775. *Transition-metal Peroxy-complexes. Part I. The Violet Perchromates.*

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The formulæ of the violet perchromates have been investigated by determining the stoicheiometry and molecularity of the ammonium and potassium salts, by studying their chemical behaviour, and by measurement of their absorption spectra. The results indicate that the basic formula of the perchromate ion is $[Cr^{VI}O(O_2)_2OH]^-$.

The infrared spectra of a number of other peroxy-complexes of chromium have been measured and are discussed.

Two series of " perchromates " have been reported. The " red " salts, variously formulated [1, 2] as $[Cr_2O_{12}]^{6-}$, $[Cr_2O_{13}]^{6-}$, and $[Cr_2O_{15}]^{6-}$, are now known [3] to contain the mononuclear ion $[Cr(O_2)_4]^{3-}$, in which four peroxy-groups are tetrahedrally disposed about a

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[1] Reedy, *J. Amer. Chem. Soc.*, 1930, **52**, 1851.

[2] Martinez and Porter, *Anales real Soc. españ. Fís. Quím.*, 1952, **48**, *B*, 879.

[3] Stromber and Brosset, *Acta Cryst.*, 1960, **14**, 441.

chromium(V) atom. The structure of the anion of the " violet " salts has not been established, and the stoicheiometry of the three known salts (the parent acid has not been isolated) is not known with certainty.

The violet potassium, ammonium, and thallium(I) perchromate are prepared by the action of hydrogen peroxide on neutral or very slightly acidic solutions of the corresponding dichromates,[4] or by the action of " blue perchromic acid " (CrO_5) solutions on potassium cyanide or hydroxide.[5, 6] The apparently related compounds $M^I{}_2CrO_6$ have also been reported.[7, 8]

Various formulæ and structures have been proposed for these salts. Wiede,[5] who first isolated them, suggested M^IOCrO_4,H_2O; Riesenfeld *et al.*[9] and Glasner [10] considered them to be $M^IH_2CrO_7$, and Rumpf [11] suggested M^IHCrO_6. Schwarz and Giese [12] prepared an anhydrous thallous perchromate of empirical formula Tl^ICrO_6, thus disproving the M^IO,CrO_4,H_2O and $M^IH_2CrO_7$ formulæ, and on the basis of permanganate titrations concluded that the anion was binuclear, $[Cr_2O_{12}]^{2-}$. Klemm and Werth [13] demonstrated that the potassium salt was only very feebly paramagnetic ($\chi_M = 172 \times 10^{-6}$ c.g.s.u.; possibly temperature-independent paramagnetism) so that it seemed likely that the chromium was sexivalent in the compound.

The salts are violently explosive, seventeen explosions having occurred during our work. Traces of organic material appear to be primarily responsible for this, and the stability is also affected by slight temperature gradients or shock.

Formula of the Violet Perchromate Anion.—(*a*) *Determination of the stoicheiometry and molecularity of the salts.* By using anhydrous solvents a potassium salt free from water of crystallization was prepared for the first time: it did not differ from the hydrated salt in properties except that it appeared to be even more unstable. Analyses of the salts indicated the empirical formula M^IHCrO_6,nH_2O ($n = 0$ when $M = Tl^+$ or K^+; $n = 1$ for $M = NH_4{}^+$). These results agree with those of Schwarz and Giese.[12] $M^IH_2CrO_7$ is not a possible formulation because, apart from the fact that it conflicts with the analytical data on the potassium and thallium salts, it would require the chromium to be septa- or quinquevalent which is excluded by the magnetic results.

A direct hydrogen analysis, by combustion of a large quantity of the anhydrous potassium salt in a current of oxygen, indicated the presence of one atom of hydrogen per atom of chromium. Although the accuracy of such a determination cannot be great owing to the small amount of hydrogen, spectroscopic evidence (see below) also indicates the presence of hydrogen in the anhydrous potassium salt.

The molecularity of the potassium and ammonium salts was measured by observing the depression in the eutectic point of an ice–potassium nitrate–water mixture. In the case of the potassium salt the molecularity of the anion alone is measured since potassium is a common cation. The results (Table 1) show conclusively that the anion is mononuclear in both cases.

The molar conductivity of ammonium perchromate in water was 111 and in methanol 109 ohm^{-1} $cm.^2$.

