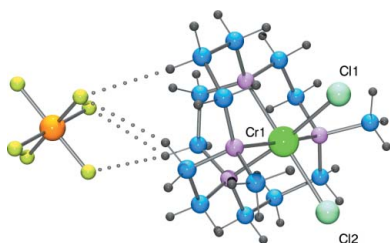# research communications

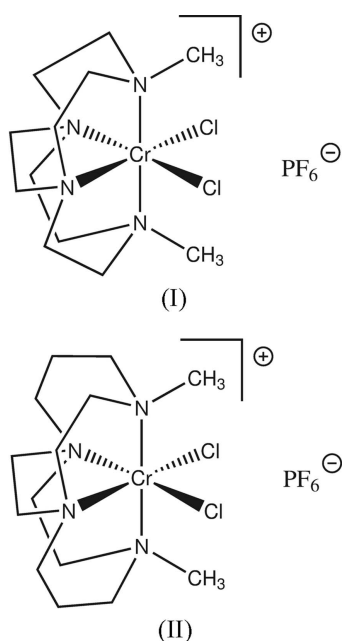# Crystal structures of two cross-bridged chromium(III) tetraazamacrocycles

Timothy J. Prior,[a]* Danny L. Maples,[b] Randall D. Maples,[b] Wesley A. Hoffert,[c] Trenton H. Parsell,[c] Jon D. Silversides,[a] Stephen J. Archibald[a] and Timothy J. Hubin[b]

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The crystal structure of dichlorido(4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane)chromium(III) hexafluoridophosphate, $[CrCl_2(C_{12}H_{26}N_4)]PF_6$, (I), has monoclinic symmetry (space group $P2_1/n$) at 150 K. The structure of the related dichlorido(4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)chromium(III) hexafluoridophosphate, $[CrCl_2(C_{14}H_{30}N_4)]PF_6$, (II), also displays monoclinic symmetry (space group $P2_1/c$) at 150 K. In each case, the $Cr^{III}$ ion is hexacoordinate with two *cis* chloride ions and two non-adjacent N atoms bound *cis* equatorially and the other two non-adjacent N atoms bound *trans* axially in a *cis*-V conformation of the macrocycle. The extent of the distortion from the preferred octahedral coordination geometry of the $Cr^{III}$ ion is determined by the parent macrocycle ring size, with the larger cross-bridged cyclam ring in (II) better able to accommodate this preference and the smaller cross-bridged cyclen ring in (I) requiring more distortion away from octahedral geometry.

## 1. Chemical context

Ethylene cross-bridged tetraazamacrocycles were introduced to coordination chemists in 1990 by Weisman and Wong (Weisman *et al.*, 1990). Since then, their transition metal complexes have become important to the fields of oxidation catalysis (Yin *et al.*, 2007; Dong *et al.*, 2013), medical/biological imaging (Boswell *et al.*, 2004; Sprague *et al.*, 2007; Silversides *et al.*, 2011) and chemokine receptor antagonism (Lewis *et al.*, 2005; Valks *et al.*, 2006; Smith *et al.*, 2012) due to the combination of restricted macrocycle configuration and kinetic inertness inherent to these ligands. Chromium(III) complexes have played an important role in characterizing new ligands due to their relative kinetic inertness (Cotton & Wilkinson, 1988). Yet, to date, only one report of the chromium coordination chemistry of these macrobicyclic ligands has appeared in the literature (Maples *et al.*, 2009). In order to expand the range of metal ions that can be coordinated by these remarkable ligands (Hubin, 2003), we are exploring further the structural chemistry of chromium cross-bridged tetraazamacrocyclic complexes and report synthesis and crystal structures of dichlorido(4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane)chromium(III) hexafluoridophosphate, (I), and dichlorido(4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)chromium(III)hexafluoridophosphate, (II).

**Figure 2**
The molecular entities of (II), with atoms shown as displacement ellipsoids at the 50% probability level.

**Table 1**
Hydrogen-bond geometry (Å, °) for (I).

| $D-\mathrm{H}\cdots A$ | $D-\mathrm{H}$ | $\mathrm{H}\cdots A$ | $D\cdots A$ | $D-\mathrm{H}\cdots A$ |
|---|---|---|---|---|
| C1—H1A···F6$^i$ | 0.99 | 2.53 | 3.347 (4) | 140 |
| C1—H1B···F3$^{ii}$ | 0.99 | 2.46 | 3.410 (5) | 162 |
| C2—H2A···F4$^i$ | 0.99 | 2.48 | 3.407 (4) | 155 |
| C3—H3A···F1$^{iii}$ | 0.99 | 2.51 | 3.500 (4) | 177 |
| C4—H4A···F6$^{iv}$ | 0.99 | 2.36 | 3.175 (4) | 139 |
| C6—H6B···F4 | 0.99 | 2.30 | 3.238 (4) | 158 |
| C1—H1A···Cl1 | 0.99 | 2.82 | 3.393 (4) | 118 |
| C4—H4B···Cl2 | 0.99 | 2.63 | 3.137 (3) | 112 |
| C5—H5A···Cl2 | 0.99 | 2.74 | 3.324 (3) | 118 |
| C6—H6A···Cl2$^v$ | 0.99 | 2.77 | 3.447 (3) | 126 |
| C8—H8B···Cl1 | 0.99 | 2.73 | 3.203 (4) | 110 |
| C12—H12B···Cl2 | 0.98 | 2.78 | 3.329 (4) | 116 |

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (iii) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (v) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$.



(I)

(II)

## 2. Structural commentary

Each of the title compounds crystallizes with a single positively-charged metal complex and one $PF_6^-$ anion in the asymmetric unit. The metal ion in each complex adopts a distorted octahedral geometry. The N atoms of each macrocycle occupy four coordination sites, while two chloride ions in a *cis* arrangement complete the coordination of Cr$^{III}$. This so-called *cis*-V conformation, expected to be dictated by the ligand cross-bridge, is apparent for both of the complexes structurally characterized here. Figs. 1 and 2 illustrate the local
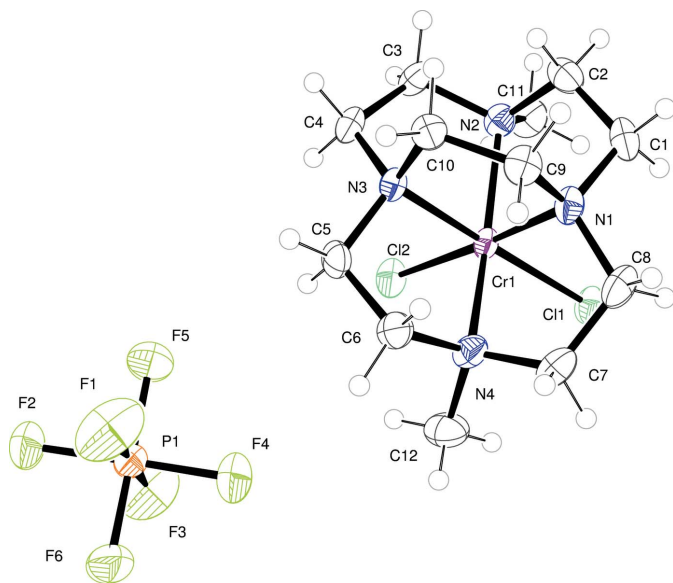
geometry about Cr$^{III}$ in (I) (dimethyl bridged-cyclen complex) and (II) (dimethyl bridged-cyclam complex), respectively. Apparently, neither the identity of the metal ion, nor that of the alkyl substituents affects this conformation. This same conformation has been seen in all known metal complexes with ethylene cross-bridged cyclam and cyclen ligands.

