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Second-sphere coordination in anion binding: *trans*-bis(ethylenediamine-κ^2N,N')dinitrocobalt(**III**) periodate

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In the title complex, $[Co(NH_2CH_2CH_2NH_2)_2(NO_2)_2](IO_4)$, the cations are situated on two sets of inversion centres and are linked by pairs of complementary N—H···O hydrogen bonds into columns arranged in an approximately hexagonal manner. The periodate anions can be envisaged as occupying triangular hollows above and below approximate hexagonal close-packed layers of *trans*-bis(ethylenediamine-κ^2N,N')-dinitrocobalt(III) cations.

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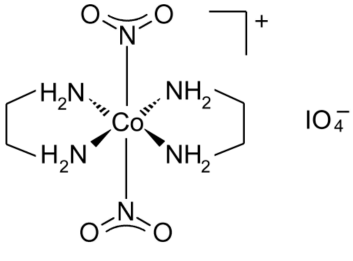
Key indicators

Single-crystal X-ray study
T = 180 K
Mean σ(C–C) = 0.002 Å
R factor = 0.015
wR factor = 0.041
Data-to-parameter ratio = 26.4

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

Comment

In the course of studies to explore cobalt(III) complexes as potential anion receptors, we have recently reported the crystal structures of several salts of *trans*-dinitrobis(ethylenediamine-*N*,*N*′)cobalt(III), including $[trans\text{-}Co(en)_2(NO_2)_2]^+$ dichromate and saccharinate (Sharma, Sharma, Bala & Venugopalan, 2005; Sharma, Sharma, Bala, Quiros & Salas, 2005). The $[Co(en)_2(NO_2)_2]^+$ cation has also been characterized in the crystal structures of numerous other complex salts. The *cis* isomer of the cation is most prevalent among these, having been observed, for example, in combination with halide anions (Bernal, 1985; Frederiksen *et al.*, 1988), polyatomic anions, such as nitrite (Bernal *et al.*, 1990; Marsh, 1997), and organic anions, such as malate and tartrate (Sun *et al.*, 1998; Frederiksen *et al.*, 1988; Sun *et al.*, 2000). The *trans* isomer has been observed less frequently, in combination with iodide and thiocyanate (Bernal & Cetrullo, 1986), and with nitrate (Bortin, 1976). Notably, in the context of this report, the *trans* isomer has previously been characterized in combination with the tetrahedral anions perchlorate and tetrafluoroborate, BF_4^-. The perchlorate salt has been reported on two occasions. One structure is isostructural with the BF_4^- salt, space group $P\overline{1}$, a = 6.718 (1), b = 13.595 (1) and c = 15.637 (1) Å, and α = 114.015 (4), β = 95.196 (3) and γ = 94.984 (3)°, with Z = 4 (Maxcy & Turnbull, 1999). A second structure has also been suggested, in space group $P\overline{1}$, with a = 6.581 (2), b = 8.274 (1) and c = 12.660 (3) Å, and α = 77.28 (2), β = 76.58 (2) and γ = 75.20 (2)°, with Z = 2 (Bernal *et al.*, 1999). The two structures appear to be identical: transformation of the Bernal structure by the matrix (1 0 0, 0 1 −1, −1 1 1) gives a = 6.581, b = 13.513 and c = 15.864 Å, and α = 113.76, β = 95.53 and γ = 93.50°. In the smaller unit cell, the perchlorate anions display orientational disorder, which is mostly resolved on moving to the larger cell. The title periodate complex, $[trans\text{-}Co(en)_2(NO_2)_2]^+(IO_4^-)$, (I) (Fig. 1), exhibits a structure different from that of the perchlorate and BF_4^- salts.



