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cis-Bromidobis(ethylene-1,2-diamine)(methylamine)cobalt(III) dibromide

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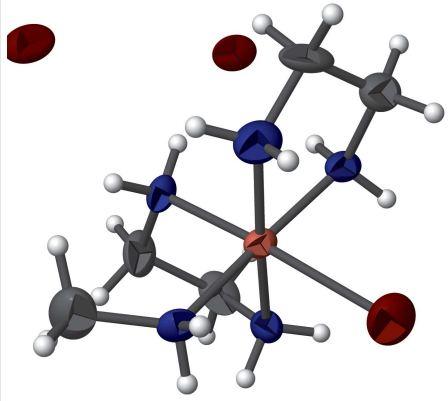
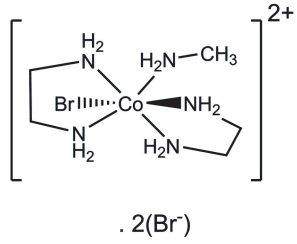
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $[CoBr(CH_5N)(C_2H_8N_2)_2]Br_2$, the cobalt(III) ion has a distorted octahedral coordination environment and is ligated by four N atoms in the equatorial plane, with an additional N atom and a Br^- ion occupying the axial positions. In the crystal, the complex cation and the two counter-anions are linked *via* N—H···Br and C—H···Br hydrogen bonds, forming a supramolecular framework.

3D view



Chemical scheme



Structure description

Mixed-ligand cobalt(III) complexes exhibit antitumor, antibacterial, antimicrobial, radiosenzitation and cytotoxicity activities (Sayed *et al.*, 1992; Teicher *et al.*, 1990; Arslan *et al.*, 2009; Delehanty *et al.*, 2008). Cobalt is an essential and integral component of vitamin B12 and is therefore found physiologically in most tissues. Cobalt(III) complexes are known for their involvement in electron-transfer and ligand-substitution reactions, which find applications in chemical and biological systems. Our present research concerns the design and synthesis of cobalt(III) complexes with the objective of understanding of their structure–reactivity correlations. Substituting an amino ligand for the $MeNH_2$ moiety can yield complexes of similar structure, but with differing electron-transfer rates (Anbalagan, 2011; Anbalagan *et al.*, 2011).

The molecular structure of the title compound is illustrated in Fig. 1. The cobalt(III) ion has a distorted octahedral coordination environment and is ligated by four N atoms (N1, N2, N3 and N5) in the equatorial plane, with N atom (N4) and the Br^- ion (Br1) occupying the axial positions. The Co1—N(ethylene-1,2-diamine) bond lengths vary from

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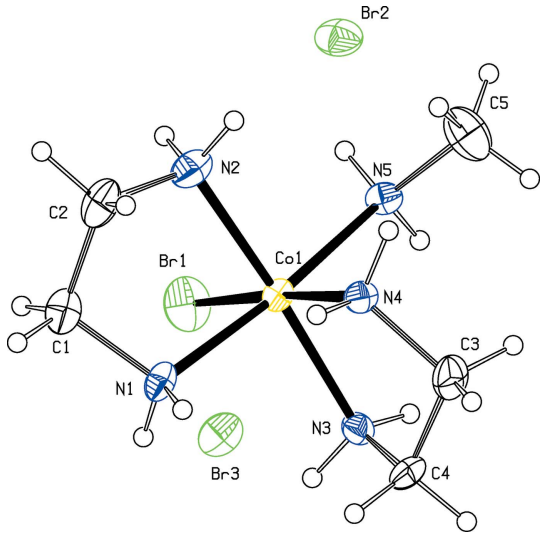

Figure 1
Molecular structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 30% probability level.

1.958 (7) to 1.966 (7) Å, comparable with the values reported [1.962 (7) to 1.957 (8) Å] in the literature (Lee *et al.*, 2007; Ramesh *et al.*, 2008; Anbalagan *et al.*, 2009; Ravichandran *et al.*, 2009). The Co1—N5 (methylamine) bond length is 1.983 (7) Å, which is also similar to the values of 1.9722 (2) to 1.988 (2) Å reported previously (Manimaran *et al.*, 2018).

