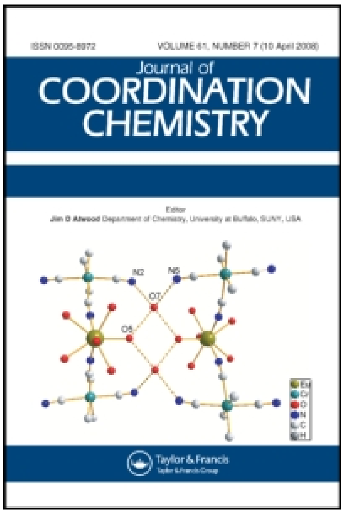

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Second sphere coordination complexes via hydrogen bonding: synthesis, spectroscopic characterization, crystal structure and packing of <i>trans</i> -$[Co(en)_2Cl_2]_2CdI_4$

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Second sphere coordination complexes via hydrogen bonding: synthesis, spectroscopic characterization, crystal structure and packing of *trans*-$[Co(en)_2Cl_2]_2CdI_4$

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Single crystal X-ray structure determination of green single crystals of *trans*-$[Co(en)_2Cl_2]_2CdI_4$ revealed that *trans*-$[Co(en)_2Cl_2]^+$ has octahedral geometry around cobalt(III). Supramolecular hydrogen bonding networks $[NH_{en}^+ \cdots I_{anion}^-]$ in the second coordination sphere and electrostatic forces stabilize crystal lattice. This suggests that *trans*-$[Co(en)_2Cl_2]^+$ is a promising anion receptor for tetraiodocadmate(II).

Keywords: Cobalt(III); Second sphere coordination; Supramolecular chemistry; Tetraiodocadmate(II); Hydrogen bonding; X-ray crystallography

1. Introduction

Coordination of anionic guest species by hydrogen bonds is an area of supramolecular chemistry that continues to attract attention because of the crucial role anions play in biological processes, medicine, catalysis and molecular assembly. The design and synthesis of synthetic anion receptors (binding agents) is a challenging task because of their different shapes and sizes, different charges and pH sensitivity. One class of anions is halocadmates(II).

Recovery of halocadmates(II) is important due to their peculiar properties (related to their polymorphic behavior), impurity, electronic configurations and lattice locations, which are key problems in semiconductor physics [1–3]. Cadmium complexes play an important role in supramolecular [4], bioinorganic [5] and luminescence research [6]. Complex cadmium(II) halide salts are known with cadmium to halide proportions of 1 : 3, 1 : 4, 1 : 5 and 1 : 6 [7]. The structure of the cations and number of hydrogen bonds are important factors to determine the shape of cadmium(II) halide complex anions. The shapes of the complex anions are variable, tetrahedral [8, 9], complex chain

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structures [10–12] and two-dimensional layered structures [13]. The size, shape and charge of the cation plays a role in stabilizing the anion, for example, $CuCl_4^{2-}$ (distorted tetrahedral) is precipitated by R_4N^+, $CuCl_4^{2-}$ (square planar) is precipitated by $[Pt(NH_3)_4]^{2+}$, $CuCl_5^{3-}$ (trigonal bipyramidal) is precipitated by $[Cr(NH_3)_6]^{3+}$ and $CuCl_6^{4-}$ (octahedral) is precipitated by biguanidinium(2+) ion.

Cobalt(III) has applications [14] – as a catalyst in the synthesis and hydrolysis of peptides [15] and as the central metal atom [16] in vitamin B_{12}. Cobalt has influence on human pathophysiological conditions, either from its absence in the body leading to anemic symptoms [17] or in excess leading to toxic effects resulting in heart disease [18]. The role of cobalt(III) complexes in the treatment of biological disorders is well established as potential anti-tumor agents [19].

We chose to study cationic cobaltammines as anion receptors due to their relative inertness towards ligand substitution, their ease of synthesis (in excellent yields) from readily available materials and possibility of ethylenediamine NH_2 hydrogens in $NH \cdots O$ (anion) hydrogen bonding interactions. This article reports the potential of *trans*-$[Co(en)_2Cl_2]^+$ as an anion receptor for tetraiodocadmate(II).

