

- (25) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).
 (26) A. P. Gaughan, Jr., K. S. Bowman, and Z. Dori, *Inorg. Chem.*, **11**, 601 (1972).
 (27) In addition to various local programs for the CDC 6400 and 7600 computers, modified versions of the following programs were employed: Zalkin's *FORDAP* Fourier summation program, Johnson's *ORTEP* thermal ellipsoid plotting program, Busing and Levy's *ORFFE* error function program, and Lawton's *TRACER* cell reduction program. Our full-matrix least-squares program *NUCLS*, in its nongroup form, closely resembles the Busing-Levy *ORFLS* program. Our absorption program, *AGNOST*, incorporates the Coppens-Leiserowitz-Rabinovich logic for gaussian integration. Modifications of these programs for the 7600 computer at Lawrence-Berkeley Laboratory were made by Professor K. N. Raymond.
 (28) (a) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.2A; (b) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *ibid.*, Table 2.2C; (c) D. T. Cromer and D. Liberman, *ibid.*, Table 2.3.1.
 (29) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).
 (30) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 793 (1965).
 (31) C-H = 0.95 Å, C-C-H = 120° (sp²), H-C-H = 109.5° (sp³), dihedral angle 90°, B(H) = 1.0 Å² + B(C).
 (32) See paragraph at end of paper regarding supplementary material.
 (33) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. **11** (1958).
 (34) Except those structures which involve orthometalation of the aryl group where the angle is *ca.* 120°; see ref 35.
 (35) F. W. B. Einstein, A. B. Gilchrist, G. W. Rayner-Canham, and D. Sutton, *J. Amer. Chem. Soc.*, **94**, 645 (1972).
 (36) J. J. deLange, J. M. Robertson, and I. Woodward, *Proc. Roy. Soc., Ser. A*, **171**, 398 (1939).
 (37) D. A. Snyder and D. L. Weaver, *Inorg. Chem.*, **9**, 2760 (1970).
 (38) The negative sign indicates a distance on the opposite side of the plane from the Rh atom.
 (39) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Wiley, New York, N. Y., 1972.
 (40) A. P. Gaughan, Jr., Z. Dori, and J. A. Ibers, *Inorg. Chem.*, **13**, 1657 (1974).

Contribution from the Department of Inorganic and Structural Chemistry,
The University, Leeds LS2 9JT, England

New Complexes of Pentaamminechromium(III) with Oxalate, Glycinate, Sulfate, and Iodate as Ligands. Loss of Ammonia from Chromium(III)-Ammine Complexes

T. RAMASAMI, ROLAND K. WHARTON, and A. GEOFFREY SYKES*

Received April 19, 1974

AIC402548

Complexes of general formula $[\text{Cr}(\text{NH}_3)_5\text{X}]^{(3-n)+}$ with $\text{X}^{n-} = \text{HC}_2\text{O}_4^-$, $\text{NH}_3^+\text{CH}_2\text{CO}_2^-$, SO_4^{2-} , and IO_3^- have been prepared as perchlorate and, in the case of $\text{X}^{n-} = \text{IO}_3^-$, perchlorate-iodate salts. Elemental analyses, uv-visible and ir spectra, and charge determinations have been used to characterize the complexes. Kinetic studies are also reported and support formulations in which X^{n-} is monodentate. It has not been possible to repeat preparations of iodato complexes $[\text{Co}(\text{NH}_3)_5\text{IO}_3]^{2+}$ and $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{IO}_3]^{2+}$ previously described, and data obtained suggest that earlier assignments are incorrect. To our knowledge no other metal-pentaammine complexes with iodate as a ligand have been reported. The relative effectiveness of different X^{n-} ligands on the rate of aquation of ammonia in these and other pentaamminechromium(III) complexes is considered.

Whereas the vast majority of cobalt(III)-ammine complexes are extremely inert to loss of ammonia, the situation with chromium(III) is less clear-cut.¹ Reactions which $[\text{Cr}(\text{NH}_3)_5\text{NO}_3]^{2+}$,² $[\text{Cr}(\text{NH}_3)_5\text{O}_2\text{CR}]^{2+}$ (R = CHCl_2 , CH_2Cl , CH_3),³ and other chromium(III) complexes¹ undergo suggest that ammonia is much more readily displaced. Pentaamminechromium(III) complexes ($\text{X}^{n-} = \text{HC}_2\text{O}_4^-$, $\text{NH}_3^+\text{CH}_2\text{CO}_2^-$, and SO_4^{2-}), the cobalt(III) analogs of which are readily prepared, have not previously been isolated. Procedures for the preparation of these complexes are reported in this paper. At the same time because of its relevance to the efficiency of procedures described, processes involving ammonia loss are considered. Different categories of reaction are defined and possible mechanisms are discussed.

The preparation of the iodato complex falls in a different category in that ammonia loss is not significant. Duval⁴ and Lobanov⁵ have previously reported the preparation of iodato complexes of cobalt(III). Since the procedures which they used were of possible relevance to the preparation of $[\text{Cr}(\text{NH}_3)_5\text{IO}_3]^{2+}$, attempts were made to repeat their work.

Experimental Section

Samples of $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{NO}_3)_3 \cdot \text{NH}_4\text{NO}_3$ were prepared⁶ and converted to the perchlorate salt using standard procedures. The complex *cis*- $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2](\text{ClO}_4)_3$ was obtained by the method of Hoppenjans and Hunt.⁷

Preparation of Pentaammineoxalatochromium(III) Perchlorate. Oxalic acid, AR (8 g), was dissolved in a 95:5 methanol (AR)-water mixture (200 ml), and $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ (1 g) was added. The mixture was maintained at *ca.* 20° for 5-6 hr, after which $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ crystals were removed by filtration. The solution was concentrated by rotary evaporation at 35-40° and a mixture of $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$, $[\text{Cr}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{H}]^{2+}$, and $[\text{Cr}(\text{NH}_3)_4\text{C}_2\text{O}_4]^{+}$ was precipitated by the addition of 1:1 ethanol-ether and cooling in ice. The orange precipitate was dissolved in 0.3 M HClO_4 also at

0° which was then passed down an ice-cooled Dowex 50W-X2 (100-200 mesh) resin column (12 cm × 1 cm). Three bands were observed and the first (red) band, which was later identified as $[\text{Cr}(\text{NH}_3)_4\text{C}_2\text{O}_4]^{+}$, eluted with a solution containing 0.3 M LiClO_4 and 0.2 M HClO_4 . Under these conditions one of the two remaining bands (both of which are orange) moved about 2 cm down the column. Using an eluent mixture of 0.8 M LiClO_4 -0.2 M HClO_4 both orange bands were eluted, with a separation of about 5 cm between the two bands at the end of the elution. The solution containing the first orange band was cooled to 0° when crystals were obtained. The ir spectrum of these is illustrated in Figure 1. The elution characteristics of the complex on the ion-exchange column, together with the ammonia to chromium ratio of 4.9:1, as determined using micro Kjeldahl and chromate analyses, indicate a formulation $[\text{Cr}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{H}](\text{ClO}_4)_2$. The second orange fraction obtained from the column gave a visible spectrum in agreement with that of $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ and corresponded to the unreacted starting material.

Preparation of Pentaammineglycinatochromium(III) Perchlorate. Glycine, AR (9 g), was dissolved in *ca.* 30 ml of 1 M HClO_4 to give a final pH of *ca.* 3.0. The solution was then warmed to 50° and $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ (5 g) was added, the temperature being maintained at 50° for 10 min. By the addition of suitable amounts of NaClO_4 and subsequent cooling it was possible to crystallize what later proved to be a mixture of $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ and $[\text{Cr}(\text{NH}_3)_5(\text{O}_2\text{CCH}_2\text{NH}_3)](\text{ClO}_4)_3$, leaving a red supernatant liquid. The mixed crystals were filtered off, washed with alcohol and ether, and then dissolved in 500 ml of methanol (AR) with stirring. The glycinate component of the mixture was soluble and readily separated from the insoluble aquo species. The methanolic solution was then concentrated by rotary evaporation and the glycinato product precipitated by the addition of a 1:1 alcohol-ether mixture. The orange product was recrystallized three times from 20-ml quantities of 1 M HClO_4 . *Anal.* Calcd for $[\text{Cr}(\text{NH}_3)_5(\text{O}_2\text{CCH}_2\text{NH}_3)](\text{ClO}_4)_3$: C, 4.71; H, 3.94; N, 16.48; Cl, 20.8; Cr, 10.2. Found: C, 4.7; H, 4.2; N, 16.2; Cl, 20.65; Cr, 10.2.

