ACTA CHEMICA SCANDINAVICA 26 (1972) 2847–2854

The Mode of Decomposition of the Oxalatotetrammine-chromium(III) Cation in Dilute Acidic Solution

D. A. HOUSE*

Chemistry Department A, Technical University of Denmark, DK-2800 Lyngby, Denmark

In 0.025 *F* $HClO_4$, the $Cr(NH_3)_4ox^+$ cation hydrolyses *via* $Cr-NH_3$ bond rupture to form $Cr(NH_3)_3(OH_2)ox^+$. This triammine subsequently looses another NH_3 molecule to form $Cr(NH_3)_2(OH_2)_2ox^+$ as the relatively stable end product. At 34.8°, the consecutive first order rate constants for these processes are 2.25×10^{-5} and 1.28×10^{-5} sec^{-1}, respectively. The tetra-, tri-, and diammine cations have been isolated from the reaction solutions by ion-exchange chromatography and characterized in solution by their visible absorption spectral parameters and metal:ligand ratios.

The rates and mode of water substitution in a variety of Cr(III) polyamine complexes have been extensively studied especially by Garner and his coworkers.[1–3] In many cases, Cr–N bond rupture competes with Cr–X substitution, in both acidic and basic solution.[2,3] In some instances, *e.g.* with α-$Cr(trien)ox^+$ and $Cr(en)_2ox^+$,** Cr–N bond rupture appears to be the only substitution process in dilute acidic ($[H^+] \lesssim 2F$) solution under both thermal [4–7] and photolytic [8] conditions.

Similar $Cr-NH_3$ bond rupture in Cr(III) ammine complexes has only been poorly documented,[1] partly due to the difficulty in characterizing the decomposition products. The photolytic hydrolysis of $Cr(NH_3)_5Cl^{2+}$ has been shown to yield *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ as a major product [9] but this has not been identified in the thermal aquation process.[10]

We have investigated the thermal hydrolysis of the $Cr(NH_3)_4ox^+$ cation in dilute acidic solution and find, in agreement with previous studies with other $Cr(N_4)ox^+$ cations, that Cr–N bond rupture is the primary mode of hydrolysis, with no evidence of oxalate release.

---

* On leave from the Department of Chemistry, University of Canterbury, Christchurch, New Zealand.

** Abbreviations used: ox = oxalato ion, $C_2O_4^{2-}$; en = ethylenediamine, $NH_2(CH_2)NH_2$; trien = triethylenetetramine, $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$; enH = monoprotonated ethylenediamine cation; trienH = monoprotonated triethylenetetramine cation.

RESULTS

Two new complex cations, *viz.* $Cr(NH_3)_3(OH_2)ox^+$ and $Cr(NH_3)_2(OH_2)_2ox^+$, have been isolated by ion-exchange chromatography from aged solutions of $Cr(NH_3)_4ox^+$ in 0.025 *F* $HClO_4$ at 34.8°. These complexes have been characterized in solution by Cr:NH_3:ox ratios and their visible absorption spectral parameters are presented in Table 1 and Fig. 1.

Table 1. Visible absorption maxima and minima (320 – 600 nm) for some Cr(III) amine oxalato and aquo complexes at 22 – 24° in acidic aqueous solution.[a]

Complex	H^+, *F*	λ_{max}[b]	λ_{min}[b]	λ_{max}[b]	Ref.
α-$Cr(trien)ox^+$	HNO_3, 2	370 (104)	420 (33.7)	495 (147)	7
$Cr(en)_2ox^+$	$HClO_4$, 1	371 (87)		493 (91)	6
$Cr(NH_3)_4ox^+$	$HClO_4$, 0.025 – 0.6	375[c] (59.0)	428 (14.5)	500 (47.5)	this work
cis-$Cr(NH_3)_4(OH_2)_2^{3+}$	$HClO_4$, 1	366 (26.6)	419 (7.8)	495 (36.1)	21
	HNO_3, 0.05	368 (23.1)		494 (31.4)	25
$Cr(trienH)(OH_2)ox^{2+}$	HNO_3, 2	392 (63.2)	450 (20.0)	520 (63.2)	7
$Cr(en)(enH)(OH_2)ox^{2+}$	$HClO_4$, 1	391 (65)		521 (64)	6
$Cr(NH_3)_3(OH_2)ox^+$	$HClO_4$, 0.1	380 (58.5)	444 (13.6)	515 (43.3)	this work
1,2,6-$Cr(NH_3)_3(OH_2)_3^{3+}$	$HClO_4$, 3	373 (25.6)	427 (8.0)	503 (25.6)	13
$Cr(en)(OH_2)_2ox^+$	H_2O (?)	395 (~63)[d]		526 (~63)[d]	24 8
$Cr(NH_3)_2(OH_2)_2ox^+$	$HClO_4$, 0.1	389 (48.3)	457 (10.2)	537 (37.7)	this work
trans-$Cr(NH_3)_2(OH_2)_4^{3+}$	$HClO_4$, 3	382 (18.5)	441 (5.3)	521 (21.0)	14

