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ISSN 2414-3146

cis-Bromidobis(1,2-diaminoethane-κ^2N,N')(ethylamine-κN)cobalt(III) dibromide

S. Manimaran,[a]* M. Manjunathan,[b] E. Govindan,[c] K. Sambathkumar[d] and K. Anbalagan[e]

[a]Department of Physics, Thanthai Hans Rover College, Perambalur 621 220, India, [b]Department of Chemistry, BWDA Arts and Science College, Tindivanam 604 304, India, [c]Department of Physics, Thiruvalluvar University College of Arts and Science, Thiruvennainallur 607 203, India, [d]P.G. Research Department of Physics, A.A. Govt. Arts College, Villupuram, India, and [e]Department of Chemistry, Pondicherry University, Pondicherry 605 014, India. *Correspondence e-mail: drmanirec@gmail.com

Received 5 March 2018
Accepted 10 June 2018

Edited by S. Bernès, Benemérita Universidad Autónoma de Puebla, México

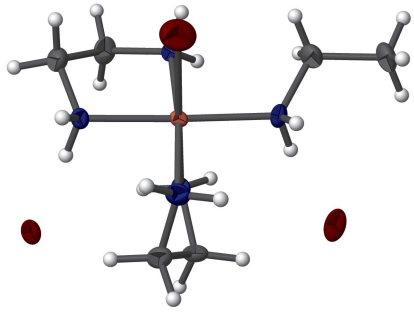
Keywords: crystal structure; cobalt(III); diaminoethane; hydrogen bonding.

CCDC reference: 785726

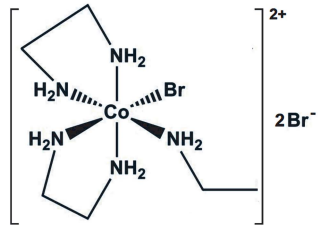
Structural data: full structural data are available from iucrdata.iucr.org

In the title complex, $[CoBr(C_2H_7N)(C_2H_8N_2)_2]Br_2$, the Co^{III} centre has a distorted octahedral coordination environment, and is surrounded by four N atoms in the equatorial plane, with an additional N atom and the Br atom occupying the axial positions. The complex is isostructural with the Cl compound for which the X-ray structure has also been reported [Anbalagan, Mahalakshmi & Ganeshraja (2011). *J. Mol. Struct.* **1005**, 45–52]. In the crystal, the complex cation and the two counter-anions are linked *via* N—H···Br hydrogen bonds, forming a three-dimensional network.

3D view



Chemical scheme



Structure description

Mixed-ligand cobalt(III) complexes have potential applications in the fields of antitumor, antibacterial, antimicrobial, radiosensitization and cytotoxicity activities (Sayed *et al.*, 1992; Teicher *et al.*, 1990; Delehanty *et al.*, 2008). Cobalt is an essential and integral component of vitamin B_{12} and is therefore found physiologically in most tissues. Complexes of cobalt are useful for nutritional supplementation to provide cobalt in a form which effectively increases the bioavailability, for instance, through the production of vitamin B_{12} by microorganisms present in the gut. In addition, cobalt(III) complexes are known for electron-transfer and ligand-substitution reactions, which are of interest in some chemical and biological systems.

Our current research deals with the design and synthesis of cobalt(III) complexes with the aim of understanding the correlation between their structure and reactivity. Substituting an amino ligand such as $MeNH_2$ by a different amine can afford structurally

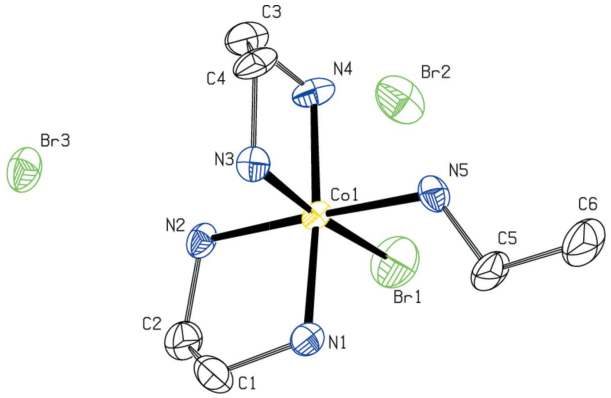


Figure 1
Molecular structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level. All H atoms omitted

