



# Crystal structure of hexakis(urea- $\kappa$ O)chromium(III) dichromate bromide monohydrate from synchrotron X-ray data

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**Keywords:** crystal structure; chromium(III) complex; urea ligand; bromide salt; hydrogen bonding; synchrotron data

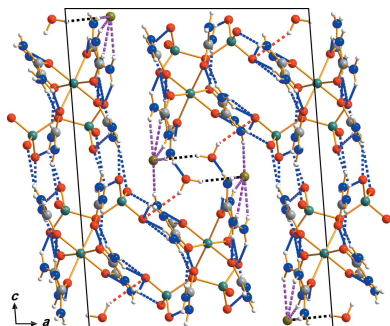
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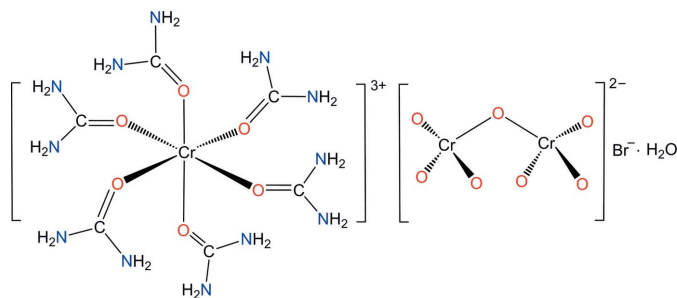
**Supporting information:** this article has supporting information at journals.iucr.org/e

The title bromide salt,  $[\text{Cr}\{\text{CO}(\text{NH}_2)_2\}_6](\text{Cr}_2\text{O}_7)\text{Br}\cdot\text{H}_2\text{O}$ , is isotypic to the corresponding chloride salt. Within the complex cation, the  $\text{Cr}^{\text{III}}$  atom is coordinated by six O atoms of six urea ligands, displaying a slightly distorted octahedral coordination environment. The Cr–O bond lengths involving the urea ligands are in the range 1.9534 (13)–1.9776 (12) Å. The  $\text{Cr}_2\text{O}_7^{2-}$  anion has a nearly staggered conformation, with a bridging angle of 130.26 (10)°. The individual components are arranged in rows extending parallel to [100]. The  $\text{Br}^-$  anion links the complex cation, as well as the solvent water molecule, through  $\text{N}-\text{H}\cdots\text{Br}$  and  $\text{O}-\text{H}\cdots\text{Br}$  hydrogen-bonding interactions. The supramolecular architecture also includes  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonding between urea N–H and water O–H donor groups and the O atoms of the  $\text{Cr}_2\text{O}_7^{2-}$  anion as acceptor atoms, leading to a three-dimensional network structure.

## 1. Chemical context

Counter-ionic species in coordination compounds play important roles in chemistry, pharmacy, molecular assembly, biology and catalysis, as well as contributing significantly to environmental pollution; however, their binding characteristics have not received much recognition (Martínez-Mañez & Sancenón, 2003; Fabbrizzi & Poggi, 2013). The study of the anion or cation effect in octahedral metal complexes may be expected to yield a great variety of new structures and properties of both chemical and biological significance. Chromium is usually found in trivalent and hexavalent oxidation states in soil, ground water and seawater (Cespon-Romero *et al.*, 1996).  $\text{Cr}^{\text{III}}$  is an essential element in mammals for maintaining efficient glucose, lipid and protein metabolism. On the other hand,  $\text{Cr}^{\text{VI}}$  is toxic and recognized as a carcinogen to humans and wildlife. The dichromate ion is environmentally important due to its high toxicity (Yusof & Malek, 2009) and its use in many industrial processes (Goyal *et al.*, 2003). Recently, the ionic reactions between hexavalent chromium(III) and inorganic oxoanions (such as  $\text{Cr}_2\text{O}_7^{2-}$  or  $\text{CrO}_4^{2-}$ ) in aqueous solution have been investigated. It was found that  $[\text{Cr}(\text{urea})_6]^{3+}$  is suitable to target these oxoanions (Bala *et al.*, 2013). Previously, the crystal structure of  $[\text{Cr}(\text{urea})_6](\text{Cr}_2\text{O}_7)\text{Cl}\cdot\text{H}_2\text{O}$  has been reported (Bondar *et al.*, 1984). This complex crystallizes in the monoclinic space group  $P2_1/n$  with four formula units in a cell of dimensions  $a = 13.782$  (2),  $b = 10.393$  (1),  $c = 17.794$  (3) Å and  $\beta = 94.86$  (2)°. Within our broader study of  $\text{Cr}^{\text{III}}$  complexes as industrial materials (Choi & Lee, 2009; Choi & Moon, 2014; Moon & Choi, 2015), we report herein the preparation and crystal structure of  $[\text{Cr}(\text{urea})_6](\text{Cr}_2\text{O}_7)\text{Br}\cdot\text{H}_2\text{O}$ , (I).