[a] Numbers in parenthesis are the molar absorbancy indices, M^{-1} cm^{-1}.
[b] Wavelength nanometers.
[c] There is a pronounced shoulder on the low wavelength side of this band at approximately 365 nm (see Fig. 1).
[d] Estimated from a spectral curve in the cited reference.

By reacting solutions of $Cr(NH_3)_4ox^+$ (9 – 15 m*F*) in 0.025 *F* $HClO_4$ at 34.8° for various times and subjecting the reaction mixture to complete chromatographic separation, the rates of build up and decay of the $Cr(NH_3)_n(OH_2)_{n-4}ox^+$ cations ($n = 2, 3, 4$) were obtained. The chromatographic separation accounted for 92 ± 3 % of the initial $Cr(NH_3)_4ox^+$, and the results are presented in Fig. 2 and Table 2. No free oxalate was detected in any of the reacting solutions.

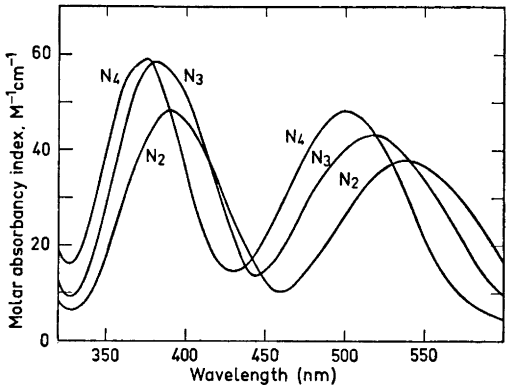

Fig. 1. Visible absorption spectra of $Cr(NH_3)_4ox^+$ (N_4) in 0.6 *F* $HClO_4$, $Cr(NH_3)_3(OH_2)ox^+$ (N_3) in 0.1 *F* $HClO_4$ and $Cr(NH_3)_2(OH_2)_2ox^+$ (N_2) in 0.1 *F* $HClO_4$ at 22 – 25°.

Table 2. Build-up and decay of $Cr(NH_3)_n(OH_2)_{4-n}ox^+$ ($n=2$, 3, 4) species.[a]

Time, h	$[N_4]_0$,[b] m*F*	$[N_4]$,[c] m*F*	Found						Calculated		
			$[N_3]$,[c] m*F*	$[N_2]$,[c] m*F*	$\sum$,[d] m*F*	c_4[e]	c_3[e]	c_2[e]	c_4[f]	c_3[f]	c_2[f]
3.5	10.50	7.00	1.98	0.35	9.43	0.750	0.212	0.038	0.722	0.253	0.025
11.0	11.70	4.74	4.78	1.54	11.06	0.428	0.430	0.140	0.408	0.445	0.147
14.0	13.90	4.00	6.10	2.70	12.80	0.312	0.475	0.211	0.320	0.472	0.208
15.75	9.08	2.32	4.07	2.13	8.52	0.273	0.478	0.249	0.273	0.475	0.247
23.0	15.00	2.00	5.63	6.13	13.76	0.145	0.410	0.445	0.150	0.405	0.445
35.0	10.01	0.68	2.92	5.81	9.41	0.072	0.311	0.617	0.060	0.325	0.615

[a] In 0.025 *F* $HClO_4$ at 34.8°C.
[b] Initial $[Cr(NH_3)_4ox^+]$, (m*F*).
[c] $[N_4]=[Cr(NH_3)_4ox^+]$, $[N_3]=[Cr(NH_3)_3(OH_2)ox^+]$ and $[N_2]=[Cr(NH_3)_2(OH_2)_2ox^+]$ found after time, *t*, (m*F*).
[d] $\sum=[N_4]+[N_3]+[N_2]$, (m*F*).
[e] $[N_4]$, $[N_3]$ and $[N_2]$ as a fraction of $\sum$.
[f] Fraction of $[N_4]$, $[N_3]$ and $[N_2]$ after time, *t*, calculated using the equations in the caption of Fig. 2.