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1C···Br3^{i}	0.89	2.77	3.574 (5)	151
N1—H1D···Br3^{ii}	0.89	2.48	3.310 (5)	155
N2—H2C···Br3	0.89	2.59	3.451 (5)	162
N2—H2D···Br2^{iii}	0.89	3.07	3.838 (5)	145
N3—H3C···Br3	0.89	2.60	3.427 (5)	155
N3—H3D···Br2	0.89	2.93	3.617 (5)	135
N4—H4C···Br2^{iv}	0.89	2.52	3.395 (6)	168
N4—H4D···Br2^{iii}	0.89	2.58	3.418 (5)	156
N5—H5C···Br2^{iv}	0.89	2.89	3.631 (5)	142
N5—H5D···Br2	0.89	2.78	3.651 (5)	166
C4—H4A···Br1^{v}	0.97	2.95	3.897 (7)	166
C4—H4B···Br2	0.97	2.91	3.566 (7)	126
C5—H5A···Br1	0.97	3.04	3.582 (8)	117

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

related complexes with different electron-transfer rates (Anbalagan, 2011; Anbalagan *et al.*, 2009). Against this background and to ascertain the molecular conformation, the structure determination of the title compound has been carried out.

The X-ray analysis confirms the molecular structure and atom connectivity as illustrated in Fig. 1. The Co—N coordination bond lengths are in agreement with those reported in the literature for Co^{III} complexes (*e.g.* Kannan *et al.*, 2013; Lee *et al.*, 2007; Ramesh *et al.*, 2008; Anbalagan *et al.*, 2009, 2011; Ravichandran *et al.*, 2009). Both ethylenediamine (en) units behave as chelating ligands, forming five-membered matallacycles with a half-chair conformation. The packing features N—H···Br interactions, forming a three-dimensional network in the crystal (Table 1 and Fig. 2). Additionally, weak C—H···Br contacts are observed (Fig. 3).

Synthesis and crystallization

A suspension of *trans*-[Co(en)$_2$Br$_2$]Br was prepared by adding drops of water to the solid (2 g). To the solid mass, about 2 ml of ethylamine was dropped for 20 min and mixed well. The grinding was continued until the colour turned from dull green to red. The reaction mixture was set aside until no further change was observed and the product was allowed to stand overnight. Finally, the solid was washed with ethanol. The resulting solid was dissolved in 5–10 ml of water pre-heated at 343 K and allowed to crystallize using hot acidified water, yielding 0.85 g of the complex. The pink crystals were filtered, washed with ethanol and dried under vacuum. X-ray quality crystals were obtained by repeated recrystallizations from hot acidified distilled water.

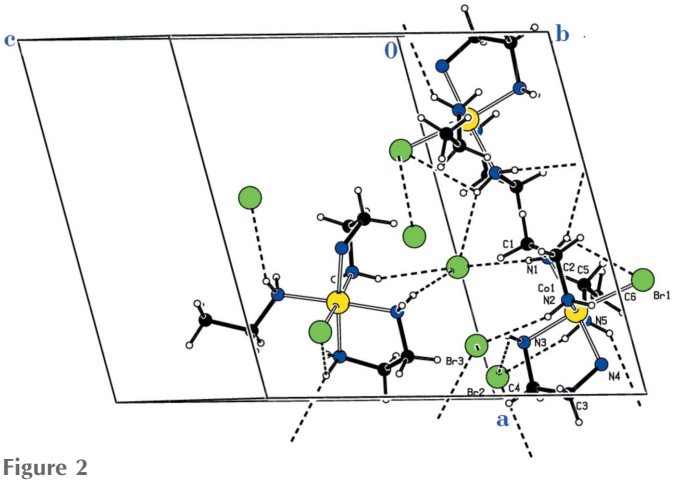


Figure 2
A packing view of the title compound approximately down the *b* axis. Intermolecular N—H···Br contacts are depicted with dashed bonds.

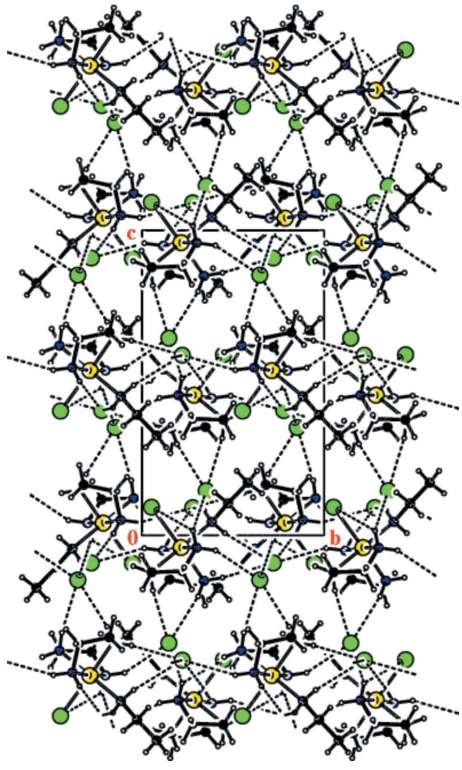


Figure 3
A packing view of the title compound down the *a* axis. Intermolecular contacts involving the Br ions are represented with dashed bonds.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

The authors thank the Department of Chemistry, Pondicherry University, for the data collection.

