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4-(Dimethylamino)pyridinium tribromido{3-[bromo/hydro(0.9/0.1)]-4-(dimethylamino)pyridine-κN^1}cobaltate(II)

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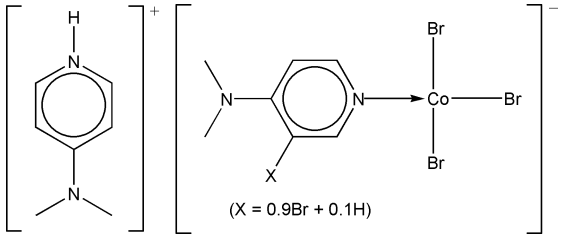
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.010 Å; disorder in main residue; R factor = 0.046; wR factor = 0.130; data-to-parameter ratio = 20.1.

The reaction of a cobalt(II) salt with 4-(dimethylamino)-pyridinium hydrobromide perbromide yielded the title compound, $(C_7H_{11}N_2)[CoBr_3(C_7H_{9.1}Br_{0.9}N_2)]$. In the anion, the Co^{II} atom is coordinated in a distorted tetrahedral geometry by three Br atoms and the pyridine N atom of a bromine-substituted 4-(dimethylamino)pyridine molecule, whose formation probably results from an incomplete substitution (90%) catalysed by the Co^{II} ion. One of the three bromine atoms bonded to the metal is disordered over two sites in a 0.9:0.1 ratio. An N—H···Br hydrogen bond connects the cation and anion.

Related literature

For bis(4-(dimethylamino)pyridinium) tetrabromidocobaltate, see: Lo & Ng (2009). For other trihalocobaltate(II) anions having a pyridine-type donor ligand, see: Bogdanović *et al.* (2001); Crane *et al.* (2004); Divjaković *et al.* (1982); Hahn *et al.* (1997); Mueller-Westerhoff *et al.* (1996); Sumner & Steinmetz (1985).



Experimental

Crystal data

$(C_7H_{11}N_2)[CoBr_3(C_7H_{9.1}Br_{0.9}N_2)]$
M_r = 615.02
Triclinic, $P\overline{1}$
a = 8.3768 (2) Å
b = 10.2622 (2) Å
c = 12.4691 (3) Å
α = 99.028 (2)°
β = 98.927 (1)°
γ = 106.933 (2)°
V = 989.57 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 8.74 mm^{-1}
T = 150 K
0.40 × 0.20 × 0.10 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.128, T_{max} = 0.475
(expected range = 0.112–0.417)
7974 measured reflections
4451 independent reflections
3019 reflections with $I > 2\sigma(I)$
R_{int} = 0.053

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.130
S = 0.97
4451 reflections
221 parameters
7 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.29 e Å^{-3}
$\Delta\rho_{min}$ = −1.04 e Å^{-3}

Table 1
Selected bond lengths (Å).

Co1—Br1	2.4086 (11)	Co1—Br3′	2.376 (9)
Co1—Br2	2.3958 (10)	Co1—N1	2.032 (5)
Co1—Br3	2.3814 (13)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···Br1	0.88	2.74	3.434 (6)	137

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2210).

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supplementary materials

Acta Cryst. (2009). E**65**, m958-m959 [**doi:10.1107/S1600536809027913**]

4-(Dimethylamino)pyridinium tribromido{3-[bromo/hydro(0.9/0.1)]-4-(dimethylamino)pyridine-κN^1}cobaltate(II)

K. M. Lo and S. W. Ng

Comment

The reaction of cobalt(II) nitrate and 4-(dimethylamino)pyridinium hydrobromide perbromide yields bis(4-(dimethylamino)pyridinium) tetrabromidocobaltate (Lo & Ng, 2009). A similar reaction with cobalt acetate in place of cobalt nitrate yields a new 4-(dimethylamino)pyridinium salt, $[C_7H_{11}N_2][CoBr_3(C_7H_{9.1}Br_{0.9}N_2)]$ (Scheme 1, Fig. 1). The Co^{II} atom is coordinated by a bromine-substituted 4-(dimethylamino)pyridine molecule, whose formation probably results from an incomplete (90%) electrophilic substitution of 4-(dimethylamino)pyridine that is probably catalyzed by the cobaltous ion.