(*b*) *Determination of the number of bonded peroxy-groups.* According to Schwarz and Giese,[12] titrations with permanganate in acid solution showed that there were 2·5 peroxy-groups per chromium atom. By the method of continuous variations, Rumpf [11] found that only two moles of hydrogen peroxide reacted with one of chromate, to give the violet

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[4] Hofmann and Hindlemaier, *Ber.*, 1904, **37**, 3405.
[5] Wiede, *Ber.*, 1898, **31**, 516.
[6] Riesenfeld, *Ber. Naturforsch. Ges. Freiburg*, 1905, **17**, 32.
[7] Hofmann and Hindlemaier, *Ber.*, 1904, **37**, 1663.
[8] Nicholson, *J. Amer. Chem. Soc.*, 1936, **58**, 2525.
[9] Riesenfeld, Kutsch, and Wohlers, *Ber.*, 1905, **38**, 1885.
[10] Glasner, *J.*, 1950, 2795.
[11] Rumpf, *Ann. Chim.* (*France*), 1937, **8**, 456.
[12] Schwarz and Giese, *Ber.*, 1933, **66**, 310.
[13] Klemm and Werth, *Z. anorg. Chem.*, 1933, **216**, 127; cf. Schwarz and Giese, *ibid.*, p. 132.

TABLE 1.

Measurement of the molecularity of the violet perchromates: ice–potassium nitrate eutectic freezing-point depressions.

C (g.-atom Cr/l.)	ΔT (°c)	K/n $(= C/\Delta T)$	C (g.-atom Cr/l.)	ΔT (°c)	K/n $(= C/\Delta T)$
Potassium salt			*Ammonium salt*		
0·043	0·068	1·58	0·041	0·144	3·88
0·059	0·087	1·47	0·048	0·162	3·74
0·066	0·100	1·52	0·065	0·230	3·92
0·088	0·135	1·53	0·086	0·252	3·24
			0·160	0·540	3·74
n in $[HCrO_6]_n^{n-} = 1{\cdot}10$			n in $[HCrO_6]_{2n}^{2n-} = 0{\cdot}45$.		

n Values calculated from $K_0 = 1{\cdot}68$ (Wiede, *Ber.*, 1897, **30**, 2178). K = Molar depression constant (K_0 at infinite dilution).

perchromates; Bobtelsky *et al.*[14] considered that the salts contained the same number of peroxy-groups as did CrO_5, but later Glasner[10] proposed the equilibrium, $HCrO_5 + H_2O_2 \rightleftharpoons H_3CrO_7$ (it was Glasner's view at that time that "blue perchromic acid" was $HCrO_5$; he now agrees[15] with its formulation as CrO_5).

The number of peroxy-groups was determined by various methods: direct measurement of peroxide by titration with cerium(IV) or permanganate, decomposition under various conditions, and conversion into CrO_5 by acidification.

Known amounts of ammonium perchromate were treated with an excess of acid ceric sulphate solution and the volume of oxygen evolved was measured. In other experiments, the ammonium salt was decomposed by water and by alkali, both in the presence of silver oxide, and the oxygen evolved was measured. Finally, studies were made of the amount of water and oxygen lost by the hydrated ammonium salt on its explosive decomposition to anhydrous ammonium dichromate: the percentage loss of weight was found to be 32·1%; the predicted value is 32·0% for 2·0 peroxy-groups and 31·4% for 2·5 peroxy-groups per chromium atom. The results of these experiments are summarized in Table 2 and indicate that there are 2·0 peroxy-groups per chromium atom.

TABLE 2.

Decomposition of the violet perchromates.

Salt	10^{-4} Mole of salt	10^{-4} Mole of O_2 evolved	Moles of O_2/moles of salt Observed	Calc. (1) *	Calc. (2) *
NH_4^+: treated with excess Ce^{4+} (acid)	0·566	1·10	1·94	2·00	2·50
	0·641	1·23	1·92		
	0·057	0·12	2·14		
K^+: treated with water + Ag_2O	1·64	1·46	0·89	1·00	1·25
	2·42	2·33	0·96		
NH_4^+: treated with water + Ag_2O	1·03	0·96	0·93	1·00	1·25
	2·20	2·37	1·08		
NH_4^+: treated with 0·1N-KOH + Ag_2O	1·23	1·35	1·10	1·00	1·25
	1·50	1·53	1·02		
	1·67	1·81	1·08		

* Ratio (moles of O_2/moles of salt) expected for (1) two and (2) 2·5 peroxy-groups per atom of chromium.