The ring size of the parent macrocycle alters the degree to which the metal ion is engulfed by the bridged macrocycle. This is most clearly evident in the N2—Cr1—N4 bond angle between two axially bound nitrogen atoms. This bond angle is 161.62 (11)° in the case of the smaller macrocycle, cylcen, while it is 171.44 (14)° for the cyclam complex. A larger bond angle, closer to linearity, indicates a better fit, or complementarity, between the ligand and the preferred octahedral geometry of the Cr$^{III}$ ion. A more subtle difference in the N1—Cr1—N3 bond angles, *viz.* the equatorially bound N atoms, shows the same trend: this angle is 83.23 (10)° for the cyclen complex and 84.18 (13)° for the cyclam complex. Finally, the Cr—N bond lengths are somewhat affected by the ligand size as well. The mean of the four Cr—N bond lengths is 2.08 Å in (I), while this average is 2.12 Å in (II). The mean value for a number of Cr—N$R_3$ bonds in the literature is 2.093 Å ($\sigma = 0.044$ Å) (Orpen *et al.*, 1989).
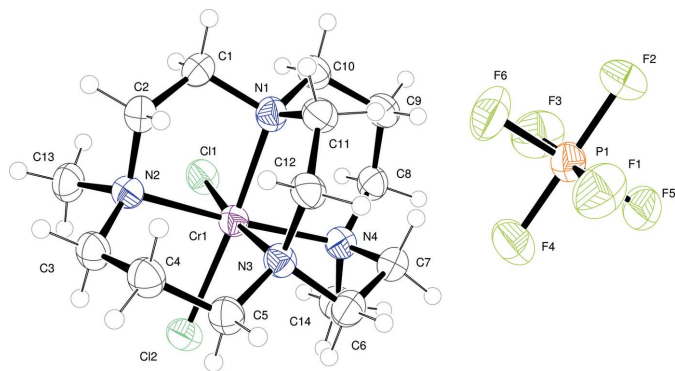


**Figure 1**
The molecular entities of (I), with atoms shown as displacement ellipsoids at the 50% probability level.

**Table 2**
Hydrogen-bond geometry (Å, °) for (II).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C1—H1$B$···F5$^i$ | 0.99 | 2.41 | 3.318 (5) | 153 |
| C2—H2$A$···F1$^{ii}$ | 0.99 | 2.50 | 3.094 (5) | 119 |
| C2—H2$A$···F6$^{ii}$ | 0.99 | 2.53 | 3.223 (6) | 127 |
| C7—H7$A$···F4 | 0.99 | 2.55 | 3.098 (6) | 115 |
| C12—H12$B$···F2$^{ii}$ | 0.99 | 2.51 | 3.393 (6) | 149 |
| C3—H3$A$···Cl2 | 0.99 | 2.73 | 3.280 (5) | 115 |
| C5—H5$B$···Cl2 | 0.99 | 2.70 | 3.287 (5) | 119 |
| C8—H8$A$···Cl1 | 0.99 | 2.70 | 3.258 (5) | 116 |
| C8—H8$B$···Cl1$^{iii}$ | 0.99 | 2.82 | 3.778 (4) | 162 |
| C10—H10$B$···Cl1 | 0.99 | 2.70 | 3.270 (5) | 117 |
| C13—H13$A$···Cl1 | 0.98 | 2.68 | 3.157 (5) | 111 |
| C13—H13$A$···Cl2$^{iv}$ | 0.98 | 2.73 | 3.572 (4) | 144 |
| C14—H14$B$···Cl2 | 0.98 | 2.69 | 3.141 (5) | 108 |

Symmetry codes: (i) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $x, -y + \frac{3}{2}, z + \frac{1}{2}$.

## 3. Supramolecular features

There are no classical hydrogen bonds present in either (I) and (II) but each structure contains a great many C—H···F and C—H···Cl interactions which generate three-dimensional arrays. These interactions were identified from the standard criterion that the distance from the hydrogen atom to the hydrogen-bond acceptor should not exceed the sum of the radius of the acceptor plus 2 Å. Tables 1 and 2 contain full details of these interactions for (I) and (II), respectively.

For (I), each $PF_6^-$ anion resides in a pocket between six metal complexes and there are C—H···F interactions to each of them. The mean C···F distance of those in Table 1 is 3.35 Å. Supplementary C—H···Cl intramolecular contacts are present and intermolecular interactions between neighbouring metal complexes are also observed. The overall effect of these intermolecular interactions is to generate an extended network. One way to describe this is in terms of puckered sheets of the cationic complex and $PF_6^-$ anions that extend in the $bc$ plane. Between these sheets further C—H···F and C—H···Cl interactions assemble these layers in an $ABAB$ fashion along $a$ to generate a densely packed three-dimensional array as shown in Fig. 3.

For (II), the arrangement is rather similar and again a three-dimensional array is constructed from nonclassical hydrogen bonds between the cations and anions. The $PF_6^-$ anion is located in a pocket formed from four metal complexes in a distorted tetrahedral arrangement and forms C—H···F interactions to each of them, with a mean C···F distance of 3.23 Å. Further C—H···Cl interactions are also present. In a similar fashion to (I), these nonclassical interactions assemble the cations and anions into puckered sheets that extend in the $bc$ plane. The sheets are then $ABAB$ stacked along $a$ as shown in Fig. 4.

## 4. Database survey

The structures of three complexes that are directly analogous to (I) have been reported. These are the manganese (Hubin *et al.*, 2001), iron (McClain *et al.*, 2006) and cobalt (Hubin *et al.*,



**Figure 3**
Crystal packing of (I), viewed perpendicular to the $bc$ plane. Dashed lines represent halide···H—C interactions.

2002) analogues. Each of these contains the metal in the trivalent state. For the Mn and Fe examples, the geometry about the metal is similar to that for Cr, but the bond angles formed by the two axially bound N atoms are smaller [155.01 (11) and 153.20 (9) °, respectively]. Similarly, the bite angles of the two equatorially bound N atoms are also noticeably smaller; these are 81.29 (11) and 78.62 (8)° for Mn and Fe analogues, respectively. However, the mean $M$—N bond length is longer for Mn and Fe examples: 2.153 and 2.167 Å, respectively. These differences in geometry reflect the smaller size of the $Mn^{III}$ and $Fe^{III}$ ions, and the possibility of a Jahn–Teller distortion for $Mn^{III}$, but the greater ligand field stabilization energy (LFSE) for $Cr^{III}$ yields shorter bond



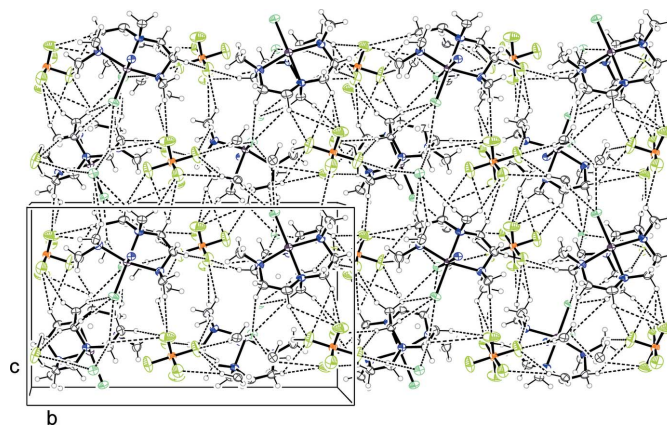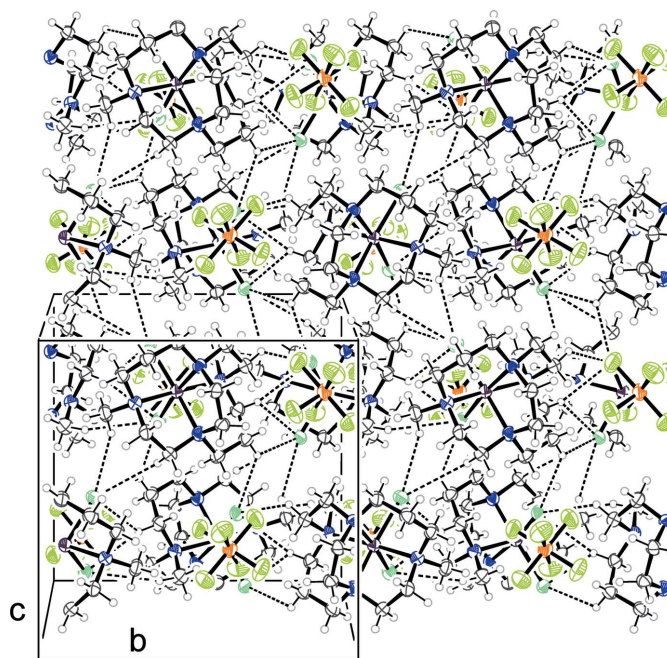**Figure 4**
Crystal packing of (II), viewed perpendicular to the $bc$ plane. Dashed lines represent halide···H—C interactions.

lengths. The Co$^{III}$ analogue is rather different because it is in a low spin state. The axial N—Co—N bond angle is 168.8 (4)° and the equatorial bond angle is 87.2 (4)°. As expected, the mean bond length is shorter for the Co case at 1.978 Å. The smaller, low-spin Co$^{III}$ ion fits into the pocket of the macrocyle better than Cr$^{III}$.

Chromium(III) complexes similar to (I) and (II) but crystallized with different anions have been reported before (Maples *et al.*, 2009). The chloride analogue of (I) has bond angles of 160.83 (19) and 83.50 (18)° about the chromium ion and a mean Cr—N bond length of 2.08 Å, which are in good agreement with (I), demonstrating the counter-anion has very little effect on the coordination about the metal. A cyclen-based macrocycle with benzyl groups replacing the methyl groups in (I), has key bond angles 160.35 (19) and 83.6 (2)° and a mean Cr—N bond length of 2.09 Å (Maples *et al.*, 2009). The pocket in the macrocycle is of a similar shape in this example but slightly enlarged because of the pendant benzyl groups.

