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Tris(ethylenediamine)nickel(II) tetraiodocadmate(II)

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The title compound, $[Ni(C_6H_{24}N_6)][CdI_4]$, contains two discrete ions, an $[Ni(en)_3]^{2+}$ (en = ethylenediamine) cation and a $[CdI_4]^{2-}$ anion. The Ni^{2+} ion is coordinated by three chelating ethylenediamine ligands in a distorted octahedral geometry while the Cd^{2+} ion binds four iodide ions in a slightly distorted tetrahedron. Both the Ni and Cd atoms lie on threefold axes of rotation. The structure is disordered at cadmium, with two alternative sites for the metal in a 97:3 ratio; the minor component of the disorder inverts the CdI_4 tetrahedron and reverses the direction of propagation of the aligned $[CdI_4]_n{}^{2-}$ units.

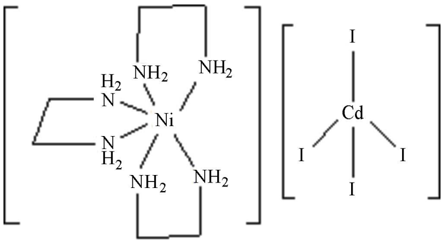
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.018
wR factor = 0.039
Data-to-parameter ratio = 27.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

There has been considerable interest in the development of chemical routes for the deposition of nickel oxide (NiO) and complex oxides containing nickel, which have a number of important industrial applications. For instance, nickel oxide is a component of electrochromic devices such as automotive mirrors and smart windows, optical or electrical gas sensors. (Ozer & Lampert, 1998). Complex (I) (Fig. 1 and Table 1) has been synthesized in a continuation of attempts to obtain suitable precursors for the deposition of complex oxides containing nickel through aerosol-assisted chemical vapour deposition (AACVD) (Sohail *et al.*, 2005).



(I)

The structure is disordered at cadmium, with two alternative sites for the metal in a 97:3 ratio; the minor component of the disorder inverts the CdI_4 tetrahedron and reverses the direction of propagation of the aligned $[CdI_4]_n{}^{2-}$ units. Only the major component of the structure is shown in Fig. 1 and discussed here. Complex (I) contains discrete $[Ni(en)_3]^{2+}$ and $[CdI_4]^{2-}$ ions, with each of the Ni and Cd atoms lying on threefold axes of rotation. The Ni^{II} ion is coordinated by three chelating ethylenediamine ligands, resulting in distorted octahedral geometry. All axial/equatorial N—Ni—N bond angles lie in the range 82.01 (10)–93.47 (12)°, showing a significant distortion, while symmetry dictates that all *trans* N—Ni—N angles are identical [173.05 (11)°], as are all Ni—N

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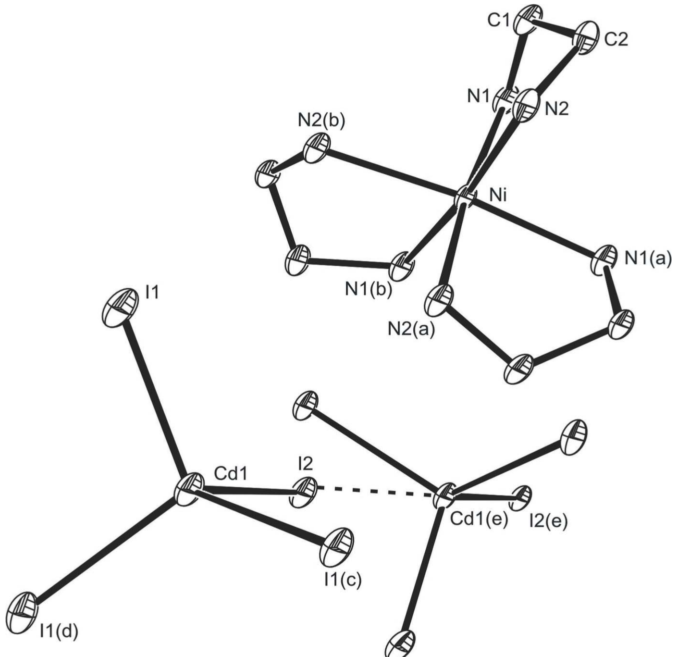

