Table 2. *Selected geometric parameters (Å, °)*

Eu—O2	2.320 (9)	Eu—O12	2.46 (1)
Eu—O5	2.36 (1)	Eu—N3	2.65 (1)
Eu—O6	2.379 (9)	Eu—N2	2.65 (1)
Eu—O10	2.405 (9)	Eu—N1	2.81 (1)
Eu—O8	2.437 (8)		
O2—Eu—O5	75.3 (3)	O10—Eu—N3	66.0 (3)
O2—Eu—O6	90.8 (3)	O8—Eu—N3	65.3 (3)
O5—Eu—O6	133.9 (3)	O12—Eu—N3	120.0 (3)
O2—Eu—O10	143.4 (3)	O2—Eu—N2	130.8 (3)
O5—Eu—O10	137.5 (3)	O5—Eu—N2	88.3 (3)
O6—Eu—O10	75.7 (3)	O6—Eu—N2	67.9 (3)
O2—Eu—O8	86.4 (3)	O10—Eu—N2	75.5 (3)
O5—Eu—O8	74.5 (3)	O8—Eu—N2	133.8 (3)
O6—Eu—O8	149.4 (3)	O12—Eu—N2	134.4 (4)
O8—Eu—O10	88.7 (3)	N3—Eu—N2	68.6 (3)
O12—Eu—O2	73.5 (3)	O2—Eu—N1	62.1 (3)
O12—Eu—O5	137.2 (4)	O5—Eu—N1	62.9 (3)
O12—Eu—O6	75.1 (4)	O6—Eu—N1	71.7 (3)
O12—Eu—O10	70.2 (3)	O10—Eu—N1	138.7 (3)
O8—Eu—O12	74.9 (3)	O8—Eu—N1	131.5 (3)
O2—Eu—N3	140.8 (3)	O12—Eu—N1	122.9 (3)
O5—Eu—N3	71.5 (3)	N3—Eu—N1	117.1 (3)
O6—Eu—N3	127.4 (3)	N2—Eu—N1	69.1 (3)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C13—H13*B*···O1	0.97 (2)	2.38 (2)	2.82 (2)	107 (1)
C19—H19*B*···O5	0.97 (2)	2.36 (2)	2.86 (2)	111 (1)

Table 3. *Dihedral angles (°) for the coordination polyhedron of [Eu(BOPTA)(H$_2$O)]$^{2-}$*

Face 1	Face 2	Angle (°)	Idealized angle (°) for D_{3h} geometry
O2—O5—O8	O6—N2—O10	176.90 (4)	180
O2—O5—O8	N1—N3—O12	173.6 (2)	180
O6—N2—O10	N1—N3—O12	173.3 (3)	180
O8—O10—O12	N1—O5—N2	138.4 (4)	146.4
O2—O6—O12	O5—N2—N3	141.3 (4)	146.4
O2—O6—N1	O8—O10—N3	139.6 (4)	146.4
O2—O6—O12	O2—O6—N1	19.2 (4)	26.4
O8—O10—O12	O8—O10—N3	22.8 (3)	26.4
O5—N2—N1	O5—N2—N3	17.5 (4)	26.4

The crystals exist as twins with a twinning plane perpendicular to the *c** reciprocal axis. Reciprocal matrices for both twins were found and the ratio between the intensities of the two twins was about 1.3. Corrections for the superimposed reflections were performed using a local program; reflections were considered to be superimposed when the distance was less than 0.012 Å^{-1} in the reciprocal lattice. It was not possible to localize the water H atoms during the refinement process.

Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELX76* (Sheldrick, 1976). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including intermolecular contact distances, have been deposited with the IUCr (Reference: NA1216). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Five New Chlorochromates of Organic Bases

PABLO A. LORENZO LUIS,[a] PEDRO MARTIN-ZARZA,[a] PEDRO GILI,[a] CATALINA RUIZ-PÉREZ,[b] M. HERNÁNDEZ-MOLINA[b] AND XAVIER SOLANS[c]

[a]*Departamento de Quimica Inorganica, Facultad de Farmica, Universidad de La Laguna, Tenerife, Canary Islands, Spain,* [b]*Departamento de Fisica Fundamental y Experimental, Universidad de La Laguna, Tenerife, Canary Islands, Spain, and* [c]*Departamento de Cristallografia, Mineralogia i Deposits Minerals, Universidad de Barcelona, Spain*

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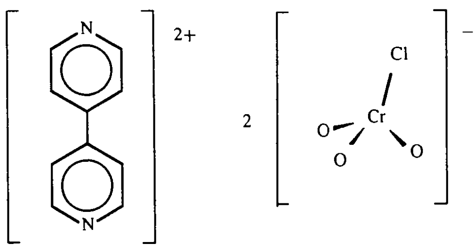
Abstract

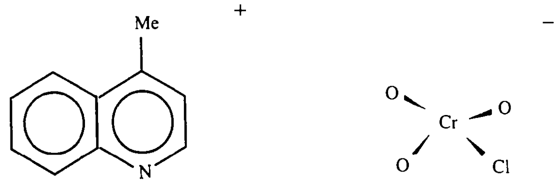
We have synthesized and characterized five new chlorochromate(VI) complexes of organic bases: 4,4′-bipyridinediium bis[chlorochromate(VI)], $(C_{10}H_{10}N_2)$-$[CrO_3Cl]_2$, 4-methylquinolinium chlorochromate(VI), $(C_{10}H_{10}N)[CrO_3Cl]$, 6-methylquinolinium chlorochromate(VI), $(C_{10}H_{10}N)[CrO_3Cl]$, *N,N′*-ethylenediaminium chloride chlorochromate(VI), $(C_2H_{10}N_2)(Cl)[CrO_3Cl]$ and (5-chloro-2-pyridyl)(2-pyridyl)ammonium chloro-

chromate(VI), $(C_{10}H_9ClN_3)[CrO_3Cl]$. The crystal and molecular structures of these compounds have been determined by X-ray crystallography and show that organic cations are bound to $[CrO_3Cl]^-$ anions by significant N···O and C···O hydrogen-bonding interactions.