The chloride analogue of (II) (Maples *et al.*, 2009) displays a similarly sized pocket; the N—Cr—N axial bond angle is 172.46 (11)° and the equatorial angle is 84.63 (11)°, while mean Cr—N bond length is 2.12 Å. In line with the observation in (I) and (II), the pocket of the cyclam-derived ligand is better able to accomodate the octahedrally surrounded Cr$^{III}$ ion and displays larger bond lengths than the cyclen equivalent.

## 5. Synthesis and crystallization

The cross-bridged ligands were prepared according to literature procedures (Weisman *et al.*, 1990; Wong *et al.*, 2000). The title complexes were prepared by a procedure slightly modified from those found in Hubin *et al.* (2001) for other trivalent metal ions. In an inert atmosphere glove-box, 1 mmol of the respective ligand was dissolved in 20 ml of anhydrous dimethylformamide in a 50 ml Erlenmeyer flask. 1 mmol of anhydrous chromium(II) chloride was added to the stirring ligand solution. The reaction was allowed to stir at room temperature overnight. The solution was then filtered through filter paper and the solvent was removed under vacuum to give blue–violet solids. In the glove-box, this divalent complex was dissolved in 20 ml of methanol in a round-bottomed flask. Five equivalents of $NH_4PF_6$ (5 mmol, 0.815 g) were dissolved in the solution. The flask was removed from the glove-box with a stopper to protect it from air. In a fume hood, a stream of nitrogen gas was directed over the surface of the solution. Four to six drops of $Br_2$ were added and the reaction was stirred for 15 min. Bright purple precipitates formed immediately. The nitrogen gas was then allowed to bubble through the solution for 15 min to remove excess $Br_2$. The flask was then stoppered and placed in a freezer for 30 min to complete the precipitation. The purple solid product was collected by vacuum filtration on a glass frit and washed with methanol and then ether. Crystals suitable for X-ray diffraction (purple blocks) were grown from the slow evaporation of aqueous solutions of the product.

**Table 3**
Experimental details.

| | (I) | (II) |
|---|---|---|
| **Crystal data** | | |
| Chemical formula | [CrCl$_2$(C$_{12}$H$_{26}$N$_4$)]PF$_6$ | [CrCl$_2$(C$_{14}$H$_{30}$N$_4$)]PF$_6$ |
| $M_r$ | 494.24 | 522.29 |
| Crystal system, space group | Monoclinic, $P2_1/n$ | Monoclinic, $P2_1/c$ |
| Temperature (K) | 150 | 150 |
| $a, b, c$ (Å) | 8.2271 (10), 19.957 (2), 12.0474 (17) | 13.6801 (19), 12.437 (2), 12.3864 (17) |
| $\beta$ (°) | 96.374 (11) | 102.028 (11) |
| $V$ (Å$^3$) | 1965.8 (4) | 2061.1 (5) |
| $Z$ | 4 | 4 |
| Radiation type | Mo $K\alpha$ | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 1.00 | 0.95 |
| Crystal size (mm) | 0.10 × 0.10 × 0.08 | 0.15 × 0.15 × 0.06 |
| | | |
| **Data collection** | | |
| Diffractometer | Stoe IPDS2 | Stoe IPDS2 |
| Absorption correction | Analytical [a face-indexed absorption correction was applied; *X-AREA* (Stoe & Cie, 2002)] | Analytical [a face-indexed absorption correction was applied; *X-AREA* (Stoe & Cie, 2002)] |
| $T_{min}$, $T_{max}$ | 0.827, 0.915 | 0.778, 0.901 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 22999, 4501, 2798 | 13450, 4158, 2073 |
| $R_{int}$ | 0.091 | 0.091 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.650 | 0.622 |
| | | |
| **Refinement** | | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.041, 0.096, 0.88 | 0.045, 0.109, 0.78 |
| No. of reflections | 4501 | 4158 |
| No. of parameters | 235 | 255 |
| H-atom treatment | H-atom parameters constrained | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.77, −0.49 | 0.33, −0.79 |

Computer programs: *X-AREA* (Stoe & Cie, 2002), *SHELXS86*, *SHELXL2013* and *SHELXTL* (Sheldrick, 2008).

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms were placed in idealised positions and refined using a riding model, with C—H = 0.98 and 0.99 Å for –CH$_3$ and –CH$_2$– groups, respectively, and with $U_{iso}$(H) values of, respectively, 1.5 and 1.2 times $U_{eq}$ of the carrier atom.

In (I), there is evidence for a very small degree of disorder (10%) in the position of the PF$_6^-$ anions. Refinement with a second orientation for this anion did not lead to a substantial improve in the fit. A model with a single orientation was therefore retained.

The structure of (II) is presented in $P2_1/n$, consistent with manganese and cobalt analogues (Hubin *et al.*, 2001, 2002), rather than the $P2_1/c$ setting of the iron analogue (McClain *et al.*, 2006) which has $\beta \simeq 120°$.

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# supporting information

## Crystal structures of two cross-bridged chromium(III) tetraazamacrocycles

**Timothy J. Prior, Danny L. Maples, Randall D. Maples, Wesley A. Hoffert, Trenton H. Parsell, Jon D. Silversides, Stephen J. Archibald and Timothy J. Hubin**

### Computing details

For both compounds, data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-AREA* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS86* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

### (I) Dichlorido(4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane)chromium(III) hexafluoridophosphate

*Crystal data*

$[CrCl_2(C_{12}H_{26}N_4)]PF_6$
$M_r = 494.24$
Monoclinic, $P2_1/n$
$a = 8.2271\ (10)$ Å
$b = 19.957\ (2)$ Å
$c = 12.0474\ (17)$ Å
$\beta = 96.374\ (11)°$
$V = 1965.8\ (4)$ Å$^3$
$Z = 4$

$F(000) = 1012$
$D_x = 1.670$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 12040 reflections
$\theta = 2.7–31.2°$
$\mu = 1.00$ mm$^{-1}$
$T = 150$ K
Block, purple
$0.10 \times 0.10 \times 0.08$ mm

*Data collection*

Stoe IPDS2
 diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 6.67 pixels mm$^{-1}$
$\omega$–scans
Absorption correction: analytical
 [a face-indexed absorption correction was
 applied; *X-AREA* (Stoe & Cie, 2002)]
$T_{min} = 0.827$, $T_{max} = 0.915$

22999 measured reflections
4501 independent reflections
2798 reflections with $I > 2\sigma(I)$
$R_{int} = 0.091$
$\theta_{max} = 27.5°$, $\theta_{min} = 2.7°$
$h = -10 \rightarrow 10$
$k = -25 \rightarrow 25$
$l = -14 \rightarrow 15$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.096$
$S = 0.88$
4501 reflections
235 parameters
0 restraints

Hydrogen site location: inferred from
 neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0474P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.77$ e Å$^{-3}$
$\Delta\rho_{min} = -0.49$ e Å$^{-3}$

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)*

|  | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cr1 | 0.21553 (5) | 0.19169 (2) | 0.20979 (4) | 0.02173 (12) |
| Cl1 | −0.06600 (7) | 0.20275 (4) | 0.17145 (7) | 0.03159 (19) |
| Cl2 | 0.25268 (8) | 0.23403 (4) | 0.03552 (7) | 0.03325 (19) |
| N1 | 0.2035 (3) | 0.15406 (14) | 0.3675 (2) | 0.0274 (6) |
| N2 | 0.2399 (3) | 0.09097 (13) | 0.1641 (2) | 0.0276 (6) |
| N3 | 0.4628 (3) | 0.18082 (13) | 0.2517 (2) | 0.0234 (5) |
| N4 | 0.2408 (3) | 0.28159 (14) | 0.2997 (2) | 0.0296 (6) |
| C1 | 0.1252 (4) | 0.08715 (17) | 0.3466 (3) | 0.0348 (8) |
| H1A | 0.0099 | 0.0927 | 0.3144 | 0.042* |
| H1B | 0.1267 | 0.0621 | 0.4177 | 0.042* |
| C2 | 0.2193 (4) | 0.04929 (17) | 0.2664 (3) | 0.0340 (7) |
| H2A | 0.1606 | 0.0074 | 0.2435 | 0.041* |
| H2B | 0.3283 | 0.0371 | 0.3042 | 0.041* |
| C3 | 0.4087 (3) | 0.08276 (17) | 0.1267 (3) | 0.0328 (8) |
| H3A | 0.3976 | 0.0776 | 0.0445 | 0.039* |
| H3B | 0.4586 | 0.0412 | 0.1599 | 0.039* |
| C4 | 0.5235 (3) | 0.14187 (17) | 0.1595 (3) | 0.0300 (7) |
| H4A | 0.6348 | 0.1249 | 0.1837 | 0.036* |
| H4B | 0.5296 | 0.1714 | 0.0940 | 0.036* |
| C5 | 0.5233 (3) | 0.25153 (16) | 0.2599 (3) | 0.0298 (7) |
| H5A | 0.5118 | 0.2726 | 0.1850 | 0.036* |
| H5B | 0.6402 | 0.2524 | 0.2899 | 0.036* |
| C6 | 0.4221 (3) | 0.28971 (17) | 0.3373 (3) | 0.0325 (8) |
| H6A | 0.4467 | 0.2726 | 0.4145 | 0.039* |
| H6B | 0.4515 | 0.3378 | 0.3372 | 0.039* |
| C7 | 0.1464 (4) | 0.27476 (19) | 0.3992 (3) | 0.0370 (8) |
| H7A | 0.0446 | 0.3014 | 0.3858 | 0.044* |
| H7B | 0.2124 | 0.2937 | 0.4655 | 0.044* |
| C8 | 0.1016 (4) | 0.20179 (19) | 0.4244 (3) | 0.0379 (8) |
| H8A | 0.1186 | 0.1940 | 0.5061 | 0.045* |
| H8B | −0.0154 | 0.1939 | 0.3988 | 0.045* |
| C9 | 0.3681 (3) | 0.14731 (18) | 0.4344 (3) | 0.0321 (7) |
| H9A | 0.3697 | 0.1062 | 0.4805 | 0.038* |
| H9B | 0.3867 | 0.1861 | 0.4854 | 0.038* |
| C10 | 0.5051 (3) | 0.14384 (16) | 0.3594 (3) | 0.0275 (7) |
| H10A | 0.6059 | 0.1633 | 0.3993 | 0.033* |
| H10B | 0.5276 | 0.0963 | 0.3429 | 0.033* |
| C11 | 0.1158 (4) | 0.06839 (19) | 0.0721 (3) | 0.0377 (8) |
| H11A | 0.0059 | 0.0742 | 0.0947 | 0.057* |