Funding information

S. Manimaran gratefully acknowledges the DST–SERB for young scientist start-up research grant (YSS/2014/000561) and DST–FIST for providing NMR facilities to the department.

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Table 2
Experimental details.

Crystal data	
Chemical formula	$[CoBr(C_2H_7N)(C_2H_8N_2)_2]Br_2$
M_r	463.95
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	300
a, b, c (Å)	12.2323 (4), 8.4841 (2), 14.8964 (4)
β (°)	107.266 (3)
V (Å^3)	1476.28 (8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	9.26
Crystal size (mm)	0.23 × 0.17 × 0.11
Data collection	
Diffractometer	Bruker SMART APEXII
Absorption correction	Multi-scan (*SADABS*; Bruker, 2008)
T_{min}, T_{max}	0.165, 0.361
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6551, 3425, 2273
R_{int}	0.027
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.689
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.047, 0.148, 1.07
No. of reflections	3425
No. of parameters	137
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.20, −2.10

Computer programs: *APEX2* and *SAINT* (Bruker, 2008), *SHELXS97* and *SHELXTL* (Sheldrick, 2008) and *SHELXL2018* (Sheldrick, 2015).

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full crystallographic data

IUCrData (2018). **3**, x180855 [https://doi.org/10.1107/S2414314618008556]

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Crystal data

$[CoBr(C_2H_7N)(C_2H_8N_2)_2]Br_2$
M_r = 463.95
Monoclinic, $P2_1/n$
a = 12.2323 (4) Å
b = 8.4841 (2) Å
c = 14.8964 (4) Å
β = 107.266 (3)°
V = 1476.28 (8) Å^3
Z = 4
$F(000)$ = 904
D_x = 2.087 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1908 reflections
θ = 25.0–2.9°
μ = 9.26 mm^{-1}
T = 300 K
Block, pink
0.23 × 0.17 × 0.11 mm

Data collection

Bruker SMART APEXII diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.165, T_{max} = 0.361
6551 measured reflections
3425 independent reflections
2273 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 29.3°, θ_{min} = 2.8°
h = −16→12
k = −10→11
l = −18→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.148
S = 1.07
3425 reflections
137 parameters
0 restraints
0 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0841P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.20 e Å^{-3}
$\Delta\rho_{min}$ = −2.10 e Å^{-3}

Special details

Refinement. All H atoms were placed in calculated positions, and refined as riding to their carrier C/N atom, with isotropic displacement parameters.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.76749 (7)	0.78619 (9)	0.04025 (6)	0.0137 (2)
Br1	0.68504 (7)	0.94805 (10)	−0.09241 (6)	0.0444 (3)
Br2	0.94231 (7)	0.27863 (8)	0.09070 (7)	0.0378 (2)
Br3	0.86031 (6)	0.85295 (8)	0.35349 (5)	0.0289 (2)
C1	0.5816 (6)	0.7765 (8)	0.1167 (6)	0.0302 (17)
H1A	0.618177	0.726722	0.176719	0.036*
H1B	0.499275	0.767240	0.103596	0.036*
C2	0.6156 (6)	0.9471 (8)	0.1194 (6)	0.0323 (18)
H2A	0.567841	1.001747	0.064538	0.039*
H2B	0.606217	0.997424	0.175153	0.039*
C3	0.9958 (6)	0.8476 (8)	0.1437 (5)	0.0278 (16)
H3A	0.981692	0.916951	0.190802	0.033*
H3B	1.074018	0.862937	0.142641	0.033*
C4	0.9771 (6)	0.6795 (8)	0.1657 (5)	0.0278 (17)
H4A	1.018388	0.655680	0.230595	0.033*
H4B	1.003559	0.609172	0.125234	0.033*
C5	0.6932 (6)	0.5267 (10)	−0.1040 (6)	0.039 (2)
H5A	0.635993	0.601290	−0.138414	0.047*
H5B	0.659449	0.464764	−0.064303	0.047*
C6	0.7241 (7)	0.4183 (10)	−0.1731 (6)	0.046 (2)
H6A	0.755801	0.479010	−0.213785	0.069*
H6B	0.656666	0.364526	−0.210005	0.069*
H6C	0.779496	0.342498	−0.139563	0.069*
N1	0.6189 (5)	0.6999 (6)	0.0412 (4)	0.0203 (12)
H1C	0.567171	0.716897	−0.014243	0.024*
H1D	0.624865	0.596314	0.050886	0.024*
N2	0.7377 (4)	0.9537 (6)	0.1208 (4)	0.0179 (11)
H2C	0.782957	0.941210	0.179387	0.021*
H2D	0.752782	1.047235	0.100142	0.021*
N3	0.8510 (4)	0.6605 (6)	0.1491 (4)	0.0186 (12)
H3C	0.832419	0.691869	0.199691	0.022*
H3D	0.831895	0.559464	0.138880	0.022*
N4	0.9159 (4)	0.8816 (6)	0.0516 (4)	0.0218 (12)
H4C	0.943442	0.843791	0.006895	0.026*
H4D	0.907846	0.985398	0.043793	0.026*
N5	0.7925 (4)	0.6151 (6)	−0.0435 (4)	0.0205 (12)
H5C	0.829306	0.657399	−0.080921	0.025*
H5D	0.839717	0.545146	−0.007231	0.025*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0142 (4)	0.0110 (4)	0.0138 (4)	−0.0004 (3)	0.0007 (3)	0.0001 (4)
Br1	0.0470 (5)	0.0451 (5)	0.0356 (5)	0.0050 (4)	0.0039 (4)	0.0083 (4)
Br2	0.0446 (5)	0.0205 (4)	0.0558 (6)	0.0005 (3)	0.0264 (4)	−0.0051 (4)