Comment

Compounds of chromium(VI) with organic bases have been shown to be selective oxidants for primary and secondary alcohols (Corey & Suggs, 1975; Davis, Sheets, Paudler & Gard, 1984). To our knowledge, the structures of the chlorochromates of pyrazinium (Pressprich, Willet, Paudler & Gard, 1990), potassium (Helmholz & Foster, 1950) and ammonium (Colton & Canterford, 1969) are known. Pyridinium chlorochromate(VI) (Corey & Suggs, 1975) has also been described but its structure is not known. We describe here the preparation, characterization and crystal and molecular structures of five new chlorochromate(VI) complexes of organic bases, 4,4′-bipyridinediium bis[chlorochromate(VI)], (1), 4-methylquinolinium chlorochromate(VI), (2), 6-methylquinolinium chlorochromate(VI), (3), *N*,*N*′-ethylenediaminium chloride chlorochromate(VI), (4), (4-chloro-2-pyridyl)(2-pyridyl)ammonium chlorochromate(VI), (5).


(1)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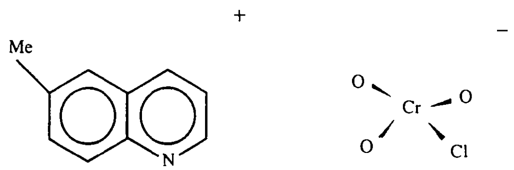
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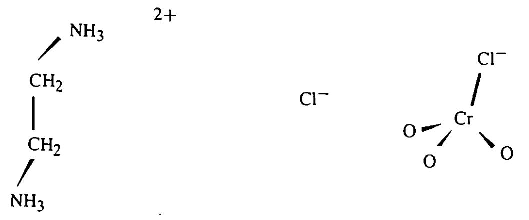
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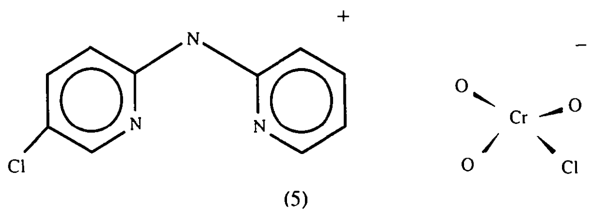
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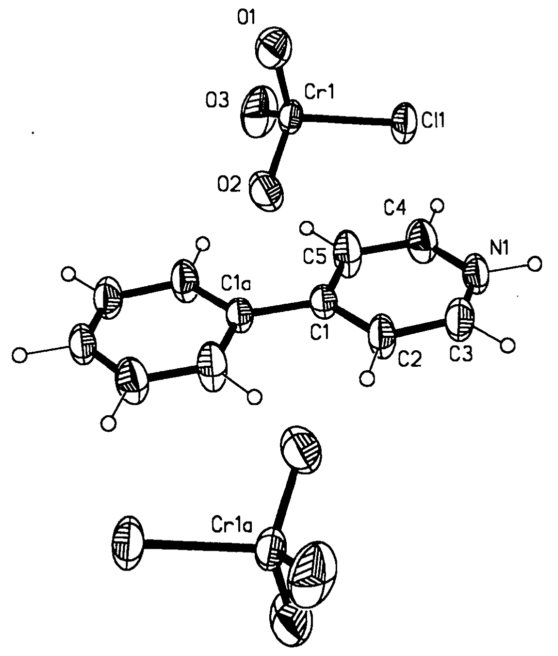

Fig. 1. Molecular structure of 4,4′-bipyridinediium chlorochromate(VI), (1), showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

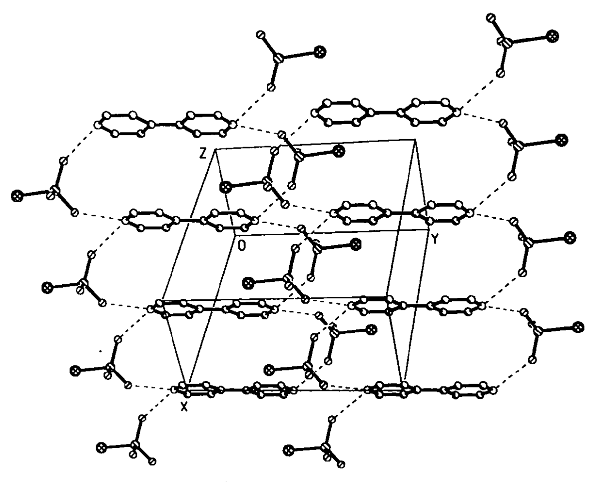

Fig. 2. Crystal structure of (1).

The chlorochromates described here can be considered to be formed by organic cations hydrogen bonded to anions, which have distorted tetrahedral geometry. The Cr—O bond distances for these compounds are found between 1.588 (4) and 1.622 (2) Å; the distance in monochromates is reported as 1.66 Å (Dobbs & Hehre, 1987) or 1.646 (2) Å (Pressprich *et al.*, 1988). The *ab initio* theoretical (SCF–MO) value obtained for Cr—O, using the double-zeta bases of valency incorporating pseudopotentials with ECP (effective core potentials) to take into account the internal electrons (Hay & Wadt, 1985), is 1.502 Å. The experimental values for Cr—Cl distances are between 2.158 (1) and 2.189 (1) Å, whereas the theoretical value is 2.340 Å.

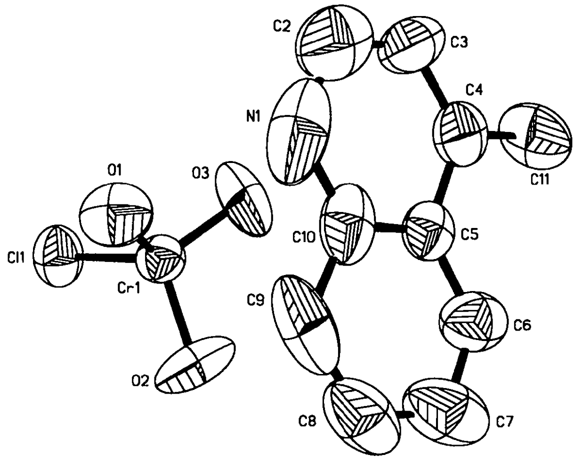

Fig. 3. Molecular structure of 4-methylquinolinium chlorochromate(VI), (2), showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