Figure 1
The structure of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 30% probability level. Only the major disorder component is shown. H atoms have been omitted.[Symmetry codes: (*a*) $-y+1, x-y, z$; (*b*) $-x+y+1, -x+1, z$; (*c*) $-x+y, -x+1, z$; (*d*) $-y+1, x-y+1, z$; (*e*) $-x+y, y, z-\frac{1}{2}$.]

bonds [2.130 (3) Å], the latter being slightly longer than analogous bonds in related compounds (Colacio *et al.*, 2003). The Cd^{II} ion in the $[CdI_4]^{2-}$ anion is coordinated by four I atoms with a distorted tetrahedral geometry.

The range of relevant I—Cd1—I bond angles, 105.377 (14)–113.237 (12)°, indicates that the geometry shows some significant deviation from regular tetrahedral, as is the case in other complexes containing $[CdI_4]^{2-}$ (Bailey & Pennington, 1995). The Cd1—I bond lengths are comparable to those of similar compounds (Bengtsson-Kloo *et al.*, 1996). The anions align to allow the cadmium centres to become linked to each other through bridging iodine ligands [I2···Cd1^e = 4.223 (1) Å] [symmetry code: (*e*) $-x+y, y, z-\frac{1}{2}$]. This interaction is weak, and consistent with a lengthening of the Cd—I2 bond [2.7889 (11)] at the limit of detection in comparison with analogous bonds involving non-bridging halogens [2.7815 (15) Å]. However, a flattening of the tetrahedron, evident from the I1—Cd—I1 angle [113.237 (12)°] is evidence of a meaningful anion–anion interaction. The distortions from octahedral and tetrahedral in both of the ions of the complex (I) may result from packing effects and are observed in other such complexes (Kallel & Bats, 1981).

Experimental

Tris(ethylenediammine)nickel(II) bromide, $[Ni(en)_3]Br_2$ (3.199 g, 6.8 mmol), and potassium tetraiodocadmate(II), $K_2[CdI_4]$ (3.62 g, 6.8 mmol), were dissolved in water (30 ml), resulting in the formation of a precipitate of complex (I). This was washed several times with distilled water and recrystallized from ethylene glycol over a two-month period at room temperature.

Crystal data

$[Ni(C_6H_{24}N_6)][CdI_4]$
$M_r = 859.02$
Trigonal, *P*3*c*1
$a = 9.023$ (5) Å
$c = 14.203$ (5) Å
$V = 1001.4$ (9) Å^3
$Z = 2$
$D_x = 2.849$ Mg m^{-3}
Mo *K*α radiation
Cell parameters from 15955 reflections
$\theta = 2.9$–30.0°
$\mu = 8.16$ mm^{-1}
$T = 150$ (2) K
Block, colourless
0.25 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.120$, $T_{max} = 0.195$
21288 measured reflections
1944 independent reflections
1937 reflections with $I > 2\sigma(I)$
$R_{int} = 0.056$
$\theta_{max} = 30.0°$
$h = -11 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.039$
$S = 1.17$
1944 reflections
72 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0075P)^2 + 1.6741P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.99$ e Å^{-3}
$\Delta\rho_{min} = -0.61$ e Å^{-3}
Absolute structure: Flack (1983), 968 Friedel pairs
Flack parameter: 0.00 (3)

Table 1
Selected geometric parameters (Å, °).