| | | | |
|---|---|---|---|
| H11B | 0.1338 | 0.0210 | 0.0559 | 0.057* |
| H11C | 0.1262 | 0.0951 | 0.0050 | 0.057* |
| C12 | 0.1830 (4) | 0.34219 (19) | 0.2353 (4) | 0.0428 (9) |
| H12A | 0.0660 | 0.3378 | 0.2103 | 0.064* |
| H12B | 0.2437 | 0.3469 | 0.1701 | 0.064* |
| H12C | 0.2012 | 0.3819 | 0.2829 | 0.064* |
| P1 | 0.74031 (9) | 0.44740 (4) | 0.22662 (7) | 0.0291 (2) |
| F1 | 0.8570 (3) | 0.43093 (16) | 0.3353 (2) | 0.0756 (8) |
| F2 | 0.8987 (2) | 0.46269 (12) | 0.1662 (2) | 0.0570 (6) |
| F3 | 0.6248 (3) | 0.46395 (16) | 0.1167 (2) | 0.0744 (8) |
| F4 | 0.5828 (3) | 0.43324 (12) | 0.2878 (2) | 0.0604 (7) |
| F5 | 0.7476 (3) | 0.37224 (11) | 0.1869 (3) | 0.0675 (8) |
| F6 | 0.7324 (3) | 0.52314 (12) | 0.2644 (3) | 0.0639 (7) |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cr1 | 0.01590 (19) | 0.0277 (3) | 0.0219 (3) | −0.00047 (18) | 0.00316 (17) | 0.0011 (2) |
| Cl1 | 0.0156 (3) | 0.0430 (5) | 0.0361 (5) | 0.0006 (3) | 0.0023 (3) | 0.0020 (4) |
| Cl2 | 0.0254 (3) | 0.0468 (5) | 0.0273 (4) | −0.0002 (3) | 0.0018 (3) | 0.0092 (4) |
| N1 | 0.0232 (11) | 0.0368 (16) | 0.0228 (14) | −0.0009 (10) | 0.0049 (10) | 0.0025 (12) |
| N2 | 0.0241 (11) | 0.0302 (15) | 0.0279 (15) | −0.0014 (10) | 0.0011 (10) | −0.0035 (12) |
| N3 | 0.0173 (10) | 0.0293 (14) | 0.0237 (13) | −0.0008 (9) | 0.0030 (9) | −0.0003 (11) |
| N4 | 0.0233 (11) | 0.0322 (15) | 0.0331 (16) | 0.0037 (10) | 0.0024 (11) | −0.0033 (12) |
| C1 | 0.0297 (15) | 0.042 (2) | 0.0334 (19) | −0.0101 (14) | 0.0055 (14) | 0.0085 (16) |
| C2 | 0.0342 (15) | 0.0284 (18) | 0.038 (2) | −0.0054 (13) | −0.0005 (14) | 0.0049 (16) |
| C3 | 0.0265 (14) | 0.0368 (19) | 0.036 (2) | 0.0060 (13) | 0.0067 (13) | −0.0101 (16) |
| C4 | 0.0200 (13) | 0.0403 (19) | 0.0306 (18) | 0.0043 (12) | 0.0073 (12) | 0.0006 (15) |
| C5 | 0.0197 (12) | 0.0329 (18) | 0.0364 (19) | −0.0056 (12) | 0.0014 (12) | 0.0017 (15) |
| C6 | 0.0244 (14) | 0.0320 (19) | 0.040 (2) | −0.0022 (12) | −0.0011 (13) | −0.0051 (15) |
| C7 | 0.0319 (15) | 0.047 (2) | 0.0324 (19) | 0.0083 (15) | 0.0065 (14) | −0.0095 (17) |
| C8 | 0.0336 (15) | 0.052 (2) | 0.0302 (18) | 0.0077 (15) | 0.0137 (14) | −0.0011 (17) |
| C9 | 0.0321 (15) | 0.0389 (19) | 0.0248 (17) | 0.0005 (14) | 0.0011 (13) | 0.0016 (15) |
| C10 | 0.0249 (13) | 0.0317 (17) | 0.0244 (17) | 0.0008 (12) | −0.0035 (12) | 0.0032 (14) |
| C11 | 0.0313 (15) | 0.045 (2) | 0.035 (2) | −0.0027 (14) | −0.0049 (14) | −0.0101 (17) |
| C12 | 0.0393 (17) | 0.034 (2) | 0.053 (3) | 0.0085 (15) | −0.0046 (16) | 0.0024 (18) |
| P1 | 0.0267 (4) | 0.0287 (4) | 0.0326 (5) | 0.0003 (3) | 0.0059 (3) | −0.0026 (4) |
| F1 | 0.0721 (16) | 0.109 (2) | 0.0429 (15) | 0.0339 (15) | −0.0032 (13) | 0.0063 (16) |
| F2 | 0.0442 (11) | 0.0542 (14) | 0.0786 (18) | −0.0083 (10) | 0.0329 (11) | −0.0070 (13) |
| F3 | 0.0674 (15) | 0.107 (2) | 0.0452 (15) | 0.0192 (15) | −0.0114 (12) | 0.0022 (15) |
| F4 | 0.0486 (12) | 0.0574 (15) | 0.0815 (19) | −0.0082 (10) | 0.0357 (12) | −0.0007 (13) |
| F5 | 0.0616 (14) | 0.0366 (13) | 0.109 (2) | −0.0068 (10) | 0.0292 (14) | −0.0234 (14) |
| F6 | 0.0456 (12) | 0.0412 (14) | 0.107 (2) | −0.0014 (10) | 0.0159 (12) | −0.0269 (14) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cr1—N3 | 2.053 (2) | C5—C6 | 1.522 (4) |
| Cr1—N1 | 2.056 (3) | C5—H5A | 0.9900 |