Experimental

Green cobalt acetate (0.70 g, 2.8 mmol) dissolved in water (2 ml) and 4-(dimethylamino)pyridinium hydrobromide perbromide (1.00 g, 2.8 mmol) dissolved in ethanol (50 ml) were mixed and the mixture was heated for one hour. The red solution was filtered; well-formed deep-blue crystals were isolated from the solution after several days.

Refinement

H atoms were placed at calculated positions (C—H = 0.95 and 0.98, N—H = 0.88 Å) and were treated as riding on their parent atoms, with U_{iso}(H) = 1.2(or 1.5)U_{eq}(C).

One of the three Br atoms that are bonded to Co1 is disordered over two positions (Br3 and Br3'). The Br3 atom is 3.5 Å from $Br4^i$ atom [symmetry code: (i) = 1-x, 1-y, 2-z]. However, as the Br3' atom is only 3.0 Å from $Br4^i$, the atom that is linked to the C2 atom should then be a mixture of Br and H atoms, with the provision that the occupancies of the Br3 and Br4 atoms are identical. As the occupancies refined to nearly 0.9:0.1, the occupancy factors were then fixed as 0.90 and 0.1 for Br3 and Br3', as well as for Br4 and H2. Other ratios, e.g. 0.85:0.15 and 0.95:0.05, gave less satisfactory *R* indices and large peaks/deep holes in the difference Fourier map. The anisotropic displacement of the minor occupant was restrained to be nearly isotropic; the Co–Br distances were restrained to within 0.01 Å of each other.

The final difference Fourier map had a peak in the vicinity of Br2 and a hole in the vicinty of Br4. The magnitudes of both could be decreased by lowering the 2θ limit to 50°.

Figures

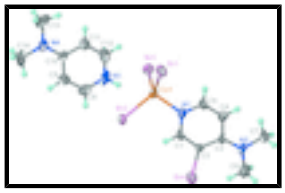


Fig. 1. Molecular structure of the title compound. Displacement ellipsoids are drawn at the 70% probability level. Minor disordered sites are omitted for clarity.

4-(Dimethylamino)pyridinium tribromido{3-[bromo/hydro(0.9/0.1)]-4- (dimethylamino)pyridine-κN^1}cobaltate(II)

Crystal data

$(C_7H_{11}N_2)[CoBr_3(C_7H_{9.1}Br_{0.9}N_2)]$	$Z = 2$
$M_r = 615.02$	$F_{000} = 591.2$
Triclinic, $P\overline{1}$	$D_x = 2.064$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.3768$ (2) Å	Cell parameters from 6987 reflections
$b = 10.2622$ (2) Å	$\theta = 2.4$–28.3°
$c = 12.4691$ (3) Å	$\mu = 8.74$ mm^{-1}
$\alpha = 99.028$ (2)°	$T = 150$ K
$\beta = 98.927$ (1)°	Block, brown
$\gamma = 106.933$ (2)°	0.40 × 0.20 × 0.10 mm
$V = 989.57$ (4) Å^3	

Data collection

Bruker APEXII CCD diffractometer	4451 independent reflections
Radiation source: fine-focus sealed tube	3019 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.053$
$T = 153$ K	$\theta_{max} = 27.5^\circ$
φ and ω scans	$\theta_{min} = 1.7^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -10 \rightarrow 10$
$T_{min} = 0.128$, $T_{max} = 0.475$	$k = -12 \rightarrow 13$
7974 measured reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.046$	H-atom parameters constrained
$wR(F^2) = 0.130$	$w = 1/[\sigma^2(F_o^2) + (0.0634P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