Cd1—I1^{i}	2.7815 (15)	Cd1*A*—I1^{i}	2.771 (4)
Cd1—I2	2.7889 (11)	Cd1*A*—I2^{ii}	2.879 (15)
		Ni—N2^{iii}	2.130 (3)
I1^{i}—Cd1—I1^{iv}	113.237 (12)	N2^{iii}—Ni—N2^{v}	92.83 (12)
I1^{i}—Cd1—I2	105.377 (14)	N2^{iii}—Ni—N1^{iii}	82.01 (10)
I1^{i}—Cd1*A*—I1^{iv}	113.90 (2)	N2—Ni—N1^{iii}	173.05 (11)
I1^{i}—Cd1*A*—I2^{ii}	104.60 (3)	N1^{iii}—Ni—N1	93.47 (12)

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

The coordinates of H atoms attached to N atoms were found in difference maps and allowed to refine freely with fixed isotropic displacement parameters. H atoms bound to C atoms were refined using a riding model, with C—H = 0.99 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. *PLATON* (Spek, 2003) reveals metrical relationships among atoms consistent with a higher symmetry space group. The highly symmetric ions also suggest the higher symmetry space group *P*$\bar{6}$*c*2. However, checking the R_{int} values, the structure is unequivocally trigonal ($\bar{3}m1$ or $\bar{3}$ symmetry; $R_{int} < 0.057$). R_{int} for any hexagonal 6/*m* or 6/*mmm* symmetry (or trigonal $\bar{3}1m$) symmetry is > 0.187. Disorder in the occupation of the anions has been resolved and refined, the principal disorder component having an occupancy of 0.972 (8). Analysis of the model considering long-range hydrogen bonds between the cation and the anion favours the 97% position of the anion.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELX97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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$[Ni(C_6H_{24}N_6)][CdI_4]$
$M_r = 859.02$
Trigonal, $P3c1$
Hall symbol: P 3 -2 " c
$a = 9.023$ (5) Å
$c = 14.203$ (5) Å
$V = 1001.4$ (9) Å^3
$Z = 2$
$F(000) = 780$
$D_x = 2.849$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 15955 reflections
$\theta = 2.9$–$30.0°$
$\mu = 8.16$ mm^{-1}
$T = 150$ K
Block, colourless
0.25 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
188 2.0° images with ω scans
Absorption correction: multi-scan (SORTAV; Blessing, 1995)
$T_{min} = 0.120$, $T_{max} = 0.195$
21288 measured reflections
1944 independent reflections
1937 reflections with $I > 2\sigma(I)$
$R_{int} = 0.056$
$\theta_{max} = 30.0°$, $\theta_{min} = 3.9°$
$h = -11 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.039$
$S = 1.17$
1944 reflections
72 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0075P)^2 + 1.6741P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.99$ e Å^{-3}
$\Delta\rho_{min} = -0.61$ e Å^{-3}
Absolute structure: Flack (1983), 968 Friedel pairs
Absolute structure parameter: 0.00 (3)