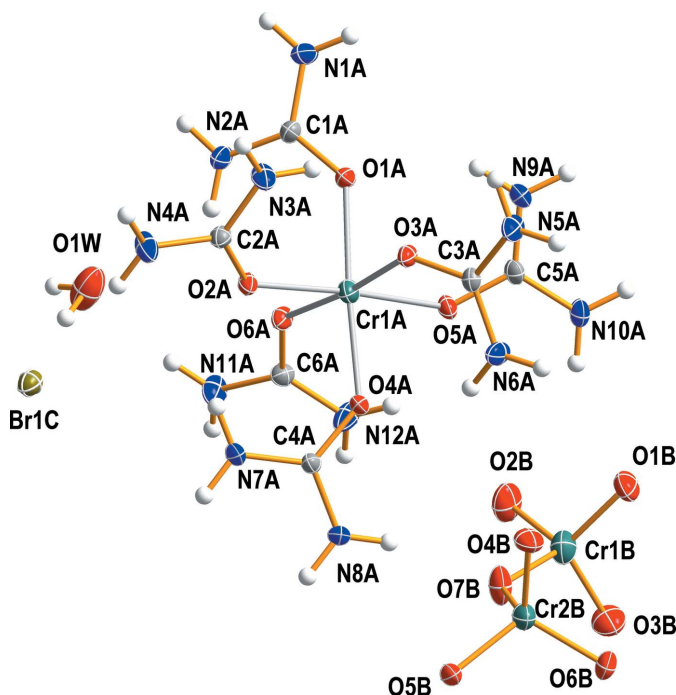


## 2. Structural commentary

In order to check if compound (I) is isotypic to  $[\text{Cr}(\text{urea})_6](\text{Cr}_2\text{O}_7)\text{Cl}\cdot\text{H}_2\text{O}$  investigated previously (Bondar *et al.*, 1984), a single-crystal X-ray structure determination was performed on the basis of synchrotron data. Compound (I) consists of the isolated complex cation  $[\text{Cr}(\text{urea})_6]^{3+}$ , together with  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{Br}^-$  counter-ions and a solvent water molecule. Comparison of the space-group type, metrics and the arrangement of the molecular components reveal (I) to be isotypic to the corresponding chloride salt. An ellipsoid plot of the molecular components of compound (I) is depicted in Fig. 1.

The  $\text{Cr}^{\text{III}}$  ion is coordinated by six urea ligands through oxygen atoms with  $\text{CrA}-\text{OA}$  bond lengths ranging from 1.9534 (13) to 1.9776 (12) Å, and with  $\text{OA}-\text{CrA}-\text{OA}$  bond angles in the range 85.10 (5)–92.95 (5)°. The  $\text{CrA}-\text{OA}$  bond lengths involving the urea ligand are in good agreement with the value of 1.9630 (17) Å for  $[\text{Cr}(\text{urea})_6](\text{BF}_4)_3$  (Górska *et al.*, 2014). They are also comparable with the corresponding lengths determined for *trans*- $[\text{Cr}(\text{nic}-O)_2(\text{cyclam})]\text{ClO}_4$  (cyclam = 1,4,8,11-tetraazacyclotetradecane; nic-*O* = *O*-coordinating nicotinate; Choi, 2009), *cis*- $[\text{Cr}(\text{ox})(\text{cyclam})]\text{ClO}_4$  (ox = oxalate; Choi *et al.*, 2004a), *cis*- $[\text{Cr}(\text{acac})(\text{cyclam})](\text{ClO}_4)_2\cdot 0.5\text{H}_2\text{O}$  (acac = acetylacetonate; Subhan *et al.*, 2011), *cis*- $[\text{Cr}(\text{ONO})_2(\text{cyclam})]\text{NO}_2$  (Choi *et al.*, 2004b) or *cis*- $[\text{Cr}(\text{edda})(\text{acac})]$  (edda = ethylenediamine-*N,N'*-diacetate; Choi *et al.*, 2012). The *trans*  $\text{O1A}-\text{Cr1A}-\text{O4A}$ ,  $\text{O3A}-\text{Cr1A}-\text{O6A}$  and  $\text{O2A}-\text{Cr1A}-\text{O5A}$  bond angles are 176.27 (5)°, 173.94 (5)°, and 175.89 (5)°, respectively. The bond lengths within the urea ligand are in the ranges of 1.263 (2)–1.276 (2) and 1.316 (2)–1.328 (2) Å for  $\text{C}=\text{O}$  and  $\text{C}-\text{N}$  bonds, respectively. The  $\text{C}=\text{O}$  bonds are slightly longer than that in free non-coordinating urea (Guth *et al.*, 1980). The isolated  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{Br}^-$  anions remain outside the coordination sphere of the cation.

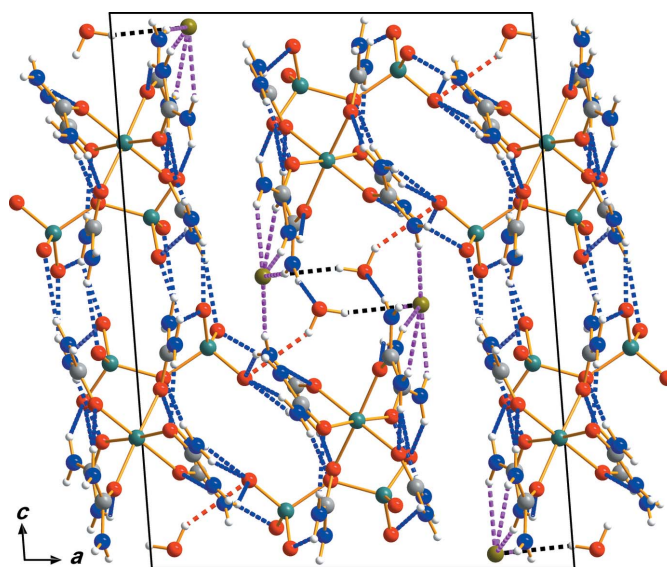
It is of interest to compare the conformation of  $\text{Cr}_2\text{O}_7^{2-}$  with that found in other ionic crystals. In the structure of compound (I) it is in a nearly staggered conformation, whereas in  $\text{K}_2\text{Cr}_2\text{O}_7$ , the tetrahedral  $\text{CrO}_4$  groups are in an almost eclipsed conformation (Brandon & Brown, 1968). As expected, the two bridging  $\text{CrB}-\text{OB}$  bonds of 1.7643 (18) and 1.8011 (17) Å are longer than the terminal  $\text{CrB}-\text{OB}$  bonds that are in the range of 1.6014 (16)–1.6299 (14) Å. The  $\text{Cr1B}-\text{O7B}-\text{Cr2B}$  bridging angle in the complex anion is 130.26 (10)°. The  $\text{OB}-\text{CrB}-\text{OB}$  bond angles in the two



**Figure 1**  
The molecular structures of the components in compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

tetrahedral  $\text{CrO}_4$  groups are between 105.21 (8) and 110.98 (10)°, indicating slight angular distortions.

