

Tris(1,2-ethanediamine- κ^2N,N')cobalt(II) triiodide iodide

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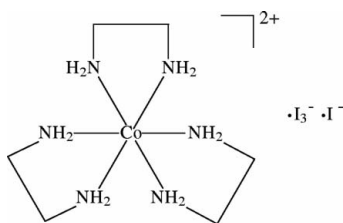
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.017; wR factor = 0.044; data-to-parameter ratio = 22.1.

The title compound, $[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_3](\text{I}_3)\text{I}$, is isostructural with the analogous Zn^{II} and Ni^{II} complexes [Wieczorrek (2000). *Acta Cryst. C* **56**, 1079–1081]. The Co^{II} atom, which has a distorted octahedral environment, and the iodide anion are located on twofold axes ($8d$ site). The central I atom of the triiodide anion is also located on a twofold axis ($8c$ site). The I_3^- anion is linear. The crystal shows inversion twinning.

Related literature

For related literature, see: Bu *et al.* (2000); Jia *et al.* (2004); Pan *et al.* (2005); Stephan & Kanatzidis (1997); Vaqueiro (2006); Vaqueiro *et al.* (2004); Varand *et al.* (1967); Wang *et al.* (2003); Wieczorrek (2000); Yu *et al.* (2001, 2002).



Experimental

Crystal data

$[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_3](\text{I}_3)\text{I}$
 $M_r = 746.84$
 Tetragonal, $I\bar{4}2d$
 $a = 14.7850$ (4) Å
 $c = 17.7221$ (9) Å
 $V = 3874.0$ (2) Å³

$Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 7.26$ mm⁻¹
 $T = 293$ (2) K
 $0.30 \times 0.20 \times 0.20$ mm

Data collection

Rigaku Mercury CCD diffractometer
 Absorption correction: multi-scan (CrystalClear; Rigaku, 2002)

$T_{\text{min}} = 0.224$, $T_{\text{max}} = 0.271$
 (expected range = 0.194–0.234)
 12658 measured reflections
 1771 independent reflections
 1766 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.017$
 $wR(F^2) = 0.044$
 $S = 0.98$
 1771 reflections
 80 parameters
 H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.43$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.02$ e Å⁻³
 Absolute structure: Flack (1983), with 772 Friedel pairs
 Flack parameter: 0.0 (5)

Table 1

Selected geometric parameters (Å, °).

I2—I3	2.9322 (2)	Co1—N13	2.282 (3)
Co1—N12	2.269 (3)	Co1—N11	2.290 (3)
I2 ⁱ —I3—I2	179.587 (17)		

Symmetry code: (i) $-x + 1, -y + 2, z$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N12—H12E \cdots I1	0.90	2.91	3.765 (3)	160
N12—H12F \cdots I1 ⁱⁱ	0.90	3.00	3.817 (3)	151
N13—H13E \cdots I3	0.90	3.15	3.874 (3)	139
N13—H13F \cdots I2 ⁱⁱⁱ	0.90	3.08	3.818 (3)	141
N13—H13F \cdots I1 ⁱⁱ	0.90	3.10	3.815 (3)	137
N11—H11E \cdots I2 ^{iv}	0.90	3.10	3.887 (3)	148
N11—H11F \cdots I2 ^v	0.90	2.92	3.735 (3)	152

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

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Siemens, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2101).

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supplementary materials

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Tris(1,2-ethanediamine- κ^2N,N')cobalt(II) triiodide iodide

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Comment

The crystal structures of tris(1,2-ethanediamine- N,N')zinc(II) triiodide iodide and tris(1,2-ethanediamine- N,N') nickel(II) triiodide iodide have been reported earlier (Wieczorrek, 2000). Herein, we report the synthesis and crystal structure of tris(1,2-ethanediamine- N,N')cobalt(II) triiodide iodide. This complex is isostructural with the Zn(II) and Ni(II) complexes.

