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A new cobalt(III) ethylenediamine complex with mixed halide counter-anions, $[Co(en)_3](Cl)(I)_2{\cdot}H_2O$

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Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.005 Å
R factor = 0.053
wR factor = 0.097
Data-to-parameter ratio = 19.1

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

The hydrothermal reaction of ethylenediamine with $CoCl_2{\cdot}6H_2O$ yielded tris(ethylenediamine-κ^2N,N')cobalt(III) chloride diiodide monohydrate, $[Co(C_2H_8N_2)_3](Cl)(I)_2{\cdot}H_2O$, which consists of $[Co(en)_3]^{3+}$ cations, Cl^- and I^- anions, and solvent water molecules. The Cl^- anions bridge the $[Co(en)_3]^{3+}$ complexes to form two-dimensional honeycomb-like layers through N—H···Cl hydrogen bonds, which stack along the c direction to form channels hosting I^- ions and water molecules.

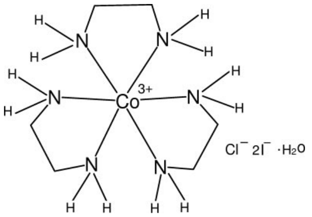
Comment

Due to the excellent coordination ability of nitrogen-containing ligands, research on transition metal complexes involving ligands which coordinate through an N atom, such as simple amines (Mitzi, 1996; Deeth *et al.*, 1984), cyanides (Wu *et al.*, 2003; Shores *et al.*, 2002), or *N*-heterocyclic rings (Hagrman *et al.*, 1999; Willett *et al.*, 2001;), has always been an active area in coordination chemistry. Within this field, great progress has been made in research on transition metal–amino complexes, including mono- (Mitzi, 1996), di- (Bu *et al.*, 2000; Ren *et al.*, 2001), tri- (Moreland & Rauchfuss, 2000) and multi-amino ligands (Goreshnik *et al.*, 2002), while transition metal di-amino complexes have been extensively studied. The asymmetric complexes $[M(\mathrm{en})_mL_n]$ (M = transition metal, en = ethylenediamine, L = anion, m = 1–3, n = 1–3), derived from the bidentate en ligand chelated to transition metals, are suitable as active intermediates or templates to produce chiral coordination complexes (Yu *et al.*, 2001; Moron *et al.*, 1994; Nakashima *et al.*, 2003). For example, Morgan *et al.* (1995) and Gray *et al.* (1997) have employed chiral metal complexes as templating agents which provide the possibility of designing chiral nanoporous materials. Chiral templates involving paramagnetic metals promote the successful synthesis of molecular ferromagnets and ferrimagnets.

It is noteworthy that the anions which balance the $[Co(en)_3]^{3+}$ complex cation are mainly of two types. Firstly, there are complexes with only one kind of anion in the system, such as $[Co(en)_3]F_3$ (Spinat *et al.*, 1981), $[Co(en)_3]Cl_3$ (Whuler *et al.*, 1975), $[Co(en)_3]Br_3$ (Nakatsu, 1962) and $[Co(en)_3]I_3$ (Matsuki *et al.*, 2001). Secondly, there are complexes with mixed anions in the system, such as $[Co(en)_3]_2(I_4)(C_2O_4)_2{\cdot}D_2O$ (Myrczek, 1997), $[Co(en)_3](Br)(C_4H_4O_6){\cdot}5H_2O$ (Kushi *et al.*, 1976), $[Co(en)_3](HgICl_3)(Cl)$ (House *et al.*, 1989) and $[Co(en)_3]_2[Fe(CN)_6]I_2{\cdot}4.6H_2O$ (Kotov & Ilyukhin, 2003). In this paper, we report the synthesis and crystal structure of the title Co^{III}–en complex with mixed halide anions, $[Co(en)_3](Cl)(I)_2{\cdot}H_2O$, (I).

