The Chemistry of Chromium(V): The Preparation and Properties of Tetrachlorobis(ethanoic acid)chromates(III) and Related Complexes

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The preparations and characterisation of the chromium(V) species [A][$CrOCl_4$] (A = pyridinium, quinolinium, isoquinolinium, NMe_4, NEt_4, or $AsPh_4$), [H_2B][$CrOCl_5$] (B = 2,2'- or 4,4'-bipyridine), and $Cs_2[CrOCl_5]$ are described, and their i.r. and electronic spectra are reported. The two lowest-energy bands in the electronic spectra of [A][$CrOCl_4$] (*ca.* 13 000 and 18 000 cm^{-1}) are assigned to $d_{xy}\rightarrow d_{xz,yz}$ and Cr–O(π)$\rightarrow$Cr–O(σ^*) transitions, respectively. The experimental data are incompatible with the energy of the band at 18 000 cm^{-1} being equated with 10*Dq* for the in-plane ligands. A recently reported preparation of [H_2-2,2'-bipy][$CrOBr_5$] is shown to be non-repeatable. A novel series of chromium(III) complexes, containing the anions $[CrX_4(HO_2CMe)_2]^-$ and $[CrX_5(HO_2CMe)]^{2-}$ (X = Cl or Br), has also been prepared, and these undergo ligand-exchange reactions to form complexes containing the anions $[CrCl_4(NCMe)_2]^-$ and $[CrCl_5(NCMe)]^{2-}$.

ALTHOUGH chromium(V) is frequently postulated as a reactive intermediate formed during the reduction of chromium(VI),[1-5] only a limited number of stable chromium(V) complexes have been isolated.[6-8] Pentachloro-oxo- and tetrachloro-oxo-chromates(V) have been known for almost 80 years,[9-12] but there are still only a few examples of these complexes which have been authentically characterised. There have been many

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investigations involving these complexes,[13-32] but much of the work (principally e.s.r. studies) appears to have been carried out with either impure or uncharacterised compounds.[24] Our initial investigations of complexes containing the anions $[CrOCl_4]^-$ and $[CrOCl_5]^{2-}$ have been reported briefly.[32] We now present our findings on this system in more detail, together with a report of a novel series of complexes containing the anions $[CrX_4(HO_2CMe)_2]^-$, $[CrX_5(HO_2CMe)]^{2-}$ (X = Cl or Br), $[CrCl_4(NCMe)_2]^-$, and $[CrCl_5(NCMe)]^{2-}$. We also detail our inability to repeat the preparation of the recently reported complex $[H_2\text{-}2,2'\text{-bipy}][CrOBr_5]$ (bipy = bipyridine).[33]

Table 1

Analytical data for chromium(v) complexes

Complex	Colour	Analysis (%) Found C	H	N	Cl	Calc. C	H	N	Cl	$\mu_{eff.}$/B.M.
$[Hpy][CrOCl_4]$	Dark red crystals	20.4	2.00	4.85	48.0	20.7	2.10	4.85	48.9	1.78
$[Hquin][CrOCl_4]$	Dark red crystals	31.6	2.50	4.05	42.1	31.8	2.35	4.10	41.7	1.75
$[Hiquin][CrOCl_4]$	Dark red crystals	32.1	2.75	4.15	41.5	31.8	2.35	4.10	41.7	1.84
$[NMe_4][CrOCl_4]$	Brown-red powder	17.1	4.45	4.95	50.1	16.9	4.25	4.95	49.95	1.80
$[NEt_4][CrOCl_4]$	Dark red crystals	28.2	6.65	4.05	41.0	28.25	5.95	4.10	41.7	1.78
$[AsPh_4][CrOCl_4]$	Yellow-brown powder	48.9	3.15		23.8	48.6	3.40		23.9	1.62
$[H_2\text{-}2,2'\text{-bipy}][CrOCl_5]$	Brown powder	30.2	2.60	6.95	43.4	29.75	2.50	6.95	43.95	1.77
$[H_2\text{-}4,4'\text{-bipy}][CrOCl_5]$	Dark brown powder	30.0	2.60	6.95	43.4	29.75	2.50	6.95	43.95	1.78
$Cs_2[CrOCl_5]$	Dark red crystals	Cs 51.7			35.0	Cs 52.0			34.7	1.85 [24]

RESULTS AND DISCUSSION

Chromium(v) *Complexes*.—A number of pentachloro-oxo- and tetrachloro-oxo-chromates(v) have been prepared by a method based on that developed by Weinland and Fiederer,[12] and these are detailed (together with magnetic moments and analytical data) in Table 1. Chromium(VI) oxide was dissolved in glacial ethanoic acid saturated with hydrogen chloride, the appropriate base (or chloride salt of the appropriate cation) dissolved in a second solution of glacial ethanoic acid (usually containing dissolved hydrogen chloride) was added, and the mixture was resaturated with hydrogen chloride to yield the desired product. Minor procedural changes can lead to products contaminated with either chromium(VI) or chromium(III) impurities. Although many of these complexes have been reported previously, only $[AsPh_4][CrOCl_4]$ [24, 29, 31, 34] and $[NEt_4][CrOCl_4]$ [24] have been well characterised. The salts $[HB][CrOCl_4]$ [B = pyridine (py) or quinoline (quin)] have been the subject of an e.s.r. study,[15] but no analytical data were published and the i.r. spectra depicted differ significantly from those of the pure products; $[NMe_4][CrOCl_4]$ has only been prepared contaminated with $[NMe_4][CrO_3Cl]$.[24] The remaining complexes have either not been spectroscopically characterised,[16] are novel, or are the subject of conflicting reports (*e.g.* $Cs_2[CrOCl_5]$ [17,21,24]). Current investigations into the e.s.r. spectra of these complexes [35,36] reveal that the pure complexes yield *g* values which differ significantly from published data.