A similar result followed from permanganate titrations. If one mole of the salt is treated with acid permanganate solution which is then back-titrated with standard ferrous solution, the oxidizing capacity of the permanganate will be decreased by one equivalent if there are 2·0 peroxy-groups bonded to chromium(VI):

$$5[CrO(O_2)_2OH]^- + 4MnO_4^- + 7H^+ = 4Mn^{2+} + 5CrO_4^{2-} + 10O_2 + 6H_2O$$

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[14] Bobtelsky, Glasner, and Bobtelsky-Chaikin, *J. Amer. Chem. Soc.*, 1945, **67**, 966.

[15] Glasner and Steinberg, *J.*, 1957, 2569.

and by two equivalents if there are 2·5 peroxy-groups:

$$2[Cr_2O_2(O_2)_5]^- + 4MnO_4^- + 8H^+ = 4Mn^{2+} + 4CrO_4^{2-} + 10O_2 + 4H_2O$$

In three consecutive runs, the oxidizing capacity decreased by 1·07, 1·00, and 1·07 equivalents of permanganate per mole or ammonium salt.

(*c*) *Relationship of the violet perchromates to blue perchromic acid.* That there is a close relation between CrO_5 and the violet perchromates has long been known,[5, 6, 9, 12, 14] but its exact nature is not clear. Rumpf's results[11] indicate that the number of peroxy-groups in the violet perchromates is the same as in CrO_5, but Glasner's[10] seem to show that CrO_5 has one peroxy-group less than the violet salts.

It has recently been proved that CrO_5 has two peroxy-groups per chromium atom,[11, 15–17] and it has been shown above that the same is true for the violet salts. Thus, conversion of a violet salt into blue perchromic acid should not involve the taking-up or release of hydrogen peroxide. This was checked by decomposing aqueous solutions of ammonium perchromate at 0° with 0·1M-hydrochloric acid, immediately extracting the CrO_5 into ether, and analyzing the ethereal layer spectrophotometrically for its chromium content (by estimation as chromate). The amount of chromium recovered was 91% (complete conversion of perchromate into CrO_5 being assumed), and, since the perchromate was pure, no peroxide was used in forming the CrO_5. The proportion of chromium extracted did not increase when potassium dichromate was mixed with the perchromate: had hydrogen peroxide been released from the perchromate on acidification of the latter, more CrO_5 would have been generated from the dichromate and the proportion of chromium in the ethereal layer would have risen. Further, addition of uranyl ion to the aqueous layer did not precipitate uranyl peroxide.

Since, then, the violet perchromates and CrO_5 are interchangeable simply by altering the pH of the solutions, they contain the same number of peroxy-groups, now established as 2·0 per chromium atom, and they probably have similar structures.

(*d*) *Spectroscopic measurements.* No strong absorption in the near-infrared or ultraviolet region was observed for methanolic or aqueous solutions of ammonium perchromate, but there was a peak at 531 mμ (ε 441) in the visible region, comparable with that[16] for CrO_5 at 580 mμ (ε ~500). A number of transition-metal peroxy-complexes have bands with molar extinction coefficients of the order of 10^3, larger than those associated with *d–d*-transitions but lower than the intensities of charge-transfer bands.[16]

The infrared spectra of a number of peroxy-complexes of chromium reported in Table 3 all include sharp bands in the region of 875 cm.$^{-1}$. Since the O–O stretching vibration occurs at 871 cm.$^{-1}$ in hydrogen peroxide[18] and around 880 cm.$^{-1}$ in organic peroxides,[19] and since K_3CrO_8, in which the only ligands are peroxy-groups, has a single absorption at 875 cm.$^{-1}$, these bands are assigned provisionally to the O–O stretching vibrations of the peroxy-ligands.* It is significant that the infrared spectra of CrO_5 and the perchromates are very similar; two sharp bands appear, one near 875 cm.$^{-1}$ (presumably an O–O stretch) and another near 930 cm.$^{-1}$ (which may be a Cr=O mode). The somewhat higher frequencies observed for ammonium perchromate may conceivably arise from hydrogen-bonding effects in the lattice. There is no band in the spectra of CrO_5 or of CrO_5,pyr which can be assigned to O–H stretching vibrations, in accordance with expectation, but spectra of anhydrous potassium perchromate have a strong peak at 3500 cm.$^{-1}$

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* These are unlikely to be Cr–O_2 stretching vibrations, since the Cr–O distances in peroxychromium compounds (cf. Table 4) are larger than in CrO_4^{2-} or $Cr_2O_7^{2-}$, so that Cr–O_2 stretches in the peroxides would occur at far lower frequencies than those under discussion.