The asymmetric unit of complex (I) is composed of two independent part-cations, in which atom Co1 resides in the 4f

position and atom Co2 in the 2*c* position, Cl^- on a twofold axis, one independent I^- anion, and one water molecule, as shown in Fig. 1. In the $[Co(en)_3]^{3+}$ cations, the Co^{III} ions display distorted octahedral coordination, surrounded by six N atoms from three neutral ethylenediamine ligands, which function as bidentate ligands, to form five-membered rings. The Co—N bond lengths are in the range 1.936 (3)–1.983 (3) Å, comparable with those found in other Co^{III}–en complexes, such as $[Co(en)_3]Cl_3$ (Whuler *et al.*, 1975) and $[Co(en)_3](FeCl_6)$ (Moron *et al.*, 1994), in which the average Co^{III}—N bond lengths are 1.96 and 1.97 Å, respectively. According to the nomenclature of Saito (1979), the configurations of the ethylenediamine rings in (I) are $\Lambda(\lambda\lambda\lambda)$ and $\Delta(\delta\delta\delta)$.



(I)

Three chloride anions bridge two Co1 complexes through N—H···Cl hydrogen bonds, with a Cl1···N11 distance of 3.305 (3) Å (Fig. 2, Table 1). Three groups are connected to three Co2 complexes *via* N—H···Cl hydrogen bonds, with a Cl1···N21 distance of 3.278 (4) Å, to form hexagonal rings, which share edges with each other to form a honeycomb-like layer in the *ab* plane (Fig. 3). These two-dimensional sheets are stacked in a parallel fashion to form a three-dimensional structure, with channels in which discrete I^- ions and water molecules are located. It is interesting that there are empty voids with a volume of 177 $Å^3$ in the crystal structure.

Similar to known complexes containing mixed halide anions, such as $[Pt(en)(Guo)_2](ClI)$ (Guo = guanosine; Garner *et al.*, 1975), *cis*-$[Cr(cyclam)(OH)(H_2O)](ClI)$ (Goodson *et al.*, 1994) and $[CuL](ICl)$ (*L* is a 24-membered hexaazadiphenol macrocyclic ligand; Kong *et al.*, 2001), in which the Cl^- and I^- anions come from the different reagents or the solution medium, the mixed Cl^- and I^- anions in (I) come from the $CoCl_2\cdot6H_2O$ reagent and a concentrated HI solution.

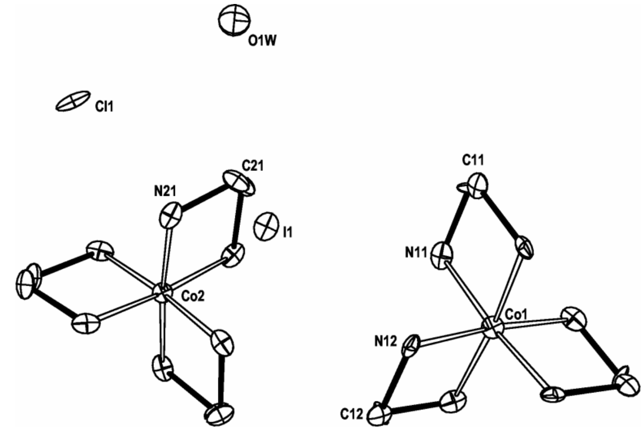


Figure 1
The asymmetric unit and symmetry-generated ligands of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

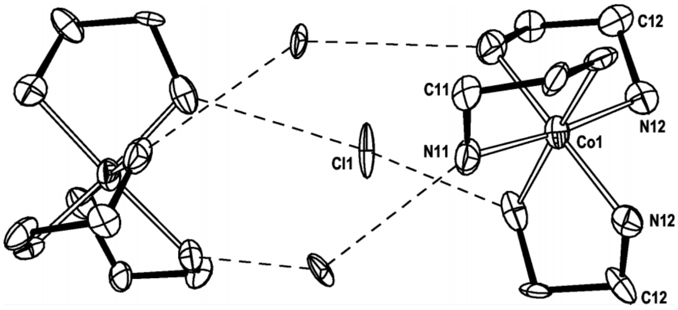


Figure 2
A view of two $[Co1(en)_3]^{3+}$ complexes bridged by Cl^- anions *via* N—H···Cl hydrogen bonds (dashed lines).

