

(1,8-Dinitro-3,6,10,13,16,19-hexaaza-bicyclo[6.6.6]icosane)cobalt(III) tribromide

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Key indicators

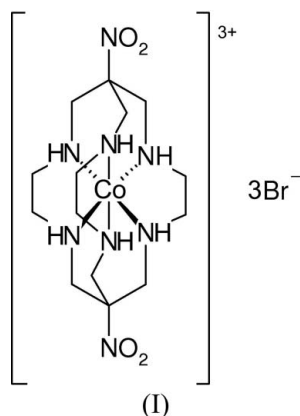
Single-crystal X-ray study  
 T = 180 K  
 Mean  $\sigma(C-C)$  = 0.003 Å  
 R factor = 0.028  
 wR factor = 0.073  
 Data-to-parameter ratio = 20.8

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

In the crystal structure of the title compound,  $[Co(C_{14}H_{30}N_8O_4)]Br_3$ , at 180 K, the cationic complexes lie on twofold rotation axes, and bromide anions lie either on twofold rotation axes or in general positions.

Comment

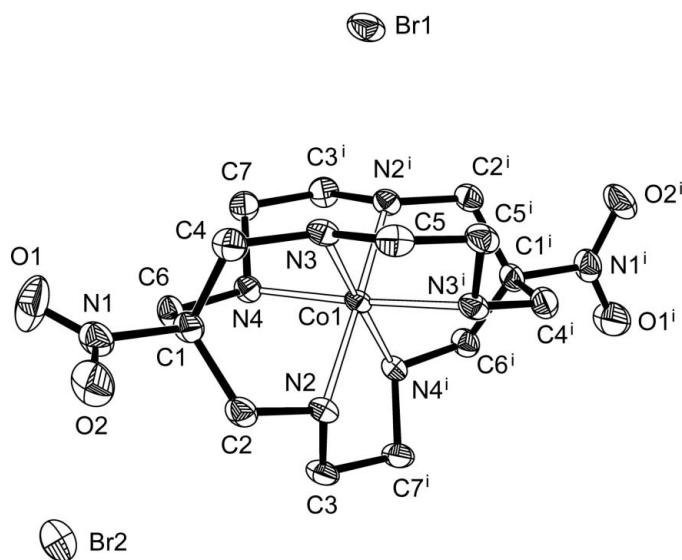
The cationic complex, denoted  $[CoR]^{3+}$ , of the title compound, (I), has been observed previously in three crystal structures:  $[CoR][C_8H_4O_{12}Sb_2]Cl \cdot 7H_2O$  (Bernhardt *et al.*, 2003),  $[CoR]Cl_3 \cdot 2H_2O$  (Clark *et al.*, 1993) and  $[CoR][C_5H_8NS_2]_3 \cdot 5H_2O$  (Achilleos *et al.*, 1989). A similar N-deprotonated complex,  $[CoR]Cl_2 \cdot 4H_2O$ , has also been reported (Geue *et al.*, 1984).



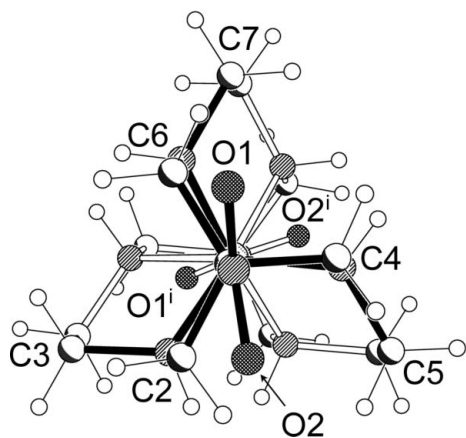
In  $[CoR]Br_3$  (Fig. 1), the complex cations lie on twofold rotation axes that pass through Co1 and the mid-point of the C5–C5<sup>i</sup> bond [symmetry code: (i)  $1 - x, y, \frac{1}{2} - z$ ]. In projection along the N1··N1<sup>i</sup> vector (Fig. 2), the triamino caps adopt a staggered arrangement, similar to that seen in the previous structures of this complex. The single symmetry-independent nitro group lies so that the plane through its three atoms appears approximately perpendicular to the C1–C4 bond in projection, and the planes of the nitro groups at each end of the complex form a dihedral angle of 77.0 (2)°. The bromide anions lie in positions that bridge the three NH··NH edges of the CoN<sub>6</sub> octahedron within the complex, accepting hydrogen bonds from both NH groups (Fig. 3 and Table 2). Atom Br2 also forms two relatively short contacts to the N atoms of adjacent nitro groups [ $Br2 \cdots N1$  and  $N1^{ii} = 3.626(2)$  Å; symmetry code: (ii)  $1 - x, y, \frac{3}{2} - z$ ]. The local environment of Br1 comprises predominantly CH<sub>2</sub> groups.

