Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{iso}/U_{eq}
Cs	0.8629 (1)	1/4	0.9831 (3)	0.060 (1)
C1	0.5742 (5)	1/4	0.9288 (14)	0.026 (2)
C2	0.6042 (4)	0.3789 (4)	0.7964 (8)	0.026 (2)
C3	0.6527 (5)	0.3297 (3)	0.5823 (9)	0.026 (2)

Table 2. *Selected geometric parameters (Å, °)*

Cs—C1	3.296 (6)	Cs—*Cp*†	3.123 (5)
Cs—C1^{i}	3.364 (6)	Cs—*Cp*^{i}	3.157 (6)
Cs—C2	3.331 (5)	Cs—C2^{ii}	3.765 (6)
Cs—C2^{i}	3.374 (5)	Cs—C3^{ii}	3.773 (6)
Cs—C3	3.386 (5)	C1—C2	1.412 (4)
Cs—C3^{i}	3.389 (6)		
Cp—Cs—*Cp*^{i}	129.71 (1)		

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

† *Cp* is the centroid of the cyclopentadienyl ring.

The structure of CsCp was refined by Rietveld (1969) analysis. A starting model based on the isostructural Rb compound in space group *Pnma* was used. The lattice parameters, the two Lorentzian peak-shape parameters of the pseudo-Voigt function (Thompson, Cox & Hastings, 1987), two asymmetry parameters due to axial divergence (Finger, Cox & Jephcoat, 1994) and the zero-point correction were refined first using the le Bail technique (le Bail, Duroy & Fourquet, 1988). Anisotropic broadening was found and refined along the chain axis. Since the shape of the Cp ring is known in very narrow limits, this additional information was used to stabilize the refinement by setting up a rigid body. In order to allow the Cp ring to relax within the plane, the length of the C—C vector was refined as an additional parameter. Refinement continued using the Rietveld technique with the scale factor, the variation of the atomic and displacement parameters. Anisotropic displacement parameters were refined for the Cs atom only. Neither absorption nor preferred orientation corrections was found to be necessary. The H atoms were included at calculated positions but were not refined.

Data collection: *SUPER* program. Cell refinement: *FULLPROF* (Rodriguez-Carvajal, 1990). Data reduction: *GUFI* (Dinnebier, 1993). Program(s) used to refine structure: *GSAS* (von Dreele & Larson, 1990). Molecular graphics: *SCHAKAL*86 (Keller, 1986). Software used to prepare material for publication: *Word for Windows* 6.0.

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Lists of raw powder data have been deposited with the IUCr (Reference: NA1280). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tris(ethylenediamine-*N*,*N*′)zinc(II) Dinitrate

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Abstract

The Zn^{II} atom in $[Zn(C_2H_8N_2)_3](NO_3)_2$ has a distorted octahedral geometry of D_3 symmetry with three ethylenediamine bidentate ligands completing the coordination.

Comment

The $[Ni(en)_3]^{2+}$ complex, where en is ethylenediamine (Swink & Atoji, 1960; Korp, Bernal, Palmer & Robinson, 1980) spontaneously resolves to give a dinitrate crystal in an uniaxial and enantiomorphic space group, allowing the single-crystal circular dichroism to be measured directly. The corresponding $[Zn(en)_3]^{2+}$ complex also spontaneously resolves into one of two optical isomers, with the conformer in this determination found to be $(\Delta\lambda\lambda\lambda)$, the same as for the corresponding

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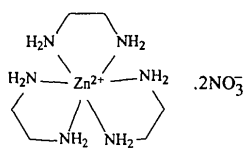

(I)

$[Ni(en)_3]^{2+}$ complex. Six other $[Zn(en)_3]^{2+}$ cations have been reported previously (Sabirov, Batsanov, Struchkov, Aleksandrov & Azizov, 1982; Muralikrishna, Mahadevan, Sastry, Seshasayee & Subramanian, 1983; Cernak, Chomic, Dunaj-Jurco & Kappenstein, 1984; Emsley, Arif, Bates & Hursthouse, 1989; Cernak, Chomic, Kappenstein & Dunaj-Jurco, 1994), with mean values of Zn—N 2.21 (3) Å, N—Zn—N 80.6 (9) and N—C—C—N 57.5 (3)°, compared with 2.193 (2) Å, 80.2 (1) and 53.7 (1)°, respectively, for the current analysis. Hydrogen bonding links the H atom on N1 to O3 on different nitrate groups [2.30 (3) and 2.48 (3) Å]. The Zn^{II} complex undergoes a phase transition at a temperature of about 141 K.

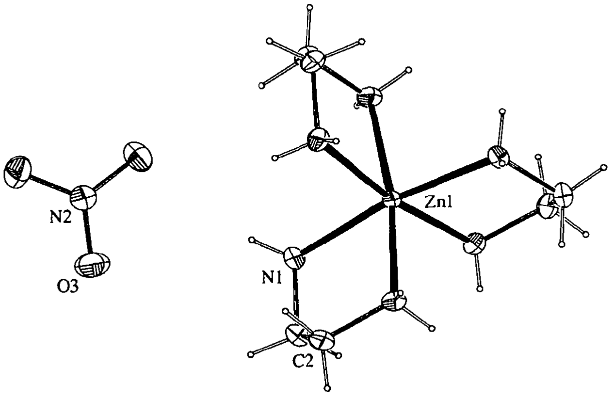

Fig. 1. *ORTEP* (in *PLUTON96*; Spek, 1996) view of tris(ethylenediamine)zinc(II) dinitrate with displacement ellipsoids at the 20% probability level.

Experimental

Ethylenediamine was added to a hot solution containing zinc nitrate and allowed to cool. The transparent crystals formed were recrystallized from water and dried.

