

## Orientalional disorder in $\Lambda$ -cobalt(III) sepulchrate trinitrate

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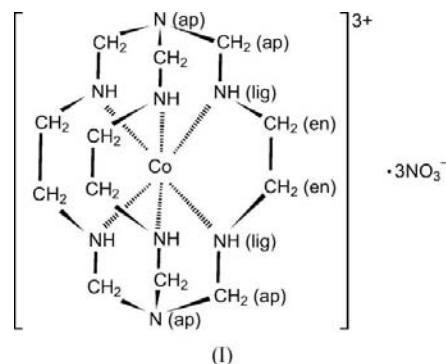
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The crystal structure of  $\Lambda$ -(1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane)cobalt(III) trinitrate,  $[\text{Co}(\text{C}_{12}\text{H}_{30}\text{N}_8)](\text{NO}_3)_3$ , consists of a sepulchrate moiety that serves as a macrobicyclic nitrogen cage for the  $\text{Co}^{3+}$  cation, which is six-coordinated by N atoms, and three nitrate anions. The Co-sepulchrate group lies on a threefold axis (site symmetry  $32$ ), as do two symmetry-related and ordered nitrate groups (site symmetry  $3$ ), with which it is connected *via*  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds [ $\text{Co}-\text{N} = 5.1452(12) \text{ \AA}$ ]. The third nitrate group is disordered as a result of symmetry requirements around the origin (site symmetry  $32$ ), and is further away from the Co-sepulchrate cage [ $\text{Co}-\text{N} = 6.3160(8) \text{ \AA}$ ]. The structure is described by applying orientational disorder over six equivalent orientations for the disordered nitrate group, which is considered as an ideal planar molecule of regular trigonal geometry with its molecular plane rotated out of the *ab* plane and the molecular centre of gravity slightly shifted away from the origin. This new model for disorder clearly improves a previous crystal structure determination.

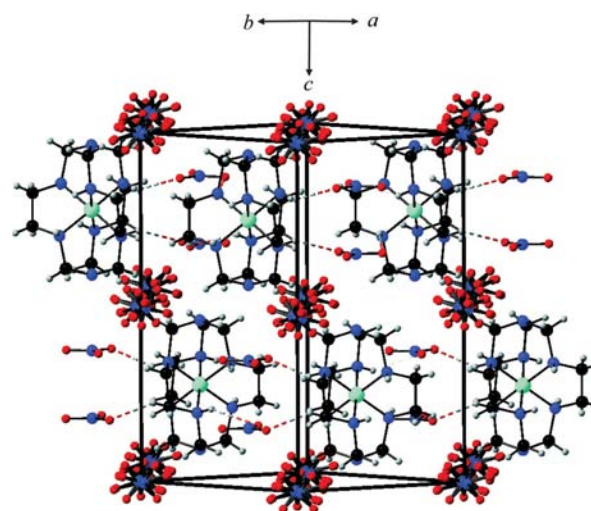
### Comment

$\Lambda$ -Cobalt(III) sepulchrate (sep) trinitrate, (I), crystallizes at room temperature in the space group  $P6_322$  (Dubicki *et al.*, 1980) (Fig. 1). Applying spectroscopic measurements, phase transitions have been observed at  $T_1 = 133 \text{ K}$  and  $T_2 = 106 \text{ K}$  (Dubicki *et al.*, 1984). By single-crystal neutron diffraction upon cooling, the appearance of satellite reflections in the diffraction pattern at  $T_1 = 133 \text{ K}$  was discovered, indicating the development of a modulated structure (Larsen *et al.*, 1988). Additional phase transitions have been observed at  $T_2 = 107 \text{ K}$  and  $T_3 = 98 \text{ K}$ . In the course of investigations of the phase transitions of  $\Lambda$ -cobalt(III) sepulchrate trinitrate, we have developed an improved model for its room-temperature crystal structure, which is presented here. The present description of the orientational disorder of one of the nitrate groups is essentially different from that of Dubicki *et al.* (1980). It will form the basis for structure models of the

incommensurate phases, which involve ordering of this nitrate group. Furthermore, Dubicki *et al.* (1980) have presented only a picture of the crystal structure and they did not give structural parameters. We present here accurate structural parameters for all atoms.