The gross crystal structure of  $[CoR]Br_3$  is conveniently considered in terms of layers parallel to the (222) planes, in which the C<sub>3</sub> axes of the central CoN<sub>6</sub> octahedra lie approxi-

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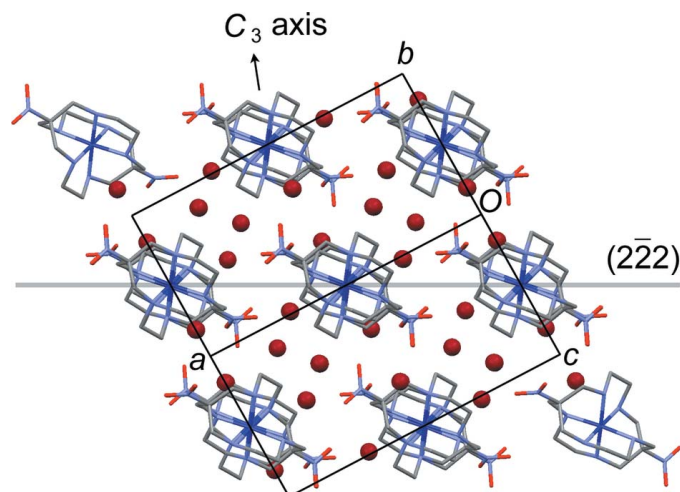
**Figure 1**  
The title complex, showing displacement ellipsoids at the 50% probability level. H atoms have been omitted. [Symmetry code: (i)  $1 - x, y, \frac{1}{2} - z$ .]



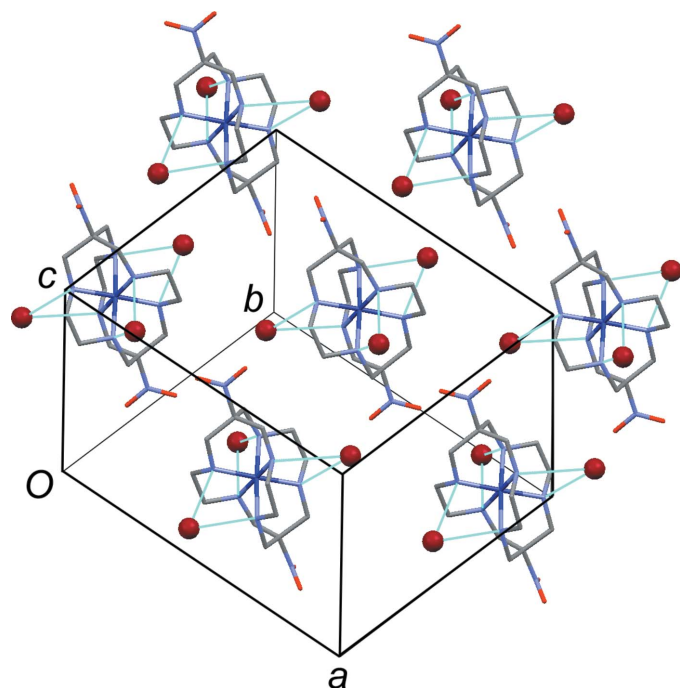
**Figure 2**  
Projection along the  $N1 \cdots N1'$  vector, with the front half of the molecule shown with solid bonds, and the back half shown with open bonds. The triamino caps adopt a staggered arrangement in projection, while the planes of the nitro groups form a dihedral angle of  $77.0^\circ$  (2°).

mately normal to the plane of the layers (Fig. 3). Projection on to a single such layer reveals an approximate hexagonal arrangement (Fig. 4). The layers stack in an *ABAB* manner, so that the complexes form an approximate hexagonal close-packed arrangement in three dimensions.

