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Chromium(III) Complexes with a Tridentate, Bidentate, or Unidentate Triethylenetetramine Ligand[1]

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Four aquotriethylenetetraminechromium(III) complexes of a type previously unreported have been synthesized and isolated in aqueous solution. In two of these complexes, 1,2,3- and 1,2,6-$Cr(trienH)(OH_2)_3^{4+}$, the normally quadridentate triethylenetetramine (trien) ligand is tridentate; in the other two complexes, $Cr(trienH_2)(OH_2)_4^{5+}$ and $Cr(trienH_3)(OH_2)_5^{6+}$, the trien ligand is bidentate and unidentate, respectively. The "partially unwrapped" trien ligands are stabilized by proton uptake. The visible absorption band maxima and minima are reported.

Introduction

Normally ethylenediamine and diethylenetriamine act, respectively, as bidentate and tridentate ligands in metal complexes. However, recently chromium(III) complexes with a bidentate or unidentate diethylenetriamine ligand have been synthesized and isolated, namely, pentaaquo(1,7-diazonia-4-azaheptane)chromium(III) cation (or, possibly, pentaaquo(1,4-diazonia-7-azaheptane)chromium(III) cation), $Cr(dienH_2)(OH_2)_5^{5+}$,[2,3] with a unidentate diethylenetriamine ligand, and tetraaquo(1-azonia-4,7-diazaheptane)chromium(III) cation, $Cr(dienH)(OH_2)_4^{4+}$,[2,3] with a bidentate diethylenetriamine ligand, the freed amino N groups being stabilized by uptake of protons. Earlier two chromium(III) complexes with a unidentate protonated ethylenediamine ligand were synthesized, namely, μ-hydroxo-enneaammine(2-aminoethylammonium)dichromium(III) chloride, $[(H_3N)_5Cr(OH)Cr(enH)(NH_3)_4]Cl_6$,[4] and pentaaquo(2-aminoethylammonium)chromium(III) cation, $Cr(enH)(OH_2)_5^{4+}$.[5]

In connection with a kinetic study of the stepwise "unwrapping" of the normally quadridentate ligand triethylenetetramine from a chromium(III) center, we have synthesized and isolated in solution four new aquotriethylenetetramine–chromium(III) complexes in which the amine ligand has a dentictity of three, two, or one. Triethylenetetramine complexes of this type apparently have not been isolated and characterized previously.

Experimental Section

1,2,6-Triaquo(1-azonia-4,7,10-triazadecane)chromium(III) Cation.—Aqueous perchloric acid solutions of this new complex were obtained by shaking 0.16 g (0.50 mFW) of *cis*-α-$[Cr(trien)Cl_2]Cl \cdot H_2O$[6] in 50 ml of 0.25 *F* $Hg(NO_3)_2$–0.1 *F* $HClO_4$ at 0–5° for 5 min, followed by chromatography at 0–3° on a 7-cm × 1-cm diameter column of H^+ Dowex AG50W-X2 cation-exchange resin (200–400 mesh). Mercury(II) and possible traces of monochloro complexes were removed with 250 ml of 1.25 *F* $HClO_4$, which also moved the triaquo complex to the bottom of the column, and then the orange band of 1,2,6-$Cr(trienH)(OH_2)_3^{4+}$ was eluted with 75–100 ml of 2 *F* $HClO_4$ at a flow rate of 5–7 ml/min to give a solution *ca.* 3 m*F* in the complex and free of other chromium species. Chlorine determinations on the complex showed no Cl was present.

Alternatively, cis-α-$[Cr(trien)Cl_2]Cl \cdot H_2O$ may be base hydrolyzed with a 100-fold excess of 0.1 *F* NaOH at 20–25° for 20 min, followed by acidification to 0.1–1 *F* $HClO_4$ at 0–10° and subsequent chromatography on a 10-cm × 1-cm diameter resin column as described above. Small amounts of $Cr(trien)(OH_2)Cl^{2+}$ or $Cr(trienH)(OH_2)_2Cl^{3+}$ are eluted by the 1.25 *F* $HClO_4$ eluent prior to elution of the triaquo complex and yields of the latter are lower than in the Hg(II) method described above.