As shown in Fig. 1, the title complex consists of one $[\text{Co}(\text{en})_3]^{2+}$ cation, one triiodide anion, and one iodide anion. The Co atom is coordinated by three ethanediamine ligands that form a distorted octahedral environment with the Co—N bond distances ranging from 2.269 (3) to 2.290 (3) Å (Table 1). It is important to stress that compounds conating $[\text{Co}(\text{en})_3]^{2+}$ cation are rare in comparison with those containing $[\text{Co}(\text{en})_3]^{3+}$ (Bu *et al.*, 2000; Jia *et al.*, 2004; Pan *et al.*, 2005; Stephan & Kanatzidis, 1997; Vaqueiro, 2006; Vaqueiro *et al.*, 2004; Varand *et al.*, 1967; Wang *et al.*, 2003; Yu *et al.*, 2001, 2002). The I—I bond distance of the linear triiodide anion in the present compound is 2.9322 (2) Å, which is in agreement with those found in $[\text{Zn}(\text{C}_2\text{H}_8\text{N}_2)_3](\text{I}_3)\text{I}$ and $[\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_3](\text{I}_3)\text{I}$. The crystal structure of the title compound is shown in Figure 2. Hydrogen bonds are formed between N atoms of the ethanediamine ligands and I atoms of triiodide and iodide anions (Table 2).

Experimental

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol, 119 mg), HI (25.6 mmol, 4 ml), ethylenediamine (15 mmol, 1 ml) and ethanol (2 ml) were heated at 453 K for two days under autogeneous pressure in a sealed 25 ml Teflon-lined stainless steel vessel, and then cooled down to room temperature within two days. Red crystals of the title compound were obtained with 25% yield (based on cobalt chloride).

Refinement

All atoms were allowed to ride on their respective parent atoms with the C—H and N—H bond distances fixed at 0.97 and 0.90 Å, respectively. H atoms were included in the refinement process with isotropic displacement parameters $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. The deepest hole in the final difference map of $-1.01 \text{ e } \text{Å}^{-3}$ is in the vicinity of the Co atom. The crystal was refined as an inversion twin.

Figures



Fig. 1. ORTEP drawing of the title compound showing 30% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

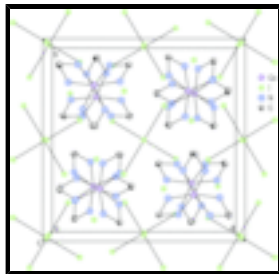


Fig. 2. Packing diagram viewed along the *c* direction.

Tris(1,2-ethanediamine-κ²N,N')cobalt(II) triiodide iodide

Crystal data

[Co(C₂H₈N₂)₃](I₃)I

M_r = 746.84

Tetragonal, *I*42*d*

Hall symbol: I -4 2bw

a = 14.7850 (4) Å

b = 14.7850 (4) Å

c = 17.7221 (9) Å

α = 90°

β = 90°

γ = 90°

V = 3874.0 (2) Å³

Z = 8

*F*₀₀₀ = 2728

D_x = 2.561 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 5670 reflections

θ = 3.0–27.5°

μ = 7.26 mm⁻¹

T = 293 (2) K

Prism, red

0.30 × 0.20 × 0.20 mm

Data collection

Rigaku Mercury CCD
diffractometer

Radiation source: rotating anode generator

Monochromator: graphite

T = 293(2) K

ω scans

Absorption correction: multi-scan
(CrystalClear; Rigaku, 2002)

*T*_{min} = 0.224, *T*_{max} = 0.271

12658 measured reflections

1771 independent reflections

1766 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.032

θ_{max} = 25.4°

θ_{min} = 3.3°

h = -16→17

k = -17→14

l = -19→21

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.017

wR(*F*²) = 0.044

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

w = 1/[σ²(*F*_o²) + (0.0313*P*)² + 5.16*P*]

where *P* = (*F*_o² + 2*F*_c²)/3

(Δ/σ)_{max} = 0.001

$S = 0.98$	$\Delta\rho_{\max} = 0.43 \text{ e } \text{\AA}^{-3}$
1771 reflections	$\Delta\rho_{\min} = -1.02 \text{ e } \text{\AA}^{-3}$
80 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), with 772 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.0 (5)

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.