(I)

The structure of (I) contains [*trans*-$Co(en)_2(NO_2)_2$]$^+$ cations situated on two sets of inversion centres. The cations may be envisaged to lie in columns along [$01\overline{1}$], linked by pairs of complementary N—H$\cdots$O hydrogen bonds (Fig. 2 and Table 2). The columns are arranged in an approximately hexagonal manner, so that the overall arrangement of the cations approximates primitive hexagonal. Considering the structure in terms of hexagonal close-packed layers of [*trans*-$Co(en)_2(NO_2)_2$]$^+$ cations in ($01\overline{1}$), the periodate anions occupy adjacent triangular hollows along [100], so that every second row of hollows is filled (Fig. 3). The positions occupied are those lined by NH_2 groups, which form hydrogen bonds to the O atoms of the periodate anions (Table 2). The periodate anions themselves adopt face-to-face staggered arrangements across centres of inversion, with $I1\cdots I1^{i}$ and $I1\cdots I1^{ii}$ separations of 4.1448 (2) and 4.2567 (2) Å, respectively [symmetry codes: (i) $2 - x, 1 - y, -z$, (ii) $1 - x, 1 - y, -z$].

The second-sphere interactions of the cation in (I) differ considerably from those of the comparable perchlorate salt, [*trans*-$Co(en)_2(NO_2)_2$]$^+$(ClO_4^-). Considering the structure of Maxcy & Turnbull (1999), the nitro groups bridge $NH_2\cdots NH_2$ edges of adjacent [*trans*-$Co(en)_2(NO_2)_2$]$^+$ cations, in an interaction similar to that observed between [*cis*-$Co(en)_2(N_3)_2$]$^+$ and the picrate anion (Sharma, Sharma, Bala & Bond, 2005). These interactions link the cations into approximately hexagonal close-packed layers in (011). In the case of [*trans*-$Co(en)_2(NO_2)_2$]$^+$(ClO_4^-), the perchlorate anions can be envisaged to occupy adjacent pairs of triangular hollows, bridging the $NH_2\cdots NH_2$ edges of each [*trans*-$Co(en)_2(NO_2)_2$]$^+$ cation (Fig. 4), with a Cl$\cdots$Cl separation of 5.161 Å within each pair.

Experimental

The complex salt [*trans*-$Co(en)_2(NO_2)_2$]NO_3 was prepared according to the literature method of Holtzclaw *et al.* (1953). [*trans*-$Co(en)_2(NO_2)_2$]NO_3 (1 g, 0.003 mol) was dissolved in water (50 ml) in a beaker. In a second beaker, sodium periodate (0.6425 g, 0.003 mol) was dissolved in water (25 ml). The solutions were mixed and yellow crystals appeared after 1 h. The complex salt is sparingly soluble in acetone and fairly soluble in dimethylsulfoxide, but insoluble in chloroform. Elemental analysis, found: Co 12.64, C 10.40, H 4.00, N 18.05%; calculated for $C_4H_{16}CoIN_6O_8$: Co 12.76, C 10.38, H 3.46, N 18.17%.

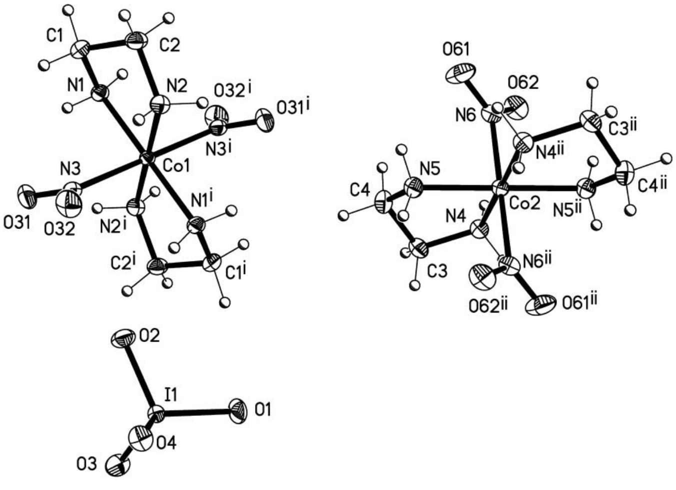


Figure 1
The ions in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $-x, 1 - y, 1 - z$; (ii) $-x, -y, -z$.]