| | | | |
|---|---|---|---|
| Cr1—N4 | 2.094 (3) | C5—H5B | 0.9900 |
| Cr1—N2 | 2.100 (3) | C6—H6A | 0.9900 |
| Cr1—Cl2 | 2.3147 (9) | C6—H6B | 0.9900 |
| Cr1—Cl1 | 2.3215 (8) | C7—C8 | 1.541 (5) |
| N1—C8 | 1.486 (4) | C7—H7A | 0.9900 |
| N1—C1 | 1.492 (4) | C7—H7B | 0.9900 |
| N1—C9 | 1.503 (4) | C8—H8A | 0.9900 |
| N2—C11 | 1.491 (4) | C8—H8B | 0.9900 |
| N2—C2 | 1.512 (4) | C9—C10 | 1.523 (4) |
| N2—C3 | 1.516 (3) | C9—H9A | 0.9900 |
| N3—C4 | 1.486 (4) | C9—H9B | 0.9900 |
| N3—C5 | 1.496 (4) | C10—H10A | 0.9900 |
| N3—C10 | 1.499 (4) | C10—H10B | 0.9900 |
| N4—C12 | 1.486 (5) | C11—H11A | 0.9800 |
| N4—C7 | 1.505 (4) | C11—H11B | 0.9800 |
| N4—C6 | 1.519 (4) | C11—H11C | 0.9800 |
| C1—C2 | 1.507 (5) | C12—H12A | 0.9800 |
| C1—H1A | 0.9900 | C12—H12B | 0.9800 |
| C1—H1B | 0.9900 | C12—H12C | 0.9800 |
| C2—H2A | 0.9900 | P1—F1 | 1.570 (3) |
| C2—H2B | 0.9900 | P1—F3 | 1.577 (3) |
| C3—C4 | 1.535 (5) | P1—F5 | 1.578 (2) |
| C3—H3A | 0.9900 | P1—F6 | 1.582 (2) |
| C3—H3B | 0.9900 | P1—F4 | 1.585 (2) |
| C4—H4A | 0.9900 | P1—F2 | 1.591 (2) |
| C4—H4B | 0.9900 | | |
| | | | |
| N3—Cr1—N1 | 83.23 (10) | N3—C5—C6 | 108.2 (2) |
| N3—Cr1—N4 | 85.68 (10) | N3—C5—H5A | 110.1 |
| N1—Cr1—N4 | 81.21 (11) | C6—C5—H5A | 110.1 |
| N3—Cr1—N2 | 80.93 (9) | N3—C5—H5B | 110.1 |
| N1—Cr1—N2 | 84.74 (11) | C6—C5—H5B | 110.1 |
| N4—Cr1—N2 | 161.62 (11) | H5A—C5—H5B | 108.4 |
| N3—Cr1—Cl2 | 91.97 (7) | N4—C6—C5 | 110.5 (3) |
| N1—Cr1—Cl2 | 175.19 (7) | N4—C6—H6A | 109.6 |
| N4—Cr1—Cl2 | 98.09 (8) | C5—C6—H6A | 109.6 |
| N2—Cr1—Cl2 | 94.91 (8) | N4—C6—H6B | 109.6 |
| N3—Cr1—Cl1 | 177.18 (8) | C5—C6—H6B | 109.6 |
| N1—Cr1—Cl1 | 93.99 (7) | H6A—C6—H6B | 108.1 |
| N4—Cr1—Cl1 | 93.50 (7) | N4—C7—C8 | 113.5 (3) |
| N2—Cr1—Cl1 | 99.27 (7) | N4—C7—H7A | 108.9 |
| Cl2—Cr1—Cl1 | 90.81 (3) | C8—C7—H7A | 108.9 |
| C8—N1—C1 | 113.3 (2) | N4—C7—H7B | 108.9 |
| C8—N1—C9 | 109.3 (3) | C8—C7—H7B | 108.9 |
| C1—N1—C9 | 110.9 (3) | H7A—C7—H7B | 107.7 |
| C8—N1—Cr1 | 106.2 (2) | N1—C8—C7 | 110.8 (2) |
| C1—N1—Cr1 | 103.6 (2) | N1—C8—H8A | 109.5 |
| C9—N1—Cr1 | 113.31 (17) | C7—C8—H8A | 109.5 |

| | | | |
|---|---|---|---|
| C11—N2—C2 | 108.1 (2) | N1—C8—H8B | 109.5 |
| C11—N2—C3 | 108.7 (2) | C7—C8—H8B | 109.5 |
| C2—N2—C3 | 111.8 (2) | H8A—C8—H8B | 108.1 |
| C11—N2—Cr1 | 114.0 (2) | N1—C9—C10 | 111.6 (3) |
| C2—N2—Cr1 | 106.88 (19) | N1—C9—H9A | 109.3 |
| C3—N2—Cr1 | 107.38 (18) | C10—C9—H9A | 109.3 |
| C4—N3—C5 | 114.0 (2) | N1—C9—H9B | 109.3 |
| C4—N3—C10 | 108.9 (2) | C10—C9—H9B | 109.3 |
| C5—N3—C10 | 111.3 (2) | H9A—C9—H9B | 108.0 |
| C4—N3—Cr1 | 106.11 (18) | N3—C10—C9 | 112.0 (2) |
| C5—N3—Cr1 | 103.27 (17) | N3—C10—H10A | 109.2 |
| C10—N3—Cr1 | 113.16 (16) | C9—C10—H10A | 109.2 |
| C12—N4—C7 | 109.0 (3) | N3—C10—H10B | 109.2 |
| C12—N4—C6 | 108.4 (2) | C9—C10—H10B | 109.2 |
| C7—N4—C6 | 110.4 (3) | H10A—C10—H10B | 107.9 |
| C12—N4—Cr1 | 114.8 (2) | N2—C11—H11A | 109.5 |
| C7—N4—Cr1 | 107.7 (2) | N2—C11—H11B | 109.5 |
| C6—N4—Cr1 | 106.47 (18) | H11A—C11—H11B | 109.5 |
| N1—C1—C2 | 108.3 (2) | N2—C11—H11C | 109.5 |
| N1—C1—H1A | 110.0 | H11A—C11—H11C | 109.5 |
| C2—C1—H1A | 110.0 | H11B—C11—H11C | 109.5 |
| N1—C1—H1B | 110.0 | N4—C12—H12A | 109.5 |
| C2—C1—H1B | 110.0 | N4—C12—H12B | 109.5 |
| H1A—C1—H1B | 108.4 | H12A—C12—H12B | 109.5 |
| C1—C2—N2 | 111.0 (3) | N4—C12—H12C | 109.5 |
| C1—C2—H2A | 109.4 | H12A—C12—H12C | 109.5 |
| N2—C2—H2A | 109.4 | H12B—C12—H12C | 109.5 |
| C1—C2—H2B | 109.4 | F1—P1—F3 | 179.36 (15) |
| N2—C2—H2B | 109.4 | F1—P1—F5 | 90.78 (16) |
| H2A—C2—H2B | 108.0 | F3—P1—F5 | 89.08 (17) |
| N2—C3—C4 | 113.5 (2) | F1—P1—F6 | 90.07 (16) |
| N2—C3—H3A | 108.9 | F3—P1—F6 | 90.06 (16) |
| C4—C3—H3A | 108.9 | F5—P1—F6 | 179.05 (17) |
| N2—C3—H3B | 108.9 | F1—P1—F4 | 91.76 (15) |
| C4—C3—H3B | 108.9 | F3—P1—F4 | 88.88 (15) |
| H3A—C3—H3B | 107.7 | F5—P1—F4 | 91.85 (13) |
| N3—C4—C3 | 110.3 (2) | F6—P1—F4 | 88.55 (13) |
| N3—C4—H4A | 109.6 | F1—P1—F2 | 88.05 (14) |
| C3—C4—H4A | 109.6 | F3—P1—F2 | 91.32 (15) |
| N3—C4—H4B | 109.6 | F5—P1—F2 | 89.00 (12) |
| C3—C4—H4B | 109.6 | F6—P1—F2 | 90.60 (13) |
| H4A—C4—H4B | 108.1 | F4—P1—F2 | 179.13 (14) |
| | | | |
| C8—N1—C1—C2 | 167.0 (3) | C7—N4—C6—C5 | 141.4 (3) |
| C9—N1—C1—C2 | −69.6 (3) | Cr1—N4—C6—C5 | 24.8 (3) |
| Cr1—N1—C1—C2 | 52.3 (3) | N3—C5—C6—N4 | −52.8 (3) |
| N1—C1—C2—N2 | −51.4 (3) | C12—N4—C7—C8 | 140.9 (3) |
| C11—N2—C2—C1 | −100.3 (3) | C6—N4—C7—C8 | −100.1 (3) |

| | | | |
|---|---|---|---|
| C3—N2—C2—C1 | 140.1 (3) | Cr1—N4—C7—C8 | 15.7 (3) |
| Cr1—N2—C2—C1 | 22.8 (3) | C1—N1—C8—C7 | −155.4 (3) |
| C11—N2—C3—C4 | 138.1 (3) | C9—N1—C8—C7 | 80.4 (3) |
| C2—N2—C3—C4 | −102.6 (3) | Cr1—N1—C8—C7 | −42.3 (3) |
| Cr1—N2—C3—C4 | 14.3 (3) | N4—C7—C8—N1 | 17.3 (4) |
| C5—N3—C4—C3 | −157.4 (3) | C8—N1—C9—C10 | −140.2 (3) |
| C10—N3—C4—C3 | 77.6 (3) | C1—N1—C9—C10 | 94.1 (3) |
| Cr1—N3—C4—C3 | −44.5 (3) | Cr1—N1—C9—C10 | −21.9 (3) |
| N2—C3—C4—N3 | 19.5 (4) | C4—N3—C10—C9 | −140.6 (3) |
| C4—N3—C5—C6 | 166.7 (3) | C5—N3—C10—C9 | 92.9 (3) |
| C10—N3—C5—C6 | −69.7 (3) | Cr1—N3—C10—C9 | −22.9 (3) |
| Cr1—N3—C5—C6 | 52.0 (3) | N1—C9—C10—N3 | 28.9 (4) |
| C12—N4—C6—C5 | −99.2 (3) | | |