Refinement. Crystal refined as inversion twin with BASF 0.5

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	1.101498 (17)	0.7500	0.1250	0.01992 (6)
I2	0.329735 (14)	0.898314 (14)	0.128322 (12)	0.02335 (5)
I3	0.5000	1.0000	0.12773 (2)	0.02203 (7)
Co1	0.77236 (4)	0.7500	0.1250	0.01965 (13)
N11	0.7898 (2)	0.61932 (19)	0.05720 (15)	0.0196 (7)
H11E	0.7419	0.5828	0.0644	0.024*
H11F	0.7938	0.6320	0.0076	0.024*
N12	0.87417 (19)	0.8274 (2)	0.05429 (15)	0.0173 (6)
H12E	0.9293	0.8021	0.0587	0.021*
H12F	0.8579	0.8261	0.0054	0.021*
N13	0.6522 (2)	0.8038 (2)	0.05786 (15)	0.0177 (7)
H13E	0.6458	0.8636	0.0659	0.021*
H13F	0.6613	0.7948	0.0082	0.021*
C11	0.8727 (3)	0.5747 (2)	0.0830 (2)	0.0238 (9)
H11A	0.9251	0.6053	0.0620	0.029*
H11B	0.8735	0.5124	0.0657	0.029*
C12	0.8767 (3)	0.9226 (2)	0.0817 (2)	0.0244 (9)
H12A	0.8258	0.9558	0.0610	0.029*
H12B	0.9319	0.9515	0.0645	0.029*
C13	0.5697 (2)	0.7554 (3)	0.08248 (15)	0.0176 (7)
H13A	0.5675	0.6964	0.0587	0.021*
H13B	0.5166	0.7891	0.0670	0.021*

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01401 (12)	0.03132 (15)	0.01442 (12)	0.000	0.000	0.00234 (13)
I2	0.02650 (11)	0.02545 (11)	0.01809 (9)	0.00195 (8)	0.00569 (11)	-0.00330 (10)
I3	0.03353 (15)	0.01645 (14)	0.01612 (13)	0.00729 (11)	0.000	0.000
Co1	0.0191 (3)	0.0207 (3)	0.0192 (3)	0.000	0.000	0.0004 (3)
N11	0.0280 (15)	0.0192 (15)	0.0118 (13)	-0.0022 (12)	0.0005 (11)	0.0009 (11)
N12	0.0169 (14)	0.0197 (14)	0.0153 (12)	-0.0011 (12)	0.0015 (11)	-0.0015 (11)
N13	0.0216 (15)	0.0195 (16)	0.0119 (12)	-0.0010 (12)	-0.0003 (11)	0.0021 (10)
C11	0.029 (2)	0.0205 (18)	0.0216 (18)	0.0043 (16)	0.0055 (15)	-0.0063 (13)
C12	0.023 (2)	0.0227 (19)	0.0275 (19)	-0.0115 (16)	0.0013 (15)	0.0020 (14)
C13	0.0163 (14)	0.0227 (16)	0.0139 (15)	0.0052 (18)	-0.0012 (11)	-0.0017 (15)

Geometric parameters (\AA , $^\circ$)