Br3	0.0349 (4)	0.0243 (4)	0.0244 (4)	0.0043 (3)	0.0040 (3)	−0.0060 (3)
C1	0.029 (4)	0.033 (4)	0.036 (4)	−0.004 (3)	0.021 (3)	−0.006 (4)
C2	0.027 (4)	0.031 (4)	0.036 (4)	0.006 (3)	0.005 (3)	−0.012 (4)
C3	0.018 (3)	0.024 (3)	0.038 (4)	−0.001 (3)	0.003 (3)	−0.006 (4)
C4	0.017 (3)	0.028 (4)	0.031 (4)	0.003 (3)	−0.004 (3)	−0.003 (3)
C5	0.025 (4)	0.040 (4)	0.046 (5)	−0.002 (3)	0.002 (4)	−0.024 (4)
C6	0.041 (5)	0.044 (5)	0.047 (5)	0.000 (4)	0.004 (4)	−0.031 (4)
N1	0.020 (3)	0.017 (3)	0.022 (3)	0.004 (2)	0.003 (2)	−0.002 (2)
N2	0.022 (3)	0.014 (2)	0.016 (3)	0.003 (2)	0.003 (2)	−0.001 (2)
N3	0.023 (3)	0.012 (2)	0.019 (3)	0.000 (2)	0.004 (2)	0.000 (2)
N4	0.018 (3)	0.019 (3)	0.027 (3)	−0.004 (2)	0.004 (2)	−0.001 (3)
N5	0.023 (3)	0.018 (3)	0.022 (3)	0.004 (2)	0.009 (2)	−0.004 (2)

Geometric parameters (Å, º)

Co1—N4	1.949 (5)	C4—H4B	0.9700
Co1—N3	1.956 (5)	C5—N5	1.483 (8)
Co1—N2	1.963 (5)	C5—C6	1.510 (11)
Co1—N1	1.963 (5)	C5—H5A	0.9700
Co1—N5	1.996 (5)	C5—H5B	0.9700
Co1—Br1	2.3717 (11)	C6—H6A	0.9600
C1—N1	1.484 (9)	C6—H6B	0.9600
C1—C2	1.503 (10)	C6—H6C	0.9600
C1—H1A	0.9700	N1—H1C	0.8900
C1—H1B	0.9700	N1—H1D	0.8900
C2—N2	1.489 (8)	N2—H2C	0.8900
C2—H2A	0.9700	N2—H2D	0.8900
C2—H2B	0.9700	N3—H3C	0.8900
C3—N4	1.458 (9)	N3—H3D	0.8900
C3—C4	1.496 (10)	N4—H4C	0.8900
C3—H3A	0.9700	N4—H4D	0.8900
C3—H3B	0.9700	N5—H5C	0.8900
C4—N3	1.496 (8)	N5—H5D	0.8900
C4—H4A	0.9700		