Preparation of Tetraammineaquoglycinatochromium(III) Perchlorate. This complex was prepared in solution by treating

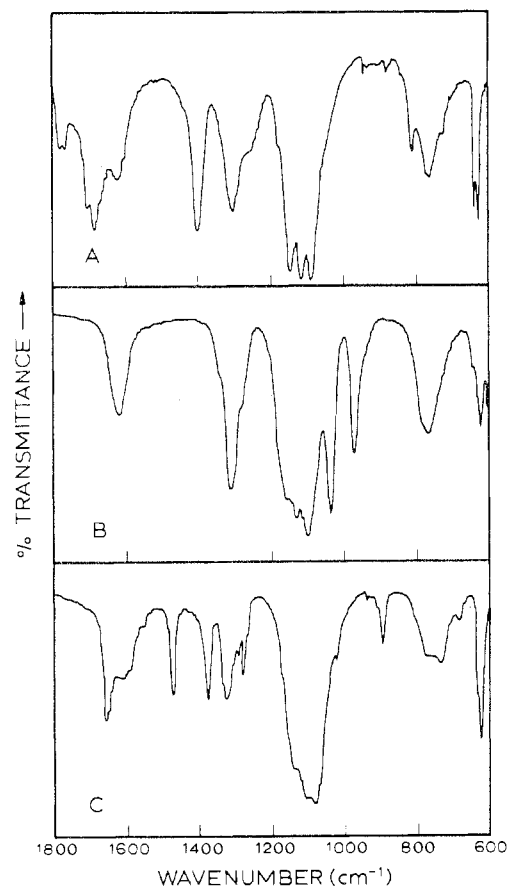


Figure 1. Infrared spectra (KBr disks) of the complexes $[\text{Cr}(\text{NH}_3)_5\text{-C}_2\text{O}_4\text{H}](\text{ClO}_4)_2$ (A), $[\text{Cr}(\text{NH}_3)_5\text{SO}_4](\text{ClO}_4)$ (B), and $[\text{Cr}(\text{NH}_3)_5\text{-O}_2\text{CCH}_2\text{NH}_3](\text{ClO}_4)_3$ (C).

$[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ or *cis*- $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2](\text{ClO}_4)_3$ with an aqueous solution of excess glycine (1:10 in the former and 1:3 in the latter) at $[\text{H}^+] = 10^{-3} M$ and 50° for 30 min. Concentrations of complex used in the preparations ranged from $(6\text{--}8) \times 10^{-3} M$. The pink complex was eluted from a Dowex 50W-X2 (100–200 mesh) ion-exchange column (12×1 cm) using a mixture of $0.9 M \text{NaClO}_4$ and $0.1 M \text{HClO}_4$. The resultant pink solution gave a spectrum with peaks at 372 (ϵ 29.5) and 510 nm (ϵ 41.7 l. mol $^{-1}$ cm $^{-1}$). Determinations of the total nitro to chromium and ammine nitrogen to chromium ratios using micro Kjeldahl and chromate analyses gave ratios of 4.9:1 and 3.9:1, respectively, when $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ was the starting material, and 4.8:1 and 3.9:1 when *cis*- $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})]^{3+}$ was used for the preparation; both are consistent with the formulation $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{O}_2\text{CCH}_2\text{NH}_3)](\text{ClO}_4)_3$.

Preparation of Nitritoglycinatotetraamminechromium(III) Perchlorate. Sodium nitrite (*ca.* 2 g) was added to a solution of $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{O}_2\text{CCH}_2\text{NH}_3)]^{3+}$ ($(7\text{--}8) \times 10^{-3} M$) at $[\text{H}^+] = 10^{-2} M$ together with a few drops of acetic acid. An additional 2 g of sodium nitrite was then added and the $[\text{H}^+]$ adjusted to $0.1 M$. After cooling at 0° for 3–4 hr the reddish orange crystals which resulted were filtered off, washed with ethanol and ether, and air-dried. *Anal.* Calcd for $[\text{Cr}(\text{NH}_3)_4(\text{ONO})(\text{O}_2\text{CCH}_2\text{NH}_3)](\text{ClO}_4)_2$: Cr, 11.9; ammine nitrogen, 12.9; total nitrogen, 19.2; organic nitrogen, 3.2. Found: Cr, 11.6; ammine nitrogen, 12.3; total nitrogen, 18.6; organic nitrogen, 3.0. The spectrum of the complex gave peaks at 360 (ϵ 186) and 485 nm (ϵ 56.2 l. mol $^{-1}$ cm $^{-1}$). The ir spectrum of the complex exhibited a band at 1040 cm^{-1} characteristic of the nitrito linkage.⁸

When the preparation was carried out at $[\text{H}^+] = \text{ca. } 10^{-4} M$, a species containing coordinated nitrite and having an overall charge of 1+ was obtained. *Anal.* Calcd for $[\text{Cr}(\text{NH}_3)_4(\text{ONO})(\text{O}_2\text{CCH}_2\text{NH}_2)](\text{ClO}_4)$: C, 7.1; H, 4.7; N, 24.8; ammine N, 16.6; Cl, 10.5; Cr, 15.3. Found: C, 7.1; H, 4.1; N, 24.7; ammine N, 16.4; Cl, 10.3; Cr, 15.1.

Preparation of Sulfatopentaamminechromium(III) Perchlorate. Sodium sulfate decahydrate (6 g) was dissolved in $2 M \text{H}_2\text{SO}_4$ (20 ml) at 50° ; $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ (1 g) was added and the resultant

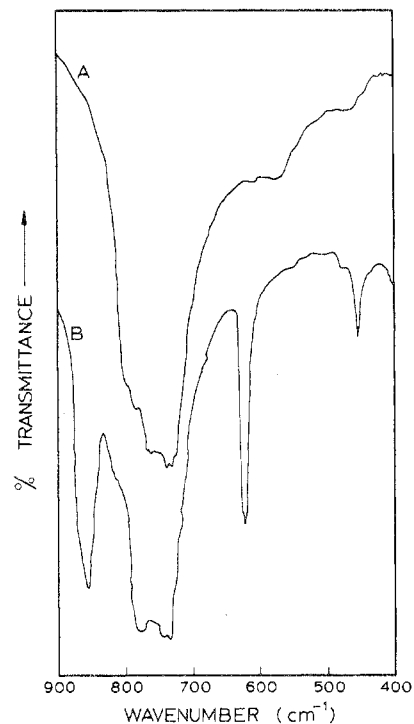


Figure 2. Infrared spectra (KBr disk) of the iodate salts of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ (A) and (Nujol) of $[\text{Cr}(\text{NH}_3)_5\text{IO}_3]^{2+}$ (B). The band at *ca.* 625 cm^{-1} is for uncomplexed perchlorate.

red solution quickly cooled to 0° by the addition of ice. Reddish orange $[\text{Cr}(\text{NH}_3)_5\text{SO}_4]^+$ was separated from other products by ion exchange using an ice-cooled Dowex 50W-X12 (200–400 mesh) resin. The complex was the second of three bands observed and was separated from the other products using $0.5 M \text{HClO}_4$ as eluent until the band is 3 cm from the bottom of the column, and $2 M \text{HClO}_4$ thereafter. The absence of free sulfate in the eluent was confirmed before the sulfato species was collected. Addition of absolute ethanol to the eluent fraction resulted in the deposition of small reddish orange crystals of the desired product. Determination of the ammonia:chromium ratio gave 4.94:1 (average value) in accordance with the formulation $[\text{Cr}(\text{NH}_3)_5\text{SO}_4](\text{ClO}_4)$. *Anal.* Calcd for $[\text{Cr}(\text{NH}_3)_5\text{SO}_4](\text{ClO}_4)$: N, 21.0; Cl, 10.5; Cr, 15.6. Found: N, 20.3; Cl, 10.4; Cr, 15.4.