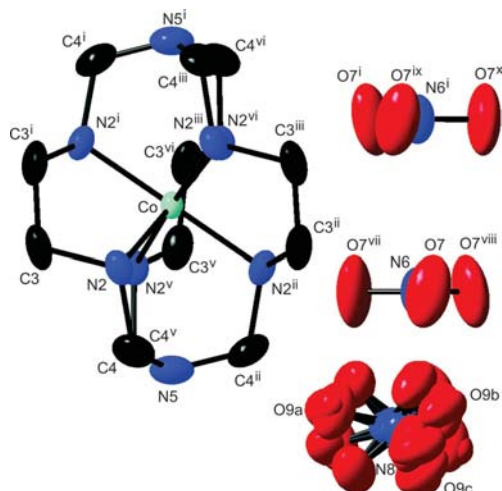


The  $\text{Co}^{3+}$  cation of (I) is located on the 32 site at  $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ , conforming to the 32 geometry of the  $[\text{Co}(\text{sep})]^{3+}$  cation. It also follows that capping atom N5 of the sepulchrate group lies on the threefold axis. The chiral N2 atoms have an S configuration (Fig. 2). All interatomic distances and angles are in good agreement with the published data for related structures (Mikami *et al.*, 1979; Dubicki *et al.*, 1980; Bacchi *et al.*, 1993*a,b*, 1996). The three N—C bonds in the sepulchrate cage, *viz.*  $\text{N}_{2\text{lig}}-\text{C}_{3\text{en}}$ ,  $\text{N}_{2\text{lig}}-\text{C}_{4\text{ap}}$  and  $\text{N}_{5\text{ap}}-\text{C}_{4\text{ap}}$ , have different lengths ( $\text{N}_{\text{lig}}$  is a ligating N atom,  $\text{C}_{\text{en}}$  is an ethylene C atom and  $\text{C}_{\text{ap}}$  is an apical C atom; see scheme and Table 1). The packing consists of layers of hydrogen-bonded  $[\text{Co}(\text{sep})]^{3+}$  cations and ordered nitrate groups (Table 2), with each  $[\text{Co}(\text{sep})]^{3+}$  cation connected to six nitrate anions and each nitrate anion to three  $[\text{Co}(\text{sep})]^{3+}$  cations. These layers are separated by layers of disordered nitrate groups (Fig. 1).



**Figure 1**

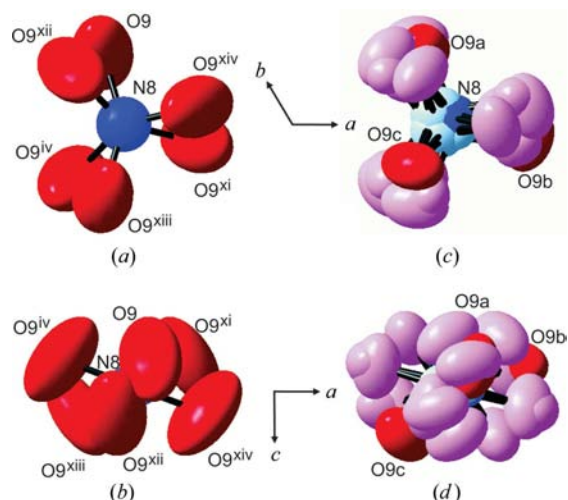
The crystal packing of (I), illustrating the  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonding involving the Co-sepulchrate cage and the ordered nitrate groups (shown as dashed lines; see Table 2 for details). The nitrate group at the origin is represented as a disordered group.


**Figure 2**

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. [Symmetry codes: (i)  $-y + 1, -x + 1, -z + \frac{1}{2}$ ; (ii)  $-y + 1, x - y + 1, z$ ; (iii)  $x, x - y + 1, -z + \frac{1}{2}$ ; (v)  $-x + y, -x + 1, z$ ; (vi)  $-x + y, y, -z + \frac{1}{2}$ ; (vii)  $-x + y + 1, -x + 1, z$ ; (viii)  $-y + 1, x - y, z$ ; (ix)  $x, x - y, -z + \frac{1}{2}$ ; (x)  $-x + y + 1, y, -z + \frac{1}{2}$ ]

Dubicki *et al.* (1980) placed atom N8 of the disordered nitrate anion at the origin with site symmetry 32. Disorder was described by atom O9 at a general position ( $x, y, z$ ) with site symmetry 1 and occupancy 0.5, spread over six equivalent positions around the origin. In the present work, the crystal structure was solved using *SUPERFLIP* (Palatinus & Chapuis, 2007) and refined with *JANA2006* (Petříček *et al.*, 2006). The position of atom O9 converged to (0.035826, 0.147196,  $-0.025571$ ) (Fig. 3). As already mentioned by Dubicki *et al.* (1984), due to symmetry, the disorder 'should be orientational in character' with six orientations of the nitrate group, each with its normal to the molecular plane tilted with respect to the crystal  $c$  axis by about  $30^\circ$ . However, this description results in chemically meaningless geometries of the nitrate anions (Table 3). In addition, the nitrate groups would be non-planar; atom N8 is  $\pm 0.102$  (1) Å out of the plane defined by the three corresponding O atoms.

