

Two cobalt(III) mono-dimethylglyoximates isolated from one reaction

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The reaction of cobalt(II) nitrate hexahydrate with dimethylglyoxime (DMGH₂) and 1,10-phenanthroline (phen) in a 1:1:2 molar ratio results in two Co^{III} mono-dimethylglyoximates having two chelating phen ligands in *cis* positions and the Co^{III} atom coordinated by six N atoms in a distorted octahedral coordination geometry. The isolated products differ in the deprotonation state of the DMGH₂ ligand. In [μ -hydrogen bis(*N,N'*-dioxidobutane-2,3-diimine)]tetrakis(1,10-phenanthroline)cobalt(III) trinitrate ethanol disolvate 1.87-hydrate, [Co₂(C₄H₆N₂O₂)(C₄H₇N₂O₂)(C₁₂H₈N₂)₄](NO₃)₃·2C₂H₆O·1.87H₂O, (I), the C₂-symmetric cation is formed with the coordination [Co(DMG)(phen)₂]⁺ cations aggregating *via* a very strong O⁻···H⁺···O⁻ hydrogen bond with an O···O distance of 2.409 (4) Å. Crystals of (I) exhibit extensive disorder of the solvent molecules, the nitrate anions and one of the phen ligands. Compound (I) is a kinetic product, not isolated previously from similar systems, that transforms slowly into (*N*-hydroxy-*N'*-oxidobutane-2,3-diimine)bis(1,10-phenanthroline)cobalt(III) dinitrate ethanol monosolvate 0.4-hydrate, [Co(C₄H₇N₂O₂)(C₁₂H₈N₂)₂](NO₃)₂·C₂H₆O·0.40H₂O, (II), with the DMGH⁻ ligand hydrogen bonded to one of the nitrate anions. In (II), the solvent molecules and one of the nitrate anions are disordered.

Comment

The coordination chemistry of the cobalt–dimethylglyoxime (DMGH₂) system has long been the subject of research that is mostly related to the study of coenzyme B₁₂ models, but synthetic, analytical, catalytic and structural aspects have also been widely addressed. In general, depending on the synthetic procedure applied (Gradinaru *et al.*, 2006), Co^{III} can form mono-, bis- and tris-dimethylglyoximates, with the most extensively studied system being Co^{III} bis-dimethylglyoximates with *trans* geometry. The fact that Co^{III} can form mixed-ligand complexes containing one dimethylglyoxime ligand and two chelating bidentate ligands, such as thiosemicarbazide (Hthsc), glycine, 2,2'-bipyridine and 1,10-phenanthroline

(phen), has been known for nearly 50 years (Ablov *et al.*, 1963). These complexes are generally formed when a Co^{II} salt, DMGH₂ and a chelating ligand are reacted in a 1:1:2 molar ratio in air to allow easy oxidation of Co^{II} to Co^{III}. To date, crystal structures have been reported for four complexes in this series: [Co^{III}(DMGH)(phen)₂](SCN)₂·2H₂O (Botoshanskii *et al.*, 1979), [Co^{III}(DMGH)(phen)₂](BF₄)₂·2H₂O (Malinovskii *et al.*, 2004), [Co^{III}(DMGH)(Hthsc)₂](NO₃)₂·2H₂O (Malinovskii *et al.*, 1977) and [Co^{III}(DMGH)(Hthsc)₂](SiF₆)·2.3H₂O (Bourosh *et al.*, 2006), in which dimethylglyoxime is monodeprotonated and the inorganic counter-ions are in the outer coordination sphere.

Among the papers retracted recently from *Acta Crystallographica Section E* due to a series of uncovered scientific frauds (Harrison *et al.*, 2010; Zhong *et al.*, 2010), three papers reported the structures of complexes formed by divalent transition metal nitrates with phen and DMGH₂ of the general formula [M^{II}(DMGH₂)(phen)₂](NO₃)₂·2H₂O, where M = Zn [Zhong *et al.*, 2007a; Cambridge Structural Database (CSD; Allen, 2002) refcode YEYGUF], Ni (Zhong *et al.*, 2007b; CSD refcode YEYGOZ) and Cu (Zhong *et al.*, 2007; CSD refcode YIQNUI). The fact that these three structures were incorrect became obvious to us when we had analysed the geometry of the dimethylglyoxime ligand using the CSD. Refinement of the crystal structures with the deposited diffraction data showed that, in all three cases, the studied compound was most probably [Co^{III}(DMGH)(phen)₂](NO₃)₂·EtOH, *i.e.* it belonged to the known series of Co^{III} mono-dimethylglyoximates. The structure of this compound has not been reported previously, and therefore we assumed incorrect identification of the protonation state of the dimethylglyoxime ligand, of the cation and its oxidation state, and of the solvent molecules. To make sure that the compound was really what we had expected, we decided to repeat the synthesis using Co(NO₃)₂·6H₂O as a substrate. There were some doubts concerning the identification of the solvent molecules due to their severe disorder, and therefore collection of new diffraction data at low temperature seemed necessary. However, as often happens, the studied system appeared to be more complicated, and at the same time more interesting, than we initially expected.