Preparation of Iodatopentaamminechromium(III). A saturated solution of sodium iodate (2 ml) at 50° containing a few crystals of iodic acid was saturated with $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$. The resultant deep red solution was rapidly cooled in an ice bath and the light red-violet powder which precipitated was filtered off, washed with ethanol and ether, and dried quickly by suction. The complex was stored over silica gel in a desiccator. Dissolution of the iodato complex in aqueous acidic media resulted in re-formation of the aquo species. Diffuse-reflectance spectra recorded for the iodato complex gave λ_{max} 383 and 529 nm and λ_{min} 437 nm; the shift to longer wavelength regions was as expected from other studies on the complexing of iodate with $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ in aqueous solution.⁹ The ir spectrum of the iodato complex, Figure 2, in the region $400\text{--}900 \text{ cm}^{-1}$ is different from that obtained for ionic iodate. The sample contains perchlorate anions (band at 625 cm^{-1}) although it is predominantly an iodate salt. The splitting of the iodate bands is as expected for the change in symmetry from C_{3v} to C_s expected for coordination of the iodate through an oxygen atom. Attempts to remove the remaining perchlorate ion using nonaqueous solvents were unsuccessful.¹⁰

Attempts to Prepare Other Iodato Complexes. The first report of an iodato complex was that by Duval⁴ in 1932. The complex, formulated as $[\text{Co}(\text{NH}_3)(\text{IO}_3)(\text{IO}_3)_2\text{-HIO}_3]$, was prepared by the reaction of iodic acid with $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$. A subsequent investigation of cobalt ammine iodate complexes by Lobanov⁵ suggested that, although iodic acid adducts are readily formed, coordination of iodate to $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ does not occur extensively in aqueous solution and precipitation of iodate salts results. Our own studies support this view. The ir spectrum reported by Duval, *et al.*,¹¹ is of little use in deciding whether the iodate is in fact coordinated to cobalt(III), since of the four frequencies quoted only one lies in the

Table I. Formula of Duval Compound by Elemental Analyses

	% Co	% I	% NH ₃
Found for Duval ^a complex	6.94	58.6–58.3	9.98
Calcd for [Co(NH ₃) ₅ IO ₃](IO ₃) ₂ ·HIO ₃	6.98	60.1	10.1
Calcd for [Co(NH ₃) ₅ H ₂ O](IO ₃) ₃ ·HIO ₃	6.83	58.8	9.85

^a See ref 4.

region expected for iodate. In view of this and the analytical data presented by Duval, Table I, we do not favor the original formulation containing a coordinated iodate and suggest a possible alternative [Co(NH₃)₅H₂O](IO₃)₃·HIO₃.

Lobanov^{5,12} has reported that the iodato complexes [Co(NH₃)₅IO₃](IO₃)₂ and [Co(NH₃)₄(H₂O)(IO₃)](IO₃)₂ are formed by heating the iodate salts of [Co(NH₃)₅H₂O]³⁺ and [Co(NH₃)₄(H₂O)]³⁺, respectively, at 130° for 4–5 hr. The iodate salts of the aquo complexes were prepared using the method of Lobanov⁵ and the complexes [Co(NH₃)₅H₂O](IO₃)₃·xH₂O and [Co(NH₃)₄(H₂O)](IO₃)₃·yH₂O maintained at 130° for 4–5 hr. A loss in weight equivalent to 3H₂O was observed in both cases, as well as slight but perceptible color change (as reported by Lobanov), but ir spectra showed no change 250–2500 cm⁻¹ from those recorded before heating. Since Lobanov assumed that both complexes were prepared as dihydrates (*i.e.*, *x* = *y* = 2), the additional loss in weight after the removal of these two waters of crystallization was attributed to the loss of a coordinated water molecule and the subsequent coordination of iodate.

Dehydration of the hydrated complexes over P₂O₅ gave weight losses¹⁰ consistent with *x* = 2 and *y* = 3. The three water molecules lost in the tetraammine case are waters of hydration; since no change in ir spectrum is observed, the inner-coordination sphere must remain intact. With the pentaammine complex it is possible that hydrogen bonding between iodate and water molecules in the lattice could result in the latter being more strongly held and therefore requiring more severe conditions for their loss. Thus, Lobanov has reported that the third water molecule is removed from the hydrated iodate salt of [Co(NH₃)₅H₂O]³⁺ with more difficulty than the others. We conclude that *x* and *y* are 3 and that in the heating experiments only waters of crystallization are lost from both iodate salts. At higher temperatures more drastic decomposition is observed.

Infrared Spectra. The spectrum of [Cr(NH₃)₅C₂O₄H](ClO₄)₂, Figure 1, shows a doublet at 1780 and 1765 cm⁻¹ which can be assigned to the asymmetric stretching frequency of a free carboxylate group. The bands at 1705, 1685, and 1400 cm⁻¹ are characteristic of asymmetric ν_7 (C=O) and ν_1 (C=O) and symmetric ν_2 (C=O), respectively.¹³ For [Cr(NH₃)₅(O₂CCH₂NH₃)](ClO₄)₃ bands at 1660 and 1380 cm⁻¹ can be assigned to the frequencies ν_{as} (C=O) and ν_2 (C=O), respectively,¹⁴ and are indicative of carboxyl group coordination. The complex [Cr(NH₃)₅SO₄](ClO₄) crystallized from the ion-exchange eluent gave an ir spectrum, Figure 1, with bands at 1040, 975, and 625 cm⁻¹ which could be assigned to the frequencies ν_3 (S=O), ν_1 (S=O), and ν_4 (S=O), respectively.¹⁵ Unfortunately the unidentate nature of the ligand in this complex could not be inferred directly from the ir spectrum since the splittings of the ν_3 (S=O) band have been overlapped by perchlorate ion vibrations.

The ir spectrum recorded for [Cr(NH₃)₅IO₃]²⁺ in dry Nujol is illustrated in Figure 2. An identical but less resolved spectrum was obtained using a KBr disk. The spectrum for ionic iodate in a similar environment is reproduced for comparison. The pyramidal IO₃⁻ ion has C_{3v} molecular symmetry and coordination through the iodine atom would preserve the symmetry of the free ion. It is therefore apparent that the iodate is coordinated through the oxygen atom, as expected, the result of which is a lowering in symmetry from C_{3v} to C_s and a lifting of the degeneracy of the ν_3 and ν_4 stretching vibrations.¹⁶ The presence of uncomplexed perchlorate is indicated by the band at 625 cm⁻¹, but vibrations in the region expected for iodate are indicative of C_{3v} → C_s splitting. Since the majority of the counteranions to the complex are iodate, the presence of ionic iodate is still manifest in the spectrum. Dasent and Waddington¹⁷ in their study on the ir spectra of metal iodates and related compounds have suggested that the extra bands observed in the region 420–480 cm⁻¹ may be due to the metal–oxygen vibration. In this context it is interesting to note that a distinct band, which is not present for ionic iodate, is observed at 455 cm⁻¹ in the spectrum of [Cr(NH₃)₅IO₃]²⁺ and may be tentatively assigned to the chromium–oxygen vibration.

UV-Visible Spectra. Details for the new carboxylato complexes

Table II. Special Details for Carboxylato Complexes, [Cr(NH₃)₅X]⁽³⁻ⁿ⁾⁺

X ⁿ⁻	λ_{max} , nm	ϵ_{max} , l. mol ⁻¹ cm ⁻¹	λ_{max} , nm	ϵ_{max} , l. mol ⁻¹ cm ⁻¹	Ref
CH ₃ CO ₂ ⁻	367	32.8	494	52.9	a
HC ₂ O ₄ ⁻	362	34.0	486	51.6	b
CH ₂ ClCO ₂ ⁻	360	32.7	483	50.3	c
CHCl ₂ CO ₂ ⁻	361	35.7	483	52.4	c
CCl ₃ CO ₂ ⁻	362	34.6	486	50.8	c
NH ₃ ⁺ CH ₂ CO ₂ ⁻	363	33.7	488	49.4	b
NH ₃ ⁺ CH ₂ CH ₂ CO ₂ ⁻	365	31.9	488	49.0	d
HIDA ^e	362	33.3	482	28.9	d

^a E. Zinato, R. Lindholm, and A. W. Adamson, *J. Inorg. Nucl. Chem.*, **31**, 449 (1969). ^b This work. ^c Reference 3. ^d T. Ramasami, unpublished work. ^e H₂IDA = iminodiacetic acid.