*Hydrogen-bond geometry (Å, º)*

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C1—H1$A$···F6[i] | 0.99 | 2.53 | 3.347 (4) | 140 |
| C1—H1$B$···F3[ii] | 0.99 | 2.46 | 3.410 (5) | 162 |
| C2—H2$A$···F4[i] | 0.99 | 2.48 | 3.407 (4) | 155 |
| C3—H3$A$···F1[iii] | 0.99 | 2.51 | 3.500 (4) | 177 |
| C4—H4$A$···F6[iv] | 0.99 | 2.36 | 3.175 (4) | 139 |
| C6—H6$B$···F4 | 0.99 | 2.30 | 3.238 (4) | 158 |
| C1—H1$A$···Cl1 | 0.99 | 2.82 | 3.393 (4) | 118 |
| C4—H4$B$···Cl2 | 0.99 | 2.63 | 3.137 (3) | 112 |
| C5—H5$A$···Cl2 | 0.99 | 2.74 | 3.324 (3) | 118 |
| C6—H6$A$···Cl2[v] | 0.99 | 2.77 | 3.447 (3) | 126 |
| C8—H8$B$···Cl1 | 0.99 | 2.73 | 3.203 (4) | 110 |
| C12—H12$B$···Cl2 | 0.98 | 2.78 | 3.329 (4) | 116 |

Symmetry codes: (i) −$x$+1/2, $y$−1/2, −$z$+1/2; (ii) $x$−1/2, −$y$+1/2, $z$+1/2; (iii) $x$−1/2, −$y$+1/2, $z$−1/2; (iv) −$x$+3/2, $y$−1/2, −$z$+1/2; (v) $x$+1/2, −$y$+1/2, $z$+1/2.

**(II) Dichlorido(4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)chromium(III) hexafluorophosphate**

*Crystal data*

[CrCl$_2$(C$_{14}$H$_{30}$N$_4$)]PF$_6$
$M_r$ = 522.29
Monoclinic, $P2_1/c$
$a$ = 13.6801 (19) Å
$b$ = 12.437 (2) Å
$c$ = 12.3864 (17) Å
$β$ = 102.028 (11)°
$V$ = 2061.1 (5) Å$^3$
$Z$ = 4

$F(000)$ = 1076
$D_x$ = 1.683 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 9091 reflections
$\theta$ = 2.6–27.9°
$\mu$ = 0.95 mm$^{-1}$
$T$ = 150 K
Block, purple
0.15 × 0.15 × 0.06 mm

*Data collection*

Stoe IPDS2
    diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 6.67 pixels mm$^{-1}$
$\omega$–scans

Absorption correction: analytical
    [a face-indexed absorption correction was
    applied; *X-AREA* (Stoe & Cie, 2002)]
$T_{min}$ = 0.778, $T_{max}$ = 0.901
13450 measured reflections

4158 independent reflections
2073 reflections with $I > 2\sigma(I)$
$R_{int} = 0.091$
$\theta_{max} = 26.3°$, $\theta_{min} = 2.6°$

$h = -17\rightarrow16$
$k = -15\rightarrow13$
$l = -15\rightarrow15$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.109$
$S = 0.78$
4158 reflections
255 parameters
0 restraints

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.052P)^2]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.33$ e Å$^{-3}$
$\Delta\rho_{min} = -0.79$ e Å$^{-3}$

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

|      | *x*          | *y*          | *z*          | $U_{iso}*/U_{eq}$ |
|------|--------------|--------------|--------------|-------------------|
| Cr1  | 0.32108 (5)  | 0.56984 (5)  | 0.21705 (5)  | 0.03357 (19)      |
| Cl1  | 0.46100 (9)  | 0.62992 (9)  | 0.33888 (8)  | 0.0431 (3)        |
| Cl2  | 0.36519 (9)  | 0.66096 (9)  | 0.07251 (8)  | 0.0423 (3)        |
| N1   | 0.2651 (3)   | 0.4975 (3)   | 0.3442 (3)   | 0.0367 (8)        |
| N2   | 0.2251 (3)   | 0.7026 (3)   | 0.2372 (2)   | 0.0368 (9)        |
| N3   | 0.1984 (3)   | 0.4956 (3)   | 0.1138 (2)   | 0.0331 (8)        |
| N4   | 0.3972 (3)   | 0.4231 (3)   | 0.1961 (3)   | 0.0384 (9)        |
| C1   | 0.2305 (4)   | 0.5917 (3)   | 0.4026 (3)   | 0.0406 (11)       |
| H1A  | 0.2892       | 0.6311       | 0.4444       | 0.049*            |
| H1B  | 0.1910       | 0.5656       | 0.4558       | 0.049*            |
| C2   | 0.1674 (4)   | 0.6666 (4)   | 0.3209 (3)   | 0.0401 (11)       |
| H2A  | 0.1057       | 0.6291       | 0.2834       | 0.048*            |
| H2B  | 0.1478       | 0.7298       | 0.3600       | 0.048*            |
| C3   | 0.1559 (3)   | 0.7420 (4)   | 0.1358 (3)   | 0.0396 (10)       |
| H3A  | 0.1966       | 0.7733       | 0.0863       | 0.048*            |
| H3B  | 0.1151       | 0.8008       | 0.1573       | 0.048*            |
| C4   | 0.0858 (3)   | 0.6599 (4)   | 0.0706 (3)   | 0.0421 (11)       |
| H4A  | 0.0419       | 0.6316       | 0.1183       | 0.051*            |
| H4B  | 0.0425       | 0.6968       | 0.0074       | 0.051*            |
| C5   | 0.1360 (3)   | 0.5661 (4)   | 0.0269 (3)   | 0.0388 (10)       |
| H5A  | 0.0838       | 0.5211       | −0.0193      | 0.047*            |
| H5B  | 0.1793       | 0.5943       | −0.0214      | 0.047*            |
| C6   | 0.2446 (4)   | 0.4113 (4)   | 0.0536 (3)   | 0.0426 (11)       |
| H6A  | 0.2768       | 0.4460       | −0.0020      | 0.051*            |
| H6B  | 0.1920       | 0.3623       | 0.0144       | 0.051*            |
| C7   | 0.3218 (4)   | 0.3474 (4)   | 0.1338 (3)   | 0.0416 (11)       |