In separate experiments, the rate of formation of free NH_4^+ was monitored by the aliquot technique using Nesslers reagent. For solutions initially 0.025 *F* in $HClO_4$ and 2 m*F* in $Cr(NH_3)_4ox^+$, linear first order rate plots were obtained for about 0.5 half-life ($\tau_{\frac{1}{2}}$), based on a calculated infinity of one ammonia released. Subsequent to this, positive deviation from linearity was observed (Fig. 3). At 34.8°, the value for the first order rate constant (k_1) for the reaction

$$Cr(NH_3)_4ox^+ + H_3O^+ \xrightarrow{k_1} Cr(NH_3)_3(OH_2)ox^+ + NH_4^+ \qquad (1)$$

was found by this method to be 2.25×10^{-5} sec^{-1}, corresponding to $\tau_{\frac{1}{2}} = 8.50$ h in good agreement with the data in Fig. 2.

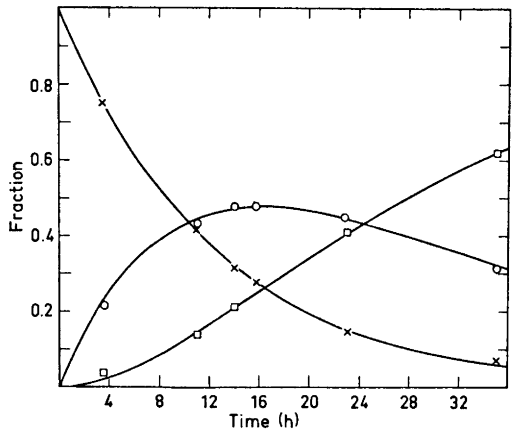

Fig. 2. Fraction of $Cr(NH_3)_n(OH_2)_{4-n}ox^+$ ($n = 2, 3, 4$) as a function of time in 0.025 *F* $HClO_4$ at 34.8°. The solid lines, are calculated from the equations, $[Cr(NH_3)_4ox^+] = c_4 = \exp(-0.0815t)$, $[Cr(NH_3)_3(OH_2)ox^+] = c_3 = -2.34\,[\exp(-0.0815t) - \exp(-0.0465t)]$ and $[Cr(NH_3)_2(OH_2)_2ox^+] = c_2 = 1 - (c_4 + c_3)$ (t = time in hours). The points ×, ○ and □ are the experimentally determined fractions c_4, c_3, and c_2, respectively, at time, t.

Thus the fraction of $Cr(NH_3)_4ox^+$ remaining at time t, in hours, under the above conditions, can be represented by the expression:

$$[Cr(NH_3)_4ox^+] \equiv c_4 = \exp(-0.0815t)$$

Trial and error calculations using the normal formulae for consecutive first order reactions [11] gave a best fit (Fig. 2) for the fraction of $Cr(NH_3)_3(OH_2)ox^+$ present at time t (in hours) as:

$$[Cr(NH_3)_3(OH_2)ox^+] \equiv c_3 = -2.34[c_4 - \exp(-0.0465t)]$$

This leads to a value of 1.28×10^{-5} sec^{-1} ($\tau_{\frac{1}{2}} = 14.9$ h) for the first order rate constant (k_1') for the reaction

$$Cr(NH_3)_3(OH_2)ox^+ + H_3O^+ \xrightarrow{k_1'} Cr(NH_3)_2(OH_2)_2ox^+ + NH_4^+ \qquad (2)$$

at 34.8°.

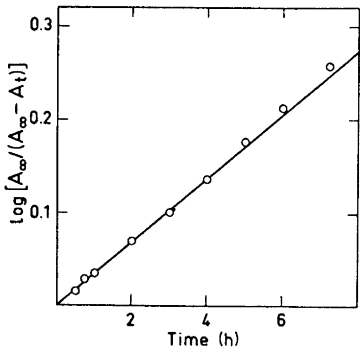

Fig. 3. First order rate plot for the release of one NH_3 from $Cr(NH_3)_4ox^+$ in 0.025 *F* $HClO_4$ at 34.8°.