Despite the report of the complex $K_2[CrOCl_5]$ in three different publications in the past 20 years [15,16,20] (none of which reports elemental analysis or i.r. data below 600 cm^{-1}), we have been unable to prepare a pure sample of this complex by any published method.[10, 12, 15, 16, 20] The sample was always contaminated with varying amounts of $K_2[CrCl_5(OH_2)]$, resulting in high magnetic moments and bands due to ν(Cr–O) at *ca.* 420—440 cm^{-1} in the i.r. spectra. The nature of the samples varied from dark red crystals (the purest samples [10]) to an orange-brown powder, depending on the method of preparation employed. A slight increase in the amount of water used in the preparation led to the formation of an almost pure form of $K_2[CrCl_5(OH_2)]$, an orange-brown powder ($\mu_{eff.}$ 3.86 B.M.).* These results are consistent with a report by Hare *et al.*[13] that $Rb_2[CrOCl_5]$

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* Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2.

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contains *ca.* 7% impurity of Cr^{III} when prepared by the published method.[11]

Despite a report that attempts to prepare bromo-oxochromates(V) by analogous routes to those used for chloro-oxochromates(V) led only to perbromide formation,[24] a brownish yellow solid, $[H_2\text{-}2,2'\text{-bipy}][CrOBr_5]$, has recently been reported to have been prepared by just such a method.[33] We have repeated this preparation under the conditions reported [33] (and with a number of variations), and find that we do indeed obtain a brownish yellow solid, which has a very similar nitrogen and bromide content, i.r. spectrum, and e.s.r. spectrum to the described complex. We also found that, assuming the given formulation, the complex had an apparent magnetic moment of *ca.* 1.7 B.M. However, the chromium content of the solid is <2% (theory: 8.31%), and the material behaves as though it were a mixture with a high perbromide content.

The i.r. assignments for $[CrOCl_4]^-$ and $[CrOCl_5]^{2-}$ are listed in Table 2. For $[CrOCl_4]^-$, the range of ν(Cr=O) is 1 016—1 022 cm^{-1} {*cf.*[37] for $[VOCl_4]^{2-}$, ν(V=O) occurs at 996—1 012 cm^{-1}} and of ν(Cr–Cl) is 380—410 cm^{-1}, with low-energy shoulders {*cf.*[38] for $[VOCl_4]^{2-}$, ν(V–Cl) occurs at 340—350 cm^{-1} with low-energy shoulders}. These are the values expected for isolated C_{4v} anions, and there is no evidence for either Cr=O · · · Cr or Cr–Cl–Cr interactions in the i.r. spectra. The only complex of this type which has been the subject of an *X*-ray crystallographic study, $[AsPh_4][CrOCl_4]$,[29,34] contains the expected C_{4v} anion. However, the quoted values of ν(Cr=O) for this complex (948,[28] 950 cm^{-1} [29]) are in error.[24,32] A detailed polarised single-crystal electronic-spectral study [29] of this complex reports that the band at 13 500 cm^{-1} in the visible spectrum shows vibronic coupling with a vibrational mode, ν at ≃920 cm^{-1}, which was assigned as the Cr=O stretching mode of the first excited state. The assignment of ν(Cr=O) in the electronic ground state as being at 1 019 cm^{-1} reinforces the assignment of the electronic transition at 13 500 cm^{-1} as being $3b_2 \rightarrow 13e$,[29] since this is a transition (essentially localised on the Cr=O moiety) from a predominantly metal orbital ($3d_{xy}$) to an orbital ($3d_{xz,yz}$) involving a significant Cr–O π-antibonding interaction. For $[CrOCl_5]^{2-}$ the range of ν(Cr=O) is 925—950 cm^{-1}, and of ν(Cr–Cl) is 330—370 cm^{-1}. Thus the vibrational modes of $[CrOCl_4]^-$ and $[CrOCl_5]^{2-}$ show the expected relations between five- and six-co-ordinate complexes.[39,40]

The electronic spectra of the chromium(V) complexes are listed in Table 2. Solution spectra (in dichloromethane) were recorded where possible, and the relative absorption coefficients of $\nu_1 : \nu_2$ confirm the findings of Garner *et al.*[29] We consider our results inconsistent with the model of the electronic structure proposed by Gray and his co-workers,[13,14] in which ν_2 is assigned as a symmetry-forbidden $^2B_2 \rightarrow {}^2B_1$ ($d_{xy} \rightarrow d_{x^2-y^2}$) transition and equated with 10*Dq* for the in-plane ligands. The magnitude of ε for ν_2 is more convincingly explained in terms of an essentially Cr–O(π)→Cr–O(σ*) transition,[29] the intensity of this absorption being an order of magnitude larger than that for the symmetry-allowed $d_{xy} \rightarrow$