Table III. Rate Constants (*k*_{obsd}) at 45° for the Chelation of Oxalate in Pentaammineoxalatochromium(III), *I* = 1.0 M (LiClO₄)

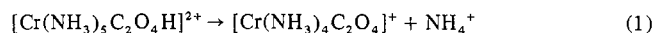
[H ⁺], M	10 ³ [complex], M	10 ⁴ · <i>k</i> _{obsd} , sec ⁻¹	[H ⁺], M	10 ³ [complex], M	10 ⁴ · <i>k</i> _{obsd} , sec ⁻¹
0.015	0.42	5.84	0.10	1.53	2.96
0.02	0.47	5.52	0.15	4.18	2.72
0.03	0.71	4.55	0.20	1.46	2.54
0.05	0.77	3.67	0.20	3.06	2.57

are listed in Table II. Remarkable similarities with regard to peak positions 364 ± 4 and 488 ± 6 nm and absorption coefficients 34 ± 2 and 51 ± 2 l. mol⁻¹ cm⁻¹, respectively, are noted.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer by means of KBr disks or Nujol mull. Kinetic runs were followed using a Unicam SP500 fitted with thermostated cell housing. A Radiometer pH meter, Type 4, with Radiometer glass (Type G202B) and calomel (Type K401) electrodes, was used for the pH measurements. The diffuse-reflectance spectrum was recorded on an SP700A scanning spectrophotometer using a white card as reference. A micro Kjeldahl apparatus similar to that described by House¹⁸ was used in the ammonia determinations. Chromium estimations were made by oxidation of the chromium(III) to chromium(VI) using hydrogen peroxide in alkaline solution, the chromium(VI) being determined spectrophotometrically at 372 nm using an absorption coefficient for chromate (CrO₄²⁻) in 1 M NaOH of 4.82 × 10³ l. mol⁻¹ cm⁻¹.

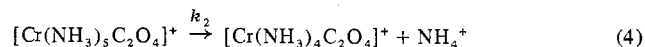
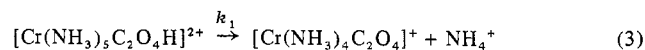
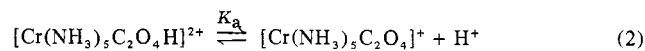
Results

Reactions of [Cr(NH₃)₅C₂O₄H]²⁺ in Solution. The complex reacts to give [Cr(NH₃)₄C₂O₄]⁺ (eq 1) which is well char-



acterized.^{19,20} The kinetics of (1) were studied at 45°, *I* = 1.0 M (LiClO₄), with [H⁺] in the range 0.015–0.2 M. At the wavelength used to follow the reaction, 373 nm, the absorption coefficients of the monodentate and bidentate oxalato complexes are 28.0 ([H⁺] = *ca.* 0.2 M) and 73.0 l. mol⁻¹ cm⁻¹, respectively. Since secondary processes involving further loss of ammonia occur before the completion of (1), it was necessary to use calculated values of the final absorbance *A*_∞. First-order plots of log (*A*_∞ - *A*_{*t*}) against time (*t*) were linear to 80–90% completion, and from the slopes (×2.303) values of the rate constant *k*_{obsd}, Table III, were evaluated.

The reaction sequence (2)–(4) gives the dependence (5).



$$k_{\text{obsd}} = \frac{k_1[\text{H}^+] + k_2K_a}{[\text{H}^+] + K_a} \quad (5)$$

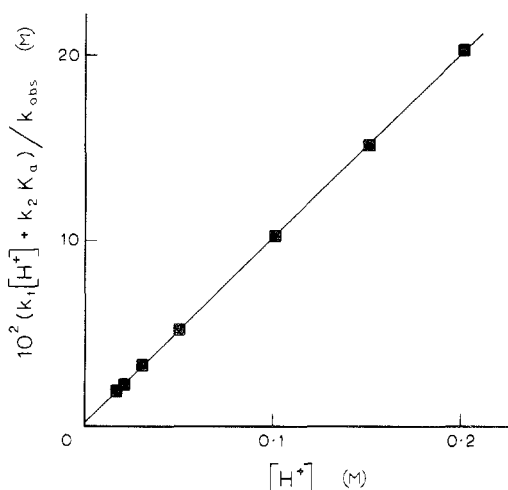


Figure 3. Dependence of $(k_1[H^+] + k_2K_a)/k_{\text{obsd}}$ on $[H^+]$ for the chelation of oxalate in pentaammineoxalatochromium(III), eq 6, at 45° and $I = 1.0 M$ (LiClO_4).

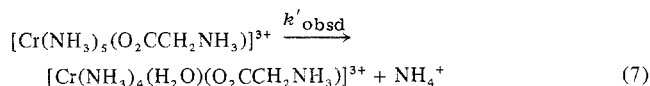
Assuming $[H^+] \gg K_a$, plots of k_{obsd} against $[H^+]^{-1}$ give some curvature but clearly indicate a positive intercept $(2.2 \pm 0.07) \times 10^{-4} \text{ sec}^{-1}$ corresponding to an $[H^+]$ -independent pathway (k_1). The slope gives k_2K_a . Equation 5 can be rearranged to eq 6. Plots of the left-hand side of (6) against $[H^+]$ are

$$\frac{k_1[H^+] + k_2K_a}{k_{\text{obsd}}} = K_a + [H^+] \quad (6)$$

linear, Figure 3. From the intercept $K_a = (2.3 \pm 0.8) \times 10^{-3} M$ at 45° , $I = 1.0 M$ (LiClO_4). Hence from a least-mean-squares treatment with weighting unity $k_2 = (3.47 \pm 1.25) \times 10^{-3} \text{ sec}^{-1}$. Errors are large in both cases because the intercept is small. The value for K_a is of the same order of magnitude as that reported²¹ for $[\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{H}]^{2+}$ ($8.8 \times 10^{-3} \text{ mol l}^{-1}$ at 25°).

Details of the complexing of oxalate to $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ ($8.3 \times 10^{-3} M$) were confirmed at $[H^+] = 1.0 \times 10^{-3} M$ and 50° with $0.1 M$ oxalate. Under these conditions the release of ammonia as determined by the micro Kjeldahl technique after ion-exchange separation of reactant solutions parallels the conversion of $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ to $[\text{Cr}(\text{NH}_3)_4\text{C}_2\text{O}_4]^+$ as monitored spectrophotometrically ($\lambda 389 \text{ nm}$, $\epsilon 58 \text{ l. mol}^{-1} \text{ cm}^{-1}$) for 30% of the reaction (see comments in ref 20 regarding the incidence of secondary reactions), Table IV. The rate constant of $(1.2 \pm 0.3) \times 10^{-4} \text{ sec}^{-1}$ is in satisfactory agreement with the value $0.98 \times 10^{-4} \text{ sec}^{-1}$ previously reported.²⁰ Thus at $[H^+] = 1.0 \times 10^{-3} M$ and with $0.1 M$ oxalate there is no significant buildup of $[\text{Cr}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{H}]^{2+}$ or of another possible intermediate, $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{C}_2\text{O}_4\text{H}]^{2+}$. Reaction proceeds mainly *via* k_2 in (4), which for the conditions specified is an order of magnitude faster than the rate of oxalate entry into the coordination sphere of $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ ($3.0 \times 10^{-4} \text{ sec}^{-1}$ at 45°).²²

Reaction of $[\text{Cr}(\text{NH}_3)_5(\text{O}_2\text{CCH}_2\text{NH}_3)]^{3+}$ in Solution. Aquation of ammonia ligands as in (7) is observed in aqueous



solution with $[H^+] > 10^{-2} M$, and chelation of the glycine is not evident. We consider first the evidence for this assignment.