In an attempt to obtain k_1 by a third method, the spectral changes of $Cr(NH_3)_4ox^+$ (1.3 m*F*) in 0.025 *F* $HClO_4$, at 34.8° were measured at various times. Initial isosbestic points at 520(44.2), 436(16.0) and 379 nm (57.5 M^{-1} cm^{-1}) were lost after about 4 h and calculation of the rate constant was not persued as the spectral changes were small. However, these observed isosbestic points are in reasonable agreement with those predicted from Fig. 1 for reaction (1) at 520(43.2), 437(15.8) and 378 nm (58.0 M^{-1} cm^{-1}).

Independent measurements of k_1' by the NH_3 release method, from chromatographically isolated solutions of $Cr(NH_3)_3(OH_2)ox^+$ were not undertaken as both the triammine cation and free NH_4^+ (generated in the primary process) were eluted from the ion-exchange column in the same fractions. No variation in column length, concentration of eluting agent or flow rate tried, gave fractions of $Cr(NH_3)_3(OH_2)ox^+$ that were sufficiently concentrated for reaction rate studies and free from a high background of NH_4^+.

Nevertheless, the above results suggest that the mode of decomposition of the $Cr(NH_3)_4ox^+$ cation in dilute acidic solution can be represented by (1) and (2) with the secondary hydrolysis being 1.75 times slower than the primary reaction. The rate of hydrolysis of the diammine cation appears to be at least an order of magnitude slower.

DISCUSSION

The $Cr(NH_3)_n(OH_2)_{4-n}ox^+$ *cations.* The absorption spectral parameters of $Cr(NH_3)_4ox^+$ have previously been reported by Kyuno, Kamada and Tanaka.[12] Their data for the molar absorbancy indices are approximately 12 % higher than those obtained here (Table 1). However, the agreement between the peak height ratios and the position of the maxima is good. In both investigations $[Cr(NH_3)_4ox]NO_3.H_2O$ has been used as the source of this cation and although the analytical data reported by Kyuno *et al.* correspond to the anhydrous compound, this would only give a discrepancy of about 5 %. The absorption spectral parameters reported here have been obtained from both weighed amounts of the solid and chromatographically isolated solutions of the cation, covering a threefold variation in concentration, with excellent agreement between the two methods.

Other points of interest from the visible absorption spectra are the well developed shoulder on the low wavelength side of the 375 nm band of $Cr(NH_3)_4ox^+$ (at about 365 nm) and a more poorly defined shoulder on the high wavelength side of the 380 nm band of $Cr(NH_3)_3(OH_2)ox^+$ (at about 390 nm) (Fig. 1). Both the 390 and 537 mn bands of $Cr(NH_3)_2(OH_2)_2ox^+$ appear to be symmetrical.

There are potentially two distinguishable isomers possible for the $Cr(NH_3)_3(OH_2)ox^+$ cation, *viz.* H_2O *trans* to an oxalate oxygen (peripheral triammine) or H_2O *trans* to an ammonia (facial triammine). Only one form appears to be produced in the hydrolysis of $Cr(NH_3)_4ox^+$ although the possibility that the $Cr(NH_3)_3(OH_2)ox^+$ formed is an isomeric mixture cannot be completely eliminated. Nevertheless, no variation in spectral parameters, outside experimental error, was observed for the several chromatographically

isolated fractions containing $Cr(NH_3)_3(OH_2)ox^+$ despite a large variation in reaction time used to generate this species.

Similar arguments suggest that only one of the three possible $Cr(NH_3)_2(OH_2)_2ox^+$ isomers (*trans* NH_3-cis H_2O, *trans* H_2O-cis NH_3 or *cis* NH_3-cis H_2O) is formed. The simple kinetic data obtained also support the hypothesis that only one $Cr(NH_3)_3(OH_2)ox^+$ species is produced, as a mixture might be expected to give at least two $Cr(NH_3)_2(OH_2)_2ox^+$ isomeric products at different rates.