1,2,3-Triaquo(1-azonia-4,7,10-triazadecane)chromium(III) Cation.—A solution consisting chiefly of 1,2,6-$Cr(trienH)(OH_2)_3^{4+}$ prepared by the above base hydrolysis and acidification was rapidly heated to 70–80° and aged for 5–10 min to convert the 1,2,6-triaquo complex to a mixture of 1,2,3-$Cr(trienH)(OH_2)_3^{4+}$ and $Cr(trienH_2)(OH_2)_4^{5+}$. Chromatography of portions (0.5–1 mFW of total Cr) of this solution at 0° on a 30-cm × 1-cm diameter resin column (same resin as above) usually required *ca.* 2000 ml of 1.5 *F* $HClO_4$ eluent at a flow rate of 1–3 ml/min to effect separation of the red 1,2,3-$Cr(trienH)(OH_2)_3^{4+}$ band from the $Cr(trienH_2)(OH_2)_4^{5+}$ left as a magenta band occupying the top 15 cm of the column; the magenta band was manually removed and saved (see below); then the 1,2,3-triaquo complex was eluted off the column with 50 ml of 3–4 *F* $HClO_4$ to give a 2–3 m*F* solution of the pure complex. Chlorine determinations on the complex gave negative results.

Tetraaquo(1,4-diazonia-7,10-diazadecane)chromium(III) Cation or Tetraaquo(1,10-diazonia-4,7-diazadecane)chromium(III) Cation.—The magenta band of resin manually removed in the procedure immediately above was eluted with 50–100 ml of 4 *F* $HClO_4$ at 0–5° with a flow rate of 1–3 ml/min to yield 5–10 m*F* solutions of pure $Cr(trienH_2)(OH_2)_4^{5+}$.

Pentaaquo(1,4,7-triazonia-10-azadecane)chromium(III) Cation or Pentaaquo(1,4,10-triazonia-7-azadecane)chromium(III) Cation.—Typically, 0.24 g (0.75 mFW) of *cis*-α-$[Cr(trien)Cl_2]Cl \cdot H_2O$ was dissolved in a 100-fold excess of 0.1 *F* NaOH and aged 20 min at 20–25°; then the solution was acidified to 1 *F* $HClO_4$ with 6 *F* $HClO_4$, giving mainly 1,2,6-$Cr(trienH)(OH_2)_3^{4+}$, with some $Cr(trien)(OH_2)Cl^{2+}$ or $Cr(trienH)(OH_2)_2Cl^{3+}$. This acidic mixture was aged for 250 min at 80° and then cooled to 0° and charged onto a 20-cm × 1-cm diameter resin column (as above). Approximately 3000–4000 ml of 1.25 *F* $HClO_4$ was used at a flow rate of 1–3 ml/min to elute a gray-blue band spectrally identified as $Cr(OH_2)_6^{3+}$; then 2000 ml of 1.5 *F* $HClO_4$ was used to elute a second gray band identified spectrally as a Cr(III) dinuclear species, apparently either $(H_2O)_5CrOCr(OH_2)_5^{4+}$ or $(H_2O)_5Cr(OH)_2Cr(OH_2)_5^{4+}$,[7] and to separate a lower magenta band of $Cr(trienH_2)(OH_2)_4^{5+}$ from a wide higher purple band of $Cr(trienH_3)(OH_2)_5^{6+}$. A center cut of the purple band was manually isolated and separately eluted at 0–3° with 60–80 ml of 4 *F* $HClO_4$ to give a purple solution *ca.* 5 m*F* in $Cr(trienH_3)(OH_2)_5^{6+}$, free from other Cr species.

Analytical Methods.—Visible absorption spectra were obtained with a Cary Model 11 recording spectrophotometer and matched 10-cm silica cells; the reference cell was filled with the

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(1) (a) Work partly supported under Contract AT(04-3)-34, Project No. 170, between the U. S. Atomic Energy Commission and the University of California. This paper constitutes Report No. UCLA-34P170-13 to the AEC. (b) Abbreviations used: en, ethylenediamine, $H_2N(CH_2)_2NH_2$; pn, propylenediamine, $CH_3CH(NH_2)CH_2NH_2$; ibn, isobutylenediamine, $H_2NCH_2C(CH_3)_2NH_2$; dien, diethylenetriamine, $H_2N(CH_2)_2NH(CH_2)_2NH_2$; trien, triethylenetetramine, $H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$.