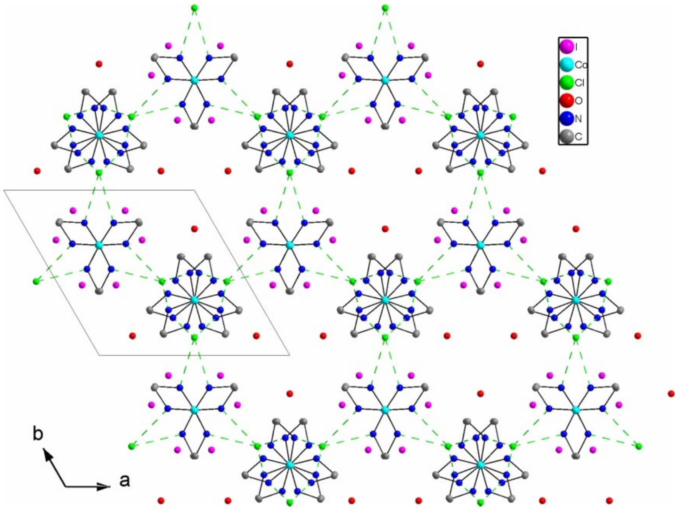


Figure 3
The crystal structure of (I), viewed along the *c* axis. H atoms have been omitted.

Experimental

A mixture of $CoCl_2\cdot6H_2O$ (0.5 mmol, 119 mg), HI (4 ml), ethylenediamine (1 ml) and ethanol (2 ml) was heated at 453 K for 2 d under autogeneous pressure in a sealed 25 ml Teflon-lined stainless steel vessel, and then cooled down to room temperature over 2 d. The resulting mixture was filtered and orange prismatic crystals of (I) were obtained from the filtrate after several days (yield 30% based on $CoCl_2\cdot6H_2O$).

Crystal data

$[Co(C_2H_8N_2)_3](Cl)(I)_2\cdot H_2O$
M_r = 546.51
Hexagonal, $P6_322$
a = 11.2374 (8) Å
c = 24.648 (3) Å
V = 2695.5 (4) $Å^3$
Z = 6
D_x = 2.020 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 425 reflections
θ = 3.2–27.5°
μ = 4.54 mm^{-1}
T = 293 (2) K
Prism, orange
0.40 × 0.30 × 0.20 mm

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Data collection

Rigaku Mercury CCD area-detector diffractometer	1588 independent reflections
ω scans	1081 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SPHERE* in *CrystalClear*; Rigaku, 2002)	$R_{\rm int} = 0.099$
$T_{\rm min} = 0.288$, $T_{\rm max} = 0.404$	$\theta_{\rm max} = 25.0°$
16 790 measured reflections	$h = -13 \rightarrow 13$
	$k = -13 \rightarrow 13$
	$l = -29 \rightarrow 29$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0013P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.053$	$(\Delta/\sigma)_{\rm max} = 0.003$
$wR(F^2) = 0.097$	$\Delta\rho_{\rm max} = 1.72$ e Å^{-3}
$S = 1.01$	$\Delta\rho_{\rm min} = -0.93$ e Å^{-3}
1588 reflections	Absolute structure: Flack (1983), with 578 Friedel pairs
83 parameters	Flack parameter = 0.09 (14)
H atoms treated by a mixture of independent and constrained refinement	

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

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D\cdots A$	D—H$\cdots$$A$
N21—H21$A$$\cdots$Cl1	0.90	2.42	3.278 (4)	160
N11—H11$A$$\cdots$Cl1$^{\rm i}$	0.90	2.61	3.305 (3)	135

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

Water H atoms were located from a difference Fourier map, and refined with the O—H bond distance restrained to 0.93 Å. All other H atoms were allowed to ride on their respective parent atoms, with C—H distances of 0.97 Å and N—H distances of 0.90 Å, and were included in the structure factor calculations with assigned isotropic displacement parameters of $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(C,N). The centers of the voids are situated at (0,0,0) and $(0,0,\frac{1}{2})$, and the highest residual peak is located around the voids. When the peak was assigned as lattice water, the site-occupancy factor was very small and so this water was omitted from the structure.

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* and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL*.

