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ISSN 2414-3146

3,3′-Dimethyl-1,1′-methylenediimidazolium tetrabromidocobaltate(II)

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Received 17 July 2018
Accepted 27 August 2018

Edited by H. Ishida, Okayama University, Japan

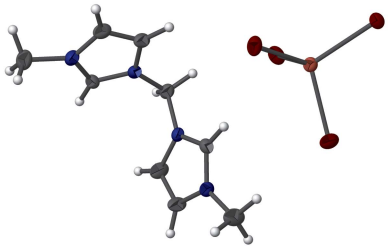
Keywords: cobalt; imidazolium; tetrahedral; crystal structure.

CCDC reference: 1863993

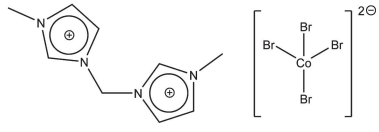
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $(C_9H_{14}N_4)[CoBr_4]$, was obtained as single crystals directly in very low yield as a side product in the reaction of 1,1′-bis(1-methylimidazolium)acetate bromide and $CoBr_2$. The title compound consists of an imidazolium-based dication and a tetrabromidocobaltate(II) complex anion, which are connected *via* C—H···Br interactions in the crystal. The dihedral angle between the imidazolium rings in the cation is 72.89 (16)°. The Co^{II} ion in the anion is coordinated tetrahedrally by four bromide ligands [Co—Br = 2.4025 (5)–2.4091 (5) Å and Br—Co—Br = 106.224 (17)–113.893 (17)°]. The compound exhibits a high melting point (>300°C) and is a light-blue solid under ambient conditions.

3D view



Chemical scheme



Structure description

In recent years, there have been enormous efforts in the field of artificial photosynthesis by converting CO_2 with water and light to hydrocarbons and just recently a review of concept article regarding photocatalytic CO_2 reduction using TiO_2-based materials under controlled reaction conditions has been published (Moustakas & Strunk, 2018). Furthermore, homogeneous catalytic CO_2 hydrogenation to formates using Ir-based catalysts is an intensively studied research field because of the demand for formic acid as a key industrial chemical and 1,1′-bis(*N*-methylimidazolium)acetate bromide, $[(MIm)_2CHCOO]Br$, has been investigated as a carboxylate-functionalized ligand for Ir^{I} and Ir^{III} complexes (Puerta-Oteo & Hölscher *et al.*, 2018). The title compound was obtained as individual crystals by decarboxylation of the cation in the reaction of $[(MIm)_2CHCOO]Br$ and $CoBr_2$ in a boiling mixture of $MeNO_2$ and MeCN. It can be seen from Fig. 1 that $(DMDIm)[CoBr_4]$ is characterized by an imidazolium-based dication and a tetrabromidocobaltate(II) complex anion. The complex anion consists of a Co^{II} ion coordinated tetrahedrally by four bromido ligands. In the crystal, C—H···Br interactions

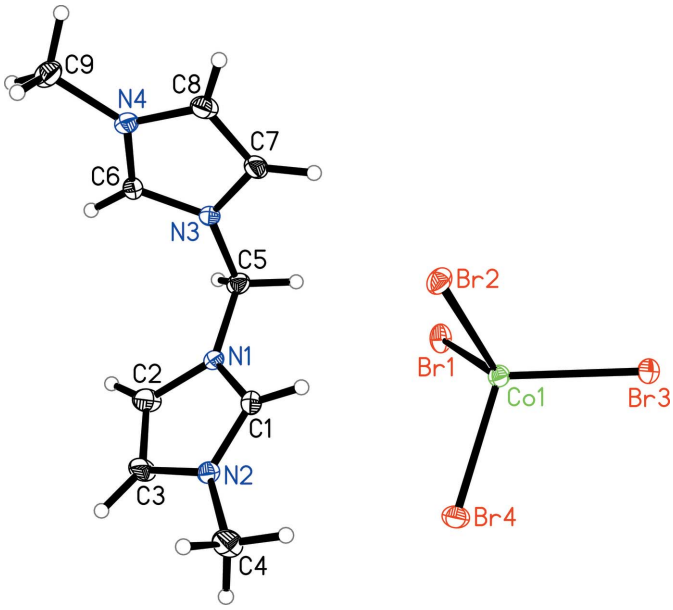


Figure 1
Molecular structure of the title compound with atom labelling and displacement ellipsoids drawn at 30% probability level.

are observed (Fig. 2 and Table 1). All bond lengths and angles within the cation as well as the complex anion are in expected ranges (Ahrens & Strassner, 2006; Kozlova *et al.*, 2009; Peppel & Köckerling, 2010; Peppel *et al.*, 2017).