2. Experimental

2.1. *Materials*

Analytical grade reagents were used without purification. The compound *trans*-$[Co(en_2)Cl_2]Cl$ was prepared by the literature method [20].

2.2. *Instruments*

C, H and N were estimated microanalytically by an automatic Perkin Elmer 2400 CHN elemental analyzer and cobalt was determined gravimetrically by the standard method [21]. Infrared spectra was recorded using a Perkin Elmer spectrum RX FT-IR system using Nujol mulls with KBr plates. ^1H and ^{13}C NMR were recorded in D_2O using a JEOL AL 300 MHz FT NMR spectrometer with TMS as internal reference. The UV/Visible spectrum was recorded using a Hitachi 330 spectrometer in H_2O.

2.3. *Synthesis of* trans-*$[Co(en)_2Cl_2]_2CdI_4$ (II)*

trans-$[Co(en)_2Cl_2]Cl$ was synthesized according to literature procedures [20]. An aqueous solution of one gram (0.003 mol) of *trans*-$[Co(en)_2Cl_2]Cl$ was dissolved in 30 mL of water and filtered using fine filter paper. This was added to 1.23 g (0.0017 mol) of potassium tetraiodocadmate(II) dissolved in minimum water.

Potassium tetraiodocadmate(II) used in the reaction was synthesized according to the following scheme:

$$CdCl_2 + 2KI \longrightarrow CdI_2 + 2KCl$$
$$CdI_2 + 2KI \longrightarrow K_2CdI_4$$

Table 1. Crystal data and structure refinement parameters of *trans*-$[Co(en)_2Cl_2]_2CdI_4$.

Empirical formula	$C_8H_{32}CdCl_4Co_2I_4N_8$
Formula weight	1120.08
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions (Å)	
a	19.983(5)
b	12.236(3)
c	24.634(5)
Volume ($Å^3$)	6024(2)
Z, Calculated density ($Mg\,m^{-3}$)	8, 2.470
Absorption coefficient (mm^{-1})	6.256
$F(000)$	4144
Crystal size (mm^3)	$0.42 \times 0.10 \times 0.10$
θ range for data collection	2.04–27.48°
Limiting indices	$-25 \leq h \leq 25$, $-14 \leq k \leq 15$, $-31 \leq l \leq 31$
Reflections collected/unique	45273/6874 [R(int) = 0.0509]
Completeness to $\theta = 27.48$	99.8%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6874/0/245
Goodness-of-fit on F^2	1.074
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0784$, $wR_2 = 0.2430$
R indices (all data)	$R_1 = 0.0861$, $wR_2 = 0.2538$
Extinction coefficient	0.00074(15)
Largest diff. peak and hole ($e\,Å^{-3}$)	2.622 and −4.703

Green crystals of *trans*-$[Co(en)_2Cl_2]_2CdI_4$ appeared within 30 min of mixing the two reactants and were collected by drawing off the mother liquor and air-dried (yield 80%). The complex is soluble in water and DMSO but insoluble in ethanol and acetone. The complex salt decomposes at 180°C. The elemental analysis is consistent with the composition *trans*-$[Co(en)_2Cl_2]_2CdI_4$. Found: (%) C, 8.5; H, 2.8; N, 10.0; Co, 10.5. Calculated: C, 8.7; H, 2.8; N, 9.8; Co, 10.3. Solubility: 0.4 g 100 mL^{-1} at 25°C, $K_{sp} = 1 \times 10^{-5}$.

2.4. *X-ray crystallography*

Intensity data for a crystal with dimensions $0.42 \times 0.10 \times 0.10\,mm^3$ were measured at room temperature on a Rigaku Saturn70 CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined by full-matrix least-squares using SHELXTL-97 [22]. The high residual electron density remaining is due to ripples in the region of the iodide (the distance between the Q1 and I2 is 0.74 Å). Crystallographic data are given in table 1. Selected interatomic parameters are given in table 2 and the numbering scheme employed is shown in figure 1 drawn using SHELXTL-97.