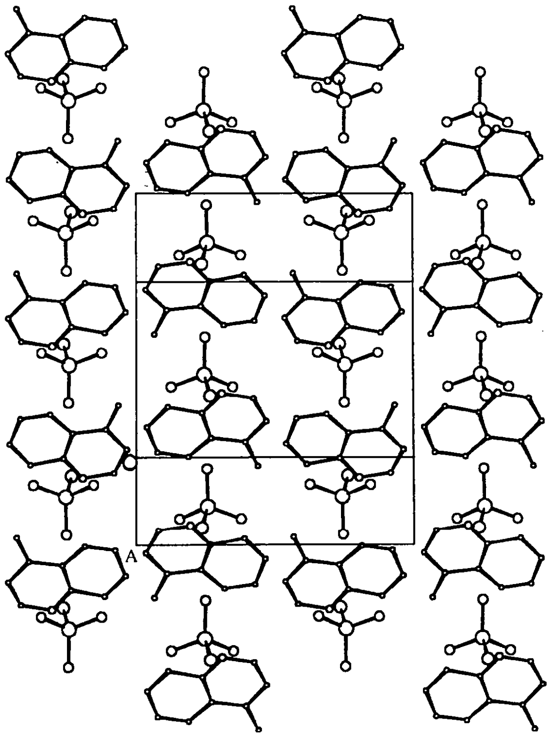

Fig. 4. Crystal structure of (2).

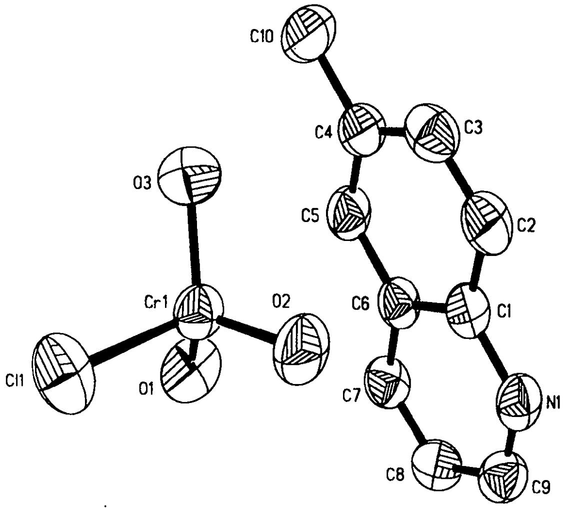

Fig. 5. Molecular structure of 6-methylquinolinium chlorochromate(VI), (3), showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

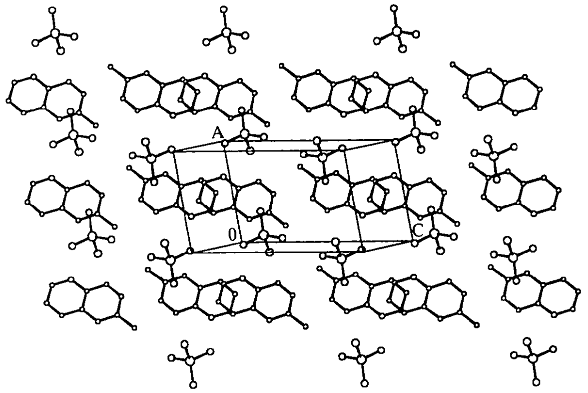

Fig. 6. Crystal structure of (3).

The experimental angles around chromium deviate significantly from the ideal tetrahedral value of 109.47°, within the range 106.2 (1)–113.7 (2)°, while the theoretical values lie between 106.5 and 112.3°. Geometric optimizations were performed using *GAUSSIAN*92 (Frisch *et al.*, 1992).

The organic cations are bound to the anions by hydrogen bonds of the type N—H···O, with N···O distances of 2.760 (3)–3.209 (5) Å, similar to the literature values (Pimentel & McClellan, 1960), and N—H···O angles of 119.9 (2)–161.1 (4)°. There are also some relatively short contacts: C···O = 3.094 (5) Å with C—H···O > 120°. These interactions cannot be considered as hydrogen bonds, but they do indicate some degree of polarization (Pressprich *et al.*, 1990). In the pyrazinium chlorochromate there are also N—H···N contacts between organic cations (Pressprich *et al.*, 1990).

The tetrahedral distortion of the anions has been calculated using the equations: $\Delta l = 1/4\Sigma[(R_i - R)/R]^2$ and $\Delta\alpha = 1/6\Sigma[(\alpha_i - 109.47)/109.47]^2$, where R_i is an individual Cr—O or Cr—Cl distance, R the mean Cr—O or Cr—Cl distance and α_i an individual O—Cr—O or O—Cl—O angle, respectively. We have compared the chlorochromates described here with K[CrO$_3$Cl] (Helmholz & Foster, 1950) and (pyrazinium)[CrO$_3$Cl] (Pressprich *et al.*, 1990). As a consequence of the ionic interaction between the cation and the anion, potassium chlorochromate shows the largest distortion ($\Delta l \times 10^2 = 2.60$ and $\Delta\alpha \times 10^4 = 7.50$). The calculated distorsions, Δl and $\Delta\alpha$ are similar for all organic chlorochromates ($\Delta l \times 10^2 = 2.06$ and $1.90 \leq \Delta\alpha \times 10^4 \leq 6.60$).

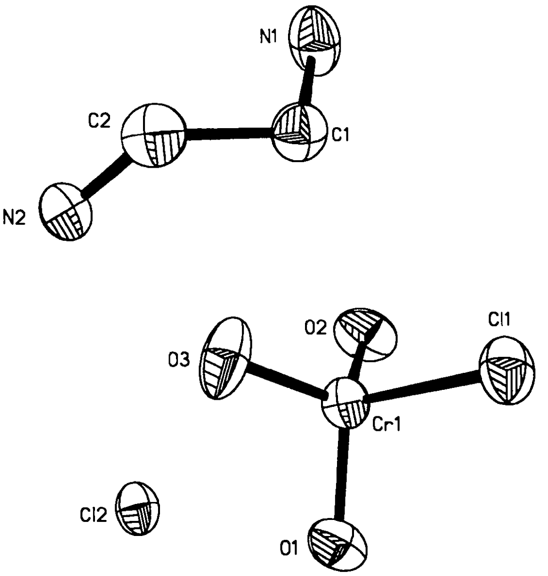

Fig. 7. Molecular structure of *N,N'*-ethylenediaminium chloride chlorochromate(VI), (4), showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