By comparison, the chloride anions in the structure of  $[CoR]Cl_3 \cdot 2H_2O$  (Clark *et al.*, 1993) occupy positions similar to those occupied by bromide in  $[CoR]Br_3$ . However, one chloride anion in  $[CoR]Cl_3 \cdot 2H_2O$  serves as a bridge between two  $NH \cdots NH$  edges in neighbouring complexes, thereby adopting essentially square-planar coordination. The complexes may again be envisaged to lie in layers [in the  $(1\bar{1}0)$  planes], with the square planes around  $Cl^-$  lying approximately in the plane of the layers. Thus, the  $C_4$  axes of the central  $CoN_6$  octahedra lie close to the normal to the plane of the layers in this case (Fig. 5). This arrangement introduces



**Figure 3**  
The structure may be considered in terms of layers of complexes parallel to the  $(2\bar{2}2)$  planes, with the  $C_3$  axes of the central  $CoN_6$  octahedra pointing approximately perpendicular to the planes of the layers. The layers are stacked in an *ABAB* manner.



**Figure 4**  
Projection on to the plane of a single layer in the  $(2\bar{2}2)$  planes, showing the approximate hexagonal arrangement of complexes. Hydrogen bonds are shown as solid blue lines.

gaps between the chloride anions that are associated with the remaining  $NH \cdots NH$  edges of the  $CoN_6$  octahedra, which are bridged by water molecules.

## Experimental

$[Co(\text{ethylenediamine})_3]I_3$  (2.5 g) and anhydrous  $Na_2CO_3$  (1.5 g) were dissolved in water (90 ml).  $CH_3NO_2$  (5 ml) and 37% aqueous formaldehyde (40 ml) were added with stirring and the yellow–brown solution was warmed to 313 K for *ca* 2 h. The mixture was then cooled

in an ice bath, and the yellow solid deposited was collected under suction and redissolved in *ca* 30 ml of hot 1 M acetic acid. Concentrated HBr (15 ml) was added and the mixture was cooled slowly, yielding crystals suitable for X-ray analysis.

Crystal data

[Co(C<sub>14</sub>H<sub>30</sub>N<sub>8</sub>O<sub>4</sub>)]Br<sub>3</sub>  
*M<sub>r</sub>* = 673.12  
 Monoclinic, C2/c  
*a* = 15.9928 (7) Å  
*b* = 13.4357 (6) Å  
*c* = 10.7799 (4) Å  
 β = 92.111 (2)°  
*V* = 2314.75 (17) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.932 Mg m<sup>-3</sup>  
 Mo Kα radiation  
 Cell parameters from 6123 reflections  
 θ = 2.6–28.2°  
 μ = 5.96 mm<sup>-1</sup>  
*T* = 180 (2) K  
 Block, orange  
 0.20 × 0.20 × 0.20 mm

Data collection

Bruker–Nonius X8APEX-II CCD diffractometer  
 Thin-slice ω and φ scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)  
*T<sub>min</sub>* = 0.224, *T<sub>max</sub>* = 0.304  
 13612 measured reflections  
 2852 independent reflections  
 2451 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.030  
 θ<sub>max</sub> = 28.3°  
*h* = -20 → 21  
*k* = -15 → 17  
*l* = -14 → 9

Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.028  
*wR*(*F*<sup>2</sup>) = 0.073  
*S* = 1.03  
 2852 reflections  
 137 parameters  
 H-atom parameters constrained  
*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0375*P*)<sup>2</sup> + 4.1623*P*]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> = 0.001  
 Δρ<sub>max</sub> = 0.89 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.64 e Å<sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