(2) D. K. Lin and C. S. Garner, *Inorg. Nucl. Chem. Lett.*, **5**, 481 (1969).

(3) D. K. Lin and C. S. Garner, *J. Amer. Chem. Soc.*, **91**, 6637 (1969).

(4) G. Schwarzenbach and B. Magyar, *Helv. Chim. Acta*, **45**, 1454 (1962).

(5) R. F. Childers, Jr., K. G. Vander Zyl, Jr., D. A. House, R. G. Hughes, and C. S. Garner, *Inorg. Chem.*, **7**, 749, 2678 (1968).

(6) D. A. House and C. S. Garner, *J. Amer. Chem. Soc.*, **88**, 2156 (1966).

(7) M. Ardon and R. A. Plane, *ibid.*, **81**, 3197 (1959).

same solution without the Cr(III) complexes. The methods for Cr and Cl analyses have been described earlier.[8]

Results and Discussion

The new complexes with a "partially unwrapped" triethylenetetramine ligand, namely, 1,2,3- and 1,2,6-$Cr(trienH)(OH_2)_3^{4+}$ (tridentate trien), $Cr(trienH_2)(OH_2)_4^{5+}$ (bidentate trien), and $Cr(trienH_3)(OH_2)_5^{6+}$ (unidentate trien), are intermediates in the stepwise aquation of *cis*-α-$Cr(trien)Cl_2^+$ to $Cr(OH_2)_6^{3+}$ and can be isolated by cation-exchange chromatography of aquation reaction solutions aged for increasing times. For preparative purposes, it is easier to synthesize the 1,2,6-triaquo complex from *cis*-α-$[Cr(trien)Cl_2]Cl \cdot H_2O$ by Hg(II)-catalyzed acid hydrolysis in $HClO_4$ or with some loss of purity by base hydrolysis in NaOH followed by acidification with $HClO_4$. The 1,2,6-triaquo complex serves as a source of the 1,2,3 (facial) isomer and the tetraaquo complex by concurrent isomerization and aquation in $HClO_4$ and under more vigorous conditions aquates to the pentaaquo complex. Although chromatography is generally still necessary, the mixtures obtained are simpler to chromatograph (see Experimental Section).

Each of the above complexes with a "partially unwrapped" triethylenetetramine ligand is stabilized in acidic medium by rapid protonation of each of the amino N atoms freed upon rupture of a Cr–N bond. We have found spectrophotometrically, for example, that $Cr(trienH_2)(OH_2)_4^{5+}$ rapidly (<5 min at 0°) rechelates at pH 7–11 to give 1,2,6-$Cr(trienH)(OH_2)_3^{4+}$ after acidification with $HClO_4$.

Our attempts to detect $Cr(trien)(OH_2)_2^{3+}$ or isolate it from the Hg(II)-catalyzed aquation or acidified base hydrolysis reaction solutions have not been successful. Moreover, methods described earlier[9] as giving orange species tentatively characterized as $Cr(trien)(OH_2)_2^{3+}$ have been shown in this work to yield 1,2,6-$Cr(trienH)(OH_2)_3^{4+}$. Additional experiments designed to search for the diaquo complex were made by adding NaOH to 1,2,6-$Cr(trienH)(OH_2)_3^{4+}$ at 0° to give a pH of 8–9 in one case and 9–10 in another, allowing the solution to stand at 0° for *ca.* 5 and 15 min, respectively, to allow possible rechelation (see above for rechelation of the tetraaquo complex) to the dihydroxo complex, then rapidly scanning the visible absorption spectrum at 15–20°, and finally rapidly making the solution 0.1 *F* in $HClO_4$ and rapidly scanning the spectrum to search for diaquo absorption bands. In the basic medium the spectrum showed bands at 383 and 537 nm ($\epsilon_{537}/\epsilon_{383} = 0.94$) in the first case and 379 and 532 nm ($\epsilon_{532}/\epsilon_{379} = 0.95$) in the second case; comparison with the spectra of *cis*-$Cr(en)_2(OH)_2^+$ (377, 526 nm, $\epsilon_{526}/\epsilon_{377} = 0.96$),[10] *trans*-$Cr(en)_2(OH)_2^+$ (396, 503 nm, $\epsilon_{503}/\epsilon_{396} = 1.1$),[10] and 1,2,6-$Cr(dien)(OH)_3$ (380, 575 nm, $\epsilon_{575}/\epsilon_{380} = 0.87$)[11] suggests that at least in the second case nearly complete rechelation to *cis*-$Cr(trien)(OH)_2^+$ may have occurred. In any case, the spectrum of the rapidly acidified solutions is identical with that of the 1,2,6-triaquo starting complex. Thus, if rechelation actually occurs in base to form the dihydroxo complex, it must aquate ~100% at 15–20° within the 45-sec time taken to acidify and scan the spectrum. The reason for the apparent lability of the diaquo complex is unknown.