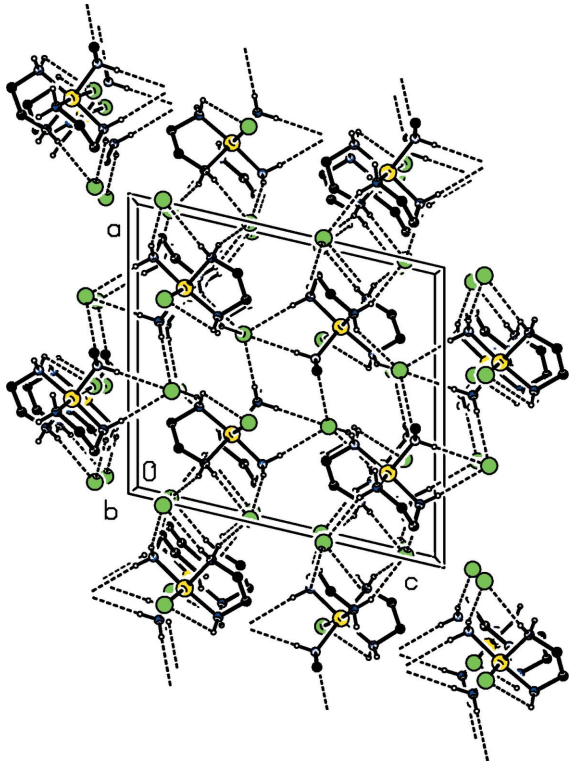

Figure 2
A view along the *b* axis of the crystal packing of the title compound. The N—H···Br hydrogen bonds are shown as dashed lines (Table 1). For clarity, C-bound H atoms have been omitted unless involved in hydrogen bonding.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H*B*···Br3^{i}	0.90	2.67	3.484 (7)	151
N1—H*A*···Br3	0.90	2.52	3.389 (8)	163
N4—H0*AB*···Br2	0.90	2.73	3.485 (7)	142
N4—H0*AA*···Br3	0.90	2.52	3.374 (7)	158
N2—H3*AA*···Br2	0.90	2.66	3.498 (10)	156
N5—H2*AB*···Br2^{ii}	0.90	2.56	3.452 (7)	171
N5—H2*AA*···Br2^{iii}	0.90	2.58	3.447 (7)	161
N3—H1*AC*···Br3	0.90	2.55	3.387 (8)	154
N3—H1*AD*···Br2^{ii}	0.90	2.61	3.511 (7)	174
C5—H11*A*···Br2	0.96	2.85	3.813 (13)	176

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$[CoBr(CH_5N)(C_2H_8N_2)_2]Br_2$
M_r	449.90
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, *b*, *c* (Å)	13.2883 (8), 7.5686 (5), 14.3602 (9)
β (°)	103.261 (6)
V (Å^3)	1405.75 (15)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	9.73
Crystal size (mm)	0.23 × 0.17 × 0.11
Data collection	
Diffractometer	Bruker SMART APEXII area-detector
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	5583, 2458, 1398
R_{int}	0.076
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.057, 0.143, 0.89
No. of reflections	2458
No. of parameters	128
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.31, −1.14

Computer programs: *APEX2* and *SAINT* (Bruker, 2008), *SHELXS97* (Sheldrick 2008), *SHELXL97* (Sheldrick 2008), *PLATON* (Spek, 2009), *SHELXTL* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

Both five-membered chelate rings adopts twisted conformations (on the C1—C2 and C3—C4 bonds), and their mean planes are inclined to each other by 80.2 (5)°.

In the crystal, molecules are linked by a series of N—H···Br hydrogen bonds and a C—H···Br hydrogen bond, leading to the formation of a supramolecular framework (Fig. 2 and Table 1)

Synthesis and crystallization

To a suspension of 2 g of *trans*-$[Co(en)_2Br_2]Br$, made into a paste using 3–4 drops of water, *ca* 2 ml of methylamine was

added dropwise over 20 min with mixing. The mixture was ground until the colour changed from dull green to red. The reaction mixture was set aside until no further change was observed and then left to stand overnight. Finally, the solid was washed with ethanol, then dissolved in 5–10 ml of water pre-heated to 343 K and allowed to crystallize using hot acidified water (yield 0.75 g). The crystals were filtered off, washed with ethanol and dried under vacuum. Pink block-like crystals were obtained by repeated recrystallization from hot acidified distilled water.