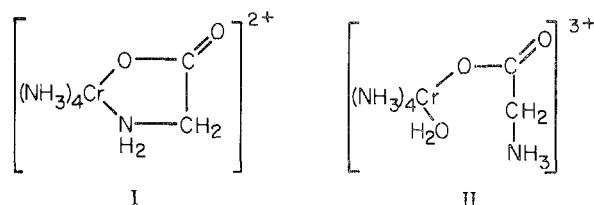
The spectrum of the principal product (>ca. 90%) from the aquation of $[\text{Cr}(\text{NH}_3)_5(\text{O}_2\text{CCH}_2\text{NH}_3)]^{3+}$ following ion-exchange separation of the products is the same as that obtained from the reaction of glycine with $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ or *cis*- $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$. The ammonia:chromium and

Table IV. The Reaction of Oxalate ($0.1 M$) with $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ ($7.8 \times 10^{-3} M$) at 50° and $[H^+] = 1.0 \times 10^{-3} M$, $I = 1.0 M$ (NaClO_4)

Time, min	Ammonia released/ chromium- (III), ^a %	Formation of $[\text{Cr}(\text{NH}_3)_4\text{C}_2\text{O}_4]^{+}$, ^b %
10	7.96	8.0
20	15.1	14.7
30	19.3	18.7
50	26.2	26.1

^a Determined using the micro Kjeldahl technique. ^b Concentration determined by chromate analysis after ion-exchange separation. Identity of the product was confirmed by uv-visible spectrophotometry ($\epsilon 58 \text{ l. mol}^{-1} \text{ cm}^{-1}$ at $\lambda 389 \text{ nm}$ for $[\text{Cr}(\text{NH}_3)_4(\text{C}_2\text{O}_4)]^{+}$).

total nitrogen:chromium ratios obtained for the main reaction products (see Experimental Section) agree within experimental error. Estimation of the charge on the species using the method of Cady and Connick²³ yielded a value of 2.73 and confirmed structure II rather than I. Addition of sodium nitrite to the



reaction product resulted in the formation of a nitrito complex (for details see preparation in Experimental Section), also indicating the presence of an aquo ligand in the starting material, since nitrite does not directly displace ammonia ligands.²⁴ Further evidence was provided by titration of the species with base which indicated the presence of a group with $pK_a \approx ca. 4.2$. Other attempts to obtain I were unsuccessful. It is concluded that chelation is not a favored process when the amine group of the glycine is protonated.

The kinetics of the aquation of ammonia from the monodentate glycinate complex were studied as a function of temperature at 550 nm , $I = 1.0 M$ (LiClO_4), $[H^+] = 0.01\text{--}0.5 M$. At this wavelength absorption coefficients for $[\text{Cr}(\text{NH}_3)_5(\text{O}_2\text{CCH}_2\text{NH}_3)]^{3+}$ and $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{O}_2\text{CCH}_2\text{NH}_3)]^{3+}$ are 9.6 and $24.0 \text{ l. mol}^{-1} \text{ cm}^{-1}$, respectively. Owing to secondary processes it was necessary to use calculated values of A_∞ corresponding to the completion of (7). First-order plots of $\log(A_\infty - A_t)$ against time (t) were linear to 70–80% with $[H^+] > 0.01 M$; deviations thereafter and nonlinearity at lower $[H^+]$ values are due to secondary processes. Values of k'_{obsd} , which were independent of $[H^+]$ over the range $0.01\text{--}0.5 M$, were calculated from the slopes of the linear portions of such plots and are listed in Table V. From the temperature dependence of k'_{obsd} , $\Delta H^\ddagger = 24.2 \pm 0.2 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -1.3 \pm 0.7 \text{ cal K}^{-1} \text{ mol}^{-1}$. The latter are similar to values obtained for ammonia loss from the complexes $[\text{Cr}(\text{NH}_3)_5(\text{O}_2\text{CR})]^{3+}$ ($R = \text{CH}_2\text{Cl}, \text{CHCl}_2$), Table VI. Quantitative estimates of the ammonia released over a 30-min period from a solution of $[\text{Cr}(\text{NH}_3)_5(\text{O}_2\text{CCH}_2\text{NH}_3)]^{3+}$ at 25° , with $[H^+]$ initially adjusted to $1.0 \times 10^{-4} M$, indicated that the rate of ammonia loss was about an order of magnitude faster than that observed in the range $[H^+] = 0.01\text{--}0.5 M$. Similar effects are apparent for other pentaamminechromium(III) complexes with nitrate and acetate as ligands. At 25° and $[H^+] = 1.0 \times 10^{-4} M$ the amount of ammonia lost per chromium(III) during 30 min was 18.4% with $8.3 \times 10^{-3} M$ $[\text{Cr}(\text{NH}_3)_5(\text{O}_2\text{CCH}_2\text{NH}_3)]^{3+}$ (final $[H^+] < 10^{-5} M$).

Reactions of $[\text{Cr}(\text{NH}_3)_5\text{SO}_4]^{3+}$ in Solution. Ammonia ligands are released and quantitative estimates at $[H^+] = 1.0 \times 10^{-2} M$ indicated 33% of ammonia per chromium atom over a period of 30 min at 25° . This figure suggests that the rate of ammonia

Table V. Rate Constants (k_{obsd}) for the Loss of Ammonia from the $[\text{Cr}(\text{NH}_3)_5(\text{O}_2\text{CCH}_2\text{NH}_3)]^{2+}$, $I = 1.0 M$ (LiClO_4)

Temp, °C	$[\text{H}^+], M$	$10^3 [\text{complex}], M$	$10^4 k'_{\text{obsd}}, \text{sec}^{-1}$
40	0.1	2.18	0.44
45	0.01	2.18	0.82
	0.1	4.51	0.82
	0.2	2.18	0.84
	0.5	2.18	0.84
50	0.01	2.18	1.45
	0.2	2.18	1.48
	0.5	2.18	1.41
55	0.01	2.18	2.81
	0.1	2.18	2.77
60	0.01	2.18	4.94
	0.1	2.21	4.87
	0.1	5.52	4.82
	0.5	2.18	4.85

Table VI. Comparison of Activation Parameters for Ammonia Loss from Pentaamminechromium(III) Complexes Containing Monodentate Carboxylate Ligands

Ligand	$\Delta H^\ddagger, \text{kcal mol}^{-1}$	$\Delta S^\ddagger, \text{cal K}^{-1} \text{mol}^{-1}$	Ref
$\text{NH}_3^+\text{CH}_2\text{CO}_2^-$	24.2 ± 0.24	-1.31 ± 0.7	This work
$\text{CH}_2\text{ClCO}_2^-$	25.3 ± 0.5	4.8 ± 1.7	3
$\text{CHCl}_2\text{CO}_2^-$	24.7 ± 0.6	0.9 ± 2.0	3

loss is comparable to that for $[\text{Cr}(\text{NH}_3)_5(\text{O}_2\text{CCH}_3)]^{2+}$ under similar conditions. Visible scan spectra indicated that subsequent reactions of $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{SO}_4)]^+$ are incident at an early stage. We were unable to isolate the primary product.

Reactions of $[\text{Cr}(\text{NH}_3)_5\text{IO}_3]^{2+}$ in Solution. A rapid equilibration of $[\text{Cr}(\text{NH}_3)_5\text{IO}_3]^{2+}$ to give $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ and iodate without rupture of the metal-oxygen bond is observed.^{9,25} Solutions of the iodato complex were prepared *in situ* by the addition of an excess of the oxy anion to $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$. Quantitative estimates of ammonia loss from solutions of $[\text{Cr}(\text{NH}_3)_5\text{IO}_3]^{2+}$ were made in two runs at 25°, with $[\text{H}^+] = 1.0 \times 10^{-4} M$ (initially), $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} = 8.3 \times 10^{-3} M$, and $[\text{IO}_3^-] = 0.1$ and $0.15 M$, respectively. The ammonia released per total chromium(III) over a period of 30 min was 11 and 15%, respectively. Under these conditions *ca.* 50 and 75% of the $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ is present as $[\text{Cr}(\text{NH}_3)_5\text{IO}_3]^{2+}$.

Formation and Stability of Other Complexes. Rapid complexing with $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ is also observed on addition of excess sulfite ($t_{1/2} < 5$ msec at 25°, $[\text{H}^+] = 10^{-3} M$) and selenite. Solutions of $[\text{Cr}(\text{NH}_3)_5\text{SO}_3]^+$ and $[\text{Cr}(\text{NH}_3)_5\text{SeO}_3]^+$ were prepared *in situ* and the loss of ammonia was determined at 25°.