For a proper description of the disordered nitrate group, orientational disorder of the complete nitrate group as a rigid body has been applied. Due to its rotation out of the  $ab$  plane, the threefold axis of the molecule does not coincide with the threefold axis of the space group. Therefore, it is not appropriate to fix the nitrate group on the origin. Thus, the molecular centre of gravity (represented by central atom N8) was shifted slightly away from the origin and then refined. In the final model, atom N8 converged to a position at [0.0269 (13), 0.0106 (13), 0.0018 (5)], which is displaced from the origin by *ca.* 0.2 Å. As the site symmetry of the origin is 32, five additional equivalent positions are generated for the nitrate rigid body, leading in total to six equivalent N-atom positions and 18 equivalent O-atom positions. By applying this model of orientational disorder, 62 instead of 60 parameters have to be refined, but now the disordered nitrate group can be defined as being planar with O–N–O angles of  $120^\circ$ . The proper geometry is also reflected in smaller anisotropic displacement


**Figure 3**

(a) and (b) Comparison of the model proposed by Dubicki *et al.* (1980), employing the refined parameters, and the present data. (c) and (d) The rigid-body model for the disordered nitrate group, viewed along the  $c$  and  $b$  axes, respectively. All figures are at the same scale. The generated disordered positions in (c) and (d) are shown in a paler colour. [Symmetry codes: (iv)  $-y, x - y, z$ ; (xi)  $-x + y, -x, z$ ; (xii)  $-x, -x + y, -z$ ; (xiii)  $x - y, -y, -z$ ; (xiv)  $y, x, -z$ ]

parameters for atoms N8 and O9 (Fig. 3). In addition, all statistical refinement parameters are considerably improved, *viz.*  $S$  from 2.48 to 2.25,  $R_{\text{obs}}$  from 0.038 to 0.034, and  $wR_{\text{obs}}$  from 0.058 to 0.052.

## Experimental

$\Delta$ -Cobalt(III) sepulchrate trinitrate crystals were prepared at the Research School of Chemistry, Australian National University, Canberra, Australia, and a sample was supplied by Professor Alan M. Sargeson (Creaser *et al.*, 1982). A crystal suitable for X-ray analysis was selected directly from the sample as prepared and fixed on a glass fibre. As the crystals are stable in air, no special coating was necessary.

### Crystal data

$[\text{Co}(\text{C}_{12}\text{H}_{30}\text{N}_8)](\text{NO}_3)_3$	$Z = 2$
$M_r = 531.4$	Mo $K\alpha$ radiation
Hexagonal, $P6_322$	$\mu = 0.94 \text{ mm}^{-1}$
$a = 8.4945$ (5) Å	$T = 295 \text{ K}$
$c = 15.9195$ (13) Å	$0.30 \times 0.15 \times 0.10 \text{ mm}$
$V = 994.80$ (12) Å <sup>3</sup>	

### Data collection

MarIP mar345dtb diffractometer	49907 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2008)	1404 independent reflections
$T_{\text{min}} = 0.693, T_{\text{max}} = 0.747$	1322 reflections with $I > 3\sigma(I)$
	$R_{\text{int}} = 0.025$

### Refinement

$R[F^2 > 3\sigma(F^2)] = 0.034$	$\Delta\rho_{\text{max}} = 0.46 \text{ e \AA}^{-3}$
$wR(F^2) = 0.053$	$\Delta\rho_{\text{min}} = -0.37 \text{ e \AA}^{-3}$
$S = 2.25$	Absolute structure: Flack (1983),
1404 reflections	1404 Friedel pairs
62 parameters	Flack parameter: 0.13 (3)
H atoms treated by a mixture of independent and constrained refinement	

**Table 1**

Selected geometric parameters (Å, °).

Co1—N2	1.9752 (15)	C4—N5	1.417 (3)
N2—C3	1.482 (3)	N6—O7	1.2222 (17)
N2—C4	1.518 (2)	N8—O9 <sub>a</sub>	1.204 (17)
C3—C3 <sup>i</sup>	1.515 (2)		
N2—Co1—N2 <sup>ii</sup>	91.05 (6)	N2—C4—N5	113.19 (18)
N2—Co1—N2 <sup>iii</sup>	90.89 (6)	C4—N5—C4 <sup>ii</sup>	114.36 (13)
C3—N2—C4	113.91 (14)		

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

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2 <sup>iv</sup> ···O7 <sup>iv</sup>	0.83 (2)	2.463 (19)	3.231 (3)	154 (2)

Symmetry code: (iv)  $-y, x - y, z$ .

In the first step, all H atoms were positioned geometrically and refined using a riding model, with N—H = 0.87 Å and C—H = 0.96 Å, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ . In the next step, the position of atom H2, which is involved in hydrogen bonding, was released and freely refined, to give N—H = 0.83 (2) Å.

The crystal is twinned by merohedry, containing two twin domains related to each other by inversion. The refined volume fractions converged to  $V_1 = 0.87$  (3) and  $V_2 = 0.13$  (3) for the first and second domains, respectively.