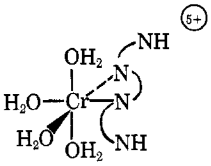
Characterization of the new complexes has been based upon their mode of formation, their aquation product, their chromatographic behavior, their d–d absorption spectra, and determinations of their charge per Cr atom using a modification[8] of the method of Beukenkamp and Herrington,[12] as described below.

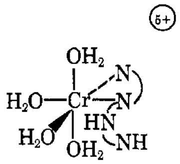
Chromatography and spectral scans made during the reactions (with isosbestic points found at the proper locations in accord with predicted values, as will be described in a later paper bearing on the kinetics) have shown that the 1,2,3- and 1,2,6-triaquo complexes aquate to the tetraaquo complex, which in turn aquates to the pentaaquo complex, which itself aquates to $Cr(OH_2)_6^{3+}$, thus establishing the genetic relationships. All the aquations are slow at room temperature.

Charge per Cr atom determinations gave values of 4.17+–4.20+ and 4.0+ for 1,2,3- and 1,2,6-$Cr(trienH)(OH_2)_3^{4+}$, respectively, and 5.20+–5.22+ for $Cr(trienH_2)(OH_2)_4^{5+}$. A charge determination was not made on the pentaaquo complex since its chromatographic behavior (see below) showed it to have a charge higher than 5+ and since it aquated directly to the known complex $Cr(OH_2)_6^{3+}$.

Rates of elution from a cation-exchange column were in the following order: $Cr(trienH_3)(OH_2)_5^{6+}$ eluting slowest, $Cr(trienH_2)(OH_2)_4^{5+}$ next, 1,2,3-$Cr(trienH)(OH_2)_3^{4+}$ next, and 1,2,6-$Cr(trienH)(OH_2)_3^{4+}$ fastest. Part of the assignment of the triaquo isomers is based on the slower elution of the 1,2,3 isomer with its higher electric dipole moment, in accord with general observations that a cis or facial species elutes more difficultly than its trans or meridial isomer.

The visible absorption maxima and minima, arising from d–d transitions in the Cr(III) center, are given in Table I, together with data for related chromium(III)–aquoamine complexes. In general the band wavelengths for species of the same chromophore type and symmetry are in excellent agreement, strongly supporting the chemical formulas assigned to each of the new complexes. The d–d spectral comparison further supports the above isomeric assignments for the $Cr(trienH)(OH_2)_3^{4+}$ isomers. The spectra (and the other lines of evidence) do not distinguish which N atoms of the trien ligand are bonded to the Cr(III) ion; *e.g.*, the d–d spectra of the two possible geometric isomers of $Cr(trienH_2)(OH_2)_4^{5+}$





would be expected to be essentially identical. Stated differently, we do not know whether the trien ligand "unwraps" from the Cr(III) center progressively from the primary amino N atom first freed, with the secondary amino N atoms then breaking their Cr–N bonds, or whether first one primary amino N atom aquates and then the other.

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[8] D. A. House, R. G. Hughes, and C. S. Garner, *Inorg. Chem.*, **6**, 1077 (1967).

[9] C. Y. Hsu and C. S. Garner, *Inorg. Chim. Acta*, **1**, 17 (1967).

[10] F. Woldbye, *Acta Chem. Scand.*, **12**, 1079 (1958).

[11] S. H. Caldwell and D. A. House, *J. Inorg. Nucl. Chem.*, **31**, 811 (1969).