With sulfite an experiment was carried out in which the ammonia released was determined at intervals, Table VII. Reactant concentrations were $[\text{SO}_3^{2-}] = 0.1 M$, $[\text{NaClO}_4] = 0.1 M$, and $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} = 8.3 \times 10^{-3} M$. The pH was monitored throughout and was maintained in the region 3.01–3.20 by the addition of small increments of $0.5 M \text{HClO}_4$. It appears from the data that one ammonia per chromium atom is labilized initially. However other processes occur and cation-exchange separation of the products indicated a number of products. There was no evidence for a product containing chelated sulfite, *e.g.*, $[\text{Cr}(\text{NH}_3)_4\text{SO}_3]^+$, and one of the products may be a disulfite complex. For reaction times in excess of *ca.* 90 min there was evidence for the buildup of a dimeric chromium(III) species.

Quantitative estimation of the ammonia lost from a solution of $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ ($8.3 \times 10^{-3} M$), containing $0.1 M \text{Na}_2\text{SeO}_3$ maintained at 25° and having an initial $[\text{H}^+]$ of $1.0 \times 10^{-4} M$, indicated the release of only <3% of ammonia per chromium(III).

Table VII. Loss of Ammonia $[\text{Cr}(\text{NH}_3)_5\text{SO}_3]^+$ (*ca.* $8 \times 10^{-3} M$) at 25°, $[\text{Na}_2\text{SO}_3] = 0.1 M$ and $[\text{NaClO}_4] = 0.1 M^a$

Time, min	Ammonia released/ $\text{Cr(III)},^b \%$	Time, min	Ammonia released/ $\text{Cr(III)},^b \%$
30	16	200	84
60	30	240	94
90	47	300	97
150	71		

^a The pH was maintained in the range 3.01–3.20 by the addition of $0.5 M$ perchloric acid as the reaction proceeded. ^b Determined using the micro Kjeldahl technique. Average values from two runs are given.

Contrary to the statement in ref 2 and in agreement with other reports²⁶ we observe significant decomposition of $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ at pH 4 and 6 over a 30-min period. The change in spectrum at 25° for a run with $8.3 \times 10^{-3} M$ complex and initial pH 4.0 is substantial and determination of the ammonia lost per chromium(III) over a period of 30 min gave a value of 7% indicating the effectiveness of hydroxide ligand labilization ($\text{p}K_a$ for $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ is *ca.* 5.2^{27,28} and only *ca.* 10% of the hydroxo form is present at any one time). Solutions of the aquo complex adjusted to pH 6 exhibited rapid color changes to the red-violet hydroxo form and the rate of ammonia loss under these conditions is rapid. The pH was monitored for a typical run at 25° and $[\text{NaClO}_4] = 0.1 M$ and showed a steady increase with time until after 35 min a pH of 8.2 was reached and precipitation of a light green solid (probably hydrated chromium(III) hydroxide²⁹) occurred.

Guastalla and Swaddle² have reported a relatively rapid loss of ammonia from $[\text{Cr}(\text{NH}_3)_5\text{NO}_3]^{2+}$ at pH 6 and 25°. At pH 4 and 25° we observe 79% of the 1:1 (*i.e.*, per chromium(III)) ammonia loss; $[\text{Cr}(\text{NH}_3)_5\text{NO}_3]^{2+} = 8.3 \times 10^{-3} M$, which is in keeping with their results.

Discussion

Difficulties which are experienced in isolating iodato complexes stem from the high lability of the iodate.^{9,30} The procedure described for the isolation of $[\text{Cr}(\text{NH}_3)_5\text{IO}_3]^{2+}$ makes use of the rapid complexing of iodate with aquometal ions which occurs with the retention of the metal-oxygen bond.⁹ The reaction is extensive when high concentrations of $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ and iodate are used. We have not been able to repeat the preparations of $[\text{Co}(\text{NH}_3)_5\text{IO}_3](\text{IO}_3)_2$ and $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{IO}_3)](\text{IO}_3)_2$ as described by Lobanov⁵ and seriously question the approach used by Duval.³¹ No other preparations of pentaammine complexes with coordinated iodate have been reported. Lobanov³² has also reported that the complex $[\text{Co}(\text{NH}_3)_3(\text{IO}_3)_3] \cdot \text{H}_2\text{O}$ may be prepared by the addition of iodate to an aqueous solution of $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]^{3+}$. The ir spectrum of this iodato complex³³ in the region 400–900 cm^{-1} is similar to that recorded for $[\text{Cr}(\text{NH}_3)_5\text{IO}_3]^{2+}$. Furthermore, since the one water of crystallization may be easily removed with no change in the resultant ir spectrum,³³ the presence of coordinated iodate is confirmed.

Processes involving loss of ammonia make preparation of complexes $\text{Cr}(\text{NH}_3)_5\text{X}^{(3-n)+}$ with $\text{X}^{n-} = \text{oxalate}$, glycinate, and sulfate more difficult. The aquation of ammonia from complexes *cis*- and *trans*- $[\text{Cr}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^{3+}$, $[\text{H}^+] = 0.5$ – $1.0 M$, has recently been studied^{34,35} and rate constants at 70° are in the range $(1.1$ – $17.6) \times 10^{-6} \text{sec}^{-1}$.³⁴ No special effects appear to be operative in these reactions, unlike those now to be considered.

The kinetic behavior observed for the chelation of oxalate in $[\text{Cr}(\text{NH}_3)_5\text{C}_2\text{O}_4]^+$ is entirely consistent with a previous study²⁰ reporting the complexing of oxalate with $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$. The latter was studied at $[\text{H}^+] = 10^{-3}$ – $10^{-4} M$ under which conditions the monodentate oxalato complex

is a transient intermediate, and release of ammonia parallels the formation of $[\text{Cr}(\text{NH}_3)_4\text{C}_2\text{O}_4]^+$ from spectrophotometric measurements, Table IV. It is concluded that under these conditions the chelation step occurs relatively rapidly with the displacement of ammonia. At $[\text{H}^+]$ values $>10^{-2} M$ the chelating arm of the oxalate in $[\text{Cr}(\text{NH}_3)_5(\text{C}_2\text{O}_4)]^+$ becomes protonated and rate constants for the conversion to $[\text{Cr}(\text{NH}_3)_4(\text{C}_2\text{O}_4)]^+$, Table III, are slower. Clearly one mode of ammonia loss from chromium(III)-ammine complexes is that observed when chelate ring formation occurs. We note that the cobalt(III) complexes $[\text{Co}(\text{NH}_3)_5(\text{C}_2\text{O}_4)]^+$ and $[\text{Co}(\text{NH}_3)_4(\text{C}_2\text{O}_4)]^+$ are both well characterized³⁶ but that conversion of $[\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4]^+$ to $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]^+$ with displacement of ammonia does not occur readily. The difference in behavior is most likely attributable to the preference which chromium(III) often exhibits for substitution by an $\text{S}_\text{N}2$ mechanism.³⁷ Pentaamminecobalt(III) complexes have been shown to undergo substitution by an $\text{S}_\text{N}1$ mechanism,³⁸ although when chelation can occur it has been suggested that here also some $\text{S}_\text{N}2$ character may prevail.³⁹

The cobalt(III) complex $[\text{Co}(\text{NH}_3)_5(\text{O}_2\text{CCH}_2\text{NH}_3)]^{3+}$ is known⁴⁰ to have an acid dissociation constant of $3.16 \times 10^{-9} \text{ l. mol}^{-1}$ and by analogy the glycinate ligand in $[\text{Cr}(\text{NH}_3)_5(\text{O}_2\text{CCH}_2\text{NH}_2)]^{2+}$ is expected to be extensively protonated over the $[\text{H}^+]$ range investigated. It is not surprising therefore that chelation in the case of the glycine complex is not favored. Instead aquation of an ammonia ligand is observed with no dependence on $[\text{H}^+]$ in the range 0.01–0.50 *M*. This effect is as reported³ for pentaamminechromium(III) complexes containing acetate and substituted acetate (with the exception of trifluoroacetate) as ligands. With carbonate a "cartwheel" rotation of the ligand is envisaged to explain the carbonate-catalyzed oxygen exchange of $[\text{Cr}(\text{NH}_3)_5\text{OH}]^{2+}$ with solvent water²⁶ and catalyses by CO_2 of substitution at chromium(III).⁴¹ A not too dissimilar process of transient chelation of the acetate ligand, when this is sufficiently basic, can be envisaged to account for ammonia loss. Olson⁴² has identified the same labilizing effect of acetate in the reaction of $[\text{Cr}(\text{H}_2\text{O})_5\text{O}_2\text{CCH}_3]^{2+}$ with EDTA and proposed the term anchimeric cis effect. Sulfate, as well as nitrate² and nitrite,²⁴ most likely labilize cis ammonias in a similar way. It is apparent that the acidity of the medium reduces the effectiveness of sulfate to labilize ammonias and in 3 *M* perchloric acid aquation of the sulfate also occurs with the formation of $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ which crystallizes from solution.