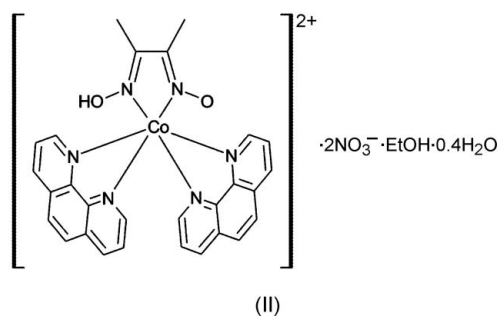
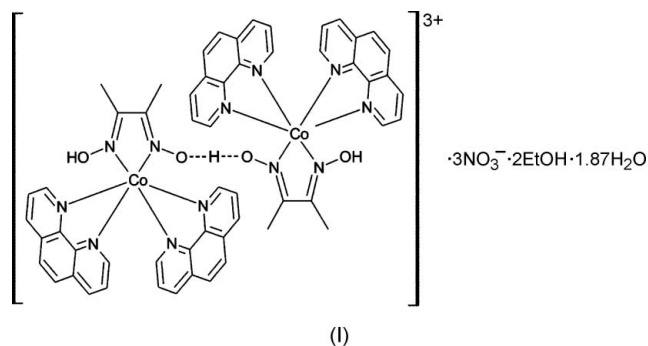
The first reaction was carried out under anaerobic conditions and resulted in the Co^{II} complex [Co^{II}(phen)₂(H₂O)₂](NO₃)₂, with an interesting uncommensurately modulated crystal structure that will be reported elsewhere. This reaction showed that under the applied conditions DMGH₂ does not react with Co^{II}. The second reaction was carried out under aerobic conditions to allow easy oxidation of Co^{II} to Co^{III}. As the reaction proceeded, precipitation of small red needle-shaped crystals of [μ -hydrogen bis(*N,N'*-dioxidobutane-2,3-diimine)]tetrakis(1,10-phenanthroline)cobalt(III) trinitrate ethanol disolvate 1.87-hydrate, (I), was observed, followed by the appearance of dark-red block-shaped crystals of (*N*-hydroxy-*N'*-oxidobutane-2,3-diimine)bis(1,10-phenanthroline)cobalt(III) dinitrate ethanol monosolvate 0.4-hydrate, (II). A few crystals of both types were isolated from the solution and the reaction mixture was left aside for a period of 3 d, during

which time the majority of the needle-shaped crystals transformed to dark-red blocks.

The diffraction quality of the crystals was checked, revealing in the case of the needles monoclinic symmetry and poor diffraction with a large amount of diffuse scattering, signalling extensive crystal disorder, whereas the dark-red block-shaped crystals gave good diffraction patterns and the unit-cell parameters agreed reasonably well with those reported for the three retracted structures (Zhong *et al.*, 2010; CSD refcodes: YEYGOZ, YEYGUF and YIQNUI). Both types of crystal, when left in air, decomposed slowly to a powder. In order to obtain larger needle-shaped crystals, the reaction was repeated a few more times, but the less-stable and apparently kinetic product (I) appeared only once, forming a few larger crystals, one of which was used for the X-ray structural analysis at 130 K.