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. 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 (Å²)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Cd1	0.3333	0.6667	0.29989 (3)	0.01805 (12)	0.972 (2)
Cd1A	0.3333	0.6667	0.1989 (10)	0.013 (4)	0.028 (2)
I1	0.27173 (3)	0.34346 (3)	0.24797 (2)	0.02170 (7)	
I2	0.3333	0.6667	0.49626 (2)	0.01908 (9)	
Ni	0.6667	0.3333	0.50028 (5)	0.01247 (13)	
N1	0.8571 (4)	0.5390 (4)	0.5815 (2)	0.0175 (6)	
H10A	0.815 (6)	0.555 (6)	0.633 (3)	0.021*	
H10B	0.935 (7)	0.520 (6)	0.598 (4)	0.021*	
N2	0.6844 (4)	0.5391 (3)	0.4181 (2)	0.0170 (6)	
H20A	0.731 (7)	0.546 (6)	0.367 (3)	0.02*	
H20B	0.589 (7)	0.523 (6)	0.407 (3)	0.02*	
C1	0.9232 (4)	0.6989 (4)	0.5266 (2)	0.0179 (6)	
H1A	1.0109	0.7079	0.4815	0.021*	
H1B	0.9773	0.7986	0.5695	0.021*	
C2	0.7773 (4)	0.6991 (4)	0.4738 (2)	0.0180 (6)	
H2A	0.6979	0.707	0.519	0.022*	
H2B	0.8228	0.7994	0.4313	0.022*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.01746 (15)	0.01746 (15)	0.0192 (2)	0.00873 (8)	0	0
Cd1A	0.011 (5)	0.011 (5)	0.019 (7)	0.005 (2)	0	0
I1	0.02936 (12)	0.02101 (11)	0.01761 (10)	0.01474 (9)	−0.00047 (8)	−0.00215 (8)
I2	0.01780 (12)	0.01780 (12)	0.02164 (18)	0.00890 (6)	0	0
Ni	0.01157 (18)	0.01157 (18)	0.0143 (3)	0.00578 (9)	0	0
N1	0.0161 (13)	0.0168 (13)	0.0189 (14)	0.0078 (11)	−0.0035 (10)	−0.0007 (10)
N2	0.0179 (13)	0.0171 (13)	0.0176 (14)	0.0100 (11)	−0.0020 (10)	0.0006 (9)
C1	0.0142 (14)	0.0146 (13)	0.0213 (15)	0.0045 (12)	−0.0008 (11)	−0.0007 (11)
C2	0.0187 (14)	0.0135 (13)	0.0228 (15)	0.0089 (12)	−0.0003 (12)	0.0002 (12)

Geometric parameters (Å, º)

Cd1—Cd1A	1.434 (15)	Ni—N1	2.130 (3)
Cd1—I1^{i}	2.7815 (15)	Ni—N1^{vi}	2.130 (3)
Cd1—I1^{ii}	2.7815 (15)	N1—C1	1.477 (4)
Cd1—I1	2.7815 (15)	N1—H10A	0.86 (5)
Cd1—I2	2.7889 (11)	N1—H10B	0.84 (5)
Cd1A—I1^{i}	2.771 (4)	N2—C2	1.484 (4)
Cd1A—I1^{ii}	2.771 (4)	N2—H20A	0.82 (5)

Cd1A—I1	2.771 (4)	N2—H20B	0.81 (5)
Cd1A—I2^{iii}	2.879 (15)	C1—C2	1.516 (5)
I2—Cd1A^{iv}	2.879 (15)	C1—H1A	0.99
Ni—N2^{v}	2.130 (3)	C1—H1B	0.99
Ni—N2^{vi}	2.130 (3)	C2—H2A	0.99
Ni—N2	2.130 (3)	C2—H2B	0.99
Ni—N1^{v}	2.130 (3)		