TABLE 2

I.r. and electronic spectra of chromium(V) complexes

	I.r. spectra (cm^{-1})		Electronic spectra (10^3 cm^{-1}) [a]		
			$^2B_2 \rightarrow {}^2E$		Charge-transfer transitions
Complex	ν(Cr=O)	ν(Cr–Cl)	$\nu_1(d_{xy} \rightarrow d_{xz,yz})$	ν_2[Cr–O(π)→Cr–O(σ*)]	
$[Hpy][CrOCl_4]$	1 019	398, 382s, d, 343 (sh)	13.3	18.5	23.0, 25.8, 31.5, 39.3, 43.1
$[Hquin][CrOCl_4]$	1 016	397s, 347 (sh)	13.1,	17.8	*ca.* 23.5, *ca.* 27.0 (sh), 32.8, 45.2
			13.2 (14) [b]	18.2 (160) [b]	
$[Hiquin][CrOCl_4]$	1 016	398s, 348 (sh)	13.1	18.1	22.5, 24.8vbr, d, 30.1, *ca.* 37.5br (sh)
$[NMe_4][CrOCl_4]$	1 016	408 (sh), *ca.* 380s, br	12.4	18.1	21.0 (sh), *ca.* 23.0, *ca.* 26.5vbr, *ca.* 37.0vbr (sh)
$[NEt_4][CrOCl_4]$	1 022	395s, 348 (sh)	13.2	18.0	*ca.* 22.0br (sh), 26.3, 31.0, 37.3
			13.2 (19) [b]	18.2 (124) [b]	22.5 (sh), (1 600), 24.7 (2 400), *ca.* 26.0 (sh), (2 200), *ca.* 32.0 (sh), (3 200), 44.2 (18 000) [b]
$[AsPh_4][CrOCl_4]$	1 019	398s	13.3	18.0	*ca.* 22.5 (sh), *ca.* 26.5br (sh), 29.2br, 31.5 (sh), 36.5
			13.0 (19) [b]	18.1 (129) [b]	*ca.* 23.0 (sh), (1 650), 24.8 (2 300), *ca.* 25.7 (sh), (2 200), 36.8 (8 600), 37.8 (10 000), 38.8 (10 000) [b]
$[H_2\text{-}2,2'\text{-bipy}][CrOCl_5]$	*c*	366s	12.1	19.2 (sh)	23.3 (sh), 24.8, 34.4, 37.5, 44.9
$[H_2\text{-}4,4'\text{-bipy}][CrOCl_5]$	*c*	354s	11.8	*ca.* 19.0 (sh)	24.0, *ca.* 28.0 (br), 37.2, 43.8
$Cs_2[CrOCl_5]$	927	334s, 312 (sh)	11.4	19.1	*ca.* 20.2 (sh), 22.8, 31.2, *ca.* 37.7 br (sh), *ca.* 45.5
' $K_2[CrOCl_5]$ '	948	343s, 313 (sh)	13.4 [d]	*ca.* 17.0 (sh) [d]	21.0, 24.8, 31.9, *ca.* 37.0 (sh), *ca.* 46.5

[a] Reflectance spectra, unless otherwise stated. [b] Solution spectra in CH_2Cl_2; molar absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses. [c] Obscured by ligand bands. [d] Probably due to a chromium(III) impurity.

s = Strong, d = doublet, br = broad, and sh = shoulder.

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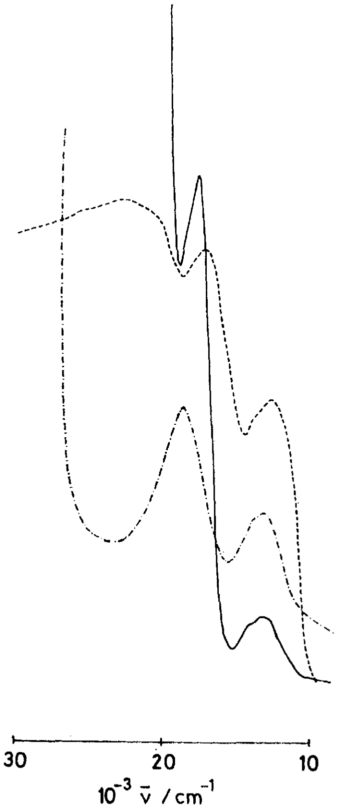
$d_{xz,yz}$ transition (ν_1). A solution of [Hquin][$CrOCl_4$] in dichloromethane yielded Cr^{III} after a few hours. The absorption coefficients quoted in Table 2 for this complex were obtained by extrapolating the value of ε as a function of time to the time when the solution was prepared. The Figure illustrates visible spectra of a freshly prepared red-brown solution [ν_1 at 13 200 (15), ν_2 at 18 200 cm^{-1} (117)] and a fully reduced purple sample [ν_1 at 13 400 (34), ν_2 at 19 200 cm^{-1} (60)].* It is interesting to note that the electronic spectra obtained by earlier workers[24] for [$CrOCl_4$]$^-$ in the reducing solvent ethanenitrile more closely resemble that of the decomposed sample. Solutions of [$AsPh_4$][$CrOCl_4$] in dichloromethane were slowly reduced over a period of days to give a purple solid.