Structure solution revealed that (I) has the formula $\{[\text{Co}^{\text{III}}(\text{DMG})(\text{phen})_2]_2\text{H}\}(\text{NO}_3)_3 \cdot 2\text{EtOH} \cdot 1.87\text{H}_2\text{O}$ and consists of crystallographically C_2 -symmetric $\{[\text{Co}^{\text{III}}(\text{DMG})(\text{phen})_2]_2\text{H}\}^+$ cations in which two identical $[\text{Co}^{\text{III}}(\text{DMG})(\text{phen})_2]^+$ units are connected by a very strong $\text{O}^- \cdots \text{H}^+ \cdots \text{O}^-$ hydrogen bond, with the H atom located on a twofold axis passing through the middle of the $\text{O} \cdots \text{O}$ distance [2.409 (4) Å] (Fig. 1*a* and Table 2). This distance is *ca* 0.1 Å shorter than the $\text{O} \cdots \text{O}$ distances of strong intramolecular hydrogen bonds formed in typical Co^{III} *trans* bis-dimethylglyoximates. In the dimethylglyoximate ligand, the N12–O12 bond length of 1.287 (3) Å clearly shows that one oxime group is fully deprotonated, whereas the N11–O11 bond length of 1.342 (3) Å in the second oxime group has a value intermediate between fully deprotonated and fully protonated states, which is in accord with the observed formation of $[\text{DMG} \cdots \text{H} \cdots \text{DMG}]^{3-}$ anionic species coordinated by two Co centres. To balance the positive charge of the Co cations,

which was assumed to be 3+, one and a half of the nitrate anions had to be located in the asymmetric unit. One anion, designated *B* in Fig. 1(*b*) and disordered over two overlapping positions, was easily identified. The missing half-anion was



sought among a difficult-to-interpret cluster of electron-density peaks found around the twofold axis. Closer examination showed that this C_2 -symmetric cluster results from the superposition of a disordered group of atoms, having half occupancy, that belong to a nitrate anion (designated *A*) and a

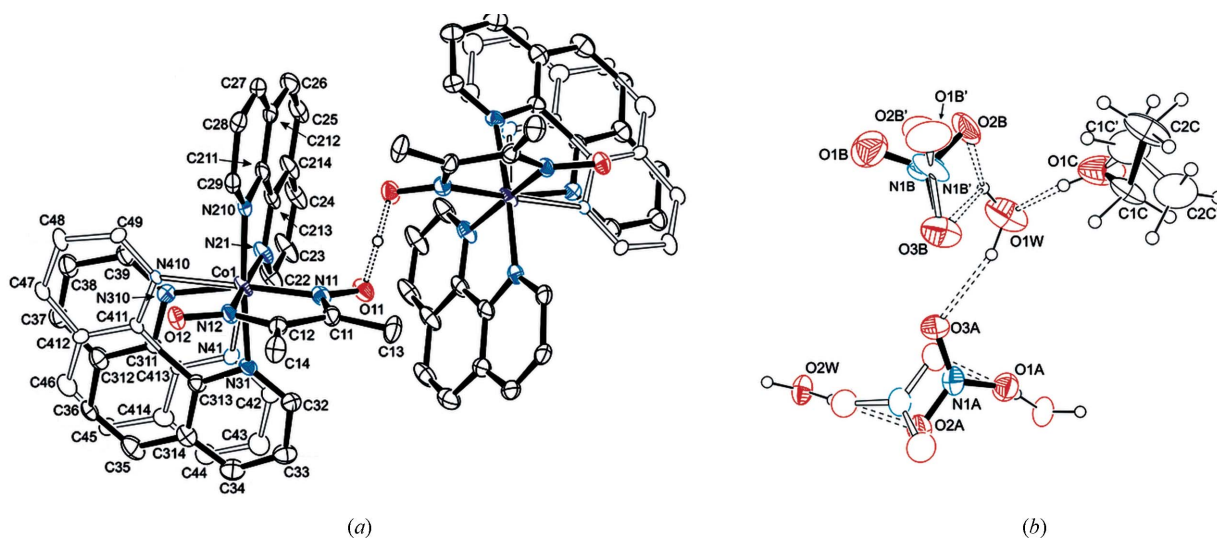


Figure 1

The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. (a) The C_2 -symmetric coordination cation $\{[\text{Co}(\text{DMG})(\text{phen})_2]_2\text{H}\}^+$ with the very strong $\text{O}^- \cdots \text{H}^+ \cdots \text{O}^-$ hydrogen bond (double dashed lines). The atoms of the phen ligand in the minor position are represented by ellipsoids with boundaries. The only H atom shown is that in the very strong hydrogen bond. (b) The nitrate anions and the solvent molecules of (I). Hydrogen bonds are shown as dashed lines and the disordered positions are differentiated by the displacement ellipsoid type.