S = 0.97	$(\Delta/\sigma)_{max}$ = 0.001
4451 reflections	$\Delta\rho_{max}$ = 1.29 e Å^{-3}
221 parameters	$\Delta\rho_{min}$ = −1.04 e Å^{-3}
7 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Br1	0.26488 (9)	0.68358 (8)	0.54136 (5)	0.0375 (2)	
Br2	0.64945 (8)	0.59464 (7)	0.69989 (5)	0.03080 (18)	
Br3	0.49021 (18)	0.89737 (12)	0.84679 (11)	0.0315 (3)	0.90
Br3'	0.531 (2)	0.8775 (13)	0.8695 (11)	0.068 (5)	0.10
Br4	0.30233 (9)	0.25573 (8)	0.96716 (6)	0.0350 (2)	0.90
Co1	0.41492 (10)	0.67837 (9)	0.72097 (7)	0.0271 (2)	
N1	0.2478 (6)	0.5344 (5)	0.7796 (4)	0.0280 (12)	
N2	−0.0965 (6)	0.2792 (5)	0.9321 (4)	0.0276 (12)	
N3	0.6361 (7)	0.7246 (6)	0.4462 (5)	0.0414 (15)	
H3	0.5580	0.6723	0.4751	0.050*	
N4	1.0006 (7)	0.9742 (6)	0.3157 (4)	0.0318 (12)	
C1	0.2977 (8)	0.4510 (6)	0.8403 (5)	0.0267 (13)	
H1	0.4135	0.4540	0.8492	0.032*	
C2	0.1936 (7)	0.3618 (6)	0.8904 (5)	0.0226 (12)	
H2'	0.2368	0.3026	0.9293	0.027*	0.10
C3	0.0191 (7)	0.3572 (6)	0.8846 (5)	0.0248 (13)	
C4	−0.0282 (8)	0.4425 (7)	0.8152 (5)	0.0320 (15)	
H4	−0.1438	0.4404	0.8015	0.038*	
C5	0.0825 (8)	0.5267 (7)	0.7677 (6)	0.0338 (15)	
H5	0.0420	0.5830	0.7239	0.041*	
C6	−0.0620 (10)	0.1971 (10)	1.0125 (8)	0.063 (3)	
H6A	0.0449	0.2503	1.0660	0.094*	
H6B	−0.0516	0.1101	0.9737	0.094*	
H6C	−0.1559	0.1756	1.0518	0.094*	
C7	−0.2699 (8)	0.2868 (7)	0.9146 (6)	0.0377 (16)	
H7A	−0.3213	0.2596	0.8349	0.057*	
H7B	−0.2661	0.3824	0.9433	0.057*	
H7C	−0.3385	0.2234	0.9537	0.057*	
C8	0.7904 (10)	0.7112 (7)	0.4577 (5)	0.0362 (16)	
H8	0.8148	0.6441	0.4962	0.043*	
C9	0.9138 (9)	0.7919 (7)	0.4155 (5)	0.0320 (15)	
H9	1.0236	0.7811	0.4254	0.038*	
C10	0.8813 (7)	0.8921 (6)	0.3568 (4)	0.0240 (13)	
C11	0.7136 (9)	0.9012 (7)	0.3454 (5)	0.0360 (16)	
H11	0.6826	0.9655	0.3062	0.043*	
C12	0.5987 (9)	0.8172 (8)	0.3908 (6)	0.0405 (17)	
H12	0.4871	0.8243	0.3831	0.049*	
C13	0.9613 (11)	1.0765 (8)	0.2567 (6)	0.051 (2)	

