Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Second-sphere coordination in anion binding: *cis*-diazidobis(ethylenediamine-κ^2N,N')cobalt(III) picrate

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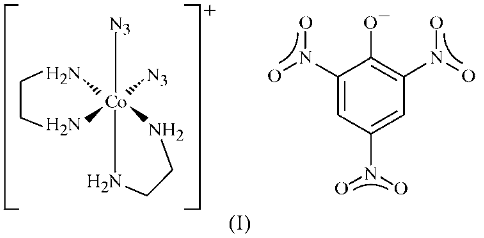
Received 30 March 2005
Accepted 18 April 2005
Online 13 May 2005

In the title compound, $[Co(N_3)_2(C_2H_8N_2)_2](C_6H_2N_3O_7)$, the cations share $NH_2\cdots NH_2$ edges with picrate anions *via* second-sphere N—H⋯O hydrogen bonds.

Comment

We are currently engaged in studies to explore cobalt(III) complexes as potential anion receptors and have previously reported the crystal structures of some *cis*-diazidobis(ethylenediamine)cobalt(III) salts (Sharma *et al.*, 2003). The $[cis\text{-}Co(N_3)_2(en)_2]^+$ cation (en is ethylenediamine) has also been characterized as a nitrate salt (Padmanabhan *et al.*, 1968; Kastner *et al.*, 1989). In continuation of our interest in this class of compounds, we describe here the synthesis and crystal structure of the title complex salt, $[cis\text{-}Co(N_3)_2(en)_2](C_6H_2N_3O_7)$, (I) (Fig. 1).



(I)

The cation and anion in (I) are segregated into layers lying approximately in the (004) planes. The $[cis\text{-}Co(N_3)_2(en)_2]^+$ cations form bilayers, into which the azide ligands interdigitate (Fig. 2). Within these bilayers, several N—H⋯N hydrogen bonds are formed with acceptor N atoms of the azide moieties (Table 2). The interactions N8—H8*B*⋯N3 and N7—H7*A*⋯N6 are formed to the terminal (non-coordinated) N atom of each azide moiety, with the N—H vector in each case being close to collinear with the N_3 axis. The interactions N10—H10*A*⋯N1 and N10—H10*B*⋯N4 are formed with acceptor N atoms bound directly to atom Co1. In these cases, the geometry at the N-atom acceptor is such that the interaction can be envisaged as involving a lone pair of electrons on an sp^2-hybridized N atom.

In the layers of picrate anions, the benzene rings lie approximately perpendicular to the layer planes, forming a herring-bone-type arrangement (Fig. 3). One NO_2 group of

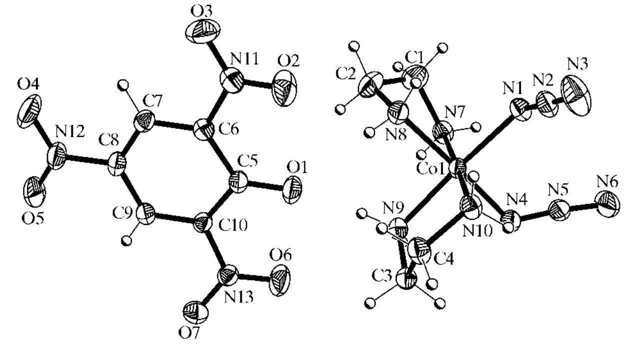


Figure 1
The molecular units in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radius.

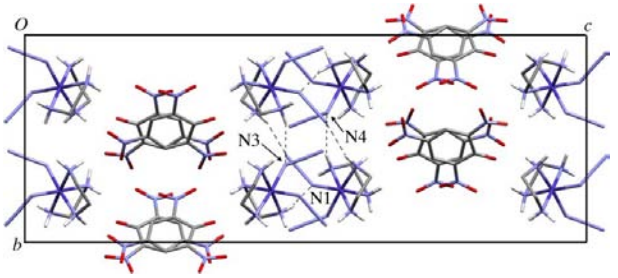


Figure 2
A projection along [100], showing bilayers of $[trans\text{-}Co(N_3)_2(en)_2]^+$ cations and layers of picrate anions lying approximately in (004). N—H⋯N hydrogen bonds are depicted as dashed lines in the central $[trans\text{-}Co(N_3)_2(en)_2]^+$ bilayer and the acceptor atoms are labelled. Atoms N1, N3 and N4 are at the symmetry positions $(\frac{1}{2}-x, 1-y, \frac{1}{2}+z)$, $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$ and $(x, \frac{1}{2}-y, \frac{1}{2}+z)$, respectively. H atoms bound to C atoms have been omitted for clarity.