It is confirmed that the  $[\text{Cr}(\text{urea})_6]^{3+}$  moiety in compound (I) may be used as a potential receptor for  $\text{Cr}_2\text{O}_7^{2-}$  anions due to its high positive charge and the large number of hydrogen-bond donor groups of its six urea ligands.



**Figure 2**  
The crystal packing of compound (I), viewed perpendicular to the *ac* plane. Dashed lines represent hydrogen-bonding interactions of the types  $\text{N}-\text{H}\cdots\text{O}$  (blue),  $\text{N}-\text{H}\cdots\text{Br}$  (pink),  $\text{O}-\text{H}\cdots\text{O}$  (red) and  $\text{O}-\text{H}\cdots\text{Br}$  (black).

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1A—H1A1···O2B <sup>i</sup>	0.87	2.42	3.051 (3)	129
N1A—H1A2···Br1C <sup>ii</sup>	0.87	2.60	3.4031 (18)	155
N2A—H2A1···O6A	0.87	2.20	2.890 (2)	136
N2A—H2A1···O1W	0.87	2.58	3.230 (3)	132
N2A—H2A2···Br1C <sup>ii</sup>	0.87	2.73	3.5121 (17)	150
N3A—H3A1···O3A	0.87	2.23	2.866 (2)	130
N3A—H3A2···O5B <sup>iii</sup>	0.87	2.21	2.972 (2)	147
N4A—H4A1···Br1C	0.87	2.55	3.4070 (18)	171
N4A—H4A2···O5B <sup>iii</sup>	0.87	2.11	2.900 (2)	151
N5A—H5A1···O6B <sup>i</sup>	0.87	2.52	3.174 (2)	133
N5A—H5A2···O3B <sup>iv</sup>	0.87	2.33	3.108 (2)	150
N6A—H6A1···O4A	0.87	2.17	2.914 (2)	143
N6A—H6A2···O1B <sup>iv</sup>	0.87	2.15	2.920 (2)	147
N7A—H7A1···O2A	0.87	2.12	2.865 (2)	143
N7A—H7A2···O4B <sup>v</sup>	0.87	2.24	3.092 (2)	168
N8A—H8A1···O7B	0.87	2.03	2.883 (2)	166
N8A—H8A2···O5B <sup>v</sup>	0.87	2.04	2.875 (2)	162
N9A—H9A1···O1A	0.87	2.22	2.954 (2)	141
N9A—H9A2···O6B <sup>iv</sup>	0.87	2.21	2.997 (2)	150
N10A—H10A···O1B	0.87	2.29	3.028 (2)	142
N10A—H10B···O4B <sup>iv</sup>	0.87	2.39	3.184 (2)	151
N11A—H11A···O1W	0.87	2.04	2.892 (3)	167
N11A—H11B···Br1C <sup>vi</sup>	0.87	2.57	3.4031 (18)	162
N12A—H12A···O5A	0.87	2.27	2.982 (2)	140
N12A—H12A···O2B	0.87	2.54	3.051 (2)	118
N12A—H12B···Br1C <sup>vi</sup>	0.87	2.85	3.6242 (18)	149
O1W—H1O1···Br1C	0.85 (1)	2.51 (1)	3.332 (2)	163 (3)
O1W—H2O1···O5B <sup>vii</sup>	0.84 (1)	2.57 (2)	3.315 (3)	149 (3)

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

### 3. Supramolecular features

The individual molecular or ionic components of (I) are arranged in rows extending parallel to [100]. The packing in the crystal structure of (I) involves not only hydrogen bonds of the type N—H···O between urea amino donor groups and the O acceptor atoms of carbonyl groups, the water molecule, or the Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> anion, but also N—H···Br hydrogen bonding between the urea amino groups and the Br<sup>-</sup> anion (Table 1). O—H···Br interactions involving the water molecule are also observed. All these interactions are responsible for the formation of an intricate three-dimensional hydrogen-bonded network in (I) (Fig. 2).

### 4. Synthesis and crystallization

All chemicals were reagent-grade materials and used without further purification. Chromium(III) tribromide hexahydrate was obtained from Aldrich Chemical Co. and used as supplied. [Cr(urea)<sub>6</sub>]Br<sub>3</sub>·3H<sub>2</sub>O was used as the starting material and was prepared according to literature procedures (Brauer, 1965), except that chromium(III) tribromide hexahydrate was used in place of chromium(III) trichloride hexahydrate (Flint & Palacio, 1979). A 0.5 g sample of [Cr(urea)<sub>6</sub>]Br<sub>3</sub>·3H<sub>2</sub>O was dissolved in 20 mL of water. Potassium dichromate (0.22 g), dissolved in 10 mL of water, was added to this solution. The mixture was refluxed at 353 K for 10 min and then cooled to room temperature. Green crystals of (I) suitable for X-ray