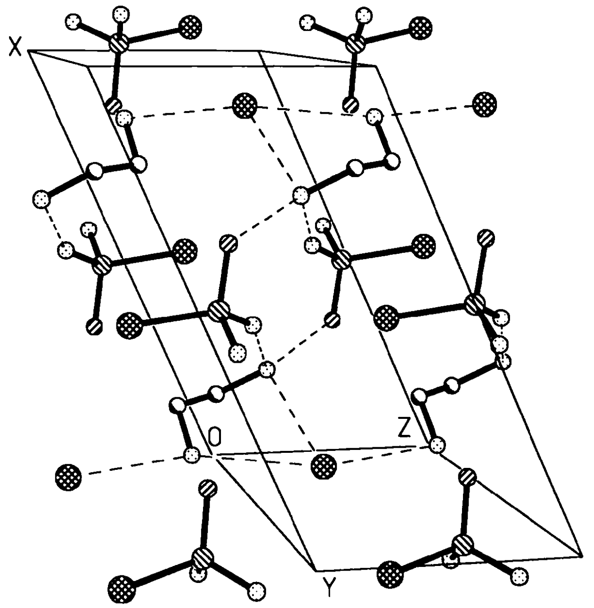

Fig. 8. Crystal structure of (4).

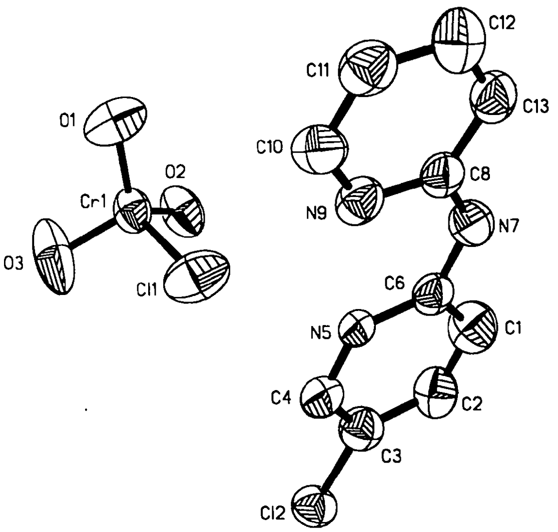

Fig. 9. Molecular structure of (5-chloro-2-pyridyl)(2-pyridyl)ammonium chlorochromate(VI), (5), showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

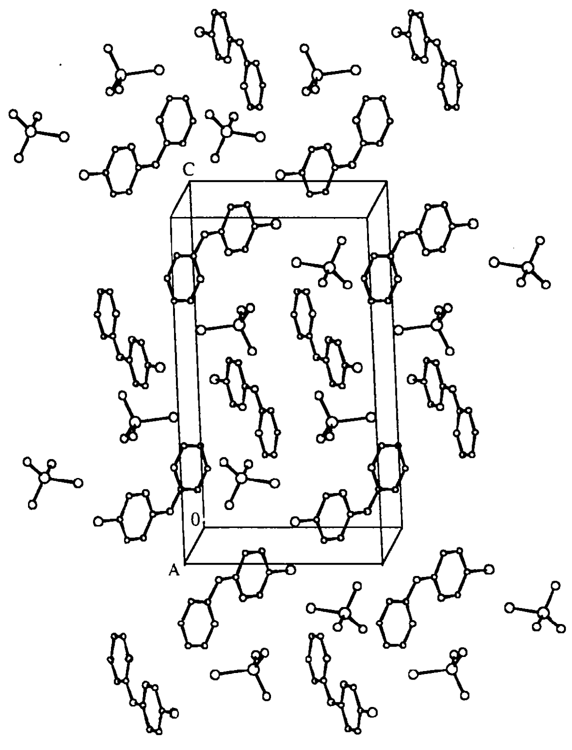

Fig. 10. Crystal structure of (5).

The IR spectra of the compounds show bands at 961–944 cm^{-1}, which correspond to the asymmetric stretching vibration ν_{as}(Cr—O). The bands at 915–904 cm^{-1} are due to the symmetric stretching vibration ν_s(Cr—O), while the bands at 440–432 cm^{-1} correspond to ν_s(Cr—Cl) (Nakamoto, 1986; Ciéslak-Golonga, 1991).

For the interpretation of the electronic spectra, we used the orbital energies for the $[CrO_3Cl]^-$ anion calculated by the $X(\alpha)$-scattered-wave method (Miller, Tinti & Case, 1989). Thus, the bands at 454–440 nm (2.77 eV) correspond to a $1a_2 \rightarrow 10e$ transition (calculated 2.9 eV), whereas the bands at 357–350 nm (3.43 eV) correspond to a $9e \rightarrow 10e$ transition (calculated 3.25 eV).

Experimental

For compound (1), an aqueous solution (15 cm^3, 6 *M* in HCl) of 4,4′-bipyridyl (0.78 g, 5 mmol) was added to another aqueous solution (15cm^3, 6 *M* in HCl) containing CrO_3 (1 g, 10 mmol) at room temperature. The mixture was stirred and a large amount of orange solid formed. The solid product was dissolved in hot aqeuous HCl (6 *M*) giving an orange solution, from which orange crystals were obtained after 10 days. Elemental analysis: found C 27.69, H 2.27, N 6.51%; $C_{10}H_{10}N_2Cr_2O_6Cl_2$ requires C 27.99, H 2.35, N 6.53%.

For compound (2), an aqueous solution (15 cm^3, 6 *M* in HCl) of 4-methylquinoline (1.43 g, 10 mmol) was added to another aqueous solution (15cm^3, 6 *M* in HCl) containing CrO_3 (1 g, 10 mmol) at room temperature. The mixture was stirred and a large amount of yellow solid was formed. The solid product was dissolved in a hot aqueous HCl (6 *M*) solution. An orange solution was formed, from which red–orange crystals were obtained after 12 days. Elemental analysis: found C 42.89, H 3.69, N 4.84%; $C_{10}H_{10}NCrO_3Cl$ requires C 42.95, H 3.60, N 5.00%.