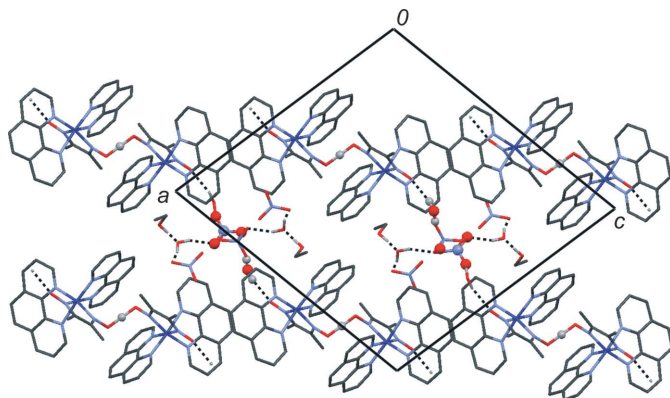


Figure 2

The crystal packing of (I), showing chains of $[\text{Co}(\text{DMG})(\text{phen})_2]_2\text{H}^+$ coordination cations formed *via* π - π stacking interactions between phen ligands. Disorder is only shown for the nitrate anion and the water molecule located around a twofold axis. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted.

water molecule (O2W) (Fig. 1*b*). In addition to the components indicated above, the asymmetric unit of (I) also contains another water molecule (O1W), with an occupancy of 0.436 (7), and an ethanol solvent molecule disordered over two positions with a common hydroxy group.

The main component of (I), *viz.* the $[\text{Co}^{\text{III}}(\text{DMG})(\text{phen})_2]_2\text{H}^+$ cation, has the Co^{III} atom in a distorted octahedral coordination geometry, with two chelating phen ligands in *cis* positions. The dihedral angles between the best planes of the chelating ligands are in the range 83.42 (8)–88.00 (10) $^\circ$ and the bite angles of the chelate rings are in the range 82.36 (11)–83.44 (11) $^\circ$. One of the phen ligands is disordered over two coplanar positions related by *ca* 13 $^\circ$ rotation around the

$\text{N12}\cdots\text{N21}$ vector. The coordination geometry around the Co^{III} centre in (I) is given in Table 1.

The disordered phen ligand shows a large number of short $\text{C}-\text{H}\cdots\text{O}$ contacts with the surrounding disordered nitrate anions and disordered solvent molecules, some of which are most probably repulsive. The occupancy of water molecule O1W is correlated with the minor position of the disordered phen ligand, whereas the occupancies of the alternative positions of the ethanol solvent molecule are correlated with the disorder of the *B* nitrate anion. In contrast, the well ordered phen and DMG ligands do not form any unusually short contacts with the disordered part of the structure, with the shortest $\text{H}\cdots\text{O}$ distance of 2.36 Å occurring for $\text{C13}-\text{H13B}\cdots\text{O2A}(1-x, -1+y, \frac{1}{2}-z)$ between the DMG methyl group and the nitrate *A* anion.

In the $[\text{Co}^{\text{III}}(\text{DMG})(\text{phen})_2]_2\text{H}^+$ cation, the atoms connected by the strong $\text{O}^-\cdots\text{H}^+\cdots\text{O}^-$ hydrogen bond are buried within a niche formed inside the cation by the ordered phen ligands and dimethylglyoximate units. In the crystal structure, the cations form extended chains along $[\bar{1}01]$ *via* π - π stacking interactions between the disordered phen units, which are additionally supported by $\text{C}-\text{H}\cdots\text{O}$ interactions between phen H atoms and atom O12¹ [symmetry code: (i) $\frac{3}{2}-x, \frac{1}{2}-y, -z$] from the deprotonated oxime group. The packing arrangement in (I) is illustrated in Fig. 2.

The asymmetric unit of the second reaction product, the dark-red block-shaped crystals of (II), consists of the $[\text{Co}^{\text{III}}(\text{DMGH})(\text{phen})_2]_2^{2+}$ cation, one ordered and one disordered nitrate anion, and disordered ethanol and water solvent molecules (Fig. 3). Taking into account the occupancies of the solvent molecules derived from the structure refinement, the formula of (II) is $[\text{Co}^{\text{III}}(\text{DMGH})(\text{phen})_2](\text{NO}_3)_2\cdot 0.40\text{H}_2\text{O}\cdot\text{EtOH}$. The dimethylglyoxime ligand is monodeprotonated, as evidenced by the oxime-group N–O bond lengths [$\text{N11}-$