An alternative explanation of the ammonia labilization so far considered is similar to that proposed by Zinato and coworkers³ following their studies on $[\text{Cr}(\text{NH}_3)_5\text{O}_2\text{CCH}_3]^{2+}$ and related complexes. According to their interpretation hydrogen bonding between the carbonyl oxygen of the carboxylate and a cis ammonia weakens the chromium–ammonia bond. Following Olson's⁴² lead we suggest instead that for this mechanism to be effective the chromium–nitrogen bond has to be strengthened and that labilization results in much the same way as in the conjugate-base mechanism. This mechanism is indirectly supported by the fact that an $[\text{H}^+]^{-1}$ dependence is observed for the aquation of ammonia ligands in complexes of the type $[\text{Cr}(\text{NH}_3)_5\text{X}]^{(3-n)+}$, e.g., $\text{X}^{n-} = \text{O}_2\text{CCH}_2\text{R}$ ($\text{R} = \text{CH}_3, \text{CH}_2\text{Cl}, \text{CHCl}_2$) and $\text{O}_2\text{CCH}_2\text{NH}_3^+$ at $[\text{H}^+] < 10^{-2} M$. Other examples of hydrogen bonding between carboxylate and ammonia ligands have been reported in X-ray crystallographic studies.⁴³ This mechanism could also apply for complexes where X^{n-} is not a carbonyl-containing ligand, since most of the anions which have been reported to labilize ammonia ligands in pentaamminechromium(III) complexes are capable of participating in hydrogen-bond formation, viz., $\text{X} = \text{ONO}^-$ and SO_4^{2-} . The behavior of nitrate is more difficult to account for since it has no basic properties,

and strong hydrogen-bonding giving rise to ammonia labilization is difficult to envisage. On balance we are inclined to attribute the ammonia labilization to the $\text{S}_\text{N}2$ character of the substitution, but we do not exclude effects arising from hydrogen bonding.

Ammonia loss is observed from $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ at $\text{pH} > 4$ and is attributable to the formation of the conjugate base $[\text{Cr}(\text{NH}_3)_5\text{OH}]^{2+}$. Labilization of the ammonias is believed to result from the nature of the bonding of the hydroxide to the metal. Sulfite, like iodate, readily complexes with $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ with retention of the metal–oxygen bond. Subsequent ammonia loss is observed which may be attributable to either of the mechanisms previously considered. Alternatively it is possible that the principal effect is similar to that observed for $[\text{Co}(\text{NH}_3)_5\text{SO}_3]^+$ ⁴⁴ and other cobalt(III) complexes^{45–47} where the sulfite ligand exerts a trans-labilizing effect. The reaction in the case of $[\text{Co}(\text{NH}_3)_5\text{SO}_3]^+$ is unusually rapid ($t_{1/2} = \text{ca. } 1 \text{ min}$ at 25° in acidic solution).⁴⁴ The effect observed for chromium(III) is much less dramatic but may originate in the same manner. Thus isomerization to the S-bonded form may be invoked and the lability results from π bonding of the sulfur atom to the metal (this may be particularly effective due to the similarities of sulfur and metal orbitals). No clear-cut labilizing effect is observed for solutions containing selenite and iodate complexes, and ammonia loss which is observed may result from the presence of $[\text{Cr}(\text{NH}_3)_5\text{OH}]^{2+}$. The absence of an effect here may be due in part to the increased size of the iodine and selenium atoms preventing any of the mechanisms so far considered from operating.

Finally, it has been reported²⁵ that in solution free nitrate (1.5 *M*) and, to a lesser extent, sulfate labilize ammonia ligands of $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$. It seems unlikely that the anions are effective from the outer-coordination sphere and a mechanism in which inner-sphere complexing precedes ammonia loss provides a more satisfactory explanation. It has also been observed that at $[\text{H}^+] = \text{ca. } 10^{-3} M$ free oxalate does not react directly with $[\text{Cr}(\text{NH}_3)_6]^{3+}$ or $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ and that slow aquation to form the aquo complex precedes coordination of the oxalate ligand.⁴⁸

In conclusion, it is apparent that the loss of ammonia from chromium(III)-ammine complexes may be considered in different categories. The effect with $[\text{Cr}(\text{NH}_3)_5(\text{C}_2\text{O}_4)]^+$ is clearly the result of the readiness with which chelate ring formation occurs. The labilization of ammonia by glycine, acetate (and substituted acetates), nitrate, nitrite, sulfate, and sulfite could be the result of transient chelation and/or hydrogen bonding. The effect with hydroxide on the other hand is best explained in terms of the bonding of the OH^- ligand to the metal.

Acknowledgment. T. R. is grateful to the Government of India for the award National Merit Scholarship and R. K. W. to the University of Leeds for the award of a Henry Ellison Fellowship.

Registry No. $[\text{Cr}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{H}](\text{ClO}_4)_2$, 53229-26-8; $[\text{Cr}(\text{NH}_3)_5(\text{O}_2\text{CCH}_2\text{NH}_3)](\text{ClO}_4)_3$, 53229-29-1; $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{O}_2\text{CCH}_2\text{NH}_3)](\text{ClO}_4)_3$, 53229-32-6; $[\text{Cr}(\text{NH}_3)_4(\text{ONO})(\text{O}_2\text{CCH}_2\text{NH}_3)](\text{ClO}_4)_2$, 53229-35-9; $[\text{Cr}(\text{NH}_3)_5\text{SO}_4](\text{ClO}_4)$, 53229-37-1; $[\text{Cr}(\text{NH}_3)_5\text{IO}_3]^{2+}$, 52843-02-4; $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$, 32700-25-7; *cis*- $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2](\text{ClO}_4)_3$, 41733-15-7; glycine, 56-40-6; $[\text{Cr}(\text{NH}_3)_5\text{SO}_3]^+$, 53229-38-2.

References and Notes

- C. S. Garner and D. A. House, *Transition Metal Chem.*, **6**, 59 (1970).
- G. Guastalla and T. W. Swaddle, *J. Chem. Soc., Chem. Commun.*, **61** (1973); *Can. J. Chem.*, **52**, 527 (1974).
- E. Zinato, C. Furlani, G. Lanna, and P. Ricciardi, *Inorg. Chem.*, **11**, 1746 (1972).
- R. Duval, *Ann. Chim. (Paris)*, [10] **18**, 241 (1932).