Synthesis and crystallization

The title compound, (DMDIm)[$CoBr_4$] (DMDIm = $C_9H_{14}N_4$), was obtained in very low yield as a side product in the reaction of [$(MIm)_2CHCOO$]Br (Puerta-Oteo & Hölscher *et al.*, 2018; Puerta-Oteo & Jiménez *et al.*, 2018) and $CoBr_2$. In order to obtain the basic characteristics of bulk (DMDIm)[$CoBr_4$], it

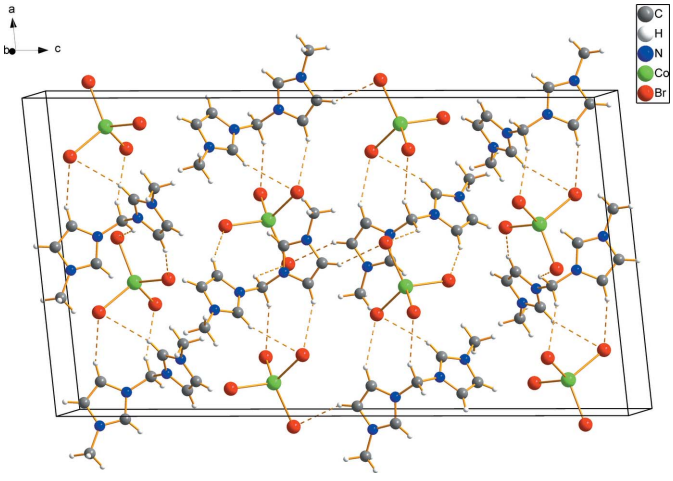


Figure 2
A packing diagram of the title compound viewed along the *b* axis, showing the C—H···Br interactions (dashed lines).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···Br2	0.95	2.92	3.829 (3)	161
C2—H2···Br4^{i}	0.95	2.84	3.679 (3)	148
C4—H4*A*···Br1^{ii}	0.98	2.90	3.560 (3)	126
C5—H5*A*···Br1	0.99	2.78	3.705 (3)	156
C5—H5*B*···Br3^{i}	0.99	2.92	3.578 (3)	124
C6—H6···Br1^{iii}	0.95	2.88	3.558 (2)	129
C7—H7···Br2	0.95	2.87	3.665 (3)	142
C8—H8···Br3^{iv}	0.95	2.83	3.699 (3)	153

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$(C_9H_{14}N_4)[CoBr_4]$
M_r	556.81
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	150
a, *b*, *c* (Å)	15.7782 (15), 7.4076 (7), 28.567 (3)
β (°)	95.7271 (19)
V (Å^3)	3322.2 (5)
Z	8
Radiation type	Mo *K*α
μ (mm^{-1})	10.64
Crystal size (mm)	0.24 × 0.10 × 0.07
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.34, 0.52
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21756, 4017, 3421
R_{int}	0.030
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.660
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.024, 0.048, 1.05
No. of reflections	4017
No. of parameters	165
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.51, −0.38

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *XP* in *SHELXTL* and *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *DIAMOND* (Putz & Brandenburg, 1999) and *publCIF* (Westrip, 2010).

was synthesized directly on the gram scale from (DMDIm)Br_2 (Cao *et al.*, 2016; Nirmala *et al.*, 2017; García-Fernández *et al.*, 2018) and $CoBr_2$ in 1:1 stoichiometry. (DMDIm)Br_2 (1.54 g, 4.57 mmol) was added in one portion to a stirred solution of $CoBr_2$ (1.00 g, 4.57 mmol) in 100 ml of acetonitrile. The suspension was heated under reflux for 4 h and the light-blue precipitate was filtered off, washed thoroughly with Et_2O and dried *in vacuo* (T = 80°C, P = 4 mbar, yield: 2.50 g, 98%). Analytical data for (DMDIm)[$CoBr_4$]: m.p. 310–312°C, EA for $C_9H_{14}Br_4CoN_2$ % (calc.): C 19.66 (19.41), H 2.37 (2.53), N 9.08 (10.06), Br 57.80 (57.40), Co 10.46 (10.62). UV/Vis (diffuse reflectance, absorbance): λ_{max} = 726, 702, 671, 645, 604, 590, 579, 563, 484, 472, 465, 435, 426, 398, 344 nm; UV/Vis (MeCN, saturated solution, 25°C, absorbance): λ_{max} = 699, 634, 618, 305, 278 nm.