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References

Brandenburg, K. (1999). *DIAMOND*. Version 2.1c. Crystal Impact GbR, Bonn, Germany.

Bu, X. H., Feng, P. Y. & Stucky, G. D. (2000). *Chem. Mater.* **12**, 1505–1507.

Deeth, R. J., Hitchman, M. A. & Sachs, H. (1984). *Inorg. Chem.* **23**, 1310–1320.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Garner, A. W., Timberlake, J. W., Engel, P. S. & Melaugh, R. A. (1975). *J. Am. Chem. Soc.* **97**, 7379–7380.

Goodson, P. A., Glerup, J., Hodgson, D. J., Michelsen, K. & Rychlewska, U. (1994). *Inorg. Chem.* **33**, 359–366.

Goreshnik, E., Leblanc, M. & Maisonneuve, V. (2002). *Z. Anorg. Allg. Chem.* **628**, 162–166.

Gray, M. J., Jasper, J. D., Wilkinson, A. P. & Hanson, J. C. (1997). *Chem. Mater.* **9**, 976–980.

Hagrman, P. J., Hagrman, D. & Zubieta, J. (1999). *Angew. Chem. Int. Ed.* **38**, 2638–2684.

House, D. A., McKee, V. & Robinson, W. T. (1989). *Inorg. Chim. Acta*, **160**, 71–76.

Kong, D. Y., Martell, A. E., Motekaitis, R. J. & Reibenspies, J. H. (2001). *Inorg. Chim. Acta*, **317**, 243–251.

Kotov, V. Yu. & Ilyukhin, A. B. (2003). *Mendeleev Commun.* **13**, 169–170.

Kushi, Y., Kuramoto, M. & Yoneda, H. (1976). *Chem. Lett.* pp. 135–136.

Matsuki, R., Shiro, M., Asahi, T. & Asai, H. (2001). *Acta Cryst.* E**57**, m448–m450.

Mitzi, D. B. (1996). *Chem. Mater.* **8**, 791–800.

Moreland, A. C. & Rauchfuss, T. B. (2000). *Inorg. Chem.* **39**, 3029–3036.

Morgan, K., Gainsford, G. & Milestione, N. (1995). *J. Chem. Soc. Chem. Commun.* pp. 425–426.

Moron, M. C., Palacio, F. & Pons, J. (1994). *Inorg. Chem.* **33**, 746–753.

Myrczek, J. (1997). *Pol. J. Chem.* **71**, 844–847.

Nakashima, T., Mishiro, J., Ito, M., Kura, G., Ikuta, Y., Matsumoto, N., Nakajima, K. & Kojima, M. (2003). *Inorg. Chem.* **42**, 2323–2330.

Nakatsu, K. (1962). *Bull. Chem. Soc. Jpn*, **35**, 832–839.

Ren, C. X., Zhu, H. L. Yang, G. & Chen, X. M. (2001). *J. Chem. Soc. Dalton Trans.* pp. 85–90.

Rigaku (2002). *CrystalClear.* Version 1.35. Rigaku Corporation, 3–9–12 Akishima, Tokyo, Japan.

Saito, Y. (1979). *Inorganic Molecular Dissymmetry*, pp. 56–59. Berlin: Springer-Verlag

Shores, M. P., Sokol, J. J. & Long, J. R. (2002). *J. Am. Chem. Soc.* **124**, 2279–2292.

Siemens (1994). *SHELXTL.* Release 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Spinat, P., Whuler, A. & Brouty, C. (1981). *J. Appl. Cryst.* **14**, 211–212.

Whuler, P. A., Brouty, C. & Spinat, P. (1975). *Acta Cryst.* B**31**, 2069–2076.

Willett, R. D., Pon, G. & Nagy, C. (2001). *Inorg. Chem.* **40**, 4342–4352.

Wu, A.-Q., Cai, L.-Z., Chen, W.-T., Guo, G.-C. & Huang, J.-S. (2003). *Acta Cryst.* C**59**, m491–m493.

Yu, J. H., Wang, Y., Shi, Z. & Xu, R. R. (2001). *Chem. Mater.* **13**, 2972–2978.

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