For compound (3), an aqueous solution (15 cm^3, 6 *M* in HCl) of 6-methylquinoline (1.43 g, 10 mmol) was added to another aqueous solution (15 cm^3, 6 *M* in HCl) containing CrO_3 (1 g, 10 mmol) at room temperature. The mixture was stirred and a large amount of yellow solid was formed. The solid product was dissolved in hot aqueous HCl (6 *M*) giving an orange solution from which red–orange crystals were obtained after 12 days. Elemental analysis: found C 42.44, H 3.60, N 4.91%; $C_{10}H_{10}NCrO_3Cl$ requires C 42.95, H 3.60, N 5.00%.

For compound (4), an aqueous solution (15 cm^3, 6 *M* in HCl) of *N,N*′-ethylendiamine (0.60 g, 10 mmol) was added to another aqueous solution (15 cm^3, 6 *M* in HCl) containing CrO_3 (1 g, 10 mmol) at room temperature. The mixture was stirred and a large amount of orange solution was formed, from which orange crystals were obtained after 10 days. Elemental analysis: found C 9.98, H 4.36, N 12.07%; $C_2H_{10}N_2CrO_3Cl_2$ requires C 10.29, H 4.29, N 12.02%.

For compound (5), an aqueous solution (15 cm^3, 6 *M* in HCl) of 2,2′-bipyridylamine (1.71 g, 10 mmol) was added to another aqueous solution (15 cm^3, 6 *M* in HCl) containing CrO_3 (1 g, 10 mmol) at room temperature. The mixture was stirred and a large amount of orange solid formed. The solid product was dissolved in hot aqueous HCl (6 *M*) giving an orange solution, from which orange crystals were obtained after 3 days. Elemental analysis: found C 34.43, H 2.59, N 11.79%; $C_{10}H_9N_3CrO_3Cl_2$ requires C 34.90, H 2.64, N 12.21%.

Elemental analyses (C, H and N) were performed in a Carlo Erba 1106 automatic analyser. The IR spectra were obtained with a Nicolet 710 FT–IR spectrophotometer in the 4000–250 cm^{-1} range, using KBr pellets. Electronic spectra as diffuse refluctance were recorded on a Perkin-Elmer 550S spectrophotometer, dispersing all samples in $BaSO_4$.

Compound (1)

Crystal data

$(C_{10}H_{10}N_2)[CrO_3Cl]_2$
M_r = 429.1
Monoclinic
$P2_1/n$
a = 11.871 (2) Å
b = 11.586 (3) Å
c = 5.707 (2) Å
β = 98.75 (2)°
V = 775.8 (2) Å^3
Z = 2
D_x = 1.837 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 4–15°
μ = 1.77 mm^{-1}
T = 293 K
Prism
0.25 × 0.15 × 0.15 mm
Orange

Data collection

Philips PW1100 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1750 measured reflections
1605 independent reflections
1575 observed reflections [$I > 3\sigma(I)$]

R_{int} = 0.055
θ_{max} = 30°
$h = -16 \rightarrow 16$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 8$
2 standard reflections
frequency: 60 min
intensity decay: <5%

Refinement

Refinement on F
R = 0.052
wR = 0.058
S = 1.32
1543 reflections
101 parameters
$w = 1/[\sigma^2(F) + 0.01201F^2]$

$(\Delta/\sigma)_{max}$ = 0.0460
$\Delta\rho_{max}$ = 0.460 e Å^{-3}
$\Delta\rho_{min}$ = −1.09 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (1)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Cr(1)	0.19321 (3)	0.01823 (5)	0.17182 (4)	0.0358 (1)
Cl(1)	0.20261 (3)	0.20643 (2)	0.14810 (6)	0.0501 (3)
O(1)	0.0923 (3)	−0.0096 (3)	0.3174 (9)	0.0754 (13)
O(2)	0.3142 (2)	−0.0233 (3)	0.3060 (6)	0.0572 (10)
O(3)	0.1742 (3)	−0.0345 (3)	−0.0915 (6)	0.0723 (13)
N(1)	0.4499 (2)	0.2935 (2)	0.8964 (5)	0.0398 (8)
C(1)	0.4905 (2)	0.0626 (2)	0.9778 (5)	0.0312 (8)
C(2)	0.5407 (3)	0.1463 (3)	1.1358 (7)	0.0439 (10)
C(3)	0.5177 (3)	0.2610 (3)	1.0895 (7)	0.0490 (12)
C(4)	0.4001 (4)	0.2168 (3)	0.7402 (7)	0.0483 (12)
C(5)	0.4186 (4)	0.1016 (3)	0.7761 (7)	0.0494 (11)

Table 2. *Selected geometric parameters (Å, °) for (1)*

Cr(1)—Cl(1)	2.189 (1)	N(1)—C(4)	1.332 (4)
Cr(1)—O(1)	1.591 (4)	C(1)—C(2)	1.395 (4)
Cr(1)—O(2)	1.596 (2)	C(1)—C(5)	1.400 (5)
Cr(1)—O(3)	1.606 (4)	C(2)—C(3)	1.374 (5)
N(1)—C(3)	1.317 (4)	C(4)—C(5)	1.363 (5)
O(1)—Cr(1)—O(2)	112.5 (2)	C(3)—N(1)—C(4)	121.5 (3)
O(1)—Cr(1)—O(3)	113.7 (2)	C(2)—C(1)—C(5)	117.0 (3)
O(2)—Cr(1)—O(3)	108.8 (2)	C(1)—C(2)—C(3)	119.7 (3)
Cl(1)—Cr(1)—O(1)	106.5 (1)	N(1)—C(3)—C(2)	121.0 (3)
Cl(1)—Cr(1)—O(2)	106.2 (1)	N(1)—C(4)—C(5)	120.5 (4)
Cl(1)—Cr(1)—O(3)	108.8 (1)	C(1)—C(5)—C(4)	120.3 (3)

Compound (2)

Crystal data

$(C_{10}H_{10}N)[CrO_3Cl]$
$M_r = 279.6$
Monoclinic
$P2_1/c$
$a = 9.685\ (2)$ Å
$b = 11.679\ (2)$ Å
$c = 11.022\ (2)$ Å
$\beta = 112.28\ (3)°$
$V = 1153.6\ (4)$ Å^3
$Z = 4$
$D_x = 1.610$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6–18°$
$\mu = 1.21$ mm^{-1}
$T = 293$ K
Prism
0.25 × 0.13 × 0.12 mm
Red–orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3012 measured reflections
2769 independent reflections
1961 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0113$
$\theta_{\rm max} = 29.97°$
$h = -13 \rightarrow 12$
$k = -3 \rightarrow 16$
$l = 0 \rightarrow 15$
2 standard reflections
frequency: 60 min
intensity decay: <10%