| | | | |
|---|---|---|---|
| H7A | 0.2891 | 0.3073 | 0.1856 | 0.050* |
| H7B | 0.3549 | 0.2949 | 0.0931 | 0.050* |
| C8 | 0.4513 (3) | 0.3706 (4) | 0.3011 (3) | 0.0408 (11) |
| H8A | 0.5060 | 0.4190 | 0.3371 | 0.049* |
| H8B | 0.4825 | 0.3035 | 0.2816 | 0.049* |
| C9 | 0.3879 (4) | 0.3433 (4) | 0.3847 (3) | 0.0421 (11) |
| H9A | 0.3353 | 0.2922 | 0.3496 | 0.051* |
| H9B | 0.4309 | 0.3055 | 0.4474 | 0.051* |
| C10 | 0.3379 (3) | 0.4366 (4) | 0.4302 (3) | 0.0405 (11) |
| H10A | 0.3021 | 0.4089 | 0.4862 | 0.049* |
| H10B | 0.3901 | 0.4869 | 0.4679 | 0.049* |
| C11 | 0.1794 (3) | 0.4237 (4) | 0.3005 (3) | 0.0395 (10) |
| H11A | 0.1286 | 0.4316 | 0.3463 | 0.047* |
| H11B | 0.2038 | 0.3485 | 0.3080 | 0.047* |
| C12 | 0.1300 (3) | 0.4441 (4) | 0.1802 (3) | 0.0402 (11) |
| H12A | 0.1056 | 0.3749 | 0.1454 | 0.048* |
| H12B | 0.0713 | 0.4913 | 0.1777 | 0.048* |
| C13 | 0.2856 (4) | 0.7989 (4) | 0.2819 (3) | 0.0443 (11) |
| H13A | 0.3262 | 0.7820 | 0.3548 | 0.053* |
| H13B | 0.2407 | 0.8589 | 0.2883 | 0.053* |
| H13C | 0.3294 | 0.8189 | 0.2318 | 0.053* |
| C14 | 0.4760 (4) | 0.4407 (4) | 0.1303 (4) | 0.0469 (12) |
| H14A | 0.5234 | 0.4952 | 0.1666 | 0.056* |
| H14B | 0.4447 | 0.4653 | 0.0560 | 0.056* |
| H14C | 0.5116 | 0.3731 | 0.1252 | 0.056* |
| P1 | 0.12310 (10) | 0.10057 (10) | 0.18374 (9) | 0.0430 (3) |
| F1 | 0.0182 (2) | 0.0745 (3) | 0.1049 (2) | 0.0696 (9) |
| F2 | 0.0958 (3) | 0.0212 (2) | 0.2740 (2) | 0.0688 (9) |
| F3 | 0.2260 (2) | 0.1297 (3) | 0.2639 (2) | 0.0718 (9) |
| F4 | 0.1495 (2) | 0.1810 (2) | 0.0940 (2) | 0.0637 (8) |
| F5 | 0.1746 (2) | 0.0057 (2) | 0.1317 (2) | 0.0615 (8) |
| F6 | 0.0718 (2) | 0.1974 (2) | 0.2371 (2) | 0.0664 (9) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cr1 | 0.0378 (4) | 0.0298 (4) | 0.0323 (3) | −0.0011 (3) | 0.0054 (3) | −0.0001 (3) |
| Cl1 | 0.0451 (7) | 0.0383 (6) | 0.0423 (5) | −0.0058 (5) | 0.0008 (5) | 0.0013 (4) |
| Cl2 | 0.0466 (7) | 0.0428 (7) | 0.0379 (5) | −0.0023 (5) | 0.0096 (5) | 0.0057 (4) |
| N1 | 0.040 (2) | 0.0317 (19) | 0.0366 (17) | 0.0027 (17) | 0.0037 (16) | 0.0002 (14) |
| N2 | 0.045 (2) | 0.033 (2) | 0.0333 (16) | 0.0000 (17) | 0.0082 (16) | 0.0005 (14) |
| N3 | 0.032 (2) | 0.0315 (19) | 0.0345 (16) | −0.0029 (16) | 0.0053 (15) | 0.0008 (14) |
| N4 | 0.043 (2) | 0.035 (2) | 0.0374 (17) | 0.0034 (18) | 0.0077 (16) | 0.0012 (15) |
| C1 | 0.052 (3) | 0.035 (3) | 0.035 (2) | 0.002 (2) | 0.011 (2) | −0.0052 (17) |
| C2 | 0.047 (3) | 0.031 (2) | 0.044 (2) | 0.003 (2) | 0.013 (2) | −0.0005 (18) |
| C3 | 0.040 (3) | 0.036 (3) | 0.040 (2) | 0.004 (2) | 0.0009 (19) | 0.0013 (18) |
| C4 | 0.042 (3) | 0.040 (3) | 0.042 (2) | 0.004 (2) | 0.003 (2) | 0.004 (2) |
| C5 | 0.039 (3) | 0.037 (3) | 0.037 (2) | 0.001 (2) | 0.0000 (19) | 0.0011 (18) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C6 | 0.050 (3) | 0.037 (3) | 0.041 (2) | 0.002 (2) | 0.008 (2) | −0.0053 (19) |
| C7 | 0.052 (3) | 0.034 (2) | 0.040 (2) | 0.003 (2) | 0.011 (2) | −0.0031 (19) |
| C8 | 0.043 (3) | 0.036 (3) | 0.040 (2) | 0.010 (2) | 0.003 (2) | 0.0025 (18) |
| C9 | 0.044 (3) | 0.040 (3) | 0.040 (2) | 0.004 (2) | 0.005 (2) | 0.0066 (19) |
| C10 | 0.045 (3) | 0.038 (3) | 0.035 (2) | 0.001 (2) | 0.002 (2) | 0.0054 (18) |
| C11 | 0.043 (3) | 0.038 (2) | 0.037 (2) | −0.005 (2) | 0.007 (2) | 0.0022 (19) |
| C12 | 0.047 (3) | 0.035 (3) | 0.039 (2) | −0.009 (2) | 0.009 (2) | 0.0011 (18) |
| C13 | 0.051 (3) | 0.031 (3) | 0.049 (2) | −0.004 (2) | 0.007 (2) | −0.0061 (19) |
| C14 | 0.042 (3) | 0.050 (3) | 0.050 (2) | 0.004 (2) | 0.014 (2) | 0.005 (2) |
| P1 | 0.0498 (8) | 0.0337 (7) | 0.0480 (6) | −0.0055 (6) | 0.0157 (6) | −0.0035 (5) |
| F1 | 0.057 (2) | 0.078 (2) | 0.0717 (18) | −0.0152 (17) | 0.0075 (15) | −0.0207 (16) |
| F2 | 0.097 (3) | 0.057 (2) | 0.0623 (16) | −0.0099 (18) | 0.0399 (17) | 0.0102 (14) |
| F3 | 0.061 (2) | 0.088 (3) | 0.0633 (17) | −0.0109 (18) | 0.0054 (15) | −0.0088 (16) |
| F4 | 0.079 (2) | 0.0471 (18) | 0.0706 (17) | −0.0034 (16) | 0.0279 (16) | 0.0136 (14) |
| F5 | 0.084 (2) | 0.0391 (16) | 0.0712 (17) | 0.0070 (16) | 0.0400 (16) | −0.0038 (13) |
| F6 | 0.069 (2) | 0.0465 (18) | 0.092 (2) | −0.0049 (16) | 0.0352 (17) | −0.0261 (15) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cr1—N1 | 2.093 (3) | C6—C7 | 1.516 (6) |
| Cr1—N3 | 2.100 (3) | C6—H6A | 0.9900 |
| Cr1—N4 | 2.143 (4) | C6—H6B | 0.9900 |
| Cr1—N2 | 2.155 (4) | C7—H7A | 0.9900 |
| Cr1—Cl1 | 2.3012 (13) | C7—H7B | 0.9900 |
| Cr1—Cl2 | 2.3031 (12) | C8—C9 | 1.520 (6) |
| N1—C11 | 1.499 (5) | C8—H8A | 0.9900 |
| N1—C10 | 1.502 (5) | C8—H8B | 0.9900 |
| N1—C1 | 1.504 (5) | C9—C10 | 1.516 (6) |
| N2—C3 | 1.490 (5) | C9—H9A | 0.9900 |
| N2—C13 | 1.495 (5) | C9—H9B | 0.9900 |
| N2—C2 | 1.497 (5) | C10—H10A | 0.9900 |
| N3—C6 | 1.500 (5) | C10—H10B | 0.9900 |
| N3—C5 | 1.507 (5) | C11—C12 | 1.524 (5) |
| N3—C12 | 1.511 (5) | C11—H11A | 0.9900 |
| N4—C7 | 1.487 (6) | C11—H11B | 0.9900 |
| N4—C14 | 1.498 (5) | C12—H12A | 0.9900 |
| N4—C8 | 1.505 (5) | C12—H12B | 0.9900 |
| C1—C2 | 1.508 (6) | C13—H13A | 0.9800 |
| C1—H1A | 0.9900 | C13—H13B | 0.9800 |
| C1—H1B | 0.9900 | C13—H13C | 0.9800 |
| C2—H2A | 0.9900 | C14—H14A | 0.9800 |
| C2—H2B | 0.9900 | C14—H14B | 0.9800 |
| C3—C4 | 1.514 (6) | C14—H14C | 0.9800 |
| C3—H3A | 0.9900 | P1—F5 | 1.579 (3) |
| C3—H3B | 0.9900 | P1—F3 | 1.587 (3) |
| C4—C5 | 1.510 (6) | P1—F1 | 1.592 (3) |
| C4—H4A | 0.9900 | P1—F4 | 1.592 (3) |
| C4—H4B | 0.9900 | P1—F2 | 1.593 (3) |