The actual geometry adopted by these cations is not known. At present our assumption of a peripheral triammine and a *trans* diammine, respectively, is favoured, as these would result from an oxalate *trans* effect. The visible absorption spectra $Cr(NH_3)_3(OH_2)ox^+$ and $Cr(NH_3)_2(OH_2)_2ox^+$ are rather different from those of the (presumably [7]) facial $N-Cr(trienH)(OH_2)ox^{2+}$ and *cis* $N-Cr(en)(OH_2)_2ox^+$, respectively, (Table 1) suggesting different configurations. Also, the peripheral triammine [13] and *trans* diammine [14–16] configurations appear to be the most stable for Cr(III) in dihalo complexes, but this need not necessarily be the case in the absence of these ligands.

If these assignments are correct, it is interesting to compare the visible absorption spectra of these oxalato complexes with those of the aquo complexes of similar ammine configuration (Table 1). Although oxalate and water are usually regarded as having similar positions in the spectrochemical series, there are considerable differences in the spectra of the two sets of complexes.

The difference between the low wavelength maxima in both series is almost constant at about 8 ± 1 nm with the oxalato complexes always at higher wavelengths. However, for the minima and the high wavelength maxima the difference in position increases as the number of NH_3 groups is reduced. This is especially so for the high wavelength maxima where the differences are 5, 13, and 16 nm for the tetra-, tri-, and diammines. Again the oxalato complexes absorb at higher wavelengths. The intensity differences between the aquo and oxalato complexes are reasonably constant at about 17 ± 1 and 33 ± 3 M^{-1} cm^{-1} for the low and high wavelength maxima, respectively.

Thus, the major difference between the oxalato and aquo complexes is a progressive shift of the high wavelength maxima of the oxalato complexes to higher wavelengths, relative to the aquo ions, as the number of NH_3 groups decreases. In all three cases, the oxalato complexes have the more intense absorption.

Kinetic data. Previous work [4,7] has shown that both $Cr(en)_2ox^+$ and α-$Cr(trien)ox^+$ hydrolyse in acid solution *via* Cr–N bond rupture to give Cr(en)(enH)$(OH_2)ox^{2+}$ and $Cr(trienH)(OH_2)ox^{2+}$, respectively. The rates of bond rupture in these systems and in $Cr(NH_3)_4ox^+$, are in the order α-$Cr(trien)ox^+ > Cr(en)_2ox^+ \sim Cr(NH_3)_4ox^+$ with rate constants of 87×10^{-5}* (2 *F* HNO_3), 4.1×10^{-5}* (1 *F* HCl) and 2.25×10^{-5} (0.025 *F* HNO_3) sec^{-1}, respectively, at 34.8°. The faster reaction of the trien complex probably reflects the strain involved in the formation of three linked 5-membered ring systems.

The fact that no free oxalate is formed in these reactions is perhaps sur-

* These data have been calculated from E_a and pre-exponential values reported in the original literature.[4,7]

prising when one considers that in concentrated hydrohalic acids, these oxalato complexes react to give dihalo [17–20] or haloaquotetramine [12] products. Nevertheless, the yields are generally less than 60 % [12] and oxalate protonation followed by oxalate release probably competes with Cr–N bond rupture in these concentrated acid solutions.

EXPERIMENTAL

Materials. $[Cr(NH_3)_4ox]NO_3.H_2O$ was prepared using the literature methods.[12,21] (Found: Cr 18.2; $Cr:NH_3:C_2O_4^{2-}$ 1:3.98 ± 0.04:1.00 ± 0.02.* Calc. for $CrN_4H_{14}C_2O_4$: Cr 18.1; $Cr:NH_3:C_2O_4^{2-}$ 1:4:1.) The ion-exchange resin (Dowex 50W × 8 50/100 mesh, H^+ form) was used in an 8 × 1 cm column [22] at room temperature. Before cation adsorption, the column was pre-washed with 2 *F* (30 ml) and then 0.025 *F* (30 ml) $HClO_4$. Perchloric acid solutions were prepared by dilution of appropriate volumes of 70 % $HClO_4$. Redistilled water was used throughout. Nesslers reagent was prepared by the method of Vogel.[23]