Refinement

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

Acknowledgements

Professor J. Strunk (LIKAT, Rostock) and A. Wotzka (LIKAT, Rostock) are gratefully acknowledged for their support. The publication of this article was funded by the Open Access Fund of the Leibniz Association.

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Puerta-Oteo, R., Jiménez, M. V., Lahoz, F. J., Modrego, F. J., Passarelli, V. & Pérez-Torrente, J. (2018). *Inorg. Chem.* **57**, 5526–5543.
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full crystallographic data

IUCrData (2018). **3**, x181212 [https://doi.org/10.1107/S2414314618012129]

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Crystal data

$(C_9H_{14}N_4)[CoBr_4]$
M_r = 556.81
Monoclinic, $C2/c$
a = 15.7782 (15) Å
b = 7.4076 (7) Å
c = 28.567 (3) Å
β = 95.7271 (19)°
V = 3322.2 (5) Å^3
Z = 8
$F(000)$ = 2104
D_x = 2.227 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7863 reflections
θ = 2.6–29.7°
μ = 10.64 mm^{-1}
T = 150 K
Needle, blue
0.24 × 0.10 × 0.07 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 8.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
T_{min} = 0.34, T_{max} = 0.52
21756 measured reflections
4017 independent reflections
3421 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 28.0°, θ_{min} = 1.4°
h = −20→20
k = −9→9
l = −37→37

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.048
S = 1.05
4017 reflections
165 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0174P)^2 + 5.0295P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 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. All H atoms were placed in idealized positions with C—H = 0.95 Å (CH), 0.98 Å (CH_3) and 0.99 Å (CH_2), and were refined using a riding model with U_{iso}(H) fixed at 1.2 U_{eq}(C) for CH and CH_2, and 1.5 U_{eq}(C) for CH_3.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.17779 (16)	0.3468 (3)	0.16985 (9)	0.0226 (5)
H1	0.2215	0.3549	0.1494	0.027*
C2	0.06459 (19)	0.2588 (4)	0.20258 (10)	0.0365 (7)
H2	0.0154	0.1927	0.2090	0.044*
C3	0.09624 (18)	0.4055 (4)	0.22558 (10)	0.0345 (7)
H3	0.0736	0.4627	0.2514	0.041*
C4	0.2187 (2)	0.6162 (4)	0.21901 (11)	0.0352 (7)
H4A	0.2699	0.6163	0.2022	0.053*
H4B	0.2352	0.6125	0.2530	0.053*
H4C	0.1856	0.7259	0.2111	0.053*
C5	0.10432 (17)	0.0753 (3)	0.13384 (9)	0.0258 (6)
H5A	0.1605	0.0290	0.1268	0.031*
H5B	0.0734	−0.0247	0.1476	0.031*
C6	−0.02772 (16)	0.1664 (3)	0.08457 (9)	0.0211 (5)
H6	−0.0664	0.1509	0.1077	0.025*
C7	0.09043 (18)	0.1725 (4)	0.04886 (9)	0.0288 (6)
H7	0.1485	0.1624	0.0431	0.035*
C8	0.02555 (18)	0.2265 (4)	0.01830 (9)	0.0289 (6)
H8	0.0291	0.2609	−0.0135	0.035*
C9	−0.13247 (18)	0.2793 (4)	0.02105 (10)	0.0352 (7)
H9A	−0.1756	0.2208	0.0383	0.053*
H9B	−0.1409	0.2439	−0.0121	0.053*
H9C	−0.1378	0.4107	0.0236	0.053*
N1	0.11685 (13)	0.2222 (3)	0.16801 (7)	0.0207 (4)
N2	0.16702 (13)	0.4578 (3)	0.20512 (7)	0.0213 (4)
N3	0.05644 (13)	0.1343 (3)	0.09049 (7)	0.0215 (4)
N4	−0.04719 (14)	0.2232 (3)	0.04118 (7)	0.0244 (5)
Co1	0.40230 (2)	0.18136 (5)	0.12715 (2)	0.02171 (8)
Br1	0.32770 (2)	−0.08576 (4)	0.14779 (2)	0.03035 (7)
Br2	0.31206 (2)	0.32678 (4)	0.06547 (2)	0.02916 (7)
Br3	0.54182 (2)	0.12285 (3)	0.10318 (2)	0.02435 (6)
Br4	0.41673 (2)	0.37353 (4)	0.19523 (2)	0.03257 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0196 (13)	0.0244 (13)	0.0243 (13)	0.0013 (10)	0.0036 (10)	0.0008 (10)
C2	0.0333 (16)	0.0497 (18)	0.0283 (15)	−0.0198 (14)	0.0118 (12)	−0.0084 (13)
C3	0.0315 (16)	0.0500 (18)	0.0245 (14)	−0.0140 (13)	0.0145 (12)	−0.0106 (13)
C4	0.0391 (17)	0.0269 (14)	0.0414 (17)	−0.0133 (13)	0.0127 (14)	−0.0077 (13)
C5	0.0256 (14)	0.0225 (13)	0.0281 (14)	0.0020 (11)	−0.0034 (11)	−0.0035 (11)
C6	0.0201 (13)	0.0210 (12)	0.0225 (12)	0.0014 (10)	0.0034 (10)	−0.0006 (10)
C7	0.0245 (14)	0.0374 (15)	0.0255 (14)	−0.0073 (12)	0.0073 (11)	−0.0086 (12)
C8	0.0315 (15)	0.0342 (15)	0.0216 (13)	−0.0082 (12)	0.0052 (11)	−0.0039 (11)
C9	0.0300 (16)	0.0420 (17)	0.0321 (16)	0.0043 (13)	−0.0054 (13)	0.0039 (13)