3. Results and discussion

trans-dichlorobis(ethylenediamine)cobalt(III) has played a pivotal role in the development of coordination chemistry. The preparation of common

Table 2. Bond lengths [Å] and angles [°] for *trans*-$[Co(en)_2Cl_2]_2CdI_4$.

I(1)–Cd(1)	2.7915(12)	C(1)–C(2)	1.48(2)
I(2)–Cd(1)	2.7593(13)	C(3)–C(4)	1.51(3)
I(3)–Cd(1)	2.7274(14)	Co(2)–N(8)	1.952(12)
I(4)–Cd(1)	2.7754(14)	Co(2)–N(7)	1.957(10)
Co(1)–N(2)	1.944(13)	Co(2)–N(6)	1.966(11)
Co(1)–N(3)	1.954(13)	Co(2)–N(5)	1.981(9)
Co(1)–N(4)	1.958(11)	Co(2)–Cl(3)	2.237(3)
Co(1)–N(1)	1.961(10)	Co(2)–Cl(4)	2.254(2)
Co(1)–Cl(1)	2.247(3)	N(5)–C(5)	1.458(19)
Co(1)–Cl(2)	2.264(3)	N(6)–C(6)	1.31(3)
N(1)–C(1)	1.491(16)	N(7)–C(7)	1.58(2)
N(2)–C(2)	1.51(2)	N(8)–C(8)	1.43(2)
N(3)–C(3)	1.38(3)	C(5)–C(6)	1.47(3)
N(4)–C(4)	1.43(2)	C(7)–C(8)	1.49(3)
I(3)–Cd(1)–I(2)	106.21(4)	C(1)–C(2)–N(2)	105.6(12)
I(3)–Cd(1)–I(4)	102.40(5)	N(3)–C(3)–C(4)	112.9(14)
I(2)–Cd(1)–I(4)	118.03(5)	N(4)–C(4)–C(3)	106.7(16)
I(3)–Cd(1)–I(1)	111.29(4)	N(8)–Co(2)–C(7)	86.2(5)
I(2)–Cd(1)–I(1)	111.33(4)	N(8)–Co(2)–N(6)	179.3(5)
I(4)–Cd(1)–I(1)	107.24(4)	N(7)–Co(2)–N(6)	93.9(5)
N(2)–Co(1)–N(3)	94.3(7)	N(8)–Co(2)–N(5)	93.8(5)
N(2)–Co(1)–N(4)	179.3(5)	N(7)–Co(2)–N(5)	179.3(4)
N(3)–Co(1)–N(4)	85.0(6)	N(6)–Co(2)–N(5)	86.0(5)
N(2)–Co(1)–N(1)	85.4(5)	N(8)–Co(2)–Cl(3)	91.2(3)
N(3)–Co(1)–N(1)	179.0(5)	N(7)–Co(2)–Cl(3)	89.6(3)
N(4)–Co(1)–N(1)	95.3(4)	N(6)–Co(2)–Cl(3)	89.5(3)
N(2)–Co(1)–Cl(1)	90.2(4)	N(5)–Co(2)–Cl(3)	89.7(3)
N(3)–Co(1)–Cl(1)	90.0(4)	N(8)–Co(2)–Cl(4)	89.3(3)
N(4)–Co(1)–Cl(1)	89.9(3)	N(7)–Co(2)–Cl(4)	90.1(3)
N(1)–Co(1)–Cl(1)	89.0(3)	N(6)–Co(2)–Cl(4)	90.0(3)
N(2)–Co(1)–Cl(2)	91.1(4)	N(5)–Co(2)–Cl(4)	90.6(3)
N(3)–Co(1)–Cl(2)	90.7(4)	Cl(3)–Co(2)–Cl(4)	179.39(14)
N(4)–Co(1)–Cl(2)	88.8(3)	C(5)–N(5)–Co(2)	108.5(9)
N(1)–Co(1)–Cl(2)	90.3(3)	C(6)–N(6)–Co(2)	111.3(11)
Cl(1)–Co(1)–Cl(2)	178.52(13)	C(7)–N(7)–Co(2)	107.8(10)
C(1)–N(1)–Co(1)	109.2(8)	C(8)–N(8)–Co(2)	111.7(11)
C(2)–N(2)–Co(1)	110.0(8)	N(5)–C(5)–C(6)	112.1(14)
C(3)–N(3)–Co(1)	108.4(12)	N(6)–C(6)–C(5)	117.9(16)
C(4)–N(4)–Co(1)	111.6(10)	C(8)–C(7)–N(7)	108.4(12)
C(2)–C(1)–N(1)	108.7(13)		