Refinement

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

Acknowledgements

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full crystallographic data

IUCrData (2018). **3**, x180819 [https://doi.org/10.1107/S2414314618008192]

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Crystal data

$[CoBr(CH_5N)(C_2H_8N_2)_2]Br_2$
M_r = 449.90
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 13.2883 (8) Å
b = 7.5686 (5) Å
c = 14.3602 (9) Å
β = 103.261 (6)°
V = 1405.75 (15) Å^3
Z = 4
$F(000)$ = 872
D_x = 2.126 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2458 reflections
θ = 2.9–25.0°
μ = 9.73 mm^{-1}
T = 293 K
Block, pink
0.23 × 0.17 × 0.11 mm

Data collection

Bruker SMART APEXII area-detector 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
5583 measured reflections
2458 independent reflections
1398 reflections with $I > 2\sigma(I)$
R_{int} = 0.076
θ_{max} = 25.0°, θ_{min} = 2.9°
h = −15→15
k = −9→8
l = −9→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.143
S = 0.89
2458 reflections
128 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0788P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.31 e Å^{-3}
$\Delta\rho_{min}$ = −1.14 e Å^{-3}

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br3	−0.00338 (8)	0.22334 (16)	0.61657 (8)	0.0449 (4)
Br2	0.37617 (8)	0.41487 (18)	0.63897 (7)	0.0469 (4)
Br1	0.32768 (9)	−0.27534 (18)	0.87914 (9)	0.0592 (4)
Co1	0.27166 (8)	0.01016 (18)	0.82199 (8)	0.0246 (3)
N1	0.1517 (5)	−0.0985 (11)	0.7355 (5)	0.032 (2)
HB	0.1244	−0.1818	0.7670	0.038*
HA	0.1030	−0.0159	0.7145	0.038*
N4	0.2206 (5)	0.2493 (10)	0.7838 (5)	0.0280 (19)
H0AB	0.2733	0.3175	0.7753	0.034*
H0AA	0.1731	0.2444	0.7280	0.034*
N2	0.3397 (6)	−0.0143 (13)	0.7154 (5)	0.043 (2)
H3AA	0.3696	0.0888	0.7059	0.051*
H3AB	0.3894	−0.0972	0.7295	0.051*
C3	0.1739 (8)	0.3276 (15)	0.8585 (8)	0.047 (3)
HC	0.1244	0.4184	0.8312	0.057*
HD	0.2269	0.3804	0.9086	0.057*
C2	0.2630 (8)	−0.0653 (17)	0.6268 (6)	0.048 (3)
H0AC	0.2306	0.0396	0.5944	0.058*
H0AD	0.2974	−0.1275	0.5838	0.058*
C5	0.4424 (9)	0.2794 (17)	0.9017 (9)	0.060 (4)
H11A	0.4280	0.3193	0.8365	0.090*
H11B	0.5157	0.2798	0.9275	0.090*
H11C	0.4096	0.3569	0.9387	0.090*
C1	0.1843 (8)	−0.1797 (16)	0.6525 (7)	0.043 (3)
H1AB	0.2126	−0.2965	0.6694	0.051*
H1AA	0.1253	−0.1908	0.5987	0.051*
N5	0.4021 (5)	0.0986 (11)	0.9053 (5)	0.028 (2)
H2AB	0.3964	0.0815	0.9659	0.033*
H2AA	0.4524	0.0254	0.8962	0.033*
N3	0.1931 (6)	0.0318 (11)	0.9218 (5)	0.033 (2)
H1AC	0.1588	−0.0694	0.9258	0.039*
H1AD	0.2368	0.0513	0.9787	0.039*
C4	0.1200 (7)	0.1775 (16)	0.8991 (8)	0.043 (3)
H2AD	0.0993	0.2165	0.9563	0.052*
H2AC	0.0588	0.1402	0.8524	0.052*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br3	0.0442 (6)	0.0487 (8)	0.0409 (6)	0.0165 (5)	0.0082 (5)	0.0065 (6)