Kinetic methods. All hydrolysis reactions were conducted in stoppered volumetric flasks covered with Al foil. For the kinetic runs monitored by NH_4^+ formation, 5 ml aliquots were taken at known times from 100 ml of 2.00 m*F* $Cr(NH_3)_4ox^+$ in 0.025 *F* $HClO_4$ at 34.8°. These aliquots were added to < 45 ml of ice-cold water containing Nesslers reagent (2 ml) and made up to 50 ml with water. A yellow colour developed immediately and the absorbance at 420 nm, with a slit width of 0.10 mm, was measured in a 1.00 cm cell within 3 min after mixing. This time allowed the cell to warm to 10–15° (to prevent fogging) and at this temperature interference by NH_3 release from the Cr–NH_3 species present in the alkaline solution was reduced to a minimum. The reference cell contained a solution consisting of Nesslers reagent (2 ml), 0.025 *F* $HClO_4$ (5 ml) and water (43 ml). Standards were prepared using 1.00 m*F* NH_4^+ (10 ml). Under these conditions, a solution 0.200 m*F* in NH_3 gave an absorbance of 0.563 ± 0.005 and the first order rate data were calculated using this absorbance as the "infinity" value. The absorbance data at time, *t*, were corrected for a small zero-time absorbance obtained 5–10 min after dissolving the solid complex in the 34.8° 0.025 *F* $HClO_4$.

Ion exchange chromatography. Samples of $[Cr(NH_3)_4ox]NO_3.H_2O$ (130–250 mg) were dissolved in 50 ml of 0.025 *F* $HClO_4$ and allowed to hydrolyse at 34.8° for various times (3.5–35 h). The reacted solution was run through a cation-exchange column and the effluent collected for oxalate analysis. Previous workers have shown that this procedure gives quantitative oxalate recovery.[7] The resulting red band was eluted with 0.1 *F* $HClO_4$ at a flow rate of 3–4 ml/min and 5 to 6, 50 ml fractions were collected. After the 5th fraction, the column contained an orange band about 2 cm from the top and 2 cm long, and a pale red band or "tail" on the last cm. The red tail was removed with a further 50 ml of 0.1 *F* $HClO_4$ and the remaining orange band was eluted with 1 or 2, 50 ml fractions of 0.6 *F* $HClO_4$. The number of 50 ml, 0.1 *F* and 0.6 *F* $HClO_4$ fractions was sometimes varied, depending on the reaction time. The visible absorption spectrum of each fraction was recorded and the solutions were analysed for Cr, NH_3, and oxalate. Molar absorbancy indices were calculated on the basis of the Cr analysis.

The analytical data, absorption band maxima and absorbancy indices showed that $Cr(NH_3)_n(OH_2)_{4-n}ox^+$ and NH_4^+ cations ($n = 2,3,4$) are present in the effluent fractions and these are eluted in the order, $Cr(NH_3)_2(OH_2)_2ox^+$ in fractions 1 and 2, $Cr(NH_3)_3(OH_2)ox^+$ plus NH_4^+ in fractions 4, 5, and 6, and $Cr(NH_3)_4ox^+$ in the 0.6 *F* $HClO_4$ fractions. Fraction 3 was always a mixture of di- and triammines except at short reaction times (< 6 h), when the amount of diammine is small.

$Cr:NH_3:C_2O_4^{2-}$ ratios in fractions containing the $Cr(NH_3)_2(OH_2)_2ox^+$ and $Cr(NH_3)_3(OH_2)ox^+$ cations were 1:1.98 ± 0.04:1.00 ± 0.02 and 1:–:0.98 ± 0.04, respectively, where the numbers quoted are the mean ± the standard deviation of 7 diammine and 10 triammine analyses. Ammonia ratios could not be determined for the triammine because of interference from free NH_4^+.

* The numbers quoted are the mean ± the standard deviation of the analysis of 6 separate $Cr(NH_3)_4ox^+$ samples isolated in solution by ion-exchange chromatography (see later).

From the known absorption spectral parameters of the components (Fig. 1, Table 1), the composition of fraction 3 was determined and the total concentration of di- tri- and tetrammine cations at the time of sampling was then calculated. These data were converted to a fraction of the total chromium species isolated and provide the experimental points in Fig. 2 and Table 2.