trans-dichlorobis(ethylenediamine)cobalt(III) salts is often difficult because of hydrolysis [23–26].

In the present work, *trans*-$[Co(en)_2Cl_2]Cl$ and potassium tetraiodocadmate(II) were reacted in appropriate molar ratios in water with the following expectation.

$$2\underset{\text{(Green)}}{trans\text{-}[Co(en)_2Cl_2]Cl} + K_2CdI_4 \xrightarrow{H_2O} \underset{\text{(Green)}}{trans\text{-}[Co(en)_2Cl_2]_2CdI_4} + 2KCl$$

The chemical composition of the complex salt, *trans*-$[Co(en)_2Cl_2]_2CdI_4$, was initially indicated by elemental analysis. Chloride ion was found to be absent so we proposed an ionic structure for the green colored crystalline solid, which is stable in air and light.

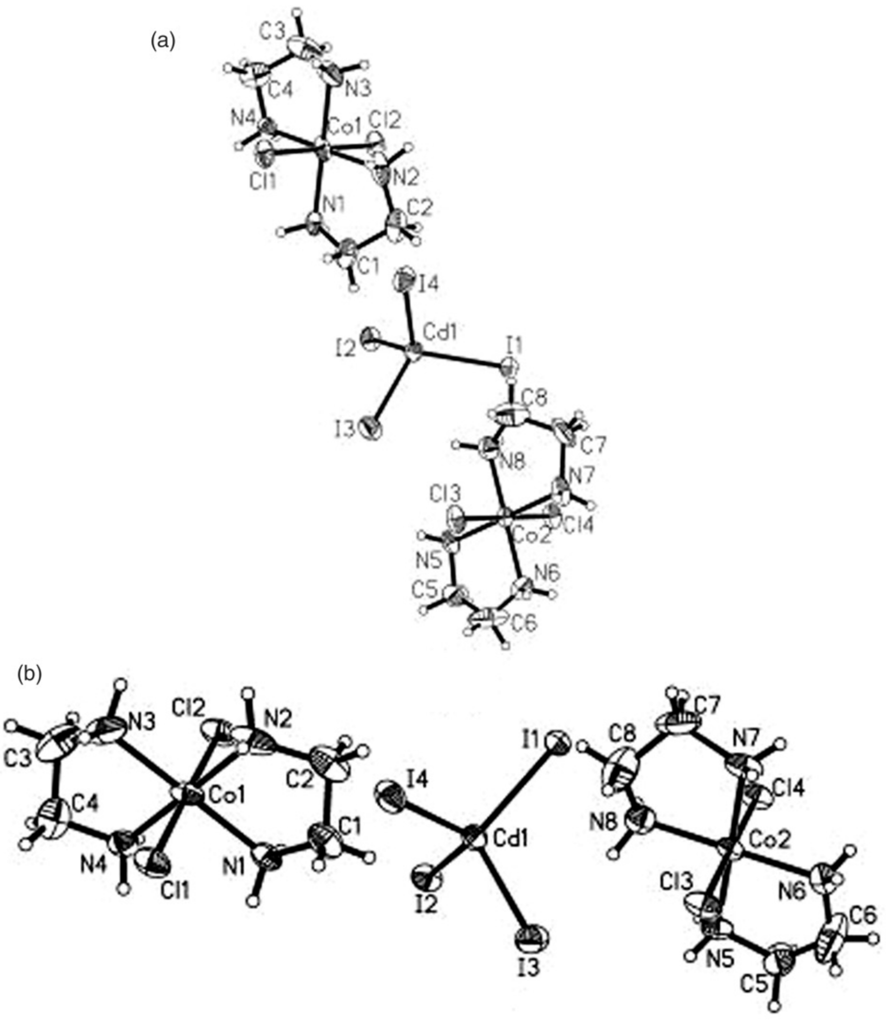

Figure 1. ORTEP diagram of *trans*-$[Co(en)_2Cl_2]_2CdI_4$ at 30% probability displacement ellipsoids.

3.1. *Measurement of solubility product*

Solubilities of ionic salts in water are classified into three categories: (a) solubility > 0.1 M (soluble), (b) solubility between 0.01 and 0.1 M (slightly soluble) and (c) solubility < 0.01 M (sparingly soluble). Solubility product measurements at room temperature show that *trans*-$[Co(en)_2Cl_2]Cl$ is readily soluble in water, whereas *trans*-$[Co(en)_2Cl_2]_2CdI_4$ is sparingly soluble in water. The solubility product of *trans*-$[Co(en)_2Cl_2]_2CdI_4$ is 1.0×10^{-5}.

3.2. *IR spectroscopy*