Crystal data

[$Co(C_2H_8N_2)_2(NO_2)_2$](IO_4)
$M_r = 462.06$
Triclinic, $P\overline{1}$
$a = 7.3556$ (4) Å
$b = 10.1773$ (5) Å
$c = 10.3602$ (5) Å
$\alpha = 79.123$ (2)°
$\beta = 74.383$ (2)°
$\gamma = 70.125$ (2)°
$V = 698.39$ (6) Å^3
$Z = 2$
$D_x = 2.197$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6850 reflections
$\theta = 3.1$–33.2°
$\mu = 3.49$ mm^{-1}
$T = 180$ (2) K
Block, yellow
0.28 × 0.20 × 0.20 mm

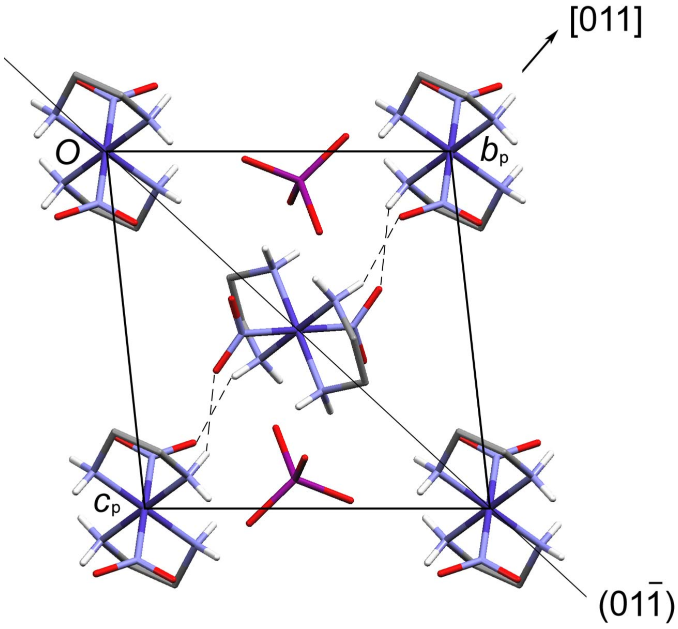


Figure 2
A projection of the structure of (I) along [100], showing the [*trans*-$Co(en)_2(NO_2)_2$]$^+$ cations linked into columns *via* complementary pairs of N—H$\cdots$O hydrogen bonds (shown as dashed lines). H atoms bound to C atoms have been omitted for clarity.

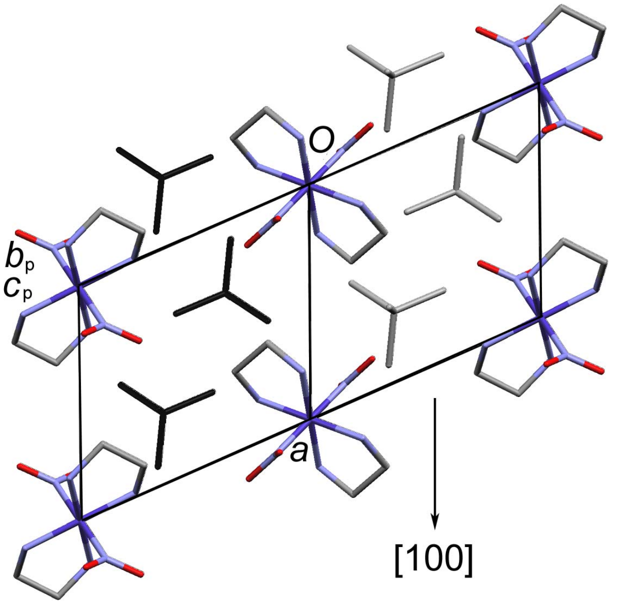


Figure 3
A projection of the structure of (I) on to a single layer of [*trans*-Co(en)$_2$(NO$_2$)$_2$]$^+$ cations in (01$\bar{1}$). Periodate anions occupy only the triangular hollows lined by NH$_2$ groups; those above the plane are shaded grey and those below the plane are shaded black. H atoms have been omitted.