N4—Co1—N3	84.9 (2)	C6—C5—H5A	108.9
N4—Co1—N2	89.1 (2)	N5—C5—H5B	108.9
N3—Co1—N2	91.9 (2)	C6—C5—H5B	108.9
N4—Co1—N1	174.2 (2)	H5A—C5—H5B	107.7
N3—Co1—N1	92.7 (2)	C5—C6—H6A	109.5
N2—Co1—N1	85.7 (2)	C5—C6—H6B	109.5
N4—Co1—N5	92.5 (2)	H6A—C6—H6B	109.5
N3—Co1—N5	89.0 (2)	C5—C6—H6C	109.5
N2—Co1—N5	178.2 (2)	H6A—C6—H6C	109.5
N1—Co1—N5	92.7 (2)	H6B—C6—H6C	109.5
N4—Co1—Br1	89.22 (16)	C1—N1—Co1	109.6 (4)
N3—Co1—Br1	174.03 (16)	C1—N1—H1C	109.8
N2—Co1—Br1	88.86 (15)	Co1—N1—H1C	109.8

N1—Co1—Br1	93.21 (17)	C1—N1—H1D	109.8
N5—Co1—Br1	90.38 (17)	Co1—N1—H1D	109.8
N1—C1—C2	107.3 (6)	H1C—N1—H1D	108.2
N1—C1—H1A	110.3	C2—N2—Co1	109.4 (4)
C2—C1—H1A	110.3	C2—N2—H2C	109.8
N1—C1—H1B	110.3	Co1—N2—H2C	109.8
C2—C1—H1B	110.3	C2—N2—H2D	109.8
H1A—C1—H1B	108.5	Co1—N2—H2D	109.8
N2—C2—C1	107.8 (6)	H2C—N2—H2D	108.2
N2—C2—H2A	110.2	C4—N3—Co1	109.7 (4)
C1—C2—H2A	110.2	C4—N3—H3C	109.7
N2—C2—H2B	110.2	Co1—N3—H3C	109.7
C1—C2—H2B	110.2	C4—N3—H3D	109.7
H2A—C2—H2B	108.5	Co1—N3—H3D	109.7
N4—C3—C4	106.9 (5)	H3C—N3—H3D	108.2
N4—C3—H3A	110.3	C3—N4—Co1	110.3 (4)
C4—C3—H3A	110.3	C3—N4—H4C	109.6
N4—C3—H3B	110.3	Co1—N4—H4C	109.6
C4—C3—H3B	110.3	C3—N4—H4D	109.6
H3A—C3—H3B	108.6	Co1—N4—H4D	109.6
C3—C4—N3	106.5 (5)	H4C—N4—H4D	108.1
C3—C4—H4A	110.4	C5—N5—Co1	119.9 (4)
N3—C4—H4A	110.4	C5—N5—H5C	107.4
C3—C4—H4B	110.4	Co1—N5—H5C	107.4
N3—C4—H4B	110.4	C5—N5—H5D	107.4
H4A—C4—H4B	108.6	Co1—N5—H5D	107.4
N5—C5—C6	113.4 (6)	H5C—N5—H5D	106.9
N5—C5—H5A	108.9		
N1—C1—C2—N2	−49.0 (8)	C3—C4—N3—Co1	37.0 (6)
N4—C3—C4—N3	−50.2 (7)	C4—C3—N4—Co1	41.0 (6)
C2—C1—N1—Co1	38.1 (7)	C6—C5—N5—Co1	171.6 (6)
C1—C2—N2—Co1	37.3 (7)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*C*···Br3^{i}	0.89	2.77	3.574 (5)	151
N1—H1*D*···Br3^{ii}	0.89	2.48	3.310 (5)	155
N2—H2*C*···Br3	0.89	2.59	3.451 (5)	162
N2—H2*D*···Br2^{iii}	0.89	3.07	3.838 (5)	145
N2—H2*D*···Br3^{iv}	0.89	3.11	3.651 (5)	121
N3—H3*C*···Br3	0.89	2.60	3.427 (5)	155
N3—H3*D*···Br2	0.89	2.93	3.617 (5)	135
N3—H3*D*···Br3^{ii}	0.89	2.96	3.665 (5)	137
N4—H4*C*···Br2^{v}	0.89	2.52	3.395 (6)	168
N4—H4*D*···Br2^{iii}	0.89	2.58	3.418 (5)	156
N5—H5*C*···Br2^{v}	0.89	2.89	3.631 (5)	142

N5—H5*D*···Br2	0.89	2.78	3.651 (5)	166
C4—H4*A*···Br1^{vi}	0.97	2.95	3.897 (7)	166
C4—H4*B*···Br2	0.97	2.91	3.566 (7)	126
C5—H5*A*···Br1	0.97	3.04	3.582 (8)	117

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