Br2	0.0452 (7)	0.0633 (10)	0.0341 (6)	−0.0063 (6)	0.0131 (5)	0.0105 (6)
Br1	0.0710 (8)	0.0415 (9)	0.0602 (8)	0.0087 (6)	0.0049 (6)	0.0089 (7)
Co1	0.0289 (7)	0.0234 (8)	0.0218 (6)	0.0044 (6)	0.0064 (5)	0.0027 (6)
N1	0.046 (5)	0.028 (6)	0.024 (4)	0.006 (4)	0.012 (4)	0.000 (4)
N4	0.031 (4)	0.019 (5)	0.037 (5)	0.004 (3)	0.013 (4)	0.004 (4)
N2	0.048 (5)	0.046 (7)	0.039 (5)	0.006 (5)	0.021 (4)	0.002 (5)
C3	0.061 (7)	0.025 (7)	0.060 (8)	0.003 (6)	0.023 (6)	−0.007 (6)
C2	0.064 (7)	0.062 (9)	0.017 (5)	0.008 (6)	0.007 (5)	−0.003 (6)
C5	0.055 (7)	0.052 (10)	0.060 (8)	−0.007 (6)	−0.013 (6)	0.007 (7)
C1	0.056 (7)	0.037 (8)	0.035 (6)	0.004 (6)	0.010 (5)	−0.002 (6)
N5	0.021 (4)	0.035 (6)	0.025 (4)	0.006 (3)	0.001 (3)	0.006 (4)
N3	0.036 (5)	0.035 (6)	0.028 (4)	−0.012 (4)	0.011 (4)	−0.004 (4)
C4	0.034 (6)	0.051 (9)	0.052 (7)	0.003 (5)	0.023 (5)	−0.018 (6)

Geometric parameters (Å, º)

Br1—Co1	2.3699 (18)	C3—HD	0.9700
Co1—N2	1.958 (7)	C2—C1	1.468 (14)
Co1—N1	1.962 (7)	C2—H0AC	0.9700
Co1—N3	1.963 (7)	C2—H0AD	0.9700
Co1—N4	1.966 (7)	C5—N5	1.475 (14)
Co1—N5	1.983 (7)	C5—H11A	0.9600
N1—C1	1.490 (11)	C5—H11B	0.9600
N1—HB	0.9000	C5—H11C	0.9600
N1—HA	0.9000	C1—H1AB	0.9700
N4—C3	1.482 (12)	C1—H1AA	0.9700
N4—H0AB	0.9000	N5—H2AB	0.9000
N4—H0AA	0.9000	N5—H2AA	0.9000
N2—C2	1.487 (12)	N3—C4	1.456 (13)
N2—H3AA	0.9000	N3—H1AC	0.9000
N2—H3AB	0.9000	N3—H1AD	0.9000
C3—C4	1.528 (15)	C4—H2AD	0.9700
C3—HC	0.9700	C4—H2AC	0.9700
N2—Co1—N1	85.3 (3)	HC—C3—HD	108.6
N2—Co1—N3	175.5 (3)	C1—C2—N2	109.1 (8)
N1—Co1—N3	90.4 (3)	C1—C2—H0AC	109.9
N2—Co1—N4	93.4 (3)	N2—C2—H0AC	109.9
N1—Co1—N4	91.8 (3)	C1—C2—H0AD	109.9
N3—Co1—N4	85.4 (3)	N2—C2—H0AD	109.9
N2—Co1—N5	90.4 (3)	H0AC—C2—H0AD	108.3
N1—Co1—N5	173.7 (3)	N5—C5—H11A	109.5
N3—Co1—N5	93.9 (3)	N5—C5—H11B	109.5
N4—Co1—N5	93.2 (3)	H11A—C5—H11B	109.5
N2—Co1—Br1	91.2 (3)	N5—C5—H11C	109.5
N1—Co1—Br1	89.0 (2)	H11A—C5—H11C	109.5
N3—Co1—Br1	90.0 (3)	H11B—C5—H11C	109.5
N4—Co1—Br1	175.4 (2)	C2—C1—N1	108.2 (9)