Electronic spectra of [Hquin][$CrOCl_4$]: (– – – –) diffuse-reflectance spectrum; (——) freshly prepared (red–brown) solution in CH_2Cl_2; and (— · — · —) reduced (purple) solution in CH_2Cl_2

Chromium(III) *Complexes*.—When the reaction mixture from which [Hquin][$CrOCl_4$] could be isolated was allowed to stand at *ca.* 0 °C for several weeks, the dark red chromium(V) complex was slowly reduced to give a bright purple chromium(III) complex, [Hquin][$CrCl_4(HO_2CMe)_2$]. Similarly, when the same reaction mixture was heated under reflux for several hours, cooled, and resaturated with hydrogen chloride, the same reduced product was obtained. The analytical data for this, and related complexes discussed in this section, are included in Table 3. The complexes formed by this method were of the general types [A][$CrCl_4(HO_2CMe)_2$], [B]$_2$[$CrCl_5(HO_2CMe)$] [A = Hquin, NMe_4, or NEt_4; B = Hpy, or isoquinolinium (Hiquin)], and [$CrCl_3$(2,2′-bipy)(HO_2CMe)]. Examination of the i.r. and electronic spectra of these complexes (Tables 4 and 5) reveals that the ethanoic acid is complexed to the chromium, and is not present in the lattice as a solvate. Relatively few complexes of co-ordinated ethanoic acid are known.[41–44] A recent *X*-ray crystallographic study[42] of [$Ni(HO_2CMe)_6$][BF_4]$_2$ revealed that ethanoic acid behaves as a unidentate ligand, co-ordinating through the oxygen of the carbonyl group. Although complexes containing the anion [$MX_4(HO_2CMe)_2$]$^-$ (M = Ti or V, X = Cl or Br) have been reported previously,[43,44] the chromium analogues have not been previously prepared. Using active chromium(III) chloride[45,46] it was possible to prepare [$CrCl_4(HO_2CMe)_2$]$^-$ complexes by saturating, for example, a mixture of $CrCl_3$, quinoline, and ethanoic acid with hydrogen chloride. However, sublimed chromium(III) chloride[46] does not react under these conditions, and we believe that the preparative route *via* CrO_3 is more convenient.

The complexes containing [$CrBr_4(HO_2CMe)_2$]$^-$ and [$CrBr_5(HO_2CMe)$]$^{2-}$ were isolated in unsuccessful attempts to prepare [$CrOBr_4$]$^-$ complexes, by an analogous route to that used for [$CrOCl_4$]$^-$ complexes. The i.r. spectra of these complex anions are listed in Table 4, together with bands observed for [NEt_4][$VCl_4(HO_2CMe)_2$].[44] The assignments of the bands due to ethanoic acid confirm that it is indeed complexed,[44] and the multiple ν(Cr–X) modes suggest that, in the case of [$CrX_4(HO_2CMe)_2$]$^-$, the complex has a *cis* configuration. ν(Cr–Cl) lies in the range 320—350 cm^{-1}, ν(Cr–Br) in the range 260—305 cm^{-1}, and ν(Cr–O) in the range 485—505 cm^{-1}, as expected for six-co-ordinate monomeric chromium(III) complexes. The reflectance spectra of the complexes are listed in Table 5. The fact that the ${}^4A_{2g}\rightarrow{}^4T_{2g}$ transition does not show any splitting is consistent with a *cis* configuration for [$CrX_4(HO_2CMe)_2$]$^-$.[47] As no splitting is observed, it is permissible to calculate *B* and *Dq* according to Griffith,[48] and calculate an average value for *Dq* and *B* for [$CrCl_6$]$^{3-}$, [$CrBr_6$]$^{3-}$, and [$Cr(HO_2CMe)_6$]$^{3+}$ by Jørgensen's law of average environment.[49] This

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* Molar absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses.

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yields 1 233 (*cf.* 1 266 cm^{-1} [50]), 1 160, and 1 612 cm^{-1} respectively for *Dq*. The value of *Dq* = 1 612 cm^{-1} for $[Cr(HO_2CMe)_6]^{3+}$ should be compared with that of 1 650 cm^{-1} for $[Cr\{CO(NH_2)_2\}_6]^{3+}$. It has been reported previously [41] that ethanoic acid has a similar ligand-field strength to urea.

TABLE 3

Analytical data for chromium(III) complexes

Complex	Colour	Found C	Found H	Found N	Found X	Calc. C	Calc. H	Calc. N	Calc. X
$[Hpy]_2[CrCl_5(HO_2CMe)]$	Purple crystals	31.8	3.70	6.25	40.0	32.05	3.60	6.25	39.45
$[Hquin][CrCl_4(HO_2CMe)_2]$	Bright purple powder	34.9	3.70	2.90	32.2	35.15	3.65	3.15	31.95
$[Hiquin]_2[CrCl_5(HO_2CMe)]$	Purple powder	43.7	3.85	5.25	32.1	43.7	3.65	5.10	32.25
$[NMe_4][CrCl_4(HO_2CMe)_2]$	Bright purple microcrystals	24.2	5.50	3.90	37.1	24.75	5.20	3.60	36.55
$[NEt_4][CrCl_4(HO_2CMe)_2]$	Pale pink powder	32.4	6.20	3.20	32.0	32.45	6.35	3.15	31.95
$[CrCl_3(2,2'\text{-bipy})(HO_2CMe)]$	Light green powder	38.4	3.25	7.05	27.8	38.35	3.50	7.45	28.3
$[Hpy]_2[CrCl_5(NCMe)]$	Purple crystals	33.3	3.55	9.55	41.2	33.5	3.50	9.75	41.15
$[Hquin][CrCl_4(NCMe)_2]\cdot MeCN$	Dark purple crystals	39.8	4.05	12.4	32.1	40.3	3.85	12.55	31.7
$[NEt_4][CrCl_4(NCMe)_2]$	Grey powder	35.1	6.50	10.5	34.6	35.5	6.45	10.35	34.9
$[Hpy]_2[CrBr_5(HO_2CMe)]$	Green microcrystals	21.9	2.20	4.25	59.2	21.45	2.40	4.15	59.5
$[Hquin][CrBr_4(HO_2CMe)_2]$	Dark brown microcrystals	25.3	2.50	2.10	51.3	25.1	2.60	2.25	51.4
$[NEt_4][CrBr_4(HO_2CMe)_2]$	Red-brown crystals	22.8	4.60	2.30	51.5	23.15	4.55	2.25	51.4
$[H_2\text{-}2,2'\text{-bipy}][CrBr_5(HO_2CMe)]$	Green powder	21.8	2.00	3.90	58.9	21.5	2.10	4.20	59.65
$[Hiquin][CrBr_4(HO_2CMe)_2]$	Brown powder	24.8	2.50	2.50	52.5 *	25.1	2.60	2.25	51.4