Cd1A—Cd1—I1^{i}	74.623 (14)	N1^{v}—Ni—N1	93.47 (12)
Cd1A—Cd1—I1^{ii}	74.623 (14)	N2^{v}—Ni—N1^{vi}	173.05 (11)
I1^{i}—Cd1—I1^{ii}	113.237 (12)	N2^{vi}—Ni—N1^{vi}	82.01 (11)
Cd1A—Cd1—I1	74.623 (14)	N2—Ni—N1^{vi}	92.08 (12)
I1^{i}—Cd1—I1	113.237 (12)	N1^{v}—Ni—N1^{vi}	93.47 (12)
I1^{ii}—Cd1—I1	113.237 (12)	N1—Ni—N1^{vi}	93.47 (12)
Cd1A—Cd1—I2	180.00 (2)	C1—N1—Ni	108.7 (2)
I1^{i}—Cd1—I2	105.377 (14)	C1—N1—H10A	106 (3)
I1^{ii}—Cd1—I2	105.377 (14)	Ni—N1—H10A	112 (3)
I1—Cd1—I2	105.377 (14)	C1—N1—H10B	112 (3)
Cd1—Cd1A—I1^{i}	75.40 (3)	Ni—N1—H10B	112 (3)
Cd1—Cd1A—I1^{ii}	75.40 (3)	H10A—N1—H10B	107 (5)
I1^{i}—Cd1A—I1^{ii}	113.90 (2)	C2—N2—Ni	108.4 (2)
Cd1—Cd1A—I1	75.4 (3)	C2—N2—H20A	112 (4)
I1^{i}—Cd1A—I1	113.9 (2)	Ni—N2—H20A	111 (3)
I1^{ii}—Cd1A—I1	113.9 (2)	C2—N2—H20B	108 (3)
Cd1—Cd1A—I2^{iii}	180	Ni—N2—H20B	110 (3)
I1^{i}—Cd1A—I2^{iii}	104.60 (3)	H20A—N2—H20B	107 (5)
I1^{ii}—Cd1A—I2^{iii}	104.60 (3)	N1—C1—C2	109.6 (3)
I1—Cd1A—I2^{iii}	104.60 (3)	N1—C1—H1A	109.8
Cd1A—I1—Cd1	29.9 (3)	C2—C1—H1A	109.8
Cd1—I2—Cd1A^{iv}	180.00 (3)	N1—C1—H1B	109.8
N2^{v}—Ni—N2^{vi}	92.83 (12)	C2—C1—H1B	109.8
N2^{v}—Ni—N2	92.83 (12)	H1A—C1—H1B	108.2
N2^{vi}—Ni—N2	92.83 (12)	N2—C2—C1	109.3 (3)
N2^{v}—Ni—N1^{v}	82.01 (10)	N2—C2—H2A	109.8
N2^{vi}—Ni—N1^{v}	92.08 (12)	C1—C2—H2A	109.8
N2—Ni—N1^{v}	173.05 (11)	N2—C2—H2B	109.8
N2^{v}—Ni—N1	92.08 (12)	C1—C2—H2B	109.8
N2^{vi}—Ni—N1	173.05 (11)	H2A—C2—H2B	108.3
N2—Ni—N1	82.01 (11)		

I1^{ii}—Cd1—Cd1A—I1^{i}	−120.000	N2^{v}—Ni—N1—C1	79.3 (2)
I1—Cd1—Cd1A—I1^{i}	120.000	N2^{vi}—Ni—N1—C1	−55.6 (13)
I1^{i}—Cd1—Cd1A—I1^{ii}	120.000	N2—Ni—N1—C1	−13.2 (2)
I1—Cd1—Cd1A—I1^{ii}	−120.000	N1^{v}—Ni—N1—C1	161.5 (2)
I1^{i}—Cd1—Cd1A—I1	−120.00	N1^{vi}—Ni—N1—C1	−104.8 (3)
I1^{ii}—Cd1—Cd1A—I1	120.00	N2^{v}—Ni—N2—C2	−106.3 (3)
II1^{i}—Cd1A—I1—Cd1	−66.50 (4)	N2^{vi}—Ni—N2—C2	160.7 (2)
I1^{ii}—Cd1A—I1—Cd1	66.50 (4)	N1^{v}—Ni—N2—C2	−64.3 (12)

I2^{iii}—Cd1A—I1—Cd1	180	N1—Ni—N2—C2	−14.6 (2)
I1^{i}—Cd1—I1—Cd1A	65.33 (2)	N1^{vi}—Ni—N2—C2	78.6 (2)
I1^{ii}—Cd1—I1—Cd1A	−65.33 (2)	Ni—N1—C1—C2	38.6 (3)
I2—Cd1—I1—Cd1A	180.000 (2)	Ni—N2—C2—C1	39.6 (3)
Cd1A—Cd1—I2—Cd1A^{iv}	0 (16)	N1—C1—C2—N2	−52.9 (3)

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