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	[Cr(CH <sub>4</sub> N <sub>2</sub> O) <sub>6</sub> ](Cr <sub>2</sub> O <sub>7</sub> )Br·H <sub>2</sub> O
<i>M<sub>r</sub></i>	726.30
Crystal system, space group	Monoclinic, <i>P2<sub>1</sub>/n</i>
Temperature (K)	243
<i>a, b, c</i> (Å)	13.774 (3), 10.474 (2), 18.123 (4)
$\beta$ (°)	94.37 (3)
<i>V</i> (Å <sup>3</sup> )	2607.0 (9)
<i>Z</i>	4
Radiation type	Synchrotron, $\lambda = 0.620$ Å
$\mu$ (mm <sup>-1</sup> )	1.97
Crystal size (mm)	0.17 × 0.08 × 0.04
Data collection	
Diffractionmeter	ADSC Q210 CCD area detector
Absorption correction	Empirical (using intensity measurements) ( <i>HKL3000sm SCALEPACK</i> ; Otwinowski & Minor, 1997)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.727, 0.920
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	27665, 7308, 5831
<i>R<sub>int</sub></i>	0.036
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.694
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.031, 0.091, 1.04
No. of reflections	7308
No. of parameters	331
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	1.02, -1.25

Computer programs: *PAL ADSC Quantum-210 ADX* (Arvai & Nielsen, 1983), *HKL3000sm* (Otwinowski & Minor, 1997), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *DIAMOND* (Putz & Brandenburg, 2007) and *publCIF* (Westrip, 2010).

structure analysis formed overnight. These were collected by filtration, washed with 2-propanol, and air dried. Yield: 65%. Elemental analysis calculated for [Cr{CO(NH<sub>2</sub>)<sub>2</sub>]<sub>6</sub>](Cr<sub>2</sub>O<sub>7</sub>)·Br·H<sub>2</sub>O: C, 9.92; H, 3.61; N, 23.14%; found: C, 10.32; H, 3.08; N, 23.38%.

### 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms bound to nitrogen were placed at calculated positions and treated as riding on their parent atoms, with N—H = 0.87 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(N). H atoms of the solvent water molecule were found from difference maps and refined with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(O) and restrained to O—H = 0.84 (1) and H···H = 1.36 (2) Å.

### Acknowledgements

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## References

- Arvai, A. J. & Nielsen, C. (1983). *ADSC Quantum-210 ADX*. Area Detector System Corporation, Poway, CA, USA.
- Bala, R., Kashyap, M., Kaur, A. & Golobic, A. (2013). *J. Mol. Struct.* **1031**, 246–253.
- Bondar, V. I., Rozman, S. P., Potekhin, K. A., Rau, V. G. & Struchkov, Yu. T. (1984). *Dokl. Akad. Nauk SSSR*, **279**, 373–376.
- Brandon, J. K. & Brown, I. D. (1968). *Can. J. Chem.* **46**, 933–941.
- Brauer, G. (1965). In *Handbook of Preparative Inorganic Chemistry*, Vol. 2. New York: Academic Press.
- Cespón-Romero, R. M., Yebra-Biurrun, M. C. & Bermejo-Barrera, M. P. (1996). *Anal. Chim. Acta*, **327**, 37–45.
- Choi, J.-H. (2009). *Inorg. Chim. Acta*, **362**, 4231–4236.
- Choi, J.-H. & Lee, S. H. (2009). *J. Mol. Struct.* **932**, 84–89.
- Choi, J.-H. & Moon, D. (2014). *J. Mol. Struct.* **1059**, 325–331.
- Choi, J.-H., Niketić, S. R., Djordjević, I., Clegg, W. & Harrington, R. W. (2012). *J. Mol. Model.* **18**, 2135–2146.
- Choi, J.-H., Oh, I.-G., Lim, W.-T. & Park, K.-M. (2004b). *Acta Cryst. C* **60**, m238–m240.
- Choi, J.-H., Oh, I.-G., Suzuki, T. & Kaizaki, S. (2004a). *J. Mol. Struct.* **694**, 39–44.
- Fabbrizzi, L. & Poggi, A. (2013). *Chem. Soc. Rev.* **42**, 1681–1699.
- Flint, C. D. & Palacio, D. J. D. (1979). *J. Chem. Soc. Faraday II*, **75**, 1159–1167.
- Górska, N., Mikuli, E. & Kótai, L. (2014). *Eur. Chem. Bull.* **3**, 474–481.
- Goyal, N., Jain, S. C. & Banerjee, U. C. (2003). *Adv. Environ. Res.* **7**, 311–319.
- Guth, H., Heger, G., Klein, S., Treutmann, W. & Scheringer, C. (1980). *Z. Kristallogr.* **153**, 237–254.
- Martínez-Máñez, R. & Sancenón, F. (2003). *Chem. Rev.* **103**, 4419–4476.
- Moon, D. & Choi, J.-H. (2015). *Spectrochim. Acta Part A*, **138**, 774–779.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography, Part A*, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Putz, H. & Brandenburg, K. (2007). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Subhan, M. A., Choi, J. H. & Ng, S. W. (2011). *Z. Anorg. Allg. Chem.* **637**, 2193–2197.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Yusof, A. M. & Malek, N. A. N. N. (2009). *J. Hazard. Mater.* **162**, 1019–1024.