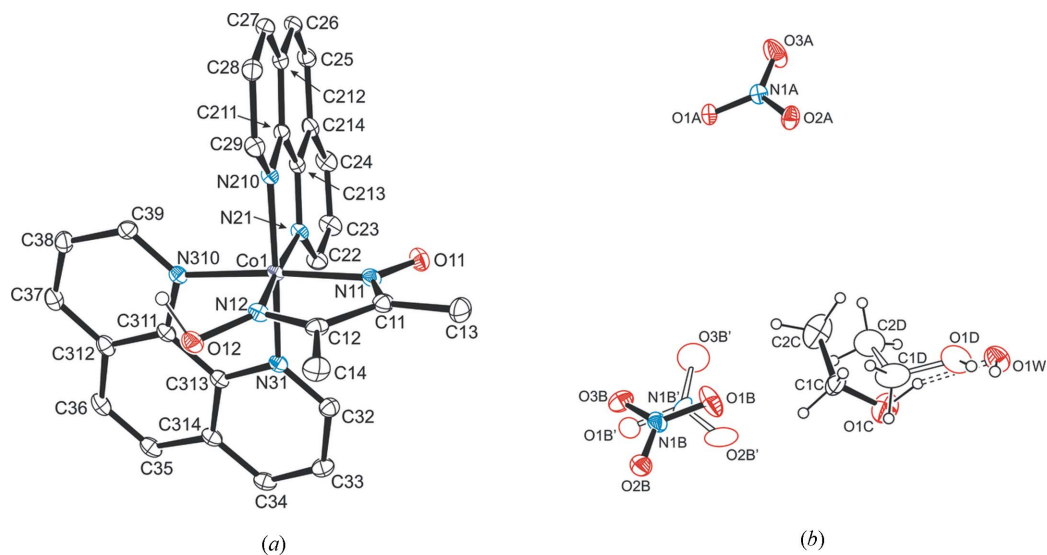
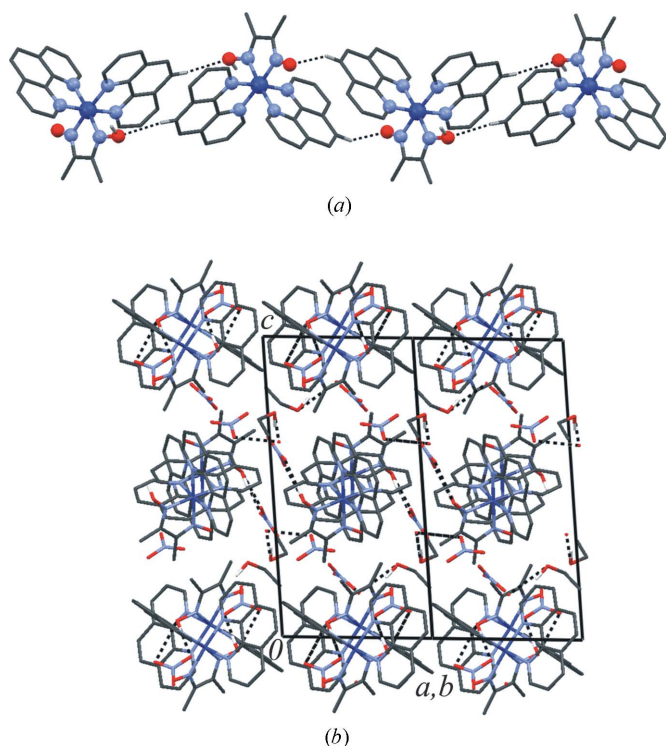


Figure 3

The structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. (a) A view of the coordination cation $[\text{Co}(\text{DMGH})(\text{phen})_2]_2^{2+}$. Only the H atom of the oxime group is shown. (b) A view of the nitrate anions and the solvent molecules. The hydrogen bond is shown as a dashed line and the disordered positions are differentiated by the displacement ellipsoid type.


Figure 4

(a) Chains formed *via* π - π stacking interactions between phen ligands and C-H...O interactions (dashed lines) in (II). (b) A view of the crystal structure of (II). The chains at $c = 0.5$ are parallel to the viewing direction, and the chains at $c = 0$ or $c = 1.0$ are approximately perpendicular to the viewing direction. Hydrogen bonds are shown as dashed lines.