[12] J. Beukenkamp and K. D. Herrington, *J. Amer. Chem. Soc.*, **82**, 3025 (1960).

TABLE I

VISIBLE ABSORPTION MAXIMA AND MINIMA OF AQUOTRIETHYLENETETRAMINECHROMIUM(III) AND RELATED COMPLEXES IN AQUEOUS SOLUTION AT 20–25°

Chromophore type[a]	Complex	$[HClO_4]$, *F*	λ_{max}, nm[b]	λ_{min}, nm[b]	λ_{max}, nm[b]
$CrNO_5$	$Cr(trienH_3)(OH_2)_5^{6+}$ [c]	3	398 (22.0)	465 (5.1)	552 (22.3)
	$Cr(dienH_2)(OH_2)_5^{5+}$ [d]	3	396 (23.4)	465 (5.3)	551 (22.4)
	$Cr(enH)(OH_2)_5^{4+}$ [e]	0.5–2	396 (21.5)	462 (5.7)	549 (22.2)
	$Cr(NH_3)(OH_2)_5^{3+}$ [f]	1	397 (21.8)		545 (22.1)
CrN_2O_4	$Cr(trienH_2)(OH_2)_4^{5+}$ [c]	2	389 (27.5)	440 (10.1)	522 (48.7)
	$Cr(dienH)(OH_2)_4^{4+}$ [d]	1	388 (27.7)	440 (11.9)	520 (48.9)
	$Cr(ibn)(OH_2)_4^{3+}$ [g]	1	390 (11.9)	440 (9.7)	518 (29.0)
	$Cr(pn)(OH_2)_4^{3+}$ [g]	1	383 (24.4)	438 (11.6)	515 (36.0)
	$Cr(en)(OH_2)_4^{3+}$ [e]	0.1–3	385 (24.3)	433 (10.7)	512 (41.7)
CrN_3O_3, facial	1,2,3-$Cr(trienH)(OH_2)_3^{4+}$ [c]	2	375 (35.6)	430 (13.8)	513 (72.0)
	1,2,3-$Cr(dien)(OH_2)_3^{3+}$ [d]	1	375 (32.2)	430 (13.3)	510 (67.0)
	1,2,3-$Cr(NH_3)_3(OH_2)_3^{3+}$ [h]	2	375 (22)	432 (6.4)	518 (34.5)
CrN_3O_3, meridial	1,2,6-$Cr(trienH)(OH_2)_3^{4+}$ [c]	2	368 (45.5)	418 (20.4)	493 (82.9)
	1,2,6-$Cr(dien)(OH_2)_3^{3+}$ [i]	1	390 (45.4)	425 (37.8)	495 (89.0)
	1,2,6-$Cr(NH_3)_3(OH_2)_3^{3+}$ [j]	3	373 (25.6)	427 (8.0)	503 (25.6)

[a] Gives numbers of amine N atoms and water O atoms directly bonded to the central Cr(III) ion. [b] Numbers inside parentheses are the molar absorbance indices (extinction coefficients) ϵ in M^{-1} cm^{-1}, defined by the relation $A = \log (I_0/I) = \epsilon cd$, where c is the molarity of the complex and d is the optical path in centimeters. [c] This research. [d] Reference 3. [e] Reference 5. [f] M. Ardon and B. E. Mayer, *J. Chem. Soc.*, 2816 (1962). [g] Reference 8. [h] C. E. Schäffer and P. Andersen, "Proceedings of the Wroclaw Symposium," Pergamon Press, London, 1964, p 571. [i] Reference 11. [j] R. G. Hughes, E. A. V. Ebsworth, and C. S. Garner, *Inorg. Chem.*, **7**, 882 (1968).

In further support of the triaquo isomeric assignments, the 1,2,6 isomer qualitatively aquates faster than the 1,2,3 isomer, as has also been observed[3] with the related 1,2,6- and 1,2,3-$Cr(dien)(OH_2)_3^{3+}$ complexes.

The new complexes probably will be useful in the synthesis of various new acido complexes with "partially unwrapped" triethylenetetramine ligands; such complexes would be generated by appropriate anation reactions.

Also under way in this laboratory is a synthetic and kinetic investigation of the "unwrapping" of the tetraethylenepentamine ligand from a Cr(III) center.

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