Analyses. Duplicate 5 ml aliquots of the effluent (50 ml fractions) from the ion-exchange column were analysed for Cr, NH_3, and oxalate. Cr was determined by oxidation of the alkaline (NaOH) aliquot with $(NH_4)_2S_2O_8$ and measuring the CrO_4^{2-} formed spectrophotometrically at 373 nm (1.00 cm cell, slit width 0.02 mm) after appropriate dilution (usually to 100 ml). Standard CrO_4^{2-} (0.100 m*F*) in dilute NaOH solution was used as a calibration for every measurement. Ammonia was determined by distillation of the NH_3 from an alkaline (NaOH) aliquot, adsorption of the distillate in saturated H_3BO_3, and titration with standard (5.00 m*F*) HCl using bromocresyl green/methyl red indicator. The warm alkaline residue was acidified with $HClO_4$ and the oxalate determined by MnO_4^- (1.00 m*F*) titration at 60°. In samples where NH_3 was not determined, an aliquot was made alkaline (NaOH), heated to 60° and then acidified with $HClO_4$ prior to the MnO_4^- titration.

Instrumentation. Visible absorption spectra (600 – 320 nm) were recorded on a Cary 11 MS-50 spectrophotometer with matched 10.00 cm cells and 0.1 *F* $HClO_4$ in the reference beam. Absorbance data for CrO_4^{2-} and NH_3 analysis were obtained at fixed wavelength using a Zeiss PMQ 11 spectrophotometer.

Acknowledgements. I thank Professor Flemming Woldbye for providing research facilities and Lic. Techn. Sven Bagger for helpful discussions.

REFERENCES

1. Garner, C. S. and House, D. A. In Carlin, R. L., Ed., *Transition Metal Chemistry*, Marcel Dekker, New York 1970, Vol. 6.
2. Ranney, S. J. and Garner, C. S. *Synthesis in Inorganic and Metal-Organic Chemistry* **1** (1971) 179.
3. Tang, S. C., Wilder, R. L., Kurimoto, R. K. and Garner, C. S. *Synthesis in Inorganic and Metal-Organic Chemistry* **1** (1971) 207.
4. Gausmann, H., Diss., Johann Wolfgang Goethe-Universität, Frankfurt am Main, Germany 1964.
5. Schläfer, H. L., Kling, O., Mähler, L. and Opitz, H. P. *Z. physik. Chem. (Frankfurt)* **24** (1960) 307.
6. Broomhead, J. A., Kane-Maguire, N. and Lauder, I. *Inorg. Chem.* **10** (1971) 955.
7. Veigel, J. *Inorg. Chem.* **7** (1968) 69.
8. Kirk, A. D., Moss, K. C. and Valentin, J. G. *Can. J. Chem.* **49** (1971) 375.
9. Manfrin, M. M., Moggi, L. and Balzani, V. *Inorg. Chem.* **10** (1971) 207.
10. Rodgers, A. and Staples, P. J. *J. Chem. Soc.* **1965** 6834.
11. Glasstone, S. *The Elements of Physical Chemistry*, Van Nostrand, New York 1946, p. 603.
12. Kyuno, E., Kamada, M. and Tanaka, N. *Bull. Chem. Soc. Japan* **40** (1967) 1848.
13. Caldwell, S. H. and House, D. A. *Inorg. Chem.* **8** (1969) 151.
14. House, D. A. *Australian J. Chem.* **22** (1969) 647.
15. Couldwell, M. C., Pickering, D. A. and House, D. A. *J. Inorg. Nucl. Chem.* **33** (1971) 3455.
16. Takeuchi, Y. and Saito, Y. *Bull. Chem. Soc. Japan* **30** (1957) 319.
17. Werner, A. *Ber.* **44** (1911) 3132.
18. Benrath, A. and Steinrath, H. *Z. anorg. allgem. Chem.* **194** (1930) 351.
19. Linhard, M. and Weigel, M. *Z. anorg. allgem. Chem.* **271** (1952) 115.
20. House, D. A. and Garner, C. S. *J. Am. Chem. Soc.* **88** (1966) 2156.
21. Hoppenjans, D. W. and Hunt, J. B. *Inorg. Chem.* **8** (1969) 505.
22. House, D. A. *J. New Zealand Inst. Chem.* **33** (1969) 75.
23. Vogel, A. I. *Quantitative Inorganic Analysis*, 3rd. Ed., Longmans, London 1961 p. 783.
24. Kirk, A. D., Moss, K. C. and Valentin, J. G. *J. Chromatog.* **36** (1968) 332.
25. Edelson, M. R. and Plane, R. A. *Inorg. Chem.* **3** (1964) 231.

Received November 25, 1971.