[16] Evans, *J.*, 1957, 4013.

[17] Schwarz and Giese, *Ber.*, 1932, **65**, 871.

[18] Schumb, Satterfield, and Wentworth, " Hydrogen Peroxide," Reinhold Publ. Corpn., New York, 1955.

[19] Bellamy, " Infra-red Spectra of Complex Molecules," Methuen, London, 1958.

TABLE 3.

Infrared spectra (cm.$^{-1}$) of chromium compounds in the range 4000—650 cm.$^{-1}$.

Complex	O–O stretch	M=O stretch	Other bands
Chromium(VI)			
CrO_3 *		969s, 893m, b	
K_2CrO_4 *		880s, b	
$K_2Cr_2O_7$		925w, 918sh, 895m, 880vs	
$(NH_4)_2CrO_4$		840b	
$(NH_4)_2Cr_2O_7$		912s, 890sh, 867vs	
$NH_4[CrOH(O_2)_2O],H_2O$	932s	980s	3500(OH), 1630(HOH)
$K[CrOH(O_2)_2O]$	876s	984m, 924s	3500(OH)s
$Tl[CrOH(O_2)_2O]$	870s	970w, 920s	3500(OH)w
CrO_5 †	864s	940s	Numerous
CrO_5,pyr ‡	875m	937s	
CrO_5,bipy ‡	890w	922s	
Chromium(V)			
K_3CrO_8	875s		1620w, 985w
$K_2[CrOCl_5]$ *		952	
Chromium(IV)			
$CrO_4(NH_3)_3$	865s		3200, 1630, 1310, 1275, 1235 (all NH_3)

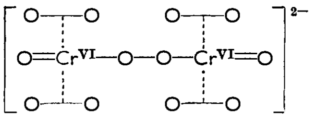
* Barraclough, Lewis, and Nyholm, *J.*, 1959, 3552.

All spectra taken in Nujol mulls, with NaCl windows, except † for CrO_5 which was in ethyl acetate solution, and K_2CrOCl_5 and K_2CrO_4 which were in formamide solutions.

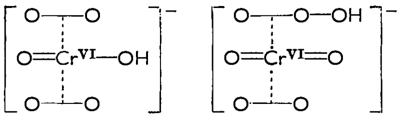
‡ Assignments uncertain owing to heavy absorption in the 800—1100 cm.$^{-1}$ region by pyridine (pyr) and bipyridyl (bipy).

which must arise from an O–H stretch; there is no band at 1630 cm.$^{-1}$ (H–O–H deformations), so it is apparent that this band does not arise from the presence of water in the molecule.

(*e*) *The structure of the violet perchromate anion.* The most commonly quoted structure [12, 13, 20] is (I), which explains the diamagnetism and stoicheiometry of the salts



(I)



(a) (II) (b)

but requires 2·5 peroxy-groups per chromium atom and requires the anion to be binuclear, both of which conflict with our results; further, the presence of a hydrogen atom is not explained. The alternative suggestions of MH_2CrO_7 and MO,CrO_4,H_2O conflict both with magnetic and with analytical results.

The evidence presented here suggests two possible structures (II, a and b). Both involve a mononuclear species in which there are two peroxy-groups per chromium(VI) atom with a single external negative charge, but differ in the placing of the proton. The peroxy-groups are assumed to be bonded side-on to the metal atoms, as is the case with $[CrO_8]^{3-}$ and $CrO_4(NH_3)_3$.

Since $Cr{-}O{-}O^-$ is probably a more basic site than is Cr=O,[21] it is possible that the hydrogen atom is bonded in a hydroperoxy- rather than in a hydroxy-group: this might also explain the difficulty in replacing it by a metal atom, to give salts $M^I{}_2CrO_6$. On the other hand, the infrared spectra of the three compounds studied have only two sharp bands in the 800—1100 cm.$^{-1}$ region (with weak third bands for the potassium and thallium

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[20] Sidgwick, "Chemical Elements and their Compounds," Oxford, 1950; Emeléus and Anderson, "Modern Aspects of Inorganic Chemistry," van Nostrand, London, 1938; Ephraim, "Inorganic Chemistry," Interscience Publ., Inc., New York, 1947.