N5—Co1—Br1	86.4 (2)	C2—C1—H1AB	110.1
C1—N1—Co1	109.6 (5)	N1—C1—H1AB	110.1
C1—N1—HB	109.7	C2—C1—H1AA	110.1
Co1—N1—HB	109.7	N1—C1—H1AA	110.1
C1—N1—HA	109.7	H1AB—C1—H1AA	108.4
Co1—N1—HA	109.7	C5—N5—Co1	124.5 (6)
HB—N1—HA	108.2	C5—N5—H2AB	106.2
C3—N4—Co1	109.9 (6)	Co1—N5—H2AB	106.2
C3—N4—H0AB	109.7	C5—N5—H2AA	106.2
Co1—N4—H0AB	109.7	Co1—N5—H2AA	106.2
C3—N4—H0AA	109.7	H2AB—N5—H2AA	106.4
Co1—N4—H0AA	109.7	C4—N3—Co1	109.8 (6)
H0AB—N4—H0AA	108.2	C4—N3—H1AC	109.7
C2—N2—Co1	110.1 (6)	Co1—N3—H1AC	109.7
C2—N2—H3AA	109.6	C4—N3—H1AD	109.7
Co1—N2—H3AA	109.6	Co1—N3—H1AD	109.7
C2—N2—H3AB	109.6	H1AC—N3—H1AD	108.2
Co1—N2—H3AB	109.6	N3—C4—C3	107.5 (7)
H3AA—N2—H3AB	108.1	N3—C4—H2AD	110.2
N4—C3—C4	106.8 (9)	C3—C4—H2AD	110.2
N4—C3—HC	110.4	N3—C4—H2AC	110.2
C4—C3—HC	110.4	C3—C4—H2AC	110.2
N4—C3—HD	110.4	H2AD—C4—H2AC	108.5
C4—C3—HD	110.4		

N2—Co1—N1—C1	14.7 (7)	Co1—N2—C2—C1	−33.9 (11)
N3—Co1—N1—C1	−166.6 (7)	N2—C2—C1—N1	45.9 (11)
N4—Co1—N1—C1	108.0 (7)	Co1—N1—C1—C2	−37.0 (10)
N5—Co1—N1—C1	−33 (3)	N2—Co1—N5—C5	77.4 (9)
Br1—Co1—N1—C1	−76.6 (6)	N1—Co1—N5—C5	125 (3)
N2—Co1—N4—C3	−172.2 (6)	N3—Co1—N5—C5	−101.7 (9)
N1—Co1—N4—C3	102.4 (6)	N4—Co1—N5—C5	−16.1 (9)
N3—Co1—N4—C3	12.1 (6)	Br1—Co1—N5—C5	168.5 (8)
N5—Co1—N4—C3	−81.6 (6)	N2—Co1—N3—C4	−59 (5)
Br1—Co1—N4—C3	3 (3)	N1—Co1—N3—C4	−75.9 (7)
N1—Co1—N2—C2	10.4 (7)	N4—Co1—N3—C4	15.9 (7)
N3—Co1—N2—C2	−6 (5)	N5—Co1—N3—C4	108.8 (7)
N4—Co1—N2—C2	−81.1 (8)	Br1—Co1—N3—C4	−164.8 (6)
N5—Co1—N2—C2	−174.3 (8)	Co1—N3—C4—C3	−39.5 (9)
Br1—Co1—N2—C2	99.3 (7)	N4—C3—C4—N3	49.1 (10)
Co1—N4—C3—C4	−36.0 (9)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H*B*···Br3^{i}	0.90	2.67	3.484 (7)	151
N1—H*A*···Br3	0.90	2.52	3.389 (8)	163
N4—H0*AB*···Br2	0.90	2.73	3.485 (7)	142

N4—H0*AA*···Br3	0.90	2.52	3.374 (7)	158
N2—H3*AA*···Br2	0.90	2.66	3.498 (10)	156
N5—H2*AB*···Br2^{ii}	0.90	2.56	3.452 (7)	171
N5—H2*AA*···Br2^{iii}	0.90	2.58	3.447 (7)	161
N3—H1*AC*···Br3	0.90	2.55	3.387 (8)	154
N3—H1*AD*···Br2^{ii}	0.90	2.61	3.511 (7)	174
C5—H11*A*···Br2	0.96	2.85	3.813 (13)	176

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