* Sample was visibly contaminated with small amounts of $[Hiquin][Br_3]$.

TABLE 4

I.r. spectra (cm^{-1}) of ethanoic acid complexes

	A[43]	B	C	D	E	F	G	H	I	J	K	L
ν(C–O)	1 658vs	1 645vs	1 636vs	1 664vs,br	1 640vs	1 643vs	1 641vs	1 650vs,br	1 663m	1 650vs	1 653m	1 660s
ν(C–O)	1 291vs	1 286s	1 301m	1 259vs	1 269s	1 268m	1 258s	1 290s	1 259m	1 266m	1 304m	1 307m
$\rho_{sym}(CH_3)$	1 016 (sh)	1 016w	*	1 019m	1 017w	1 017m	1 015w	1 019m	1 012w	1 017w	*	*
δ(COO)	634s	639s	635s	638s	629s	626s	618s	633s	618m	623m	*	632m
γ(CCO)	576w	575w	571w	591w	559m	565w	553w					
ν(M–O)	491s	504m	503, 491s,d	498m	500m	489m	485m	491s	*	486s	495w	500m
ν(M–X)	333vs,br 303s	348s 316m	357vs 324vs	333vs 303 (sh)	308 (sh) 291vs 283 (sh)	291vs 284 (sh)	303 (sh) 287 (sh) 284vs	320vs,br	318vs 293 (sh) 281 (sh)	298m 270vs	304m 261s 250 (sh)	368s 350m 329m

m = Medium and w = weak.

* Obscured by ligand bands.

A = $[NEt_4][VCl_4(HO_2CMe)_2]$, B = $[NEt_4][CrCl_4(HO_2CMe)_2]$, C = $[NMe_4][CrCl_4(HO_2CMe)_2]$, D = $[Hquin][CrCl_4(HO_2CMe)_2]$, E = $[NEt_4][CrBr_4(HO_2CMe)_2]$, F = $[Hquin][CrBr_4(HO_2CMe)_2]$, G = $[Hiquin][CrBr_4(HO_2CMe)_2]$, H = $[Hpy]_2[CrCl_5(HO_2CMe)]$, I = $[Hiquin]_2[CrCl_5(HO_2CMe)]$, J = $[Hpy]_2[CrBr_5(HO_2CMe)]$, K = $[H_2\text{-}2,2'\text{-bipy}][CrBr_5(HO_2CMe)]$, and L = $[CrCl_3(2,2'\text{-bipy})(HO_2CMe)]$.

TABLE 5

Electronic-reflectance spectra of chromium(III)–ethanoic acid complexes

Complex	*Dq*/cm^{-1}	*B*/cm^{-1}	*d–d* Transition (10^3 cm^{-1}) $^4A_{2g}\rightarrow{}^4T_{2g}$	*d–d* Transition (10^3 cm^{-1}) $^4A_{2g}\rightarrow{}^4T_{1g}$ (*F*)	Charge-transfer transitions (10^3 cm^{-1})
$[Hquin][CrCl_4(HO_2CMe)_2]$	1 350	582	13.5	19.2	31.6 (sh), 32.5, 37.1, 44.8
$[NMe_4][CrCl_4(HO_2CMe)_2]$	1 350	520	13.5	18.75	*ca.* 35.5vbr, *ca.* 43.0br
$[NEt_4][CrCl_4(HO_2CMe)_2]$	1 380	575	13.8	19.5	*ca.* 36.0vbr, *ca.* 44.5br
$[Hquin][CrBr_4(HO_2CMe)_2]$	1 320	468	13.2	18.0	*ca.* 27.0 (sh), 29.5, 32.8, 36.0, 44.5
$[Hiquin][CrBr_4(HO_2CMe)_2]$	1 300	493	13.0	18.0	*ca.* 26.0 (sh), 29.8, 36.0
$[NEt_4][CrBr_4(HO_2CMe)_2]$	1 310	574	13.1	18.7	*ca.* 26.0br (sh), 29.5, 32.8, *ca.* 37.0vbr, 43.0
$[Hpy]_2[CrCl_5(HO_2CMe)]$	1 300	562	13.0	18.5	33.5, 38.2, 42.5
$[Hiquin]_2[CrCl_5(HO_2CMe)]$	1 295	569	12.95	18.5	*ca.* 25.0 (sh), *ca.* 29.5 (sh), 30.4, *ca.* 35.5br (sh), 42.9
$[Hpy]_2[CrBr_5(HO_2CMe)]$	1 240	486	12.4	17.3	27.0vbr, *ca.* 34.0 (sh), 37.8, 43.0
$[H_2\text{-}2,2'\text{-bipy}][CrBr_5(HO_2CMe)]$	1 230	489	12.3	17.2	22.0 (sh), 23.2 (sh), 28.8, 32.4, *ca.* 37.0br, 44.3
$[CrCl_3(2,2'\text{-bipy})(HO_2CMe)]$	1 570		15.7	(22.1 (sh), 23.6, 25.1)	26.8 (sh), 29.8 (sh), 33.3, 36.7, 43.0
$[Cr\{CO(NH_2)_2\}_6]Cl_3$	1 650	620	16.5	22.8	*ca.* 35.3 (sh), 44.3