## supporting information

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## Crystal structure of hexakis(urea- $\kappa$ O)chromium(III) dichromate bromide monohydrate from synchrotron X-ray data

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### Computing details

Data collection: *PAL ADSC Quantum-210 ADX* (Arvai & Nielsen, 1983); cell refinement: *HKL3000sm* (Otwinowski & Minor, 1997); data reduction: *HKL3000sm* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Putz & Brandenburg, 2007); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### Hexakis(urea- $\kappa$ O)chromium(III) dichromate bromide monohydrate

#### Crystal data

$[\text{Cr}(\text{CH}_4\text{N}_2\text{O})_6](\text{Cr}_2\text{O}_7)\text{Br}\cdot\text{H}_2\text{O}$

$M_r = 726.30$

Monoclinic, *P2<sub>1</sub>/n*

$a = 13.774$  (3) Å

$b = 10.474$  (2) Å

$c = 18.123$  (4) Å

$\beta = 94.37$  (3)°

$V = 2607.0$  (9) Å<sup>3</sup>

$Z = 4$

$F(000) = 1460$

$D_x = 1.850$  Mg m<sup>-3</sup>

Synchrotron radiation,  $\lambda = 0.620$  Å

Cell parameters from 102484 reflections

$\theta = 0.4\text{--}33.6^\circ$

$\mu = 1.97$  mm<sup>-1</sup>

$T = 243$  K

Block, green

$0.17 \times 0.08 \times 0.04$  mm

#### Data collection

ADSC Q210 CCD area-detector  
diffractometer

Radiation source: PLSII 2D bending magnet  
 $\omega$  scans

Absorption correction: empirical (using  
intensity measurements)

(*HKL3000sm SCALEPACK*; Otwinowski &  
Minor, 1997)

$T_{\min} = 0.727$ ,  $T_{\max} = 0.920$

27665 measured reflections

7308 independent reflections

5831 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 25.5^\circ$ ,  $\theta_{\min} = 1.6^\circ$

$h = -19 \rightarrow 19$

$k = -14 \rightarrow 14$

$l = -25 \rightarrow 25$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.091$

$S = 1.03$

7308 reflections

331 parameters

3 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0607P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.01$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -1.25$  e Å<sup>-3</sup>



*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cr1A	0.48784 (2)	0.24358 (2)	0.73428 (2)	0.01814 (7)
O1A	0.40481 (9)	0.09045 (11)	0.72718 (6)	0.0269 (3)
N1A	0.33471 (14)	-0.09246 (16)	0.69010 (10)	0.0418 (4)
H1A1	0.3286	-0.1131	0.7360	0.050*
H1A2	0.3140	-0.1441	0.6547	0.050*
N2A	0.38377 (13)	0.04656 (16)	0.60403 (9)	0.0365 (4)
H2A1	0.4103	0.1185	0.5925	0.044*
H2A2	0.3627	-0.0062	0.5694	0.044*
C1A	0.37546 (13)	0.01753 (16)	0.67403 (9)	0.0251 (3)
O2A	0.58364 (9)	0.16617 (11)	0.67175 (6)	0.0247 (2)
N3A	0.61554 (13)	-0.03008 (15)	0.72164 (9)	0.0363 (4)
H3A1	0.5774	-0.0167	0.7569	0.044*
H3A2	0.6464	-0.1023	0.7194	0.044*
N4A	0.68354 (14)	0.03653 (17)	0.61675 (10)	0.0432 (4)
H4A1	0.6904	0.0939	0.5828	0.052*
H4A2	0.7140	-0.0360	0.6151	0.052*
C2A	0.62668 (13)	0.05977 (16)	0.67111 (9)	0.0247 (3)
O3A	0.55288 (9)	0.15949 (11)	0.82167 (6)	0.0242 (2)
N5A	0.58535 (13)	0.11285 (15)	0.94126 (8)	0.0351 (4)
H5A1	0.5743	0.0326	0.9316	0.042*
H5A2	0.6018	0.1370	0.9864	0.042*
N6A	0.59470 (13)	0.31974 (15)	0.90232 (9)	0.0352 (4)
H6A1	0.5899	0.3762	0.8670	0.042*
H6A2	0.6111	0.3434	0.9476	0.042*
C3A	0.57714 (12)	0.19830 (17)	0.88725 (9)	0.0228 (3)
O4A	0.56802 (9)	0.39845 (11)	0.74788 (6)	0.0244 (2)
N7A	0.66023 (14)	0.41622 (16)	0.64918 (10)	0.0432 (5)
H7A1	0.6546	0.3351	0.6395	0.052*
H7A2	0.6937	0.4649	0.6217	0.052*
N8A	0.62761 (13)	0.58826 (15)	0.72028 (9)	0.0366 (4)
H8A1	0.6004	0.6213	0.7576	0.044*
H8A2	0.6613	0.6363	0.6925	0.044*
C4A	0.61789 (12)	0.46555 (16)	0.70582 (9)	0.0228 (3)
O5A	0.39560 (9)	0.33272 (11)	0.79418 (6)	0.0268 (3)
N9A	0.34380 (13)	0.17981 (16)	0.87118 (9)	0.0365 (4)
H9A1	0.3558	0.1195	0.8401	0.044*
H9A2	0.3203	0.1609	0.9130	0.044*
N10A	0.34220 (13)	0.39063 (16)	0.90220 (9)	0.0394 (4)
H10A	0.3531	0.4702	0.8919	0.047*