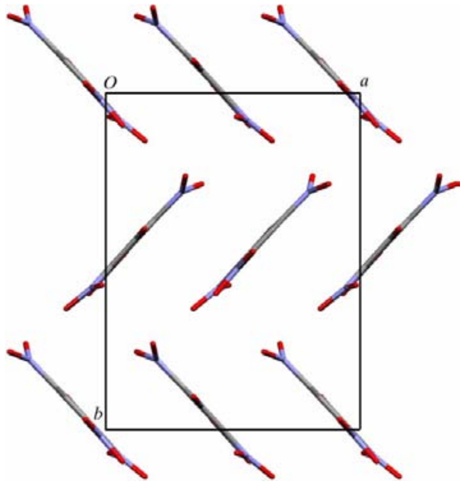


Figure 3
A projection along [001] on to the plane of a single layer of picrate anions, showing the herring-bone-type arrangement.

DOI: 10.1107/S0108270105011960

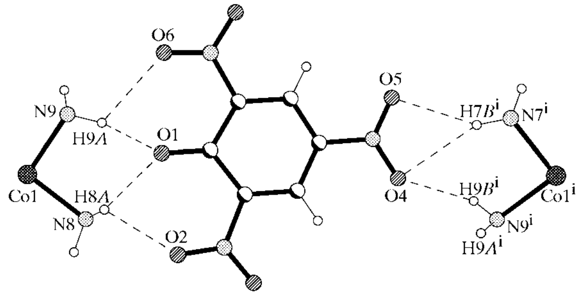


Figure 4
Second-sphere hydrogen-bond interactions between the cationic and anionic moieties. [Symmetry code: (i) $-x, \frac{1}{2}+y, \frac{1}{2}-z$.]

each anion lies approximately in the plane, and the C—O$^-$ bonds in adjacent molecules project alternately above and below the plane.

Of most interest from the perspective of anion–cation recognition is the arrangement of the second-sphere hydrogen-bond interactions at the interface between the picrate layers and the [*cis*-Co(N$_3$)$_2$(en)$_2$]$^+$ bilayers. The edge of each picrate anion that contains the phenoxy O atom interacts with an NH$_2$···NH$_2$ edge of an adjacent [*cis*-Co(N$_3$)$_2$(en)$_2$]$^+$ cation, forming complementary sets of N—H···O hydrogen bonds that are bifurcated at the N—H donor (Table 2 and Fig. 4). The remaining NO$_2$ group also interacts essentially with a single NH$_2$···NH$_2$ edge, accepting N—H···O hydrogen bonds from N7—H7 that are bifurcated at the donor (Table 1 and Fig. 4). Atom O4 of this nitrate group lies approximately along the bisector of the H9*A*—N9—H9*B* angle, slightly displaced towards H9*B*, so that it accepts N—H···O hydrogen bonds that are bifurcated at the acceptor.

Experimental

The complex salt [*cis*-Co(N$_3$)$_2$(en)$_2$]NO$_3$ was prepared according to the literature method of Staples & Tobe (1960). [*cis*-Co(N$_3$)$_2$(en)$_2$]NO$_3$ (1 g, 0.003 mol) was dissolved in water (100 ml) in a beaker. In a second beaker, NaOH (0.1362 g, 0.003 mol) was dissolved in a minimum amount of water and picric acid (0.7116 g, 0.003 mol) was added. The two clear solutions were mixed and the resulting brown precipitate was filtered off and dried in air. This solid was dissolved in a 3:1 acetone–water mixture and slow evaporation at room temperature afforded red–black single crystals of (I) suitable for X-ray structure determination within one week. The complex salt (m.p. 453 K) is soluble in water and dimethyl sulfoxide, and fairly soluble in acetone. Elemental analysis found: Co 12.04, C 24.80, H 3.82, N 37.25%; calculated for $C_{10}H_{18}CoN_{13}O_7$: Co 12.00, C 24.42, H 3.66, N 37.04%.