The disordered nitrate group is described with a rigid-body refinement. In the first step, atoms N8 and O9 were refined independently, as proposed by Dubicki *et al.* (1980). The occupancy factor of atom O9 was 0.5. As atom N8 lies at the origin, only two anisotropic displacement parameters can be refined for N8. With the (3 + 6) parameters of atom O9, 11 parameters in total are involved. In the next step, an ideal 'model molecule' was created by one N and one O atom, with N—O = 1.22 Å and ideal molecular symmetry 321 (generating an ideal planar nitrate group with three O—N—O angles of 120° each). The position of the model O atom was made refinable, according to the restrictions of the local 321 point symmetry (one parameter). Atoms N8 and O9 were then replaced by the model molecule and the position and orientation of this rigid body were refined (three parameters for displacement and three for orientation), together with the position of the model O atom. Any attempt to apply TLS refinement for the rigid body as well resulted in singularities with blocked parameters, large correlations and a nonconverging refinement. Therefore, the anisotropic displacement parameters of the atoms in the model molecule were refined independently (two for the N atom and four for the O atom). In total, 13 parameters are applied to this part of the structure.

**Table 3**Interatomic angles (°) in the disordered nitrate group derived from the model proposed by Dubicki *et al.* (1980).

Angles are given for two out of the six possible orientations.

O—N—O <sup>iv</sup>	109.1 (5)	O—N—O <sup>xi</sup>	109.1 (5)
O—N—O <sup>xiv</sup>	99.3 (5)	O—N—O <sup>xiii</sup>	149.0 (7)
O <sup>xiv</sup> —N—O <sup>iv</sup>	149.0 (7)	O <sup>xiii</sup> —N—O <sup>xi</sup>	99.3 (7)

Symmetry codes: (iv)  $-y, x - y, z$ ; (xi)  $-x + y, -x, z$ ; (xiii)  $x - y, -y, -z$ ; (xiv)  $y, x, -z$ .

Data collection: *MAR345DTB* (Klein, 2003); cell refinement: *PEAKREF* (Schreurs, 1999); data reduction: *EVAL15* (Schreurs *et al.*, 2010) and *SADABS* (Sheldrick, 2008); program(s) used to solve structure: *SUPERFLIP* (Palatinus & Chapuis, 2007); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2006); molecular graphics: *DIAMOND* (Brandenburg, 2009); software used to prepare material for publication: *JANA2006*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SU3043). Services for accessing these data are described at the back of the journal.

## References

- Bacchi, A., Ferranti, F. & Pelizzi, G. (1993a). *Acta Cryst.* **C49**, 1163–1169.  
 Bacchi, A., Ferranti, F. & Pelizzi, G. (1993b). *Acta Cryst.* **C49**, 1885–1892.  
 Bacchi, A., Ferranti, F. & Pelizzi, G. (1996). *Acta Cryst.* **C52**, 1624–1627.  
 Brandenburg, K. (2009). *DIAMOND*. Version 3.2. Crystal Impact GbR, Bonn, Germany.  
 Creaser, I. L., Geue, R. J., Harrowfield, J. M., Herlt, A. J., Sargeson, A. M., Snow, M. R. & Springborg, J. (1982). *J. Am. Chem. Soc.* **104**, 6016–6025.  
 Dubicki, L., Ferguson, J., Geue, R. J. & Sargeson, A. M. (1980). *Chem. Phys. Lett.* **74**, 393–397.  
 Dubicki, L., Ferguson, J. & Willimson, B. (1984). *J. Phys. Chem.* **88**, 4254–4258.  
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
 Klein, C. (2003). *MAR345DTB*. Version 2.2.0. Marresearch GmbH, Norderstedt, Germany.  
 Larsen, F. K., Jørgensen, P., Grønbæk Hazell, R., Lebech, B., Thomas, R., Geue, R. J. & Sargeson, A. M. (1988). *Molecular Structure: Chemical Reactivity and Biological Activity*, edited by J. J. Stezowski, J.-L. Huang & M.-C. Shao, pp. 499–504. Oxford: IUCr/Oxford University Press.  
 Mikami, M., Konno, M. & Saito, Y. (1979). *Acta Cryst.* **B35**, 3096–3098.  
 Palatinus, L. & Chapuis, G. (2007). *J. Appl. Cryst.* **40**, 786–790.  
 Petříček, V., Dušek, M. & Palatinus, L. (2006). *JANA2006*. Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic.  
 Schreurs, A. M. M. (1999). *PEAKREF*. Utrecht University, The Netherlands.  
 Schreurs, A. M. M., Xian, X. & Kroon-Batenburg, L. M. J. (2010). *J. Appl. Cryst.* **43**, 70–82.  
 Sheldrick, G. (2008). *SADABS*. Version 2008/1. Bruker AXS Inc., Madison, Wisconsin, USA.