Refinement

Refinement on F^2
$R(F) = 0.0708$
$wR(F^2) = 0.1986$
$S = 1.082$
2757 reflections
145 parameters
$w = 1/[\sigma^2(F_o^2) + (0.1421P)^2 + 0.6429P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.060$
$\Delta\rho_{\rm max} = 0.112$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.059$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cr(1)	0.16921 (7)	0.24419 (5)	0.37089 (6)	0.0493 (3)
Cl(1)	0.38921 (1)	0.26537 (1)	0.36403 (1)	0.0722 (5)
O(1)	0.1856 (5)	0.2464 (3)	0.5198 (3)	0.0793 (16)
O(2)	0.1039 (5)	0.1246 (4)	0.3035 (4)	0.1031 (19)
O(3)	0.0643 (5)	0.3444 (4)	0.2882 (4)	0.100 (2)
N(1)	0.8800 (5)	0.3065 (3)	0.5352 (3)	0.111 (3)
C(2)	0.8550 (3)	0.4208 (3)	0.5135 (3)	0.108 (4)
C(3)	0.7654 (2)	0.4648 (3)	0.3924 (3)	0.082 (3)
C(4)	0.6947 (3)	0.3900 (2)	0.2921 (2)	0.068 (2)
C(5)	0.7206 (2)	0.2682 (2)	0.3149 (2)	0.053 (2)
C(6)	0.6567 (3)	0.1873 (3)	0.2197 (3)	0.077 (2)
C(7)	0.6821 (3)	0.0766 (3)	0.2464 (2)	0.093 (3)
C(8)	0.7752 (2)	0.0393 (3)	0.3707 (2)	0.095 (3)
C(9)	0.8465 (3)	0.1149 (3)	0.4730 (2)	0.105 (3)
C(10)	0.8166 (3)	0.2354 (3)	0.4408 (3)	0.070 (2)
C(11)	0.5992 (4)	0.4353 (3)	0.1667 (3)	0.091 (3)

Table 4. *Selected geometric parameters (Å, °) for (2)*

Cr(1)—Cl(1)	2.175 (2)	C(4)—C(5)	1.450 (4)
Cr(1)—O(1)	1.588 (4)	C(4)—C(11)	1.441 (3)
Cr(1)—O(2)	1.596 (4)	C(5)—C(6)	1.373 (4)
Cr(1)—O(3)	1.591 (4)	C(5)—C(10)	1.400 (3)
N(1)—C(2)	1.360 (5)	C(6)—C(7)	1.328 (5)
N(1)—C(10)	1.290 (4)	C(7)—C(8)	1.394 (3)
C(2)—C(3)	1.386 (4)	C(8)—C(9)	1.392 (4)
C(3)—C(4)	1.371 (4)	C(9)—C(10)	1.454 (5)
O(1)—Cr(1)—O(2)	111.2 (2)	C(5)—C(4)—C(11)	122.1 (2)
O(1)—Cr(1)—O(3)	111.8 (2)	C(4)—C(5)—C(10)	116.5 (2)
O(2)—Cr(1)—O(3)	108.8 (2)	C(4)—C(5)—C(6)	123.0 (2)
Cl(1)—Cr(1)—O(1)	108.5 (2)	C(5)—C(6)—C(7)	120.6 (3)
Cl(1)—Cr(1)—O(2)	107.7 (2)	C(6)—C(7)—C(8)	121.3 (3)
Cl(1)—Cr(1)—O(3)	108.5 (2)	C(7)—C(8)—C(9)	122.3 (3)
N(1)—C(2)—C(3)	122.5 (3)	C(8)—C(9)—C(10)	115.2 (2)
C(2)—N(1)—C(10)	119.4 (3)	C(5)—C(10)—C(9)	120.2 (3)
C(2)—C(3)—C(4)	118.6 (3)	N(1)—C(10)—C(9)	115.9 (3)
C(3)—C(4)—C(11)	118.9 (3)	N(1)—C(10)—C(5)	123.9 (3)
C(3)—C(4)—C(5)	119.0 (2)	C(6)—C(5)—C(10)	120.5 (3)

Compound (3)

Crystal data

$(C_{10}H_{10}N)[CrO_3Cl]$
$M_r = 279.6$
Triclinic
$P\overline{1}$
$a = 6.748\ (5)$ Å
$b = 7.957\ (5)$ Å
$c = 11.611\ (2)$ Å
$\alpha = 104.89\ (1)°$
$\beta = 100.34\ (3)°$
$\gamma = 92.11\ (3)°$
$V = 590\ (1)$ Å^3
$Z = 2$
$D_x = 1.574$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6–18°$
$\mu = 1.18$ mm^{-1}
$T = 293$ K
Prism
0.3 × 0.2 × 0.15 mm
Red–orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3467 measured reflections
3432 independent reflections
2977 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.045$
$\theta_{\rm max} = 30°$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 10$
$l = -3 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity decay: <10%

Refinement

Refinement on F^2
$R(F) = 0.0601$
$wR(F^2) = 0.1578$
$S = 1.341$
3265 reflections
158 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0927P^2) + (0.0771P)]$
where $P = [\max(F_o^2,0) + 2F_c^2]/3$

$(\Delta/\sigma)_{\rm max} = 0.412$
$\Delta\rho_{\rm max} = 0.905$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.118$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

Table 5. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (3)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cr(1)	0.10212 (4)	0.31689 (4)	0.23002 (3)	0.0457 (1)
Cl(1)	−0.09261 (1)	0.07266 (8)	0.17072 (7)	0.0707 (2)
O(1)	0.0227 (3)	0.4343 (2)	0.1386 (2)	0.0650 (6)
O(2)	0.3295 (2)	0.2696 (3)	0.2239 (2)	0.0683 (7)
O(3)	0.0799 (3)	0.4099 (3)	0.3658 (2)	0.0697 (7)
N(1)	0.7079 (3)	0.6443 (2)	0.1580 (2)	0.0515 (6)
C(1)	0.5990 (3)	0.6896 (2)	0.2486 (2)	0.0458 (5)
C(2)	0.6587 (3)	0.6501 (3)	0.3604 (2)	0.0558 (7)
C(3)	0.5429 (4)	0.6978 (3)	0.4468 (2)	0.0593 (8)
C(4)	0.3662 (3)	0.7866 (3)	0.4279 (2)	0.0544 (8)
C(5)	0.3093 (3)	0.8249 (3)	0.3194 (2)	0.0520 (7)
C(6)	0.4241 (3)	0.7781 (2)	0.2267 (2)	0.0455 (6)
C(7)	0.3717 (3)	0.8155 (3)	0.1133 (2)	0.0535 (7)
C(8)	0.4885 (4)	0.7672 (3)	0.0268 (2)	0.0575 (7)
C(9)	0.6576 (4)	0.6799 (3)	0.0518 (2)	0.0560 (7)
C(10)	0.2466 (6)	0.8342 (5)	0.5274 (3)	0.0742 (11)