N1	0.0174 (10)	0.0245 (11)	0.0199 (10)	−0.0015 (8)	−0.0001 (8)	−0.0016 (8)
N2	0.0203 (11)	0.0242 (11)	0.0197 (10)	−0.0044 (9)	0.0035 (9)	0.0010 (9)
N3	0.0204 (11)	0.0223 (11)	0.0216 (11)	−0.0008 (8)	0.0010 (8)	−0.0053 (9)
N4	0.0221 (11)	0.0277 (12)	0.0228 (11)	−0.0028 (9)	−0.0008 (9)	−0.0027 (9)
Co1	0.02076 (18)	0.02356 (17)	0.02092 (17)	−0.00132 (14)	0.00261 (14)	0.00084 (14)
Br1	0.02704 (14)	0.02493 (13)	0.04071 (16)	−0.00168 (11)	0.01153 (12)	0.00564 (12)
Br2	0.02183 (14)	0.04087 (16)	0.02428 (13)	−0.00203 (11)	−0.00018 (10)	0.00796 (11)
Br3	0.02163 (13)	0.02442 (13)	0.02722 (14)	0.00184 (10)	0.00359 (10)	0.00110 (10)
Br4	0.03414 (16)	0.03955 (16)	0.02469 (14)	−0.01065 (12)	0.00624 (11)	−0.00815 (12)

Geometric parameters (Å, º)