H10B	0.3187	0.3706	0.9439	0.047*
C5A	0.36129 (12)	0.30050 (18)	0.85473 (9)	0.0249 (3)
O6A	0.42481 (9)	0.31007 (11)	0.64197 (6)	0.0267 (3)
N11A	0.38747 (13)	0.44107 (17)	0.54758 (9)	0.0410 (4)
H11A	0.4000	0.3802	0.5171	0.049*
H11B	0.3686	0.5155	0.5306	0.049*
N12A	0.37717 (14)	0.51221 (16)	0.66616 (9)	0.0407 (4)
H12A	0.3828	0.4985	0.7136	0.049*
H12B	0.3584	0.5866	0.6491	0.049*
C6A	0.39707 (13)	0.42046 (16)	0.62008 (9)	0.0263 (3)
Cr1B	0.43809 (2)	0.74013 (3)	0.86870 (2)	0.02751 (8)
Cr2B	0.67274 (2)	0.73371 (2)	0.89720 (2)	0.02405 (7)
O1B	0.42792 (12)	0.65095 (15)	0.93969 (8)	0.0452 (4)
O2B	0.36945 (13)	0.6882 (2)	0.79973 (9)	0.0586 (5)
O3B	0.41248 (13)	0.88526 (15)	0.88712 (10)	0.0553 (4)
O4B	0.69792 (12)	0.59234 (12)	0.92738 (9)	0.0425 (3)
O5B	0.75382 (11)	0.78025 (13)	0.84199 (8)	0.0350 (3)
O6B	0.66869 (12)	0.83207 (14)	0.96458 (8)	0.0446 (4)
O7B	0.56137 (12)	0.73256 (16)	0.84224 (9)	0.0475 (4)
Br1C	0.68438 (2)	0.24957 (2)	0.47474 (2)	0.03324 (7)
O1W	0.44307 (16)	0.2183 (3)	0.46645 (14)	0.0752 (7)
H1O1	0.5018 (9)	0.236 (3)	0.460 (2)	0.090*
H2O1	0.414 (2)	0.224 (3)	0.4242 (10)	0.090*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cr1A	0.02397 (14)	0.01721 (12)	0.01352 (12)	-0.00045 (9)	0.00324 (9)	0.00064 (8)
O1A	0.0347 (7)	0.0256 (6)	0.0205 (6)	-0.0087 (5)	0.0029 (5)	-0.0020 (4)
N1A	0.0600 (12)	0.0324 (9)	0.0328 (9)	-0.0201 (8)	0.0028 (8)	-0.0024 (7)
N2A	0.0584 (11)	0.0293 (8)	0.0217 (7)	-0.0092 (7)	0.0016 (7)	-0.0050 (6)
C1A	0.0267 (8)	0.0252 (8)	0.0233 (8)	-0.0013 (6)	0.0011 (6)	-0.0021 (6)
O2A	0.0324 (6)	0.0207 (5)	0.0219 (5)	0.0047 (5)	0.0082 (5)	0.0012 (4)
N3A	0.0517 (10)	0.0254 (7)	0.0334 (8)	0.0121 (7)	0.0141 (7)	0.0084 (6)
N4A	0.0590 (11)	0.0328 (8)	0.0412 (10)	0.0212 (8)	0.0266 (8)	0.0096 (7)
C2A	0.0294 (9)	0.0221 (7)	0.0225 (8)	0.0029 (6)	0.0015 (6)	-0.0001 (6)
O3A	0.0340 (7)	0.0222 (5)	0.0160 (5)	0.0008 (5)	-0.0004 (4)	0.0003 (4)
N5A	0.0553 (11)	0.0303 (8)	0.0189 (7)	0.0038 (7)	-0.0019 (7)	0.0039 (6)
N6A	0.0535 (10)	0.0297 (8)	0.0211 (7)	-0.0090 (7)	-0.0058 (7)	-0.0008 (6)
C3A	0.0228 (8)	0.0271 (8)	0.0185 (7)	0.0025 (6)	0.0020 (6)	0.0002 (6)
O4A	0.0318 (6)	0.0227 (6)	0.0195 (5)	-0.0069 (5)	0.0071 (5)	-0.0003 (4)
N7A	0.0638 (12)	0.0300 (8)	0.0403 (10)	-0.0118 (8)	0.0336 (9)	-0.0061 (7)
N8A	0.0521 (10)	0.0250 (7)	0.0352 (8)	-0.0146 (7)	0.0194 (8)	-0.0063 (6)
C4A	0.0260 (8)	0.0240 (7)	0.0186 (7)	-0.0051 (6)	0.0024 (6)	0.0000 (6)
O5A	0.0320 (7)	0.0264 (6)	0.0234 (6)	0.0031 (5)	0.0108 (5)	0.0025 (5)
N9A	0.0468 (10)	0.0337 (8)	0.0312 (8)	-0.0092 (7)	0.0179 (7)	0.0007 (7)
N10A	0.0522 (11)	0.0358 (9)	0.0330 (9)	0.0025 (8)	0.0224 (8)	-0.0046 (7)
C5A	0.0200 (8)	0.0314 (9)	0.0239 (8)	-0.0003 (6)	0.0060 (6)	-0.0002 (6)

O6A	0.0372 (7)	0.0231 (6)	0.0192 (5)	0.0041 (5)	-0.0018 (5)	0.0018 (4)
N11A	0.0637 (12)	0.0345 (9)	0.0242 (8)	0.0140 (8)	0.0005 (8)	0.0082 (7)
N12A	0.0614 (12)	0.0286 (8)	0.0307 (9)	0.0152 (8)	-0.0061 (8)	-0.0029 (6)
C6A	0.0281 (9)	0.0253 (8)	0.0248 (8)	0.0009 (7)	-0.0026 (7)	0.0024 (6)
Cr1B	0.03041 (16)	0.03174 (16)	0.02060 (14)	0.00408 (11)	0.00341 (11)	-0.00030 (10)
Cr2B	0.03046 (15)	0.02096 (13)	0.02202 (14)	0.00009 (10)	0.01038 (11)	-0.00170 (10)
O1B	0.0603 (10)	0.0450 (9)	0.0315 (7)	0.0022 (7)	0.0112 (7)	0.0076 (6)
O2B	0.0538 (11)	0.0844 (13)	0.0358 (9)	-0.0078 (10)	-0.0086 (7)	-0.0112 (9)
O3B	0.0664 (12)	0.0354 (8)	0.0655 (11)	0.0140 (8)	0.0136 (9)	0.0039 (8)
O4B	0.0544 (9)	0.0253 (7)	0.0493 (9)	0.0019 (6)	0.0139 (7)	0.0074 (6)
O5B	0.0439 (8)	0.0273 (6)	0.0364 (7)	-0.0072 (6)	0.0200 (6)	-0.0046 (5)
O6B	0.0658 (10)	0.0378 (8)	0.0321 (7)	-0.0006 (7)	0.0166 (7)	-0.0119 (6)
O7B	0.0365 (9)	0.0763 (12)	0.0306 (8)	0.0079 (7)	0.0076 (6)	-0.0056 (7)
Br1C	0.04246 (12)	0.02884 (10)	0.02779 (11)	0.00280 (7)	-0.00149 (8)	-0.00060 (6)
O1W	0.0493 (12)	0.0971 (16)	0.0789 (16)	-0.0032 (12)	0.0040 (11)	-0.0419 (14)