Crystal data

$[Zn(C_2H_8N_2)_3](NO_3)_2$
$M_r = 369.70$
Hexagonal
$P6_322$
$a = 8.9289 (6)$ Å
$c = 11.3327 (7)$ Å
$V = 782.46 (9)$ Å^3
$Z = 2$
$D_x = 1.56$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10$–$14°$
$\mu = 1.609$ mm^{-1}
$T = 293 (2)$ K
Plate
0.50 × 0.33 × 0.17 mm
Clear

Data collection

CAD-4 MicroVAX-controlled diffractometer
$2\theta/\omega$ scans
Absorption correction: empirical *via* ψ scan (North, Phillips & Mathews, 1983)
$T_{min} = 0.63$, $T_{max} = 0.76$
1551 measured reflections
470 independent reflections
458 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0345$
$\theta_{max} = 25°$
$h = -10 \rightarrow 9$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0246$
$wR(F^2) = 0.0584$
$S = 1.213$
470 reflections
52 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0373P)^2 + 0.0723P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.214$ e Å^{-3}
$\Delta\rho_{min} = -0.447$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.02 (4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Zn1	1/3	2/3	3/4	0.0323 (2)
N1	0.5502 (3)	0.8622 (3)	0.8542 (2)	0.0456 (5)
C2	0.7077 (3)	0.8646 (5)	0.8147 (3)	0.0574 (6)
N2	2/3	1/3	0.8903 (3)	0.0476 (7)
O3	0.6877 (3)	0.4800 (3)	0.8927 (2)	0.0757 (6)

Table 2. *Selected geometric parameters (Å, °)*

Zn1—N1	2.193 (2)	C2—C2^i	1.479 (6)
N1—C2	1.465 (3)	N2—O3	1.227 (2)
N1—Zn1—N1^i	80.2 (1)	O3^{ii}—N2—O3	119.9 (2)
N1—C2—C2^i	111.3 (2)		

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

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *PLUTON96* (Spek, 1996). Software used to prepare material for publication: *SHELXL93*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: TA1128). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-Bis(cyanamidonitrato-*N*:*O*)bis(imidazole-N^3)copper(II), $[Cu(CN_3O_2)_2(C_3H_4N_2)_2]$

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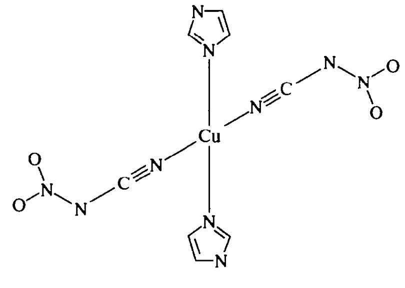
Abstract

The structure of the title compound consists of one-dimensional polymeric chains extending along the **c** direction. They are formed by linking $[Cu(NCNNO_2)_2(iz)_2]$ (iz is imidazole) units together. The cyanamidonitrate anions act as bidentate bridging ligands, with a short Cu—N(nitrile) bond of 2.011 (2) Å in the equatorial plane and a long axial Cu—O bond of 2.687 (3) Å. The Cu atom is located on a centre of symmetry and is pseudo-octahedrally coordinated by two *trans* N(imidazole) atoms [Cu—N 1.936 (2) Å] and two nitrile N atoms, and by two axial O atoms from cyanamidonitrate ligands.

Comment

Non-linear pseudo-halides with different donor atoms are potentially polydentate ligands. In the case of complexes of the MX_2L_2 type (where M = Cu^{II}, Ni^{II}, Co^{II}; X = $N(CN)_2$, $C(CN)_3$, $ONC(CN)_2$; L is a neutral ligand of pyrazole or imidazole type), it is highly probable that the anionic ligand X has a bidentate bridging function, as the coordination number of the central atom is usually six. The metal–ligand bond lengths are approximately equivalent in coordination compounds with bidentate bridging dicyanamide and tricyanomethanide, such as $[Ni\{N(CN)_2\}_2(4\text{-meiz})_2]$ (meiz is methylimidazole) (Kožíšek & Hvastijová, 1997) or $[Co\{C(CN)_3\}_2(2\text{-meiz})_2]$ (Hvastijová, Kožíšek, Kohout, Jäger & Fuess, 1995). On the other hand, in $[Cu\{C(CN)_3\}(\text{pyrazole})_4][C(CN)_3]$ or in $[Cu\{C(CN)_3\}_2(\text{pyrazole})_3]$ (Kožíšek, Hvastijová, Kohout, Mroziński & Köhler, 1991), these bond lengths are quite different. The cyanamidonitrate anion, NO_2NCN^-, contains three potential donor atoms, *i.e.* amide and nitrile N atoms and an O atom. It is preferentially coordinated through the nitrile N atom in, for example, $[Cu(NCNNO_2)_2(1\text{-methylimidazole})_4]$ (Kožíšek & Hvastijová, 1997). In $[(CH_3)_3Sn(NCNNO_2)]$ (Jäger, Tretner, Biedermann & Hartung, 1997*a*), the cyanamidonitrate is bonded in a bidentate bridging manner through the nitrile and amide N atoms. The same coordination mode is observed for the Cu^I and the Ag^I complexes of the type $[M(NCNNO_2)(PPh_3)_2]_2$ (Jäger, Tretner, Biedermann & Hartung, 1997*b*). It was therefore of interest to investigate the bonding in the title complex, (I).



(I)

X-ray analysis confirms the coordination number to be six for the central atom and the bidentate bridging function of the cyanamidonitrato ligand. The bridging mode of cyanamidonitrate through the nitrile N and nitrate O atoms observed here is preferred to that found by Jäger *et al.* (1996*a*,*b*) in Sn, Cu^I and Ag^I complexes.