H13A	0.9162	1.1366	0.3038	0.076*
H13B	0.8758	1.0282	0.1881	0.076*
H13C	1.0654	1.1334	0.2384	0.076*
C14	1.1733 (9)	0.9648 (8)	0.3293 (6)	0.048 (2)
H14A	1.2214	0.9768	0.4084	0.073*
H14B	1.2452	1.0380	0.2994	0.073*
H14C	1.1689	0.8733	0.2893	0.073*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0327 (4)	0.0541 (5)	0.0345 (4)	0.0205 (3)	0.0109 (3)	0.0188 (3)
Br2	0.0220 (3)	0.0369 (4)	0.0365 (4)	0.0102 (3)	0.0092 (3)	0.0119 (3)
Br3	0.0321 (5)	0.0292 (5)	0.0328 (5)	0.0089 (4)	0.0070 (3)	0.0071 (4)
Br3'	0.076 (9)	0.060 (7)	0.057 (7)	0.001 (5)	0.034 (6)	0.001 (5)
Br4	0.0253 (4)	0.0469 (5)	0.0403 (4)	0.0144 (3)	0.0087 (3)	0.0237 (4)
Co1	0.0236 (5)	0.0288 (5)	0.0310 (5)	0.0068 (4)	0.0110 (3)	0.0108 (4)
N1	0.025 (3)	0.030 (3)	0.031 (3)	0.008 (2)	0.009 (2)	0.011 (2)
N2	0.022 (3)	0.031 (3)	0.029 (3)	0.003 (2)	0.010 (2)	0.013 (2)
N3	0.033 (3)	0.047 (4)	0.034 (3)	−0.005 (3)	0.011 (3)	0.007 (3)
N4	0.026 (3)	0.038 (3)	0.026 (3)	0.002 (2)	0.003 (2)	0.010 (2)
C1	0.017 (3)	0.033 (4)	0.028 (3)	0.007 (3)	0.007 (2)	0.002 (3)
C2	0.023 (3)	0.023 (3)	0.025 (3)	0.009 (2)	0.008 (2)	0.010 (2)
C3	0.020 (3)	0.025 (3)	0.024 (3)	0.000 (2)	0.006 (2)	0.000 (2)
C4	0.023 (3)	0.035 (4)	0.039 (4)	0.007 (3)	0.004 (3)	0.015 (3)
C5	0.024 (3)	0.039 (4)	0.046 (4)	0.014 (3)	0.011 (3)	0.020 (3)
C6	0.036 (5)	0.085 (7)	0.083 (6)	0.017 (5)	0.021 (4)	0.058 (5)
C7	0.024 (4)	0.042 (4)	0.049 (4)	0.008 (3)	0.017 (3)	0.010 (3)
C8	0.055 (5)	0.029 (4)	0.023 (3)	0.011 (3)	0.007 (3)	0.007 (3)
C9	0.036 (4)	0.031 (4)	0.027 (3)	0.012 (3)	0.001 (3)	0.002 (3)
C10	0.027 (3)	0.025 (3)	0.015 (3)	0.003 (3)	0.002 (2)	0.003 (2)
C11	0.033 (4)	0.045 (4)	0.030 (4)	0.014 (3)	0.002 (3)	0.013 (3)
C12	0.023 (4)	0.059 (5)	0.033 (4)	0.007 (3)	0.002 (3)	0.008 (3)
C13	0.060 (5)	0.035 (4)	0.050 (5)	−0.001 (4)	0.008 (4)	0.022 (4)
C14	0.031 (4)	0.056 (5)	0.045 (5)	−0.003 (4)	0.013 (3)	−0.002 (4)

Geometric parameters (Å, °)

Co1—Br1	2.4086 (11)	C4—H4	0.9500
Co1—Br2	2.3958 (10)	C5—H5	0.9500
Co1—Br3	2.3814 (13)	C6—H6A	0.9800
Co1—Br3'	2.376 (9)	C6—H6B	0.9800
Br4—C2	1.888 (6)	C6—H6C	0.9800
Co1—N1	2.032 (5)	C7—H7A	0.9800
N1—C1	1.340 (8)	C7—H7B	0.9800
N1—C5	1.347 (8)	C7—H7C	0.9800
N2—C3	1.343 (7)	C8—C9	1.356 (9)
N2—C6	1.454 (9)	C8—H8	0.9500
N2—C7	1.461 (8)	C9—C10	1.416 (8)