There have been previous reports [51,52] that $[Hpy]_2[CrX_5]\cdot MeCO_2H$ (X = Cl or Br), formed by the reaction of pyridine with chromium(III) ethanoate in ethanoic acid–ethanoyl chloride mixtures, are solvates containing CrX_6 units. However, *X*-ray powder photography [51] has revealed them to be isostructural with the complexes $[Hpy]_2[CrX_5(HO_2CMe)]$ reported here. The product $[CrCl_3(2,2'\text{-bipy})(HO_2CMe)]$ shows spectroscopic properties typical of complexes of the general type $[CrCl_3L_2L']$.[53] The possibility of an ionic formulation {*e.g.*

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[50] G. W. A. Fowles and B. J. Russ, *J. Chem. Soc.* (*A*), 1967, 517.

[51] H. D. Hardt and G. Streit, *Z. anorg. Chem.*, 1970, **374**, 63.

[52] H. D. Hardt, M. Fleischer, and G. Streit, *Proc. 3rd Symp. Co-ordination Chem.*, 1970, **1**, 165.

[53] D. H. Brown and R. T. Richardson, *J. Inorg. Nuclear Chem.*, 1973, **35**, 755.

$[CrCl_2(2,2'\text{-bipy})_2][CrCl_4(HO_2CMe)_2]\}$ was eliminated by an examination of the spectroscopic data (Tables 4 and 5). The electronic spectrum indicated a calculated value of $Dq = 2\,055$ cm^{-1} for $[Cr(2,2'\text{-bipy})_3]^{3+}$.

Reaction of the ethanoic acid complexes with ethanenitrile yielded the corresponding ethanenitrile complexes, $[CrCl_4(NCMe)_2]^-$ and $[CrCl_5(NCMe)]^{2-}$ (see Table 3). The i.r. and electronic-spectral data for these complexes (see Table 6) reveal that the ethanenitrile is co-ordinated to the chromium, and that the $[CrCl_4(NCMe)_2]^-$ anion has a *cis* configuration. A single-crystal *X*-ray crystallographic study of $[Hquin][CrCl_4(NCMe)_2]\cdot MeCN$ has confirmed that the anion does indeed have a *cis* configuration.[54] ν(Cr–Cl) lies in the range 320—345 cm^{-1}, and *Dq* for $[Cr(NCMe)_6]^{3+}$ has been calculated as 1 875 cm^{-1} and for $[CrCl_6]^{3-}$ as 1 245 cm^{-1}. Thus for the range of complexes studied the spectrochemical series is 2,2′-bipy > MeCN > $MeCO_2H$ ~ urea > Cl^- > Br^-.

TABLE 6

I.r. and electronic spectra of ethanenitrile complexes

	I.r. spectra (cm^{-1})		Electronic spectra				
					d–d Transitions (10^3 cm^{-1})		Charge-transfer transitions (10^3 cm^{-1})
Complex	ν(C≡N)	ν(Cr–Cl)	*Dq*/cm^{-1}	*B*/cm^{-1}	$^2A_{2g}\rightarrow{}^4T_{2g}$	$^4A_{2g}\rightarrow{}^4T_{1g}$ (*F*)	
$[Hpy]_2[CrCl_5(NCMe)]$	2 320,[a] 2 294	331, 322s, d, 272 (sh)	1 350	581	13.5	19.2	31.5, 34.5 (sh), 38.0, 43.5
$[Hquin][CrCl_4(NCMe)_2]\cdot MeCN$	2 322,[a] 2 292, 2 247 [b]	340s	1 450	565	14.5	20.2	31.5 (sh), 32.3, *ca.* 35.8 (sh), 44.6
$[NEt_4][CrCl_4(NCMe)_2]$	2 334,[a] 2 302	342, 336s, d	1 460	640	14.6	20.85	32.3, 36.0 (sh), 45.0br

[a] Combination (CH_3 bend and C–C stretch) modes. [b] Due to MeCN of crystallisation.

EXPERIMENTAL

Starting Materials.—Chromium(III) chloride (sublimed; Alfa), tetraphenylarsonium chloride (Cambrian), and all the other reagents (B.D.H. or Fisons) were used without further purification, unless otherwise stated. An active form of chromium(III) chloride was prepared by heating $CrCl_3\cdot 6H_2O$ under reflux in excess of thionyl chloride [45] (Found: Cl, 66.8; Cr, 32.6. Calc. for Cl_3Cr: Cl, 67.15; Cr, 32.85%). Hexakis(urea)chromium(III) chloride was prepared by the reaction of urea with an aqueous solution of chromium(III) chloride [55] (Found: C, 14.3; H, 4.90; Cl, 20.4; N, 32.1. Calc. for $C_6H_{24}Cl_3CrN_{12}O_6$: C, 13.9; H, 4.65; Cl, 20.5; N, 32.4%). Hydrogen halides were dried (H_2SO_4) prior to use. Dichloromethane and ethanenitrile were dried (CaH_2 and P_4O_{10} respectively) and distilled prior to use.