O11 = 1.278 (2) Å and N12—O12 = 1.382 (2) Å], which are similar to those reported earlier for $[\text{Co}^{\text{III}}(\text{DMGH})(\text{phen})]^{2+}$ cations (Botoshanskii *et al.*, 1979; Malinovskii *et al.*, 2004). The N12—O12—H1O oxime group interacts *via* a hydrogen bond with the ordered nitrate anion *A* (Table 4).

The coordination geometry around the Co^{III} centre in (II) is very similar to that in (I) (Fig. 3*a* and Table 3), with the dihedral angles between the best planes of the chelating ligands in the range 84.46 (4)–89.97 (4)° and the bite angles of the three chelate rings in the range 81.89 (8)–83.98 (8)°. The volume in the crystal structure which is occupied by the solvent molecules is either occupied by a single ethanol molecule, which forms a hydrogen bond with a disordered *B* nitrate anion, or by an ethanol and a water molecule, with the water molecule serving as a bridge between ethanol and the *B* nitrate anion. The crystal structure of (II) can be seen as composed of chains of $[\text{Co}^{\text{III}}(\text{DMGH})(\text{phen})]^{2+}$ cations formed *via* π - π stacking interactions between inversion-centre-related phen ligands and C—H...O interactions between phen and DMGH[−] ligands. These chains extend along the $[\bar{1}10]$ and $[110]$ directions (Fig. 4). Similar packing motifs were observed in two other compounds containing $[\text{Co}^{\text{III}}(\text{DMGH})(\text{phen})]^{2+}$ cations (Botoshanskii *et al.*, 1979; Malinovskii *et al.*, 2004).

In summary, the two Co^{III} nitrate compounds isolated from one reaction contain coordination cations that differ in the

deprotonation state of the dimethylglyoximate ligand. In (I), there is one H atom per two DMG^{2-} anions, and a very strong $\text{O}^- \cdots \text{H}^+ \cdots \text{O}^-$ hydrogen bond connects two coordination cations into the $[\text{Co}^{\text{III}}(\text{DMG})(\text{phen})_2\text{H}]^+$ species, although this cannot pack efficiently, as reflected in the extensive crystal structure disorder. Compound (I), which is a kinetic product, transforms in solution to compound (II), with a structure similar to those of the previously reported mono-dimethylglyoximates. Moreover, (II) represents the revised structure of the three DMGH₂ complexes recently retracted from *Acta Crystallographica Section E* (Zhong *et al.*, 2010; CSD refcodes: YEYGOZ, YEYGUF, YIQNUI).

Experimental

Dimethylglyoxime (60 mg, 0.5 mmol), 1,10-phenanthroline (190 mg, 1 mmol) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (140 mg, 0.5 mmol) were dissolved in ethanol (10 ml) in a round-bottomed flask. The mixture was heated for 5 h under reflux with stirring and then filtered and the filtrate placed in a vial in a closed vessel containing diethyl ether. Within 1 d, red needle-shaped crystals of (I) and dark-red block-shaped crystals of (II) appeared. A few crystals of each type were isolated from the solution and used for X-ray analyses.

Compound (I)

Crystal data

$[\text{Co}_2(\text{C}_4\text{H}_6\text{N}_2\text{O}_2)(\text{C}_4\text{H}_7\text{N}_2\text{O}_2) \cdot (\text{C}_{12}\text{H}_8\text{N}_2)_4] \cdot (\text{NO}_3)_3 \cdot 2\text{C}_2\text{H}_6\text{O} \cdot 1.87\text{H}_2\text{O}$	$\beta = 104.353 (4)^\circ$ $V = 5921.4 (4) \text{ \AA}^3$ $Z = 4$
$M_r = 1379.76$	Mo $K\alpha$ radiation $\mu = 0.65 \text{ mm}^{-1}$ $T = 130 \text{ K}$ $0.50 \times 0.40 \times 0.40 \text{ mm}$
Monoclinic, $C2/c$	
$a = 19.0680 (8) \text{ \AA}$	
$b = 16.0170 (5) \text{ \AA}$	
$c = 20.0130 (8) \text{ \AA}$	

Data collection

Oxford XcaliburE CCD diffractometer	25463 measured reflections 5211 independent reflections 3075 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.053$
Absorption correction: multi-scan (CrysAlis Pro; Oxford Diffraction, 2009)	
$T_{\text{min}} = 0.720$, $T_{\text{max}} = 0.804$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$	183 restraints
$wR(F^2) = 0.095$	H-atom parameters constrained
$S = 0.89$	$\Delta\rho_{\text{max}} = 0.34 \text{ e \AA}^{-3}$
5211 reflections	$\Delta\rho_{\text{min}} = -0.46 \text{ e \AA}^{-3}$
614 parameters	