Table 6. *Selected geometric parameters (Å, °) for (3)*

Cr(1)—Cl(1)	2.182 (1)	C(2)—C(3)	1.368 (4)
Cr(1)—O(1)	1.622 (2)	C(3)—C(4)	1.422 (4)
Cr(1)—O(2)	1.603 (2)	C(4)—C(5)	1.364 (3)
Cr(1)—O(3)	1.597 (2)	C(4)—C(10)	1.504 (4)
N(1)—C(1)	1.372 (3)	C(5)—C(6)	1.418 (3)
N(1)—C(9)	1.324 (3)	C(6)—C(7)	1.411 (3)
C(1)—C(2)	1.407 (3)	C(7)—C(8)	1.373 (4)
C(1)—C(6)	1.416 (3)	C(8)—C(9)	1.384 (4)
O(1)—Cr(1)—O(2)	111.8 (1)	C(5)—C(4)—C(10)	121.0 (3)
O(1)—Cr(1)—O(3)	111.1 (1)	C(4)—C(5)—C(6)	120.9 (2)
O(2)—Cr(1)—O(3)	111.5 (1)	C(1)—C(6)—C(5)	118.7 (2)
Cl(1)—Cr(1)—O(1)	107.3 (1)	C(2)—C(1)—C(6)	120.6 (2)
Cl(1)—Cr(1)—O(2)	107.7 (1)	C(1)—C(2)—C(3)	118.4 (2)
Cl(1)—Cr(1)—O(3)	107.2 (1)	C(2)—C(3)—C(4)	122.5 (2)
C(1)—N(1)—C(9)	123.2 (2)	C(5)—C(6)—C(7)	123.0 (2)
N(1)—C(1)—C(6)	118.0 (2)	C(1)—C(6)—C(7)	118.3 (2)
N(1)—C(1)—C(2)	121.3 (2)	C(6)—C(7)—C(8)	120.5 (2)
C(3)—C(4)—C(10)	119.2 (2)	C(7)—C(8)—C(9)	119.3 (2)
C(3)—C(4)—C(5)	118.8 (2)	N(1)—C(9)—C(8)	120.6 (2)

Compound (4)

Crystal data

$(C_2H_{10}N_2)(Cl)[CrO_3Cl]$
$M_r = 233.02$
Monoclinic
$P2_1/n$
$a = 12.157$ (2) Å
$b = 12.265$ (3) Å
$c = 6.316$ (2) Å
$\beta = 114.50$ (3)°
$V = 856.9$ (7) Å^3
$Z = 4$
$D_x = 1.806$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 4$–15°
$\mu = 1.915$ mm^{-1}
$T = 293$ K
Prism
0.30 × 0.26 × 0.18 mm
Orange

Data collection

Philips PW1100 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2104 measured reflections
1937 independent reflections
1904 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.018$
$\theta_{\rm max} = 30°$
$h = -17 \rightarrow 15$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 8$
2 standard reflections frequency: 60 min intensity decay: <10%

Refinement

Refinement on F
$R = 0.070$
$wR = 0.086$
$S = 1.138$
1904 reflections
92 parameters
$w = 1/[\sigma^2(F) + 0.02973F^2]$

$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 1.183$ e Å^{-3}
$\Delta\rho_{\rm min} = -2.089$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 7. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (4)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cr(1)	0.9775 (1)	−0.20000 (1)	0.6476 (1)	0.0301 (3)
Cl(1)	0.9415 (1)	−0.1374 (1)	0.3007 (2)	0.0442 (6)
Cl(2)	1.1114 (1)	−0.4013 (1)	1.3093 (2)	0.0386 (5)
O(1)	1.1214 (3)	−0.2185 (4)	0.7901 (7)	0.0420 (13)
O(2)	0.9101 (5)	−0.3156 (4)	0.6185 (10)	0.0438 (18)
O(3)	0.9298 (6)	−0.1109 (5)	0.7758 (10)	0.052 (3)
N(1)	0.6333 (4)	−0.0334 (4)	0.3279 (8)	0.0385 (16)
N(2)	0.7947 (4)	0.0806 (4)	0.8048 (8)	0.0386 (15)
C(1)	0.7254 (4)	0.0553 (4)	0.3752 (9)	0.0328 (17)
C(2)	0.7322 (5)	0.1310 (4)	0.5663 (10)	0.0352 (19)

Table 8. *Selected geometric parameters (Å, °) for (4)*

Cr(1)—Cl(1)	2.188 (1)	N(1)—C(1)	1.500 (7)
Cr(1)—O(1)	1.617 (3)	N(2)—C(2)	1.510 (7)
Cr(1)—O(2)	1.609 (5)	C(1)—C(2)	1.498 (8)
Cr(1)—O(3)	1.605 (7)		
O(1)—Cr(1)—O(2)	108.8 (3)	Cl(1)—Cr(1)—O(2)	108.3 (2)
O(1)—Cr(1)—O(3)	110.4 (3)	Cl(1)—Cr(1)—O(3)	107.6 (2)
O(2)—Cr(1)—O(3)	112.6 (3)	N(1)—C(1)—C(2)	113.4 (5)
Cl(1)—Cr(1)—O(1)	109.1 (2)	N(2)—C(2)—C(1)	112.8 (4)

Compound (5)