Physical Methods and Analyses.—Electronic spectra were recorded on a Unicam SP 700C spectrophotometer, i.r. spectra on Perkin-Elmer 457 and 577 spectrophotometers. Magnetic moments were measured by the Gouy method at room temperature. *X*-Ray powder photographs were recorded using a Debye–Scherrer camera and filtered Cu-K_α radiation (λ 1.540 51 Å). Analyses (C, H, N, Cl, and Cr) were either by the Microanalyses Unit, Inorganic Chemistry Laboratory, Oxford University, or by the Butterworth Microanalytical Consultancy, Ltd.

All the preparations and manipulations were performed under dry nitrogen or *in vacuo*.

Preparations.—$[HB][CrOCl_4]$ (B = py, quin, *or* iquin). A typical preparation using pyridine is described. The mol ratio of B : Cr was 0.8 : 1.

Chromium(VI) oxide (5 g) was added to ethanoic acid (150 cm^3) and the mixture was saturated with hydrogen chloride at room temperature. A solution of pyridine (3.2 cm^3) in $MeCO_2H$ (10 cm^3), through which hydrogen chloride had been passed for *ca.* 30 s, was added, and the mixture was then resaturated with hydrogen chloride. Red crystals start to appear at this stage. The mixture was vigorously shaken for 1 h (to ensure complete dissolution of the CrO_3) and allowed to stand overnight. The red crystals were filtered off *in vacuo*, washed with $MeCO_2H$ (150 cm^3), and dried *in vacuo*. Changing the mol ratio of B : Cr to 2.2 : 1 did not produce $[CrOCl_5]^{2-}$ complexes.

$[A][CrOCl_4]$ (A = $AsPh_4$ *or* NEt_4) *and* $Cs_2[CrOCl_5]$. The preparations were as above, except that ACl (A = $AsPh_4$, NEt_4, or Cs) was used instead of B, and was dissolved in a minimum volume of $MeCO_2H$. No hydrogen chloride was passed through this solution prior to its addition to the reaction mixture. In the case of CsCl only the mol ratio of ACl : Cr was 2.2 : 1.

$[H_2B][CrOCl_5]$ (B = 2,2′- *or* 4,4′-bipy). The preparations were as for $[HB][CrOCl_4]$, except that the hydrogen chloride was passed into the solution of B in $MeCO_2H$ until precipitation of the amine hydrochloride was imminent.

$[NMe_4][CrOCl_4]$. Chromium(VI) oxide (5 g) was added to $MeCO_2H$ (150 cm^3) and the mixture was saturated with hydrogen chloride at room temperature. The mixture was frequently shaken until all the CrO_3 had dissolved (*ca.* 3 h). A solution of tetramethylammonium chloride (4.4 g) in $MeCO_2H$ (50 cm^3), through which hydrogen chloride had been passed for *ca.* 30 s, was added immediately and the mixture was then resaturated with hydrogen chloride. The red-brown powder which formed was collected immediately by filtration *in vacuo*, washed with $MeCO_2H$ (150 cm^3), and dried *in vacuo*.

Attempts to prepare this complex by an analogous method to that used for $[NEt_4][CrOCl_4]$ led to a complex heavily contaminated with $[NMe_4][CrO_3Cl]$, as found previously.[24] Any attempt to allow the reaction mixture to stand prior to filtration led to contamination with a chromium(III) complex.

‘ $K_2[CrOCl_5]$ ’. A solution of CrO_3 (6 g) in water (15 cm^3) was added to concentrated hydrochloric acid (150 cm^3) at −11 °C, which had been saturated (at −11 °C) with hydrogen chloride, and the resulting mixture was resaturated with hydrogen chloride. The mixture was allowed to stand at 0 °C for 5 min, whilst the $CrCl_2O_2$ formed in the reaction separated as a heavy red oil. The mother liquor was decanted rapidly into a flask at −11 °C,

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[54] C. K. Prout and P. D. P. Thomas, personal communication.

[55] G. Brauer, ‘ Handbuch der Präparativen Anorganischen Chemie,’ Enke, Stuttgart, 1960.

and to this was added a solution of potassium chloride (2.1 g) in water (15 cm^3). Hydrogen chloride was passed through this solution for 10 min, and the dark red crystals which formed were immediately filtered off and dried *in vacuo*. The sample was contaminated with small amounts of $K_2[CrCl_5(OH_2)]$ (Found: Cl, 54.5; Cr, 15.9; K, 24.1. Calc. for Cl_5CrK_2O: Cl, 54.8; Cr, 16.1; K, 24.2%). Any delay, or allowing the temperature to rise above 0 °C, caused rapid reduction of the product.

'$[H_2\text{-}2,2'\text{-bipy}][CrOBr_5]$'. Hydrobromic acid (*ca.* 25 cm^3), saturated with hydrogen bromide at −5 °C, was added dropwise, with stirring, to finely powdered potassium dichromate (3 g) at −5 °C until all the solid had dissolved. A solution of 2,2'-bipyridine (3 g) in hydrobromic acid (15 cm^3) at −5 °C was then added to the red solution, and the orange-yellow solid formed was filtered off immediately *in vacuo*, washed with hydrobromic acid (15 cm^3) saturated with hydrogen bromide at −5 °C, and dried *in vacuo* (Found: C, 17.8; H, 1.60; Br, 64.8; Cr, 0.90; K, 9.6; N, 4.20. Calc. for $C_{10}H_{10}Br_5CrN_2O$: C, 19.2; H, 1.60; Br, 63.85; Cr, 8.30; K, 0.00; N, 4.50%).