Compound (II)

Crystal data

$[\text{Co}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)(\text{C}_{12}\text{H}_8\text{N}_2)_2] \cdot (\text{NO}_3)_2 \cdot \text{C}_2\text{H}_6\text{O} \cdot 0.40\text{H}_2\text{O}$	$\beta = 96.744 (1)^\circ$ $V = 2979.11 (5) \text{ \AA}^3$ $Z = 4$
$M_r = 711.79$	Cu $K\alpha$ radiation $\mu = 5.15 \text{ mm}^{-1}$ $T = 130 \text{ K}$ $0.10 \times 0.10 \times 0.05 \text{ mm}$
Monoclinic, $P2_1/c$	
$a = 13.7587 (1) \text{ \AA}$	
$b = 11.9763 (1) \text{ \AA}$	
$c = 18.2055 (2) \text{ \AA}$	

Table 1Selected geometric parameters (\AA , $^\circ$) for (I).

Co1—N11	1.887 (3)	Co1—N210	1.943 (3)
Co1—N12	1.911 (2)	Co1—N310	1.894 (11)
Co1—N21	1.995 (3)	Co1—N410	2.097 (13)
Co1—N31	2.036 (12)	N11—O11	1.342 (3)
Co1—N41	1.848 (14)	N12—O12	1.287 (3)
N11—Co1—N310	168.0 (3)	N41—Co1—N210	169.7 (4)
N11—Co1—N410	174.2 (3)	N210—Co1—N31	175.5 (3)
N12—Co1—N21	172.92 (10)		

Table 2Hydrogen-bond geometry (\AA , $^\circ$) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O11—H1O \cdots O11 ⁱ	1.21	1.21	2.409 (4)	170
O1W—H1W1 \cdots O3A	0.89	1.95	2.816 (9)	163
O1W—H2W1 \cdots O2B	0.89	1.85	2.684 (9)	155
O1W—H2W1 \cdots O2B'	0.89	2.04	2.921 (13)	173
O1W—H2W1 \cdots O3B	0.89	2.42	2.940 (8)	118
O2W—H1W2 \cdots O2A	0.89	2.03	2.890 (9)	161
O2W—H2W2 \cdots O12 ⁱⁱ	0.89	2.10	2.845 (5)	140
O1C—H1C \cdots O1W	0.82	1.64	2.395 (7)	151
O1C—H1C \cdots O2B	0.82	2.38	2.884 (6)	120

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

Oxford SuperNova diffractometer	14572 measured reflections
Absorption correction: multi-scan (<i>CrysAlis Pro</i> ; Oxford Diffraction, 2009)	5254 independent reflections 4545 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.021$
$T_{\text{min}} = 0.611, T_{\text{max}} = 0.810$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	488 parameters
$wR(F^2) = 0.109$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.79 \text{ e \AA}^{-3}$
5254 reflections	$\Delta\rho_{\text{min}} = -0.49 \text{ e \AA}^{-3}$

Due to the severe disorder of the crystal structure of (I), the structure refinement was also attempted in the *Cc* space group, but the disorder persisted in this lower symmetry group too, with only a minor reduction in the *R* factor. For the refinement, restraints and constraints were imposed on the geometry of the disordered groups (DFIX, FLAT and EXYZ commands in *SHELXL97*; Sheldrick, 2008) and on the displacement parameters of the atoms from the disordered phen ligand (ISOR command in *SHELXL97*) and overlapping atoms of the ethanol solvent molecule and the nitrate *B* anion (EADP command in *SHELXL97*). The sum of the occupancy factors for the disordered phen ligands (atom labels starting with 3 and 4) was constrained to unity and for the major position the occupancy factor refined to 0.564 (7). A common occupancy factor was assumed for the major positions of the *B* nitrate anion and the ethanol *C* molecule and it refined to 0.638 (5). All C-bound H atoms were placed in calculated positions, with C—H = 0.95–98 \AA , and were refined as riding on their carrier atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The H atoms of the OH groups were either identified in difference Fourier maps or placed in calculated positions and refined as riding on their carrier atoms, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

In (II), disorder was observed for the *B* nitrate anion and the solvent molecules. The nitrate anions in disordered positions were refined as rigid groups. The sum of the occupancy factors for disor-

Table 3Selected geometric parameters (\AA , $^\circ$) for (II).