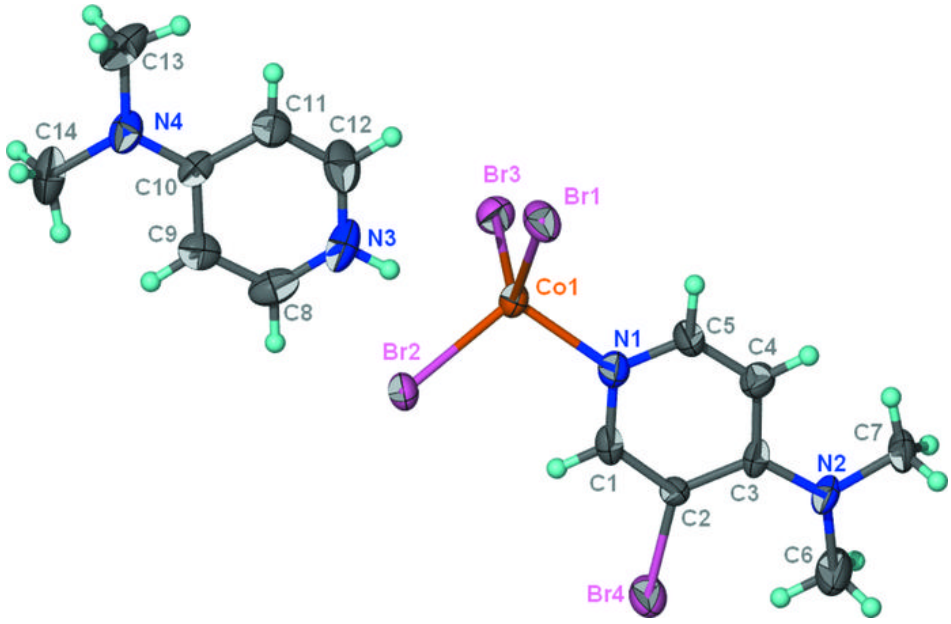
N3—C8	1.328 (9)	C9—H9	0.9500
N3—C12	1.338 (9)	C10—C11	1.421 (9)
N3—H3	0.8800	C11—C12	1.353 (9)
N4—C10	1.333 (7)	C11—H11	0.9500
N4—C13	1.456 (9)	C12—H12	0.9500
N4—C14	1.463 (9)	C13—H13A	0.9800
C1—C2	1.368 (8)	C13—H13B	0.9800
C1—H1	0.9500	C13—H13C	0.9800
C2—C3	1.439 (8)	C14—H14A	0.9800
C2—H2'	0.9500	C14—H14B	0.9800
C3—C4	1.415 (9)	C14—H14C	0.9800
C4—C5	1.350 (9)		
N1—Co1—Br3'	105.5 (5)	N2—C6—H6A	109.5
N1—Co1—Br3	107.98 (15)	N2—C6—H6B	109.5
Br3'—Co1—Br3	12.5 (4)	H6A—C6—H6B	109.5
N1—Co1—Br2	106.97 (14)	N2—C6—H6C	109.5
Br3'—Co1—Br2	104.7 (4)	H6A—C6—H6C	109.5
Br3—Co1—Br2	114.67 (5)	H6B—C6—H6C	109.5
N1—Co1—Br1	105.94 (15)	N2—C7—H7A	109.5
Br3'—Co1—Br1	123.1 (4)	N2—C7—H7B	109.5
Br3—Co1—Br1	111.17 (5)	H7A—C7—H7B	109.5
Br2—Co1—Br1	109.64 (4)	N2—C7—H7C	109.5
C1—N1—C5	116.2 (5)	H7A—C7—H7C	109.5
C1—N1—Co1	122.3 (4)	H7B—C7—H7C	109.5
C5—N1—Co1	121.2 (4)	N3—C8—C9	121.1 (6)
C3—N2—C6	125.9 (5)	N3—C8—H8	119.5
C3—N2—C7	119.4 (5)	C9—C8—H8	119.5
C6—N2—C7	114.3 (5)	C8—C9—C10	120.9 (6)
C8—N3—C12	120.3 (6)	C8—C9—H9	119.5
C8—N3—H3	119.9	C10—C9—H9	119.5
C12—N3—H3	119.9	N4—C10—C9	122.3 (6)
C10—N4—C13	120.2 (6)	N4—C10—C11	121.8 (6)
C10—N4—C14	121.2 (6)	C9—C10—C11	115.9 (6)
C13—N4—C14	118.6 (6)	C12—C11—C10	119.2 (6)
N1—C1—C2	124.6 (5)	C12—C11—H11	120.4
N1—C1—H1	117.7	C10—C11—H11	120.4
C2—C1—H1	117.7	N3—C12—C11	122.6 (6)
C1—C2—C3	120.5 (5)	N3—C12—H12	118.7
C1—C2—Br4	114.0 (4)	C11—C12—H12	118.7
C3—C2—Br4	125.5 (4)	N4—C13—H13A	109.5
C1—C2—H2'	119.8	N4—C13—H13B	109.5
C3—C2—H2'	119.8	H13A—C13—H13B	109.5
N2—C3—C4	120.3 (5)	N4—C13—H13C	109.5
N2—C3—C2	127.4 (6)	H13A—C13—H13C	109.5
C4—C3—C2	112.2 (5)	H13B—C13—H13C	109.5
C5—C4—C3	123.4 (6)	N4—C14—H14A	109.5
C5—C4—H4	118.3	N4—C14—H14B	109.5
C3—C4—H4	118.3	H14A—C14—H14B	109.5
N1—C5—C4	122.9 (6)	N4—C14—H14C	109.5