- (5) N. I. Lobanov, *Russ. J. Inorg. Chem.*, **4**, 151 (1959).
 (6) M. Mori, *Inorg. Syn.*, **5**, 132 (1957).
 (7) D. W. Hoppenjans and J. B. Hunt, *Inorg. Chem.*, **8**, 505, (1969).
 (8) W. W. Fee, C. S. Garner, and J. N. MacB. Harrowfield, *Inorg. Chem.*, **6**, 87 (1967).
 (9) R. K. Wharton, R. S. Taylor, and A. G. Sykes, *Inorg. Chem.*, **14**, 33 (1975).
 (10) R. K. Wharton, Ph.D. Thesis, University of Leeds, 1973.
 (11) R. Duval, C. Duval, and J. Lecomte, *Bull. Soc. Chim. Fr.*, 1048 (1947).
 (12) N. I. Lobanov, *Zh. Neorg. Khim.*, **2**, 1035 (1957).
 (13) J. Fujita, A. E. Martell, and K. Nakamoto, *J. Chem. Phys.*, **36**, 324 (1962).
 (14) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley, New York, N. Y., 1970, p 238.
 (15) Reference 14, p 173.
 (16) For a discussion of the infrared spectra of iodates see J. R. Durig, O. D. Bonner, and W. H. Breazeale, *J. Phys. Chem.*, **69**, 3886 (1965).
 (17) W. E. Dasent and T. C. Waddington, *J. Chem. Soc.*, 2429 (1960).
 (18) D. A. House, *Acta Chem. Scand.*, **26**, 2847 (1972).
 (19) R. Davies and R. B. Jordan, *Inorg. Chem.*, **10**, 2432 (1971).
 (20) O. Nor and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1232 (1973).
 (21) C. Andrade and H. Taube, *Inorg. Chem.*, **5**, 1087 (1966).
 (22) Calculated from data in ref 20.
 (23) H. H. Cady and R. E. Connick, *J. Amer. Chem. Soc.*, **80**, 2646 (1958).
 (24) T. C. Matts and P. Moore, *J. Chem. Soc. A*, 1632 (1971).
 (25) N. V. Duffy and J. E. Earley, *J. Amer. Chem. Soc.*, **89**, 272 (1967).
 (26) J. E. Earley and W. Alexander, *J. Amer. Chem. Soc.*, **92**, 2294 (1970); M. A. Levine, T. P. Jones, W. E. Harris, and W. J. Wallace, *ibid.*, **83**, 2453 (1961).
 (27) W. K. Wilmarth, H. Graff, and S. T. Gustin, *J. Amer. Chem. Soc.*, **78**, 2683 (1956).
 (28) J. Bjerrum, G. Schwarzenbach, and L. G. Sillen, *Chem. Soc., Spec. Publ.*, No. 7, 8 (1958).
 (29) R. Giovanoli, W. Stadelmann and H. Gamsjager, *Chimia*, **27**, 170 (1973).
 (30) G. Bazsa and H. Diebler, *Proc. Int. Conf. Coord. Chem.*, **15**, 442 (1973).
 (31) We note also that W. E. Jones and T. W. Swaddle, *Can. J. Chem.*, **45**, 2647 (1967), have not succeeded in repeating the preparation of $[\text{Co}(\text{NH}_3)_5\text{ClO}_4]^{2+}$ reported by Duval, nor has it been possible to detect the bromato complex by allowing excess NaBrO_3 to react with $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$: J. F. Ojo, unpublished work.
 (32) N. I. Lobanov, *Izv. Sekt. Platinu Drugikh Blagorod. Metal., Inst. Obshch. Neorg. Khim., Akad. Nauk SSSR*, **28**, 277 (1954).
 (33) H. Siebert, personal communication.
 (34) L. Monsted and O. Monsted, *Acta Chem. Scand.*, **27**, 2121 (1973).
 (35) G. Guastalla and T. W. Swaddle, *Inorg. Chem.*, **13**, 61 (1974).
 (36) See, for example, C. Hwang and A. Haim, *Inorg. Chem.*, **9**, 500 (1970), and references therein.
 (37) J. H. Espenson, *Inorg. Chem.*, **8**, 1554 (1969).
 (38) A. Haim, *Inorg. Chem.*, **9**, 426 (1970).
 (39) H. M. Comley and W. C. E. Higginson, *J. Chem. Soc., Dalton Trans.*, 2522 (1972).
 (40) R. Holwerda, E. Deutsch, and H. Taube, *Inorg. Chem.*, **11**, 1965 (1972).
 (41) M. T. Beck, *J. Inorg. Nucl. Chem.*, **15**, 250 (1960).
 (42) M. V. Olson, *Inorg. Chem.*, **12**, 1416 (1973).
 (43) E. B. Fleischer and R. Frost, *J. Amer. Chem. Soc.*, **87**, 3998 (1965).
 (44) J. Halpern, R. A. Palmer, and L. M. Blakley, *J. Amer. Chem. Soc.*, **88**, 2877 (1966).
 (45) J. E. Byrd and W. K. Wilmarth, *Inorg. Chim. Acta Rev.*, **5**, 7 (1971).
 (46) R. S. Murray, D. R. Stranks, and J. K. Yandell, *Chem. Commun.*, 604 (1969).
 (47) H. Siebert and G. Wittke, *Z. Anorg. Allg. Chem.*, **399**, 52 (1973).
 (48) P. J. M. O'Neill, unpublished work.

Contribution from the Departments of Chemistry, University of Connecticut, Storrs, Connecticut 06268, and Cornell University, Ithaca, New York 14850

Transition Metal Pentacoordination

ANGELO R. ROSSI and ROALD HOFFMANN*

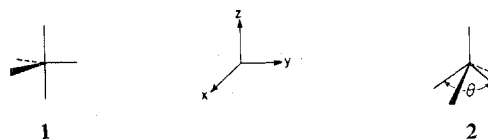
Received June 21, 1974

AIC40399E

A unified molecular orbital treatment of pentacoordinate transition metal complexes for the D_{3h} trigonal-bipyramidal and the C_{4v} square-pyramidal geometries is presented. Symmetry arguments and calculations on model compounds for which π -bonding effects are excluded yield basic σ -bonding trends. Thus the axial bond should be weaker in the trigonal bipyramid for d^0 - d^4 and d^{10} and stronger for d^8 low-spin complexes; the apical bond of a square pyramid with $\theta < 165^\circ$ is stronger for d^0 - d^6 and d^{10} and weaker for d^8 . A similar pattern is obtained for σ -substituent effects: the stronger σ donor prefers the equatorial position of a trigonal bipyramid for d^0 - d^4 , d^{10} and the axial site for d^8 ; in the square pyramid the preferred position for a stronger σ donor is apical for d^0 - d^6 and d^{10} and basal for d^8 . The substitutional preferences of substituents bearing cylindrical and single-faced π -donor and -acceptor orbitals are explored. The π interaction is greatest when the substituent is equatorial in a trigonal bipyramid, with its donor or acceptor orbital in the equatorial plane. A single-faced π acceptor will orient itself eq_\perp for d^8 - d^{10} ; a single-faced π donor, eq_\parallel . A cylindrical π acceptor will favor the equatorial site for d^8 - d^{10} ; a π donor, the axial site. In the interesting d^8 case the effect of a π acceptor on the relative bond strengths counteracts the σ effect, while a donor reinforces it. In a square pyramid the extent of π interaction varies with the degree of pyramidity. For a nearly flat square pyramid cylindrical π interaction is greatest in the basal site but changes to the apical position as the pyramidity increases. In a basal site there is always more interaction in the basal orientation.

Pentacoordinate transition metal complexes occupy a unique position in inorganic chemistry. As unstable reactive intermediates such species are commonly implicated in associative primary reactions of tetracoordinate molecules and dissociative reactions of hexacoordinate compounds.¹⁻³ When pentacoordinate molecules are stable enough to be isolated, they confront us with a fascinating geometrical problem—the choice between trigonal bipyramid, square pyramid, and even other extreme conformations, and a generally soft potential energy surface connecting these minima.⁴⁻⁷

In this paper we build on our previous analysis of the bonding in pentacoordinate phosphorus⁸ to derive a general theory of substituent effects and geometrical preferences in pentacoordinate transition metal complexes. The geometries considered in detail are the D_{3h} trigonal bipyramid, **1**, and the C_{4v} square pyramid, **2**. The electronic effects were modeled on ML_5 , where M is a metal atom of the third transition series, L a pseudoligand carrying either s orbitals alone, when the



isolated effects of σ bonding were to be studied, or a full complement of s and p orbitals. The qualitative discussion of bonding effects should be valid for metal atoms in any transition series. Details of the extended Hückel calculations are given in the Appendix.

A cautionary note must be inserted here. The arguments to be presented in this paper are primarily symmetry and overlap based, with detailed calculations playing only a supportive role. Even so, the conclusions should be viewed by the reader critically, not as the last word of theory but as the working out of the consequences of one particular model. It is legitimate to question some of the foundations of the model, for instance the crucial role we will assign to hybridization with $(n+1)p$ orbitals. And the geometrical features of transition

* To whom correspondence should be addressed at Cornell University.