*Geometric parameters (Å, °)*

Cr1A—O6A	1.9534 (13)	N7A—H7A1	0.8700
Cr1A—O4A	1.9672 (12)	N7A—H7A2	0.8700
Cr1A—O3A	1.9674 (12)	N8A—C4A	1.316 (2)
Cr1A—O5A	1.9683 (12)	N8A—H8A1	0.8700
Cr1A—O1A	1.9685 (12)	N8A—H8A2	0.8700
Cr1A—O2A	1.9776 (12)	O5A—C5A	1.273 (2)
O1A—C1A	1.271 (2)	N9A—C5A	1.325 (3)
N1A—C1A	1.324 (2)	N9A—H9A1	0.8700
N1A—H1A1	0.8700	N9A—H9A2	0.8700
N1A—H1A2	0.8700	N10A—C5A	1.317 (2)
N2A—C1A	1.318 (2)	N10A—H10A	0.8700
N2A—H2A1	0.8700	N10A—H10B	0.8700
N2A—H2A2	0.8700	O6A—C6A	1.272 (2)
O2A—C2A	1.263 (2)	N11A—C6A	1.328 (2)
N3A—C2A	1.330 (2)	N11A—H11A	0.8700
N3A—H3A1	0.8700	N11A—H11B	0.8700
N3A—H3A2	0.8700	N12A—C6A	1.316 (2)
N4A—C2A	1.327 (2)	N12A—H12A	0.8700
N4A—H4A1	0.8700	N12A—H12B	0.8700
N4A—H4A2	0.8700	Cr1B—O3B	1.6014 (16)
O3A—C3A	1.2763 (19)	Cr1B—O2B	1.6036 (17)
N5A—C3A	1.325 (2)	Cr1B—O1B	1.6045 (15)
N5A—H5A1	0.8700	Cr1B—O7B	1.8011 (17)
N5A—H5A2	0.8700	Cr2B—O6B	1.6018 (14)
N6A—C3A	1.319 (2)	Cr2B—O4B	1.6071 (14)
N6A—H6A1	0.8700	Cr2B—O5B	1.6299 (14)
N6A—H6A2	0.8700	Cr2B—O7B	1.7643 (18)
O4A—C4A	1.2753 (19)	O1W—H1O1	0.847 (10)
N7A—C4A	1.324 (2)	O1W—H2O1	0.840 (10)



O6A—Cr1A—O4A	91.26 (5)	C4A—O4A—Cr1A	134.62 (11)
O6A—Cr1A—O3A	173.94 (5)	C4A—N7A—H7A1	120.0
O4A—Cr1A—O3A	92.95 (5)	C4A—N7A—H7A2	120.0
O6A—Cr1A—O5A	92.28 (5)	H7A1—N7A—H7A2	120.0
O4A—Cr1A—O5A	85.39 (5)	C4A—N8A—H8A1	120.0
O3A—Cr1A—O5A	92.40 (5)	C4A—N8A—H8A2	120.0
O6A—Cr1A—O1A	90.94 (5)	H8A1—N8A—H8A2	120.0
O4A—Cr1A—O1A	176.27 (5)	O4A—C4A—N8A	118.05 (15)
O3A—Cr1A—O1A	85.10 (5)	O4A—C4A—N7A	122.52 (15)
O5A—Cr1A—O1A	91.51 (5)	N8A—C4A—N7A	119.42 (16)
O6A—Cr1A—O2A	85.86 (5)	C5A—O5A—Cr1A	130.34 (11)
O4A—Cr1A—O2A	90.98 (5)	C5A—N9A—H9A1	120.0
O3A—Cr1A—O2A	89.71 (5)	C5A—N9A—H9A2	120.0
O5A—Cr1A—O2A	175.89 (5)	H9A1—N9A—H9A2	120.0
O1A—Cr1A—O2A	92.18 (5)	C5A—N10A—H10A	120.0
C1A—O1A—Cr1A	133.54 (11)	C5A—N10A—H10B	120.0
C1A—N1A—H1A1	120.0	H10A—N10A—H10B	120.0
C1A—N1A—H1A2	120.0	O5A—C5A—N10A	118.60 (17)
H1A1—N1A—H1A2	120.0	O5A—C5A—N9A	122.19 (16)
C1A—N2A—H2A1	120.0	N10A—C5A—N9A	119.21 (16)
C1A—N2A—H2A2	120.0	C6A—O6A—Cr1A	134.00 (11)
H2A1—N2A—H2A2	120.0	C6A—N11A—H11A	120.0
O1A—C1A—N2A	123.02 (16)	C6A—N11A—H11B	120.0
O1A—C1A—N1A	118.16 (16)	H11A—N11A—H11B	120.0
N2A—C1A—N1A	118.82 (16)	C6A—N12A—H12A	120.0
C2A—O2A—Cr1A	134.53 (11)	C6A—N12A—H12B	120.0
C2A—N3A—H3A1	120.0	H12A—N12A—H12B	120.0
C2A—N3A—H3A2	120.0	O6A—C6A—N12A	122.57 (16)
H3A1—N3A—H3A2	120.0	O6A—C6A—N11A	117.47 (16)
C2A—N4A—H4A1	120.0	N12A—C6A—N11A	119.95 (17)
C2A—N4A—H4A2	120.0	O3B—Cr1B—O2B	110.98 (10)
H4A1—N4A—H4A2	120.0	O3B—Cr1B—O1B	110.57 (9)
O2A—C2A—N4A	118.21 (16)	O2B—Cr1B—O1B	110.20 (10)
O2A—C2A—N3A	122.64 (16)	O3B—Cr1B—O7B	108.93 (8)
N4A—C2A—N3A	119.13 (16)	O2B—Cr1B—O7B	106.82 (9)
C3A—O3A—Cr1A	132.68 (11)	O1B—Cr1B—O7B	109.24 (9)
C3A—N5A—H5A1	120.0	O6B—Cr2B—O4B	110.63 (8)
C3A—N5A—H5A2	120.0	O6B—Cr2B—O5B	109.93 (8)
H5A1—N5A—H5A2	120.0	O4B—Cr2B—O5B	110.14 (8)
C3A—N6A—H6A1	120.0	O6B—Cr2B—O7B	110.82 (8)
C3A—N6A—H6A2	120.0	O4B—Cr2B—O7B	109.98 (8)
H6A1—N6A—H6A2	120.0	O5B—Cr2B—O7B	105.21 (8)
O3A—C3A—N6A	122.05 (15)	Cr2B—O7B—Cr1B	130.26 (10)
O3A—C3A—N5A	118.32 (16)	H1O1—O1W—H2O1	104 (2)
N6A—C3A—N5A	119.63 (15)		
Cr1A—O1A—C1A—N2A	-12.6 (3)	Cr1A—O5A—C5A—N9A	-33.6 (2)
Cr1A—O1A—C1A—N1A	167.40 (14)	Cr1A—O6A—C6A—N12A	-23.3 (3)