Co1–N3	1.966 (2)	Co1–N4	1.975 (2)
Co1–N2	1.9672 (19)		
N3–Co1–N3 <sup>i</sup>	86.10 (12)	N2–Co1–N4 <sup>i</sup>	86.33 (8)
N3–Co1–N2	91.33 (8)	N3–Co1–N4	90.92 (8)
N3–Co1–N2 <sup>i</sup>	91.74 (8)	N2–Co1–N4	90.75 (8)
N2–Co1–N2 <sup>i</sup>	175.79 (12)	N4–Co1–N4 <sup>i</sup>	92.17 (12)
N3–Co1–N4 <sup>i</sup>	176.15 (8)		

Symmetry code: (i) -x + 1, y, -z + 1/2.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N2–H2...Br1 <sup>i</sup>	0.93	2.40	3.333 (2)	177
N3–H3...Br1	0.93	2.37	3.275 (2)	163
N4–H4...Br2 <sup>ii</sup>	0.93	2.35	3.268 (2)	169

Symmetry codes: (i) -x + 1, y, -z + 1/2; (ii) -x + 1, -y, -z + 1.

H atoms bound to C atoms were positioned geometrically and allowed to ride during subsequent refinement, with C–H = 0.99 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C). H atoms bound to N atoms were visible in

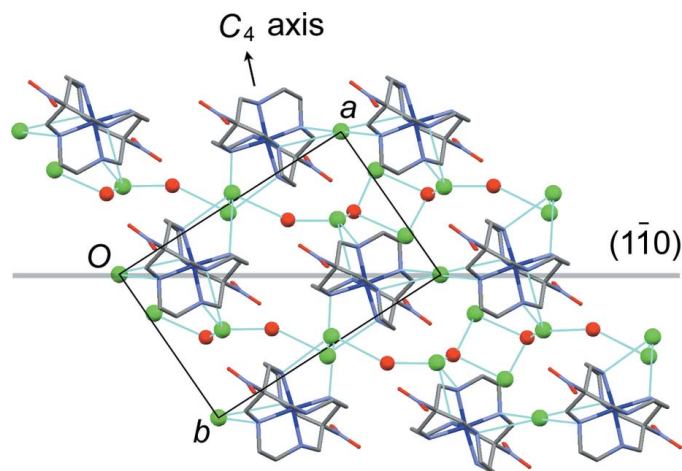


Figure 5

Layers in the chloride salt [CoR]Cl<sub>3</sub>·2H<sub>2</sub>O (Clark *et al.*, 1993) lying parallel to the (1̄10) planes. In this case, the C<sub>4</sub> axes of the central CoN<sub>6</sub> octahedra in each complex point approximately perpendicular to the layer plane, leaving gaps between the chloride anions that are occupied by water molecules. Hydrogen bonds are shown as solid blue lines. In this projection, the chloride anions in square-planar coordination environments appear at the corners of the unit cell.

difference Fourier maps, but were included in calculated positions and allowed to ride, with N–H = 0.93 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(N).

Data collection: APEX2 (Bruker–Nonius, 2004); 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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References

Achilleos, A. A., Gahan, L. R., Hambley, T. W., Healy, P. C. & Weedon, D. M. (1989). *Inorg. Chim. Acta*, **157**, 209–214.  
 Bernhardt, P. V., Dyahningtyas, T. E., Harrowfield, J. M., Kim, J.-Y., Kim, Y. & Rukmini, E. (2003). *Aust. J. Chem.* **56**, 1187–1191.  
 Bruker (2003). SAINT. Version 7.06a. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Bruker–Nonius (2004). APEX2. Version 1.0-22. Bruker–Nonius BV, Delft, The Netherlands.  
 Clark, I. J., Geue, R. J., Engelhardt, L. M., Harrowfield, J. M., Sargeson, A. M. & White, A. H. (1993). *Aust. J. Chem.* **46**, 1485–1505.  
 Geue, R. J., Hambley, T. W., Harrowfield, J. M., Sargeson, A. M. & Snow, M. R. (1984). *J. Am. Chem. Soc.* **106**, 5478–5488.  
 Sheldrick, G. M. (2000). SHELXTL. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Sheldrick, G. M. (2003). SADABS. Version 2.10. Bruker AXS Inc., Madison, Wisconsin, USA.