Data collection

Bruker Nonius X8 APEX-II CCD area-detector diffractometer
Thin–slice ω and φ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.429$, $T_{\max} = 0.498$
7750 measured reflections
4857 independent reflections
4633 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.014$
$\theta_{\max} = 33.3°$
$h = -10 \rightarrow 10$
$k = -15 \rightarrow 15$
$l = -15 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.015$
$wR(F^2) = 0.041$
$S = 1.11$
4857 reflections
184 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0191P)^2 + 0.1654P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.55$ e Å^{-3}
$\Delta\rho_{\min} = -0.78$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—N3	1.9388 (11)	Co2—N6	1.9317 (11)
Co1—N2	1.9441 (11)	Co2—N4	1.9527 (11)
Co1—N1	1.9552 (10)	Co2—N5	1.9572 (11)
N3—Co1—N3^{i}	180	N6^{ii}—Co2—N6	180
N3—Co1—N2	89.96 (5)	N6—Co2—N4	90.95 (5)
N3^{i}—Co1—N2	90.04 (5)	N6—Co2—N4^{ii}	89.05 (5)
N2—Co1—N2^{i}	180	N4—Co2—N4^{ii}	180
N3—Co1—N1	88.61 (5)	N6—Co2—N5	89.12 (5)
N3^{i}—Co1—N1	91.39 (5)	N4—Co2—N5	85.70 (5)
N2—Co1—N1	85.94 (5)	N6—Co2—N5^{ii}	90.88 (5)
N2^{i}—Co1—N1	94.06 (5)	N4—Co2—N5^{ii}	94.30 (5)
N1—Co1—N1^{i}	180	N5—Co2—N5^{ii}	180

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x, -y, -z$.

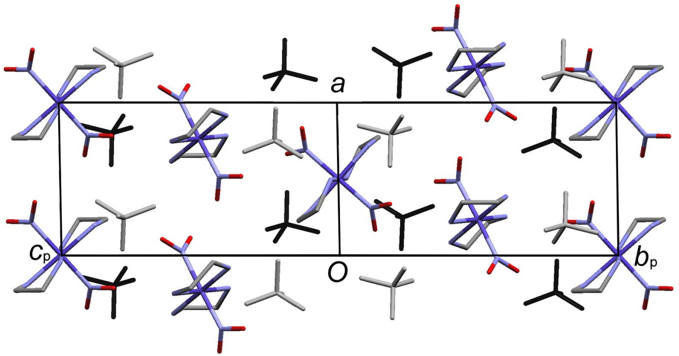


Figure 4
A projection of [*trans*-Co(en)$_2$(NO$_2$)$_2$]$^+$(ClO$_4^-$) on to a single layer of [*trans*-Co(en)$_2$(NO$_2$)$_2$]$^+$ cations in (011). Perchlorate anions occupy adjacent pairs of triangular hollows, bridging NH$_2$···NH$_2$ edges; those above the plane are shaded grey and those below the plane are shaded black. H atoms have been omitted.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*C*···O2^{i}	0.92	2.24	3.0390 (15)	145
N1—H1*D*···O3^{iii}	0.92	2.12	2.9297 (15)	146
N5—H5*A*···O4^{iv}	0.92	2.37	3.1347 (15)	141
N4—H4*D*···O1^{v}	0.92	2.33	2.9258 (15)	122
N2—H2*D*···O2^{vi}	0.92	2.60	3.3389 (16)	138
N2—H2*C*···O62^{vii}	0.92	2.20	2.9943 (16)	144
N5—H5*B*···O1^{vi}	0.92	2.39	3.0244 (16)	126
N4—H4*C*···O32^{viii}	0.92	2.34	3.0809 (17)	137
N4—H4*D*···O4^{viii}	0.92	2.54	3.3267 (15)	144

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

H atoms were placed in calculated positions and allowed to ride during subsequent refinement, with N—H = 0.92 Å and C—H = 0.99 Å, and with $U_{\rm iso}$(H) = 1.2 $U_{\rm eq}$(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*.

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