Crystal data

[Co(N$_3$)$_2$(C$_2$H$_8$N$_2$)$_2$](C$_6$H$_2$N$_3$O$_7$)
$M_r = 491.30$
Orthorhombic, *Pbca*
$a = 9.1229$ (3) Å
$b = 12.0980$ (5) Å
$c = 32.8793$ (12) Å
$V = 3628.9$ (2) Å^3
$Z = 8$
$D_x = 1.799$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 6972 reflections
$\theta = 2.7$–31.3°
$\mu = 1.02$ mm^{-1}
$T = 180$ (2) K
Block, red–black
0.25 × 0.25 × 0.20 mm

Data collection

Bruker Nonius X8 APEX-II CCD area-detector diffractometer
Thin–slice ω and φ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.703$, $T_{\max} = 0.822$
20 066 measured reflections
4649 independent reflections
3930 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.020$
$\theta_{\max} = 29.5°$
$h = -12 \rightarrow 12$
$k = -15 \rightarrow 13$
$l = -43 \rightarrow 44$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.115$
$S = 1.04$
4649 reflections
280 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0559P)^2 + 4.5267P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.39$ e Å^{-3}
$\Delta\rho_{\min} = -0.43$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—N10	1.9560 (18)	Co1—N4	1.9602 (19)
Co1—N7	1.9594 (19)	Co1—N1	1.9613 (18)
Co1—N8	1.9595 (19)	Co1—N9	1.9779 (17)
N10—Co1—N7	178.14 (8)	N8—Co1—N1	90.76 (8)
N10—Co1—N8	92.53 (8)	N4—Co1—N1	91.84 (8)
N7—Co1—N8	85.68 (9)	N10—Co1—N9	85.07 (7)
N10—Co1—N4	91.83 (8)	N7—Co1—N9	94.47 (8)
N7—Co1—N4	89.93 (8)	N8—Co1—N9	91.84 (8)
N8—Co1—N4	174.78 (8)	N4—Co1—N9	85.68 (8)
N10—Co1—N1	93.43 (8)	N1—Co1—N9	177.05 (8)
N7—Co1—N1	87.11 (8)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N7—H7*A*···N6^i	0.92	2.31	3.184 (3)	158
N7—H7*B*···O4^v	0.92	2.48	3.312 (3)	151
N7—H7*B*···O5^v	0.92	2.34	3.164 (3)	149
N8—H8*A*···O1	0.92	2.16	2.948 (3)	143
N8—H8*A*···O2	0.92	2.38	3.025 (3)	128
N8—H8*B*···N3^{ii}	0.92	2.37	3.194 (3)	149
N9—H9*A*···O1	0.92	2.02	2.839 (2)	148
N9—H9*A*···O6	0.92	2.51	3.045 (3)	117
N9—H9*B*···O4^v	0.92	2.41	2.897 (3)	113
N10—H10*A*···N1^{iii}	0.92	2.37	3.248 (3)	161
N10—H10*B*···N4^{iv}	0.92	2.66	3.336 (3)	131

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

The largest peak in the difference density map lies in the vicinity of atom Co1. All H atoms were placed in calculated positions and allowed to ride during subsequent refinement, with C—H = 0.95 Å and N—H = 0.92 Å, and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(C,N).

Data collection: *APEX2* (Bruker–Nonius, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

RS and RPS gratefully acknowledge the financial support of the UGC [grant No. F.12–38/2003(SR)]. ADB is grateful to the

Danish Natural Science Research Council (SNF) and Carlsbergfondet (Denmark) for provision of the X-ray equipment.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1132). Services for accessing these data are described at the back of the journal.

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