N1—C5—H5	118.6	H14A—C14—H14C	109.5
C4—C5—H5	118.6	H14B—C14—H14C	109.5
Br3'—Co1—N1—C1	−83.8 (6)	Br4—C2—C3—C4	−176.4 (5)
Br3—Co1—N1—C1	−96.6 (5)	N2—C3—C4—C5	177.9 (6)
Br2—Co1—N1—C1	27.3 (5)	C2—C3—C4—C5	−5.0 (9)
Br1—Co1—N1—C1	144.2 (4)	C1—N1—C5—C4	1.3 (9)
Br3'—Co1—N1—C5	90.1 (7)	Co1—N1—C5—C4	−173.0 (5)
Br3—Co1—N1—C5	77.3 (5)	C3—C4—C5—N1	1.8 (11)
Br2—Co1—N1—C5	−158.8 (5)	C12—N3—C8—C9	1.0 (10)
Br1—Co1—N1—C5	−41.9 (5)	N3—C8—C9—C10	−0.6 (10)
C5—N1—C1—C2	−0.6 (9)	C13—N4—C10—C9	−179.5 (6)
Co1—N1—C1—C2	173.6 (5)	C14—N4—C10—C9	0.0 (9)
N1—C1—C2—C3	−3.0 (9)	C13—N4—C10—C11	−0.2 (9)
N1—C1—C2—Br4	178.6 (5)	C14—N4—C10—C11	179.3 (6)
C6—N2—C3—C4	−174.2 (7)	C8—C9—C10—N4	179.1 (6)
C7—N2—C3—C4	−2.0 (9)	C8—C9—C10—C11	−0.3 (9)
C6—N2—C3—C2	9.1 (10)	N4—C10—C11—C12	−178.6 (6)
C7—N2—C3—C2	−178.7 (6)	C9—C10—C11—C12	0.7 (9)
C1—C2—C3—N2	−177.7 (6)	C8—N3—C12—C11	−0.5 (10)
Br4—C2—C3—N2	0.5 (9)	C10—C11—C12—N3	−0.3 (11)
C1—C2—C3—C4	5.4 (8)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···Br1	0.88	2.74	3.434 (6)	137

Fig. 1


C13
C14
N4
C11
C12
C10
C9
N3
C8
Br3
Br1
Co1
Br2
N1
C5
C4
C7
N2
C1
C3
C2
C6
Br4