[21] Taube, personal communication.

salts), and it is tempting to assign these to Cr=O and O–O stretching modes. If these assignments are correct, and absence of accidental overlapping of frequencies is assumed, it seems likely that there are two equivalent (O–O) groups. Recent work [22] on the infra-red spectrum of ammonium hydroperoxide indicates that the O–O stretching frequency in the hydroperoxide group (836 cm.$^{-1}$) is significantly lower than that in normal peroxides (*e.g.*, 871 cm.$^{-1}$ in hydrogen peroxide [18]) so that two peroxide stretches should be found in addition to the Cr=O stretching mode. For this reason structure (b) is favoured, but (a) cannot be excluded.

TABLE 4.

Structural data on peroxy-complexes.

Ref.	Complex	M–O distance (Å)	O–O distance (Å)	O–M–O angle
a	K_3CrO_8	1·94 and 1·88	1·49	
b	$CrO_4(NH_3)_3$	1·94	1·31	39·3°
c	$[(H_3N)_5CoO_2Co(NH_3)_5]^{5+}$	2·38	1·45	
d	BaO_2		1·49	
e	KO_2		1·28	
f	O_2		1·207	
g	H_2O_2		1·49	
h	$(NH_4)_2Cr_2O_7$	1·63 (terminal 1·91 (bridging)		

Refs.: (*a*) Cf. ref. (3). (*b*) Cf. ref. (24). (*c*) Brosset and Vannerberg, *Nature*, 1961, **190**, 714. (*d*) Abrahams and Kalnajs, *Acta Cryst.*, 1954, **7**, 838. (*e*) Abrahams and Kalnajs, *Acta Cryst.*, 1955, **8**, 502. (*f*) Tinkham and Stranberg, *Phys. Rev.*, 1955, **97**, 951. (*g*) Abrahams, Collin, and Lipscomb, *Acta Cryst.*, 1951, **4**, 15. (*h*) Byström and Wilhelmi, *Acta Chem. Scand.*, 1951, **4**, 1003.

Miscellaneous Peroxy-complexes of Chromium.—"*Di-ammonium perchromate,* $(NH_4)_2CrO_6$." The salt $(NH_4)_2CrO_6$ reported by Hofmann and Hindlemaier [7] was considered by Reisenfeld *et al.*[23] to be a mixture of H_3CrO_8 and $(NH_4)_3CrO_8$. The preparation was repeated by us and the product was found by spectral and analytical examination to be a mixture of violet ammonium perchromate and $(NH_4)_3CrO_8$.

Nicholson [8] prepared a compound which gave analyses for $(NH_4)_2CrO_6$ but had the properties of violet ammonium perchromate by reaction of a solution of CrO_5 in ethyl acetate with methanolic ammonia; the experiment was repeated and resulted in the formation of pure violet ammonium perchromate.

Diperoxytriamminechromium(IV), $Cr(O_2)_2(NH_3)_3$. A recent *X*-ray structural investigation of a crystal of this complex [24] indicates that the chromium atom is quinqueco-ordinated, with two peroxy-groups symmetrically bonded in side-on positions to the chromium atom. The O–O bond distance is exceptionally short in comparison with those in other peroxy-compounds (see Table 4); McLaren and Helmholz [24] explained this by suggesting that in the triammine the chromium is in the (+2) state with two superoxide (O_2^-) groups bonded to it, in such a way that the two unpaired electrons [25] are localized on the oxygen rather than on the chromium atom. This, however, assumes that chromium(II) must be spin-paired, which seems unlikely for a quinqueco-ordinated complex with comparatively weak-field ligands bonded to it. Further, since the O–O stretching frequency (Table 3) is substantially constant (and hence, to a first order of approximation, so is the force constant) for all the peroxy-compounds studied, and since magnetic results preclude CrO_8^{3-}, CrO_5, or the violet perchromates from having superoxide groups attached to the central atom, it seems unlikely that the compound $Cr(O_2)_2(NH_3)_3$ should contain them, especially as the existence of chromium(II), a very unstable oxidation state, would be very unusual in these circumstances. It is difficult to see why the O–O distance is so short in the complex and why the stretching frequency is not considerably higher than it is.

[22] Knop and Giguère, *Canad. J. Chem.*, 1959, **37**, 1794.

[23] Riesenfeld, Kutsch, Ohl, and Wöhlers, *Ber.*, 1905, **38**, 3380.