$[A][CrCl_4(HO_2CMe)_2]$ (A = Hquin, NEt_4, *or* NMe_4). The reaction mixture from which $[A][CrOCl_4]$ may have been isolated by filtration was heated under reflux until a dark green solution formed (*ca.* 3 h). This solution was saturated with hydrogen chloride at room temperature until the solution became dark purple, and was then allowed to stand at 0 °C for several weeks. The precipitated complex was collected by filtration *in vacuo*, washed with $MeCO_2H$ (*ca.* 150 cm^3), and dried *in vacuo*.

Attempts to prepare $[Hpy][CrCl_4(HO_2CMe)_2]$ and $[Hiquin][CrCl_4(HO_2CMe)_2]$ by this method did not produce a solid product.

$[HB]_2[CrCl_5(HO_2CMe)]$ (B = py *or* iquin). A typical preparation using pyridine is described. The mol ratio of B : Cr was 2.2 : 1.

Chromium(VI) oxide (5 g) was added to $MeCO_2H$ (150 cm^3) and the mixture was saturated with hydrogen chloride at room temperature. Pyridine (9 cm^3) was added to the mixture which was then resaturated with hydrogen chloride and heated under reflux until a dark green solution formed (*ca.* 4 h). This solution was saturated with hydrogen chloride at room temperature until the solution became dark purple, and then allowed to stand at 0 °C for several weeks. The purple crystals were collected by filtration *in vacuo*, washed with $MeCO_2H$ (*ca* 200 cm^3), and dried *in vacuo*.

Attempts to prepare $[Hquin]_2[CrCl_5(HO_2CMe)]$ by this method yielded only $[Hquin][CrCl_4(HO_2CMe)_2]$.

$[CrCl_3(2,2'\text{-bipy})(HO_2CMe)]$. The reaction mixture from which $[H_2\text{-}2,2'\text{-bipy}][CrOCl_5]$ may have been isolated by filtration was heated under reflux for 2 h, forming a pale green powder and dark green solution. The powder was filtered off *in vacuo*, washed with $MeCO_2H$ (100 cm^3), and dried *in vacuo*. Saturation of the green filtrate with hydrogen chloride yielded a blue-green form of the same complex.

Alternative methods for $[Hquin][CrCl_4(HO_2CMe)_2]$. (*a*) The reaction mixture from which $[Hquin][CrOCl_4]$ may have been isolated by filtration was stored at −20 °C for 2 months. The solid, now purple, was collected by filtration *in vacuo*, washed with $MeCO_2H$ (200 cm^3), and dried *in vacuo* (Found: C, 34.5; H, 3.70; Cl, 31.8; N, 2.90. Calc. for $C_{13}H_{16}Cl_4CrNO_4$: C, 35.15; H, 3.65; Cl, 31.95; N, 3.15%).

(*b*) A solution of quinoline (2 cm^3) in $MeCO_2H$ (5 cm^3) was added to a solution of active chromium(III) chloride (2.71 g) in $MeCO_2H$ (55 cm^3). The turquoise solution was saturated with hydrogen chloride, and the resulting purple powder was filtered off *in vacuo*, washed with $MeCO_2H$ (150 cm^3), and dried *in vacuo* (Found: C, 34.9; H, 3.50; Cl, 33.1; N, 2.94%). Sublimed chromium(III) chloride will not react under the conditions described.

$[HB][CrBr_4(HO_2CMe)_2]$ (B = quin *or* iquin) *and* $[NEt_4][CrBr_4(HO_2CMe)_2]$. A typical preparation using quinoline is described. The ratio of B : Cr (and $[NEt_4]Br$: Cr) was 0.8 : 1.

Chromium(VI) oxide (5 g) was added to $MeCO_2H$ (150 cm^3) and the mixture was saturated with hydrogen bromide at room temperature. A solution of quinoline (4.7 cm^3) in $MeCO_2H$ (10 cm^3) was added and the mixture was resaturated with hydrogen bromide, and allowed to stand at 0 °C for several weeks. The precipitated complex was filtered off *in vacuo*, washed with $MeCO_2H$ (300 cm^3), and dried *in vacuo*.

$[H_2\text{-}2,2'\text{-bipy}][CrBr_5(HO_2CMe)]$ *and* $[Hpy]_2[CrBr_5(HO_2CMe)]$.—The preparations were as above, except that mol ratios of 2,2'-bipy : Cr and py : Cr of 0.4 : 1 and 2.2 : 1 were used, respectively. A py : Cr mol ratio of 0.8 : 1 produced the desired complex, only in a much smaller yield.

$[NEt_4][CrCl_4(NCMe)_2]$, $[Hquin][CrCl_4(NCMe)_2]\cdot MeCN$ *and* $[Hpy]_2[CrCl_5(NCMe)]$. A typical preparation is described. All the ethanenitrile complexes were prepared from their ethanoic acid analogues.

Quinolinium tetrachlorobis(ethanoic acid)chromate(III) (2.2 g) was mixed with ethanenitrile (200 cm^3) and heated under reflux until complete solution was achieved (*ca.* 1 h). The purple solution was allowed to stand at −20 °C for several weeks, whence the precipitated complex was filtered off *in vacuo*, washed with MeCN (50 cm^3), and dried *in vacuo*.

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