Co1—N11	1.9118 (18)	Co1—N210	1.9460 (18)
Co1—N12	1.8949 (18)	Co1—N310	1.9942 (18)
Co1—N21	1.9609 (18)	N11—O11	1.278 (2)
Co1—N31	1.9371 (18)	N12—O12	1.382 (2)
N31—Co1—N210	175.27 (7)	N11—Co1—N310	175.85 (8)
N12—Co1—N21	174.40 (7)		

Table 4Hydrogen-bond geometry (\AA , $^\circ$) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O12—H1O \cdots O1A	0.96	1.71	2.659 (2)	169
O12—H1O \cdots O2A	0.96	2.42	2.984 (2)	117
O1W—H1W1 \cdots O2B ⁱ	1.06	1.71	2.464 (13)	124
O1W—H1W1 \cdots O2B ^j	1.06	1.73	2.782 (8)	169
O1C—H1C \cdots O1W	1.01	1.94	2.905 (11)	161
O1D—H1D \cdots O2B ⁱ	0.95	1.90	2.824 (8)	162

Symmetry code: (i) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$.

dered nitrate anions *B* and *B'* was constrained to unity. Water and ethanol *C* molecules had a common occupancy factor of $1 - p$, where *p* is the occupancy factor of the ethanol *D* molecule. The occupancy factors for the ethanol *D* molecule and the nitrate *B* anion refined to 0.597 (6) and 0.864 (4), respectively. All C-bound H atoms were placed in calculated positions, with C—H = 0.95–99 \AA , and were refined as riding on their carrier atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The H atoms of the OH groups were either identified in difference Fourier maps or placed in calculated positions and refined as riding on their carrier atoms, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. One of the H atoms of the disordered water molecule could not be located.

For both compounds, data collection: *CrysAlis Pro* (Oxford Diffraction, 2009); cell refinement: *CrysAlis Pro*; data reduction: *CrysAlis Pro*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3237). Services for accessing these data are described at the back of the journal.

References

- Ablov, A. V., Samus, N. M. & Bologa, O. A. (1963). *Zh. Neorg. Khim.* **8**, 860–870.
- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Botoshanskii, M. M., Krasnova, N. F., Simonov, Y. A., Samus', N. M., Antipin, M. I. & Malinivskii, T. I. (1979). *Zh. Strukt. Khim.* **20**, 1052–1058.
- Bourrosh, P. N., Gerbeleu, N. V., Gdaniec, M., Simonov, Y. A., Bologa, O. A. & Koropchanu, E. B. (2006). *Russ. J. Inorg. Chem.* **51**, 267–273.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Gradinaru, J., Malinivskii, S., Gdaniec, M. & Zeccin, S. (2006). *Polyhedron*, **25**, 3417–3426.
- Harrison, W. T. A., Simpson, J. & Weil, M. (2010). *Acta Cryst.* **E66**, e1–e2.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- Malinivskii, S. T., Bologa, O. A., Coropceanu, E. B. & Gerbeleu, N. V. (2004). *Crystallogr. Rep.* **49**, 807–810.
- Malinivskii, S. T., Simonov, Y. A., Ablov, A. V., Samus', N. M. & Malinivskii, T. I. (1977). *Dokl. Akad. Nauk SSSR*, **236**, 1357–1360.

- Oxford Diffraction (2009). *CrysAlis Pro*. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Zhong, H., Duan, S.-H., Hong, Y.-P., Li, M.-L., Liu, Y.-Q., Luo, C.-J., Luo, Q.-Y., Xiao, S.-Z., Xie, H.-L., Xu, Y.-P., Yang, X.-M., Zeng, X.-R. & Zhong, Q. Y. (2010). *Acta Cryst.* **E66**, e11–e12.
- Zhong, H., Yang, X.-M., Luo, C.-J. & Li, M.-L. (2007). *Acta Cryst.* **E63**, m3160–m3161.
- Zhong, H., Zeng, X.-R., Yang, X.-M., Luo, Q.-Y. & Li, M.-L. (2007a). *Acta Cryst.* **E63**, m642–m644.
- Zhong, H., Zeng, X.-R., Yang, X.-M., Luo, Q.-Y. & Li, M.-L. (2007b). *Acta Cryst.* **E63**, m639–m641.