Infrared spectrum of the newly synthesized complex has been recorded in the region 4000–400 cm^{-1} and tentative assignments have been made on the basis of earlier reports in literature [27]. The IR band at 880 cm^{-1} is assigned to CH_2 rocking region and a band at 1566 cm^{-1} to δNH_2 [28]. The absorption bands for tetraiodocadmate(II) in the far-IR region could not be observed due to limitation of the instrument.

3.3. *Electronic spectroscopy*

The electronic spectrum of the newly synthesized complex has been recorded in H_2O. The UV/visible absorption spectra show absorptions at 617, 346 and 228 nm. These absorptions correspond to d-d transitions typical for octahedral low spin cobalt(III) [29]. These transitions are from $^1A_{1g}$ ground state of cobalt(III) to singlet state $^1T_{1g}$ (low energy) and from $^1A_{1g}$ ground state to $^1T_{2g}$ (higher energy). In the complexes of the type CoA_4B_2 (*cis* or *trans*) the $^1T_{1g}$ state is split, the splitting [30] in *trans* isomer being more, thus justifying three absorption peaks in the UV–Visible spectrum of title complex salt.

3.4. *NMR spectroscopy*

NMR spectra of the complex in D_2O show a signal at 5.2 ppm attributed to nitrogen protons of ethylenediamine while CH_2 protons of ethylenediamine [31] are observed at 2.8 ppm. The ^{13}C NMR spectrum shows the characteristic signal at 44.7 ppm for carbons [32] of ethylenediamine.