I2—I3	2.9322 (2)	N13—C13	1.479 (4)
Co1—N12	2.269 (3)	N13—H13E	0.9000
Co1—N13	2.282 (3)	N13—H13F	0.9000
Co1—N11	2.290 (3)	C11—H11A	0.9700
N11—C11	1.465 (5)	C11—H11B	0.9700
N11—H11E	0.9000	C12—H12A	0.9700
N11—H11F	0.9000	C12—H12B	0.9700
N12—C12	1.489 (5)	C13—H13A	0.9700
N12—H12E	0.9000	C13—H13B	0.9700
N12—H12F	0.9000		
I2 ⁱ —I3—I2	179.587 (17)	C13—N13—Co1	108.63 (19)
N12—Co1—N13	93.02 (9)	C13—N13—H13E	110.0
N12—Co1—N11	93.51 (11)	Co1—N13—H13E	110.0
N13—Co1—N11	96.22 (10)	C13—N13—H13F	110.0
C11—N11—Co1	108.1 (2)	Co1—N13—H13F	110.0
C11—N11—H11E	110.1	H13E—N13—H13F	108.3
Co1—N11—H11E	110.1	N11—C11—H11A	109.8
C11—N11—H11F	110.1	N11—C11—H11B	109.8
Co1—N11—H11F	110.1	H11A—C11—H11B	108.2
H11E—N11—H11F	108.4	N12—C12—H12A	109.6
C12—N12—Co1	108.2 (2)	N12—C12—H12B	109.6
C12—N12—H12E	110.0	H12A—C12—H12B	108.1
Co1—N12—H12E	110.0	N13—C13—H13A	109.6
C12—N12—H12F	110.0	N13—C13—H13B	109.6
Co1—N12—H12F	110.0	H13A—C13—H13B	108.1
H12E—N12—H12F	108.4		

Symmetry codes: (i) $-x+1, -y+2, z$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
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N12—H12E···I1	0.90	2.91	3.765 (3)	160
N12—H12F···I1 ⁱⁱ	0.90	3.00	3.817 (3)	151
N13—H13E···I3	0.90	3.15	3.874 (3)	139
N13—H13F···I2 ⁱⁱⁱ	0.90	3.08	3.818 (3)	141
N13—H13F···I1 ⁱⁱ	0.90	3.10	3.815 (3)	137
N11—H11E···I2 ^{iv}	0.90	3.10	3.887 (3)	148
N11—H11F···I2 ^v	0.90	2.92	3.735 (3)	152

Symmetry codes: (ii) $y, -x+2, -z$; (iii) $-y+3/2, -x+1, z-1/4$; (iv) $-x+1, y-1/2, -z+1/4$; (v) $y, -x+1, -z$.

Fig. 1

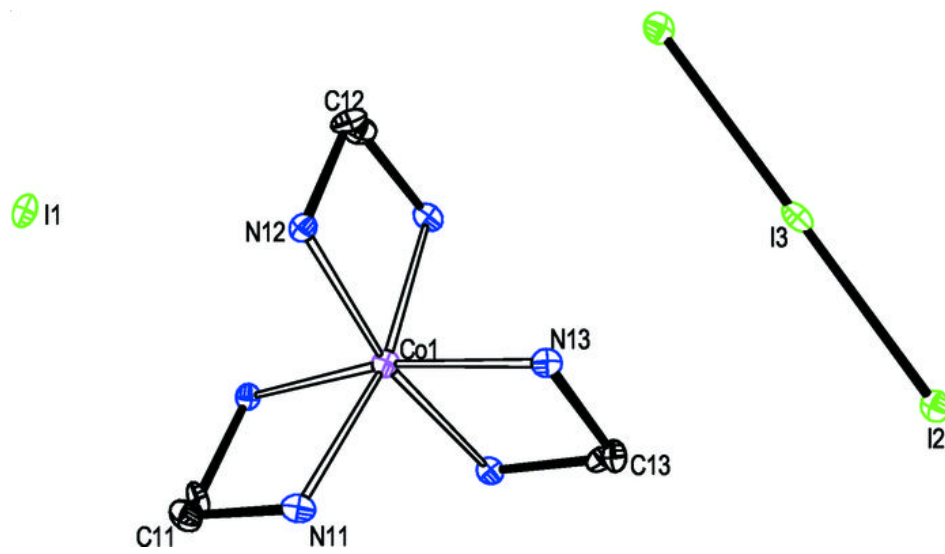


Fig. 2