Crystal data

$(C_{10}H_9ClN_3)[CrO_3Cl]$
$M_r = 342.10$
Monoclinic
$P2_1/n$
$a = 6.396$ (2) Å
$b = 10.915$ (5) Å
$c = 19.192$ (5) Å
$\beta = 92.83$ (3)°
$V = 1338.2$ (8) Å^3
$Z = 4$
$D_x = 1.698$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6$–18°
$\mu = 1.26$ mm^{-1}
$T = 293$ K
Prism
0.36 × 0.30 × 0.20 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4009 measured reflections
3874 independent reflections
2472 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.056$
$\theta_{\rm max} = 30°$
$h = -8 \rightarrow 8$
$k = -15 \rightarrow 15$
$l = -26 \rightarrow 26$
3 standard reflections frequency: 60 min intensity decay: <10%

Refinement

Refinement on F
$R = 0.056$
$wR = 0.073$
$S = 1.164$
1981 reflections
195 parameters
$w = 1/[\sigma^2(F) + 0.00242F^2]$
$(\Delta/\sigma)_{\max} = 0.023$
$\Delta\rho_{\max} = 1.050$ e Å^{-3}
$\Delta\rho_{\min} = -0.518$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 9. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (5)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cr(1)	0.12061 (2)	0.21256 (2)	0.15440 (7)	0.0516 (5)
Cl(1)	0.25239 (6)	0.39451 (4)	0.15331 (2)	0.0893 (13)
O(1)	−0.1233 (4)	0.2258 (3)	0.1696 (3)	0.082 (3)
O(2)	0.1549 (3)	0.1488 (3)	0.0810 (3)	0.065 (3)
O(3)	0.2440 (3)	0.14045 (3)	0.21514 (4)	0.110 (5)
Cl(2)	0.8154 (4)	0.5498 (2)	0.1033 (1)	0.0534 (7)
C(1)	0.3385 (4)	0.7274 (3)	0.0051 (3)	0.053 (3)
C(2)	0.5177 (4)	0.6602 (2)	0.0162 (2)	0.060 (3)
C(3)	0.5876 (2)	0.6352 (2)	0.0851 (2)	0.062 (4)
C(4)	0.4695 (3)	0.6770 (2)	0.1397 (4)	0.055 (3)
N(5)	0.2901 (2)	0.7415 (3)	0.1286 (3)	0.050 (2)
C(6)	0.2251 (3)	0.7676 (3)	0.0631 (3)	0.043 (3)
N(7)	0.0438 (3)	0.8339 (2)	0.0522 (3)	0.051 (2)
C(8)	−0.0842 (2)	0.8794 (2)	0.1001 (2)	0.043 (2)
N(9)	−0.0414 (2)	0.8567 (2)	0.1683 (2)	0.049 (2)
C(10)	−0.1715 (2)	0.8982 (3)	0.2187 (2)	0.049 (3)
C(11)	−0.3440 (2)	0.9627 (3)	0.2003 (3)	0.053 (3)
C(12)	−0.3924 (3)	0.9863 (3)	0.1297 (3)	0.057 (3)
C(13)	−0.2612 (3)	0.9450 (2)	0.0797 (2)	0.052 (3)

Table 10. *Selected geometric parameters (Å, °) for (5)*

Cr(1)—Cl(1)	2.158 (1)	N(5)—C(6)	1.335 (7)
Cr(1)—O(1)	1.608 (3)	C(6)—N(7)	1.374 (3)
Cr(1)—O(2)	1.596 (6)	N(7)—C(8)	1.356 (6)
Cr(1)—O(3)	1.583 (6)	C(8)—N(9)	1.345 (6)
Cl(2)—C(3)	1.750 (3)	C(8)—C(13)	1.381 (3)
C(1)—C(2)	1.369 (3)	N(9)—C(10)	1.383 (5)
C(1)—C(6)	1.427 (5)	C(10)—C(11)	1.341 (3)
C(2)—C(3)	1.400 (5)	C(11)—C(12)	1.398 (7)
C(3)—C(4)	1.400 (8)	C(12)—C(13)	1.382 (5)
C(4)—N(5)	1.354 (3)		
O(1)—Cr(1)—O(2)	112.1 (2)	C(1)—C(6)—N(5)	121.5 (2)
O(1)—Cr(1)—O(3)	111.4 (2)	N(5)—C(6)—N(7)	118.5 (3)
O(2)—Cr(1)—O(3)	110.3 (2)	C(1)—C(6)—N(7)	120.0 (3)
Cl(1)—Cr(1)—O(1)	107.6 (1)	C(6)—N(7)—C(8)	128.5 (3)
Cl(1)—Cr(1)—O(2)	108.8 (1)	N(7)—C(8)—C(13)	120.7 (3)
Cl(1)—Cr(1)—O(3)	106.5 (1)	N(7)—C(8)—N(9)	119.5 (2)
C(2)—C(1)—C(6)	119.8 (3)	N(9)—C(8)—C(13)	119.8 (3)
C(1)—C(2)—C(3)	118.5 (3)	C(8)—N(9)—C(10)	121.3 (2)
Cl(2)—C(3)—C(2)	121.1 (2)	N(9)—C(10)—C(11)	120.2 (4)
C(2)—C(3)—C(4)	119.0 (2)	C(10)—C(11)—C(12)	119.4 (2)
Cl(2)—C(3)—C(4)	119.9 (3)	C(11)—C(12)—C(13)	120.0 (4)
C(3)—C(4)—N(5)	122.4 (6)	C(8)—C(13)—C(12)	119.2 (3)
C(4)—N(5)—C(6)	118.8 (4)		

For (1), (2), (3) and (4), the H atoms were placed in geometrical calculated positions and included in the refinement with common isotropic displacement parameters. For (5), the H atoms were obtained from a difference Fourier map except for those bonded to N7.

Data collection and cell refinement: Philips PW 1100/20 software for (1) and (4); *CAD*-4 *Software* (Enraf–Nonius, 1989) for (2), (3) and (5). Data reduction: *PHIL* (Riche, 1981) for (1) and (4); *CAD*-4 *Software* for (2), (3) and (5). Structure solution: *SHELXS*86 (Sheldrick, 1990) for (1), (3), (4) and (5); *SIR*92 (Altomare *et al.*, 1994) for (2). Structure refinement: *SHELX*76 (Sheldrick, 1976) for (1), (4) and (5); *SHELXL*93 (Sheldrick, 1993) for (2) and (3). For all compounds, molecular graphics: *ORTEP*II (Johnson, 1976); program used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1153). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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