3.5. *Crystal structure*

The X-ray crystal structure of *trans*-$[Co(en)_2Cl_2]_2CdI_4$ has been determined by single crystal X-ray crystallography. The title complex salt crystallizes in orthorhombic space group Pbca. The complex salt is composed of discrete ions, two *trans*-$[Co(en)_2Cl_2]^+$ cations and $[CdI_4]^{2-}$ anion. In *trans*-$[Co(en)_2Cl_2]^+$, the cobalt(III) is surrounded by four nitrogen atoms originating from two coordinated ethylenediamine ligands and two chloride ligands resulting in an octahedral geometry. A comparison of bond lengths and bond angles for the cation in the title complex salts with the previously reported salts of this cation in literature [33–35] can be seen in table 3. The ionic character of tetraiodocadmate(II) is indicated by comparison of bond lengths and angles in *trans*-$[Co(en)_2Cl_2]_2CdI_4$ with those of other ionic tetraiodocadmates(II) reported in literature [36]. The average Cd–I bond length and I–Cd–I bond angles are around 2.7 Å and 109.0°, as can be seen from table 3. The corresponding values in the title complex salt are 2.75 Å and 109.1°. The Cd(II) coordination environment is tetrahedral. The Cd–I bond length in the $[CdI_4]^{2-}$ anion is approximately equal to the sum of covalent radii for Cd (1.51) and I (1.33) atoms. Besides electrostatic attraction, an intricate network of $N–H^+ \cdots I^-$ hydrogen bonds involving the second sphere coordination stabilize the crystal lattice of the salt. Each ethylenediamine coordinated to cobalt(III) is capable of acting as hydrogen bond donors through its N–H groups; hydrogen bonding parameters are given in table 4. As shown in figure 2(a), each $[CdI_4]^{2-}$ is hydrogen bonded to four different [*trans*-$Co(en)_2Cl_2]^+$ cations by $N–H \cdots I$. The hydrogen bonds interlink the [*trans*-$Co(en)_2Cl_2]^+$ and $[CdI_4]^{2-}$ building blocks into a two-dimensional framework in the *ab* plane (figure 2b). This particular arrangement is also found in *trans*-$[Co(en)_2Cl_2]_2S_4O_6$, where each tetrathionate links four Co complexes by

Table 3. A comparison of average bond lengths and angles (Å, °) for cation and anion in *trans*-$[Co(en)_2Cl_2]_2CdI_4$.

Cation

Formula of the salt	Bond lengths				Bond angles			Ref.
	Co–N	Co–Cl	C–N	C–C	N–Co–N	Co–N–C	N–Co–Cl	
[*trans*-$Co(en)_2Cl_2]N_3$	1.94(16)	2.25(5)	1.48(3)	1.50(3)	89.4(7)	109.4(12)	89.2(5)	[33]
[*trans*-$Co(en)_2Cl_2]_2S_4O_6$	1.94(2)	2.21(1)	1.48(1)	1.51(4)	85.7(1)	–	90.5(7)	[34]
[*trans*-$Co(en)_2Cl_2]ClO_3$	1.94(16)	2.25(5)	1.48(3)	1.50(3)	89.4(7)	109.4(12)	89.2(5)	[35]
[*trans*-$Co(en)_2Cl_2]BrO_3$	1.95(2)	2.25(8)	1.48(4)	1.51(4)	89.7(10)	109.2(18)	90.5(7)	[35]
[*trans*-$Co(en)_2Cl_2]_2CdI_4$	1.95(12)	2.24(3)	1.45(3)	1.49(3)	89.7(4)	109.5(8)	89.9(4)	This work

Anion

Formula of the salt	Cd–I	I–Cd–I	Ref.
Na_2CdI_4	2.79	–	[36](a)
$[C_4H_{12}N]_2CdI_4$	2.76	110.09	[36](b)
$[C_4H_{12}N_2]CdI_4$	2.78	109.97	[36](c)
trans-$[Co(en)_2Cl_2]_2CdI_4$	2.75	109.1	This work

Table 4. Hydrogen bonding parameters (Å, °) for *trans*-$[Co(en)_2Cl_2]_2CdI_4$.

D–H ··· A	d(D–H)	d(H ··· A)	d(D ··· A)	∠(DHA)
N3–H3D ··· I4^a	0.90	3.02	3.645(11)	128.2
N6–H6C ··· I4^b	0.90	2.89	3.754(10)	160.6
N6–H6D ··· I1^c	0.90	2.93	3.688(10)	143.2
N8–H8C ··· I1	0.90	2.92	3.701(10)	145.9
N8–H8D ··· I3	0.90	2.75	3.567(11)	151.5

Symmetry code: a: $0.5-x, -0.5+y, z$; b: $0.5+x, y, 1.5-z$; c: $1.5-x, -0.5+y, z$.