[24] McLaren and Helmholz, *J. Phys. Chem.*, 1959, **63**, 1279.

[25] Bhatnagar, Prakash, and Hamid, *J.*, 1938, 1428; Evans, personal communication.

EXPERIMENTAL

The violet perchromates are all explosive, the ammonium less so than the potassium salt. The thallous salt is particularly unstable. They should not be stored in a confined space, and should be kept away from heat and shock.

Potassium Perchromate (*Anhydrous*), $K[Cr(OH)(O_2)_2O]$.—This was made by treating an anhydrous ethereal solution of CrO_5 with a deficiency of ethanolic potassium hydroxide solution at −10°. The mixture was left for 5 min. and the solid *perchromate* was then filtered off as quickly as possible, washed with a little ice-cold methanol and ether, and air-dried. It is highly unstable and normally no sample may be kept at room temperatures for more than 6 hr. (Found: K, 20·0; Cr, 27·2; H, 0·6. $HCrKO_6$ requires K, 20·8; Cr, 27·6, H, 0·5%). (Hydrogen analysis: 646 mg. of product gave 37·6 mg. of water on combustion in oxygen.)

Hydrated Ammonium Perchromate, $NH_4[Cr(OH)(O_2)_2O],H_2O$.—This *salt* was prepared by the action of hydrogen peroxide on ammonium dichromate[4] (Found: Cr, 28·5; NH_4^+, 9·5. H_7CrNO_7 requires Cr, 28·1; NH_4^+, 9·7%).

Thallous Perchromate, $Tl[Cr(OH)(O_2)_2O]$.—The *salt* was prepared by double decomposition between thallous nitrate and ammonium perchromate[12] (Found: Tl, 58·5; Cr, 14·4. $CrHO_6Tl$ requires Tl, 57·8; Cr, 14·7%).

Reaction between CrO_5 *in Ethyl Acetate and Methanolic Ammonia.*—This is alleged[8] to give $(NH_4)_2CrO_6$. The experiment was repeated and the product found to be ammonium perchromate (Found: Cr, 28·1; NH_4^+, 9·2%).

Preparation of $(NH_4)_2CrO_6$ *by the Method of Hofmann and Hindlemaier.*[7]—The product consisted of a mixture of $(NH_4)_3CrO_8$ and $NH_4[Cr(OH)(O_2)_2O]$ (Found: Cr, 24·5; NH_4^+, 14·4. Calc. for $H_8CrN_2O_6$: Cr, 28·3; NH_4^+, 19·6%).

Red Potassium Perchromate, K_3CrO_8.—This was prepared by Riesenfeld's method[26] (Found: K, 39·9; Cr, 17·7. Calc. for K_3CrO_8: K, 39·5; Cr, 17·5%).

Triamminediperoxychromium(IV), $CrO_4(NH_3)_3$, was prepared by the method of Riesenfeld *et al.*[23] (Found: Cr, 30·8; NH_3, 29·7. Calc. for $CrH_9N_3O_4$: Cr, 31·1; NH_3, 30·7%), the complexes CrO_5 (1,10-phenanthroline) (Found: Cr, 17·1. Calc. for $C_{12}H_8CrN_2O_5$: Cr, 16·7%), and CrO_5(2,2′-bipyridyl) (Found: Cr, 18·7. Calc. for $C_{10}H_8CrN_2O_5$: Cr, 18·0%) by Evans's method,[16] and CrO_5(pyridine) by Wiede's method.

Various Measurements.—Molecular weights were obtained from freezing-point depressions of an ice–potassium nitrate eutectic.[28]

Infrared spectra were taken with a Perkin–Elmer model 21 recording spectrophotometer with sodium chloride optics, and visible and ultraviolet spectra with a Cary recording spectrophotometer.

Analyses were done as follows: chromium spectrophotometrically as chromate; thallium gravimetrically as dichromate; potassium gravimetrically as the tetraphenylboronate; ammonium ion gravimetrically as the chloroplatinate(VI); hydrogen by combustion as water absorbed on Drierite; ammonia volumetrically by the Kjeldahl method.

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[26] Riesenfeld, *Z. anorg. Chem.*, 1912, **74**, 48.

[27] Wiede, *Ber.*, 1897, **30**, 2178.

[28] Jahr, Brechlin, Blanke, and Rubens, *Z. anorg. Chem.*, 1952, **270**, 240; Jander and Ertel, *J. Inorg. Nuclear Chem.*, 1956, **3**, 149.