C1—N2	1.324 (3)	C6—N4	1.316 (3)
C1—N1	1.330 (3)	C6—N3	1.343 (3)
C1—H1	0.9500	C6—H6	0.9500
C2—C3	1.340 (4)	C7—C8	1.339 (4)
C2—N1	1.375 (3)	C7—N3	1.382 (3)
C2—H2	0.9500	C7—H7	0.9500
C3—N2	1.367 (3)	C8—N4	1.376 (3)
C3—H3	0.9500	C8—H8	0.9500
C4—N2	1.461 (3)	C9—N4	1.469 (3)
C4—H4A	0.9800	C9—H9A	0.9800
C4—H4B	0.9800	C9—H9B	0.9800
C4—H4C	0.9800	C9—H9C	0.9800
C5—N3	1.452 (3)	Co1—Br4	2.4025 (5)
C5—N1	1.462 (3)	Co1—Br1	2.4055 (4)
C5—H5A	0.9900	Co1—Br2	2.4067 (5)
C5—H5B	0.9900	Co1—Br3	2.4091 (5)
N2—C1—N1	108.3 (2)	C7—C8—N4	107.7 (2)
N2—C1—H1	125.9	C7—C8—H8	126.1
N1—C1—H1	125.9	N4—C8—H8	126.1
C3—C2—N1	106.9 (2)	N4—C9—H9A	109.5
C3—C2—H2	126.5	N4—C9—H9B	109.5
N1—C2—H2	126.5	H9A—C9—H9B	109.5
C2—C3—N2	107.5 (2)	N4—C9—H9C	109.5
C2—C3—H3	126.3	H9A—C9—H9C	109.5
N2—C3—H3	126.3	H9B—C9—H9C	109.5
N2—C4—H4A	109.5	C1—N1—C2	108.5 (2)
N2—C4—H4B	109.5	C1—N1—C5	126.3 (2)
H4A—C4—H4B	109.5	C2—N1—C5	125.1 (2)
N2—C4—H4C	109.5	C1—N2—C3	108.8 (2)
H4A—C4—H4C	109.5	C1—N2—C4	126.5 (2)
H4B—C4—H4C	109.5	C3—N2—C4	124.7 (2)
N3—C5—N1	111.7 (2)	C6—N3—C7	108.6 (2)
N3—C5—H5A	109.3	C6—N3—C5	125.8 (2)
N1—C5—H5A	109.3	C7—N3—C5	125.6 (2)
N3—C5—H5B	109.3	C6—N4—C8	109.0 (2)

N1—C5—H5B	109.3	C6—N4—C9	125.3 (2)
H5A—C5—H5B	107.9	C8—N4—C9	125.7 (2)
N4—C6—N3	108.1 (2)	Br4—Co1—Br1	107.348 (17)
N4—C6—H6	126.0	Br4—Co1—Br2	109.197 (18)
N3—C6—H6	126.0	Br1—Co1—Br2	106.224 (17)
C8—C7—N3	106.6 (2)	Br4—Co1—Br3	108.743 (17)
C8—C7—H7	126.7	Br1—Co1—Br3	113.893 (17)
N3—C7—H7	126.7	Br2—Co1—Br3	111.280 (16)
N1—C2—C3—N2	0.1 (3)	C2—C3—N2—C4	178.0 (3)
N3—C7—C8—N4	0.6 (3)	N4—C6—N3—C7	−0.2 (3)
N2—C1—N1—C2	1.6 (3)	N4—C6—N3—C5	177.9 (2)
N2—C1—N1—C5	179.0 (2)	C8—C7—N3—C6	−0.3 (3)
C3—C2—N1—C1	−1.0 (3)	C8—C7—N3—C5	−178.3 (2)
C3—C2—N1—C5	−178.4 (2)	N1—C5—N3—C6	−74.8 (3)
N3—C5—N1—C1	−83.8 (3)	N1—C5—N3—C7	102.9 (3)
N3—C5—N1—C2	93.2 (3)	N3—C6—N4—C8	0.6 (3)
N1—C1—N2—C3	−1.5 (3)	N3—C6—N4—C9	−177.7 (2)
N1—C1—N2—C4	−178.6 (2)	C7—C8—N4—C6	−0.8 (3)
C2—C3—N2—C1	0.9 (3)	C7—C8—N4—C9	177.5 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···Br2	0.95	2.92	3.829 (3)	161
C2—H2···Br4^{i}	0.95	2.84	3.679 (3)	148
C4—H4*A*···Br1^{ii}	0.98	2.90	3.560 (3)	126
C5—H5*A*···Br1	0.99	2.78	3.705 (3)	156
C5—H5*B*···Br3^{i}	0.99	2.92	3.578 (3)	124
C6—H6···Br1^{iii}	0.95	2.88	3.558 (2)	129
C7—H7···Br2	0.95	2.87	3.665 (3)	142
C8—H8···Br3^{iv}	0.95	2.83	3.699 (3)	153

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