Cr1A—O2A—C2A—N4A	175.80 (14)	Cr1A—O6A—C6A—N11A	157.35 (14)
Cr1A—O2A—C2A—N3A	-2.8 (3)	O6B—Cr2B—O7B—Cr1B	-39.64 (15)
Cr1A—O3A—C3A—N6A	-26.1 (2)	O4B—Cr2B—O7B—Cr1B	83.00 (13)
Cr1A—O3A—C3A—N5A	154.40 (13)	O5B—Cr2B—O7B—Cr1B	-158.42 (12)
Cr1A—O4A—C4A—N8A	150.59 (14)	O3B—Cr1B—O7B—Cr2B	78.99 (14)
Cr1A—O4A—C4A—N7A	-29.9 (3)	O2B—Cr1B—O7B—Cr2B	-161.07 (13)
Cr1A—O5A—C5A—N10A	146.75 (14)	O1B—Cr1B—O7B—Cr2B	-41.89 (15)

## Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1A—H1A1...O2B <sup>i</sup>	0.87	2.42	3.051 (3)	129
N1A—H1A2...Br1C <sup>ii</sup>	0.87	2.60	3.4031 (18)	155
N2A—H2A1...O6A	0.87	2.20	2.890 (2)	136
N2A—H2A1...O1W	0.87	2.58	3.230 (3)	132
N2A—H2A2...Br1C <sup>ii</sup>	0.87	2.73	3.5121 (17)	150
N3A—H3A1...O3A	0.87	2.23	2.866 (2)	130
N3A—H3A2...O5B <sup>iii</sup>	0.87	2.21	2.972 (2)	147
N4A—H4A1...Br1C	0.87	2.55	3.4070 (18)	171
N4A—H4A2...O5B <sup>iii</sup>	0.87	2.11	2.900 (2)	151
N5A—H5A1...O6B <sup>i</sup>	0.87	2.52	3.174 (2)	133
N5A—H5A2...O3B <sup>iv</sup>	0.87	2.33	3.108 (2)	150
N6A—H6A1...O4A	0.87	2.17	2.914 (2)	143
N6A—H6A2...O1B <sup>iv</sup>	0.87	2.15	2.920 (2)	147
N7A—H7A1...O2A	0.87	2.12	2.865 (2)	143
N7A—H7A2...O4B <sup>v</sup>	0.87	2.24	3.092 (2)	168
N8A—H8A1...O7B	0.87	2.03	2.883 (2)	166
N8A—H8A2...O5B <sup>v</sup>	0.87	2.04	2.875 (2)	162
N9A—H9A1...O1A	0.87	2.22	2.954 (2)	141
N9A—H9A2...O6B <sup>iv</sup>	0.87	2.21	2.997 (2)	150
N10A—H10A...O1B	0.87	2.29	3.028 (2)	142
N10A—H10B...O4B <sup>iv</sup>	0.87	2.39	3.184 (2)	151
N11A—H11A...O1W	0.87	2.04	2.892 (3)	167
N11A—H11B...Br1C <sup>vi</sup>	0.87	2.57	3.4031 (18)	162
N12A—H12A...O5A	0.87	2.27	2.982 (2)	140
N12A—H12A...O2B	0.87	2.54	3.051 (2)	118
N12A—H12B...Br1C <sup>vi</sup>	0.87	2.85	3.6242 (18)	149
O1W—H1O1...Br1C	0.85 (1)	2.51 (1)	3.332 (2)	163 (3)
O1W—H2O1...O5B <sup>vii</sup>	0.84 (1)	2.57 (2)	3.315 (3)	149 (3)

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