N–H ··· O hydrogen bonds [34]. The crystal architecture of *trans*-$[Co(en)_2Cl_2]_2S_4O_6$ is given in the Supplemental data. In *trans*-$[Co(en)_2Cl_2]X$, where $X = ClO_3$, BrO_3 and N_3 the packing is different although N–H ··· O/N is observed.

4. Conclusions

The potential of *trans*-$[Co(en)_2Cl_2]^+$ as anion receptor for $[CdI_4]^{2-}$ has been explored by isolating and characterizing a new anhydrous salt *trans*-$[Co(en)_2Cl_2]_2CdI_4$. X-ray crystal structure determination reveals discrete ions. Electrostatic forces and hydrogen bonding interactions involving second sphere coordination stabilize the crystal structure. The tetraiodocadmate(II) anions are sandwiched between the layers of cations and provide stability through $N–H^+ \cdots I^-$ hydrogen bonding interactions. *trans*-$[Co(en)_2Cl_2]^+$ is a promising cationic complex for molecular recognition of $[CdI_4]^{2-}$ anion in aqueous medium in contrast to other receptors which are effective in non-aqueous solvents. The solubility product measurement showed that the affinity of *trans*-$[Co(en)_2Cl_2]^+$ is greater for $[CdI_4]^{2-}$ than chloride.

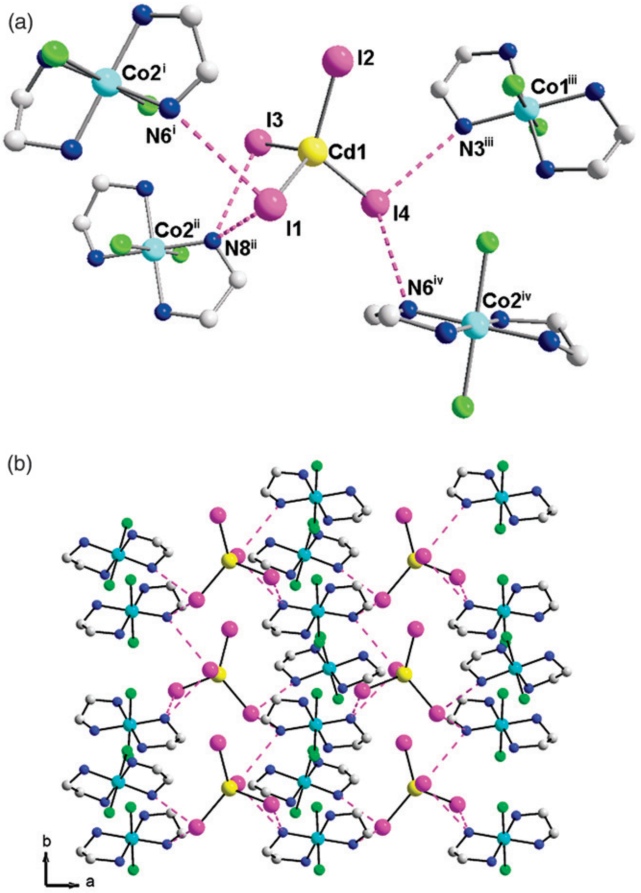

Figure 2. (a) A view of the $[CdI_4]^{2-}$ environment stabilized by hydrogen bonds [symmetry codes: (i) $-2+x$, y, $-1+z$; (ii) $-0.5-x$, $-0.5+y$, $-1+z$; (iii) $-1+x$, y, $-1+z$; (iv) $-x$, $-0.5+y$, $0.5-z$.]; (b) view of the two-dimensional hydrogen-bonding framework in *trans*-$[Co(en)_2Cl_2]_2CdI_4$.

Supplementary data

Crystallographic data for the structural analysis of the title compound has been deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK and are available free of charge from the Director on request quoting deposition number CCDC 650937 (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

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