| | | | |
|---|---|---|---|
| C5—H5A | 0.9900 | P1—F6 | 1.605 (3) |
| C5—H5B | 0.9900 | | |
| | | | |
| N1—Cr1—N3 | 84.18 (13) | N3—C6—C7 | 110.4 (3) |
| N1—Cr1—N4 | 89.33 (13) | N3—C6—H6A | 109.6 |
| N3—Cr1—N4 | 84.16 (14) | C7—C6—H6A | 109.6 |
| N1—Cr1—N2 | 85.11 (13) | N3—C6—H6B | 109.6 |
| N3—Cr1—N2 | 88.80 (14) | C7—C6—H6B | 109.6 |
| N4—Cr1—N2 | 171.44 (14) | H6A—C6—H6B | 108.1 |
| N1—Cr1—Cl1 | 91.75 (10) | N4—C7—C6 | 108.7 (4) |
| N3—Cr1—Cl1 | 172.78 (10) | N4—C7—H7A | 109.9 |
| N4—Cr1—Cl1 | 89.84 (10) | C6—C7—H7A | 109.9 |
| N2—Cr1—Cl1 | 96.82 (10) | N4—C7—H7B | 109.9 |
| N1—Cr1—Cl2 | 173.17 (11) | C6—C7—H7B | 109.9 |
| N3—Cr1—Cl2 | 92.77 (9) | H7A—C7—H7B | 108.3 |
| N4—Cr1—Cl2 | 96.45 (9) | N4—C8—C9 | 115.9 (4) |
| N2—Cr1—Cl2 | 88.73 (9) | N4—C8—H8A | 108.3 |
| Cl1—Cr1—Cl2 | 91.90 (5) | C9—C8—H8A | 108.3 |
| C11—N1—C10 | 107.4 (3) | N4—C8—H8B | 108.3 |
| C11—N1—C1 | 110.5 (3) | C9—C8—H8B | 108.3 |
| C10—N1—C1 | 106.3 (3) | H8A—C8—H8B | 107.4 |
| C11—N1—Cr1 | 111.9 (2) | C10—C9—C8 | 116.6 (4) |
| C10—N1—Cr1 | 117.3 (3) | C10—C9—H9A | 108.1 |
| C1—N1—Cr1 | 103.2 (2) | C8—C9—H9A | 108.1 |
| C3—N2—C13 | 104.7 (3) | C10—C9—H9B | 108.1 |
| C3—N2—C2 | 110.4 (3) | C8—C9—H9B | 108.1 |
| C13—N2—C2 | 108.3 (3) | H9A—C9—H9B | 107.3 |
| C3—N2—Cr1 | 116.7 (2) | N1—C10—C9 | 114.0 (3) |
| C13—N2—Cr1 | 110.7 (3) | N1—C10—H10A | 108.8 |
| C2—N2—Cr1 | 105.9 (2) | C9—C10—H10A | 108.8 |
| C6—N3—C5 | 106.6 (3) | N1—C10—H10B | 108.8 |
| C6—N3—C12 | 110.3 (3) | C9—C10—H10B | 108.8 |
| C5—N3—C12 | 108.2 (3) | H10A—C10—H10B | 107.7 |
| C6—N3—Cr1 | 104.1 (3) | N1—C11—C12 | 113.9 (3) |
| C5—N3—Cr1 | 116.2 (3) | N1—C11—H11A | 108.8 |
| C12—N3—Cr1 | 111.2 (2) | C12—C11—H11A | 108.8 |
| C7—N4—C14 | 108.1 (3) | N1—C11—H11B | 108.8 |
| C7—N4—C8 | 109.7 (3) | C12—C11—H11B | 108.8 |
| C14—N4—C8 | 104.7 (3) | H11A—C11—H11B | 107.7 |
| C7—N4—Cr1 | 107.5 (3) | N3—C12—C11 | 113.9 (4) |
| C14—N4—Cr1 | 111.4 (3) | N3—C12—H12A | 108.8 |
| C8—N4—Cr1 | 115.4 (2) | C11—C12—H12A | 108.8 |
| N1—C1—C2 | 110.6 (3) | N3—C12—H12B | 108.8 |
| N1—C1—H1A | 109.5 | C11—C12—H12B | 108.8 |
| C2—C1—H1A | 109.5 | H12A—C12—H12B | 107.7 |
| N1—C1—H1B | 109.5 | N2—C13—H13A | 109.5 |
| C2—C1—H1B | 109.5 | N2—C13—H13B | 109.5 |
| H1A—C1—H1B | 108.1 | H13A—C13—H13B | 109.5 |

| | | | |
|---|---|---|---|
| N2—C2—C1 | 109.8 (4) | N2—C13—H13C | 109.5 |
| N2—C2—H2A | 109.7 | H13A—C13—H13C | 109.5 |
| C1—C2—H2A | 109.7 | H13B—C13—H13C | 109.5 |
| N2—C2—H2B | 109.7 | N4—C14—H14A | 109.5 |
| C1—C2—H2B | 109.7 | N4—C14—H14B | 109.5 |
| H2A—C2—H2B | 108.2 | H14A—C14—H14B | 109.5 |
| N2—C3—C4 | 116.7 (4) | N4—C14—H14C | 109.5 |
| N2—C3—H3A | 108.1 | H14A—C14—H14C | 109.5 |
| C4—C3—H3A | 108.1 | H14B—C14—H14C | 109.5 |
| N2—C3—H3B | 108.1 | F5—P1—F3 | 90.73 (18) |
| C4—C3—H3B | 108.1 | F5—P1—F1 | 91.12 (17) |
| H3A—C3—H3B | 107.3 | F3—P1—F1 | 178.15 (19) |
| C5—C4—C3 | 115.3 (4) | F5—P1—F4 | 89.96 (15) |
| C5—C4—H4A | 108.5 | F3—P1—F4 | 89.57 (17) |
| C3—C4—H4A | 108.5 | F1—P1—F4 | 90.36 (17) |
| C5—C4—H4B | 108.5 | F5—P1—F2 | 90.75 (16) |
| C3—C4—H4B | 108.5 | F3—P1—F2 | 90.55 (17) |
| H4A—C4—H4B | 107.5 | F1—P1—F2 | 89.50 (18) |
| N3—C5—C4 | 115.2 (3) | F4—P1—F2 | 179.28 (19) |
| N3—C5—H5A | 108.5 | F5—P1—F6 | 179.47 (19) |
| C4—C5—H5A | 108.5 | F3—P1—F6 | 88.75 (17) |
| N3—C5—H5B | 108.5 | F1—P1—F6 | 89.40 (17) |
| C4—C5—H5B | 108.5 | F4—P1—F6 | 89.91 (17) |
| H5A—C5—H5B | 107.5 | F2—P1—F6 | 89.38 (16) |
| | | | |
| C11—N1—C1—C2 | −71.2 (4) | C8—N4—C7—C6 | 159.7 (3) |
| C10—N1—C1—C2 | 172.6 (4) | Cr1—N4—C7—C6 | 33.5 (4) |
| Cr1—N1—C1—C2 | 48.6 (4) | N3—C6—C7—N4 | −56.2 (5) |
| C3—N2—C2—C1 | 159.5 (3) | C7—N4—C8—C9 | −64.3 (5) |
| C13—N2—C2—C1 | −86.4 (4) | C14—N4—C8—C9 | −180.0 (4) |
| Cr1—N2—C2—C1 | 32.3 (4) | Cr1—N4—C8—C9 | 57.2 (4) |
| N1—C1—C2—N2 | −56.7 (5) | N4—C8—C9—C10 | −61.3 (5) |
| C13—N2—C3—C4 | 178.8 (4) | C11—N1—C10—C9 | 66.6 (5) |
| C2—N2—C3—C4 | −64.9 (5) | C1—N1—C10—C9 | −175.1 (4) |
| Cr1—N2—C3—C4 | 56.0 (5) | Cr1—N1—C10—C9 | −60.3 (4) |
| N2—C3—C4—C5 | −60.3 (5) | C8—C9—C10—N1 | 61.5 (5) |
| C6—N3—C5—C4 | −177.6 (4) | C10—N1—C11—C12 | −149.2 (4) |
| C12—N3—C5—C4 | 63.7 (5) | C1—N1—C11—C12 | 95.2 (4) |
| Cr1—N3—C5—C4 | −62.1 (4) | Cr1—N1—C11—C12 | −19.2 (5) |
| C3—C4—C5—N3 | 62.9 (5) | C6—N3—C12—C11 | 95.5 (4) |
| C5—N3—C6—C7 | 170.9 (4) | C5—N3—C12—C11 | −148.2 (4) |
| C12—N3—C6—C7 | −71.8 (4) | Cr1—N3—C12—C11 | −19.6 (4) |
| Cr1—N3—C6—C7 | 47.6 (4) | N1—C11—C12—N3 | 25.8 (5) |
| C14—N4—C7—C6 | −86.8 (4) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H⋯*A* | *D*—H | H⋯*A* | *D*⋯*A* | *D*—H⋯*A* |
|---|---|---|---|---|
| C1—H1*B*⋯F5ⁱ | 0.99 | 2.41 | 3.318 (5) | 153 |
| C2—H2*A*⋯F1ⁱⁱ | 0.99 | 2.50 | 3.094 (5) | 119 |
| C2—H2*A*⋯F6ⁱⁱ | 0.99 | 2.53 | 3.223 (6) | 127 |
| C7—H7*A*⋯F4 | 0.99 | 2.55 | 3.098 (6) | 115 |
| C12—H12*B*⋯F2ⁱⁱ | 0.99 | 2.51 | 3.393 (6) | 149 |
| C3—H3*A*⋯Cl2 | 0.99 | 2.73 | 3.280 (5) | 115 |
| C5—H5*B*⋯Cl2 | 0.99 | 2.70 | 3.287 (5) | 119 |
| C8—H8*A*⋯Cl1 | 0.99 | 2.70 | 3.258 (5) | 116 |
| C8—H8*B*⋯Cl1ⁱⁱⁱ | 0.99 | 2.82 | 3.778 (4) | 162 |
| C10—H10*B*⋯Cl1 | 0.99 | 2.70 | 3.270 (5) | 117 |
| C13—H13*A*⋯Cl1 | 0.98 | 2.68 | 3.157 (5) | 111 |
| C13—H13*A*⋯Cl2ⁱᵛ | 0.98 | 2.73 | 3.572 (4) | 144 |
| C14—H14*B*⋯Cl2 | 0.98 | 2.69 | 3.141 (5) | 108 |

Symmetry codes: (i) *x*, −*y*+1/2, *z*+1/2; (ii) −*x*, *y*+1/2, −*z*+1/2; (iii) −*x*+1, *y*−1/2, −*z*+1/2; (iv) *x*, −*y*+3/2, *z*+1/2.