.2 M hexaaquochromium(III) perchlorate (pH 2.5) and the alcohol-ether extraction procedure was omitted. Elution fractions were monitored spectrophotometrically so that the later fractions that contained hexaaquochromium(III) perchlorate after its "break through" could be rejected.

**Reaction Conditions and Analysis of Products.** All reaction mixtures were prepared to contain known initial concentrations of reactants (see Table I) and stored in the dark at room temperature (25° ± 3°) for 3–5 half-lives (based on preliminary spectral examination of similar reaction mixtures). Solutions prepared to have a pH of 2 or 3 were maintained at those levels to within ±0.2 unit of pH by periodic addition of very small amounts of concentrated perchloric acid, as needed to replace hydrogen ions consumed in hydrolysis of cyanopentaaquochromium(III). Dilution was negligible.

For analysis of products, a 10.00-ml sample was diluted to 100 ml with deionized water and added to a cation-exchange column (Bio-Rad AG 50W-X4, 100–200 mesh, 18 ml of resin, 21-cm length, 4-ml/min flow rate) which had been previously treated with 100 ml of 0.6 M  $\text{K}_2\text{SO}_4$  (adjusted to pH 2.5 with  $\text{H}_2\text{SO}_4$ ) and washed with deionized water. The loaded column was washed with deionized water, and the combined volume of effluent and wash was measured and retained for analysis. Adsorbed cations were successively eluted in separate fractions from the column using 0.2 M  $\text{K}_2\text{SO}_4$  (pH 2.5) followed by 0.6 M  $\text{K}_2\text{SO}_4$  (pH 2.5) at the end to remove the hexaaquochromium(III) ion. The volume of each elution fraction was measured before samples of it were taken for analysis. Spectra of effluent and eluted fractions were recorded using 10-cm cells and a Cary Model 14 spectrophotometer. Chromium concentrations were determined spectrophotometrically after conversion to chromate by treatment with sodium hydroxide and hydrogen peroxide.<sup>10</sup> The

molar absorptivities and peak positions found for each eluted species served to confirm its identity. Good agreement with previously reported spectral data was found.<sup>11</sup>

More detailed analyses were necessary to characterize the thiocyanate reaction mixtures, because the products were more numerous and complex. The ion-exchange procedure was the same, except that smaller elution fractions were collected. Aliquots of these were analyzed spectrophotometrically for chromium (converted to chromate),<sup>10</sup> thiocyanate (converted to the iron(III) complex),<sup>12</sup> and cyanide (converted to dicyanobis(1,10-phenanthroline)iron(II) and extracted into chloroform).<sup>13</sup>

#### Results and Discussion

Experimental conditions and analytical results are summarized in Table I for the various reactions of cyanopentaaquochromium(III) and hexaaquochromium(III). Reactivities of the two species under similar conditions are compared in Table II, based on relative yields of anation products with different anions and concentrations of reactants. Several significant conclusions can be drawn from these results: (1) anation is not facilitated during loss of a cyanide ligand upon acid attack, (2) anation is promoted by the presence of a cyanide ligand, and (3) loss of a cyanide ligand is favored once anation occurs.

In 0.5 M strong acid, loss of cyanide upon aquation of cyanopentaaquochromium(III) predominates, even in the presence of high concentrations of anions. Approximately the same amount of anation, if any, occurs as in the case of hexaaquochromium(III) treated under similar conditions. This is taken as evidence that anion substitution is negligible at the cyanide ligand site either before or during aquation.

At lower acid concentrations, over the pH range 1–3, the yields of anation products from cyanopentaaquochromium-

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Table II. Comparisons of Yields of X-Substituted Products<sup>a</sup> from [Cr(CN)(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup> and [Cr(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> under the Same Conditions

X <sup>n-</sup>	[X <sup>n-</sup> ]	[H <sup>+</sup> ]	Time, hr	% yield from	
				[Cr(CN)- (H <sub>2</sub> O) <sub>5</sub> ] <sup>2+</sup>	[Cr- (H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>
ClO <sub>4</sub> <sup>-</sup>	2.0	0.5	5	0.0	0.0
NO <sub>3</sub> <sup>-</sup>	2.0	0.5	5	2.5	0.7
Cl <sup>-</sup>	2.0	0.5	5	0.7	0.0
Br <sup>-</sup>	2.0	0.5	5	0.9	0.0
NCS <sup>-</sup>	1.5	0.5	5	18	9
NCS <sup>-</sup>	1.0	0.1	15	15	4
NCS <sup>-</sup>	1.0	0.1	30	17	8
NCS <sup>-</sup>	1.0	(pH 2)	15	24	7
NCS <sup>-</sup>	1.0	(pH 2)	30	47	10
NCS <sup>-</sup>	0.2	(pH 2)	30	12	9
NCS <sup>-</sup>	0.2	(pH 3)	30	23	9
SO <sub>4</sub> <sup>2-</sup>	2.0	0.5	5	10	4
SO <sub>4</sub> <sup>2-</sup>	0.2	0.1	15	18	6
SO <sub>4</sub> <sup>2-</sup>	0.2	(pH 2)	15	30	6
			30	40	9
SO <sub>4</sub> <sup>2-</sup>	1.0	(pH 3)	13	48	14

<sup>a</sup> See Table I for identities and amounts.

(III) increase with increasing pH, time, and anion concentration. Yields of anation products from hexaquo chromium(III) under similar conditions are lower, essentially independent of pH and dependent only on time and anion concentration. The improved stability against acid-catalyzed aquation of cyanopentaaquochromium(III) at pH 2-3 ensures a longer time for the cyanide ligand to exert its influence on substitution reactions. Its effect is clearly that of labilizing coordinated water to favor an increased rate of exchange.

The experimental results do not enable a distinction to be made as to whether the cyanide ligand exerts a trans- or a cis-labilizing effect in cyanopentaaquochromium(III). It was hoped that complexes of the type [Cr(H<sub>2</sub>O)<sub>4</sub>(CN)X]<sup>3-</sup> would be produced in sufficient yields to permit identification of their geometries, thereby revealing either cis or trans labilization. Various attempts to prepare the mixed cyanosulfato (X<sup>2-</sup> = SO<sub>4</sub><sup>2-</sup>) species failed, even at ice temperatures. Apparently, loss of cyanide is greatly enhanced once sulfate ion coordination occurs. Some success in preparing the mixed-ligand complex was realized in the case of the thio-cyanato (X = NCS) complex. Its presence in the different reaction mixtures was conclusively demonstrated; however, conditions for producing it in high yield were not found. The limited amounts produced were insufficient for detailed characterization and structure determination. Based on earlier studies<sup>2-6</sup> and lacking any new evidence to the contrary, it is believed that the cyanide ligand of cyanopentaaquochromium(III) exerts a trans- rather than a cis-labilizing effect.

Ours is believed to be the first observation of the [Cr(H<sub>2</sub>O)<sub>4</sub>(CN)(NCS)]<sup>+</sup> complex ion, and further more detailed studies are planned, provided that it can be prepared in the pure form and in higher concentration. Only small amounts were found in the reaction mixtures of the present study, along with unreacted [Cr(H<sub>2</sub>O)<sub>5</sub>(CN)]<sup>2+</sup> and various other thio-cyanato complexes. The order of elution of these species from the ion-exchange column was [Cr(H<sub>2</sub>O)<sub>3</sub>(NCS)<sub>3</sub>], [Cr(H<sub>2</sub>O)<sub>4</sub>(CN)(NCS)]<sup>+</sup>, [Cr(H<sub>2</sub>O)<sub>4</sub>(NCS)<sub>2</sub>]<sup>+</sup>, [Cr(H<sub>2</sub>O)<sub>5</sub>(CN)]<sup>2+</sup>, [Cr(H<sub>2</sub>O)<sub>5</sub>(NCS)]<sup>2+</sup>, [Cr(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>, using deionized water to remove the first, 0.2 M K<sub>2</sub>SO<sub>4</sub> (pH 2.5) to remove the next four, and 0.6 M K<sub>2</sub>SO<sub>4</sub> to remove the last of these species from the column. Identification of the red [Cr(H<sub>2</sub>O)<sub>4</sub>(CN)(NCS)]<sup>+</sup> complex ion in dilute solutions was by spectrophotometric determination of chromium, thiocyanate, and cyanide contents. Typical results gave molar ratios respec-

tively of 1.0:1.1:1.3, indicating some contamination. Analysis of known mixtures demonstrated that the method for determination of cyanide<sup>13</sup> is free of interference from either chromium or thiocyanate. Spectra of the dilute solutions, measured in a 10-cm cell, exhibited two bands in the visible region, one at approximately 530 nm of  $\epsilon \sim 46 \text{ l. mol}^{-1} \text{ cm}^{-1}$  and another at about 403 nm of  $\epsilon \sim 50 \text{ l. mol}^{-1} \text{ cm}^{-1}$ . An intense charge-transfer band appears in the near-ultraviolet spectrum.

Quantitative recovery of chromium was achieved without recourse to unusually large volumes or concentrations of elution agents. The efficiency of potassium sulfate solutions as a cation eluting agent is probably enhanced by the pronounced tendency of sulfate ions to form ion pairs with multivalent cations, thereby lowering their charge and promoting desorption. Use of perchloric acid as eluting agent, although noncomplexing, was precluded by the instability of the cyano complexes in strongly acidic solutions. No detectable amount of sulfate substitution occurred during the relatively short time required for chromatographic separation and analysis.

Solid samples of [Cr(H<sub>2</sub>O)<sub>5</sub>(CN)]SO<sub>4</sub>·H<sub>2</sub>O (containing about 10% K<sub>2</sub>SO<sub>4</sub>) exposed to moist air decompose gradually, giving off hydrogen cyanide and turning dark green. The green residue contains an appreciable amount of an anionic chromate(III) species with adsorption characteristics closely resembling those reported for the disulfatotetraquo-chromate(III) anion.<sup>14</sup>

Storage of the solid monocyno complex in tightly closed, dark containers, produced only partial decomposition.

**Registry No.** [Cr(H<sub>2</sub>O)<sub>5</sub>CN]SO<sub>4</sub>·H<sub>2</sub>O, 38782-96-6; [Cr(H<sub>2</sub>O)<sub>5</sub>(CN)](ClO<sub>4</sub>)<sub>2</sub>, 38782-97-7; [Cr(H<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>3</sub>, 27535-70-2; LiClO<sub>4</sub>, 7791-03-9; LiNO<sub>3</sub>, 7790-69-4; LiCl, 7447-41-8; LiBr, 7550-35-8; LiNCS, 556-65-0; Li<sub>2</sub>SO<sub>4</sub>, 10377-48-7.

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## Studies of Hydroxy Acid Complexes. II. Lactatobis((R)-1,2-propanediamine)cobalt(III) Complexes

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We have previously reported<sup>1</sup> the optical activity associated with complexes of the type [Co(en)<sub>2</sub>ha]<sup>+</sup> where en is ethylenediamine and ha is an optically active hydroxy acid. The configurational and vicinal effects associated with those complexes were separated out and it was found that both effects had very significant contributions to the net circular dichroism. This was contrary to results obtained for other related systems containing amino acids,<sup>2,3</sup> and this was surprising since hydroxy acids are the oxygen analogs of amino acids and one would anticipate that there should have been a great deal of similarity between the two systems. In an

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