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trans-Bis(acetonitrile)tetraaquacobalt(II) dinitrate at 150 K

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Key indicators

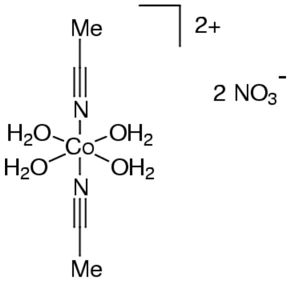
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.034
wR factor = 0.082
Data-to-parameter ratio = 14.8

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

In the title compound, $[Co(CH_3CN)_2(H_2O)_4](NO_3)_2$, the Co^{II} cations occupy crystallographic inversion centres and adopt a distorted octahedral coordination geometry, with *trans*-disposed acetonitrile ligands. Extensive hydrogen-bonding interactions between the coordinated water ligands and the nitrate counter-anions lead to the formation of a three-dimensional framework. There are substantial differences between the structure of the title compound at 150 K and the previously reported structure at 293 K.

Comment

The title compound, (I), isolated during our studies of hydrogen-bonded frameworks formed by simple aqua–metal complexes (Blake *et al.*, 2001), exists as an air-stable orange solid. An X-ray study confirmed the stoichiometry of the compound (Fig. 1). The Co^{II} centre occupies an octahedral environment with the MeCN ligands adopting a *trans* arrangement. Extensive hydrogen-bonding interactions are observed between the water molecules and the nitrate anions (Fig. 2), leading to the formation of a three-dimensional hydrogen-bonded array. Thus, each nitrate anion is hydrogen bonded to four symmetry-equivalent $[Co(CH_3CN)_2(H_2O)_4]^{2+}$ cations, with each nitrate O atom participating in hydrogen bonding. Two of the O atoms accept single hydrogen bonds from two different water-molecule donors, but the other adopts hydrogen bonds from two water molecules which are coordinated to two distinct $[Co(CH_3CN)_2(H_2O)_4]^{2+}$ cations. Each cation forms hydrogen bonds with eight different nitrate anions.



(I)

The structure of (I) has been reported previously but was determined at 293 K (Kopylovich *et al.*, 2001), as opposed to 150 K in this study. Comparison of the unit-cell dimensions of the previous and current reports reveals a significant and unexpected lengthening of the unit-cell b axis from 12.7715 (8) to 13.029 (3) Å and an increase in the value of the β angle from 117.723 (9) to 119.744 (3)°. The two structures also differ in the degree of observed disorder. Thus, in the previously

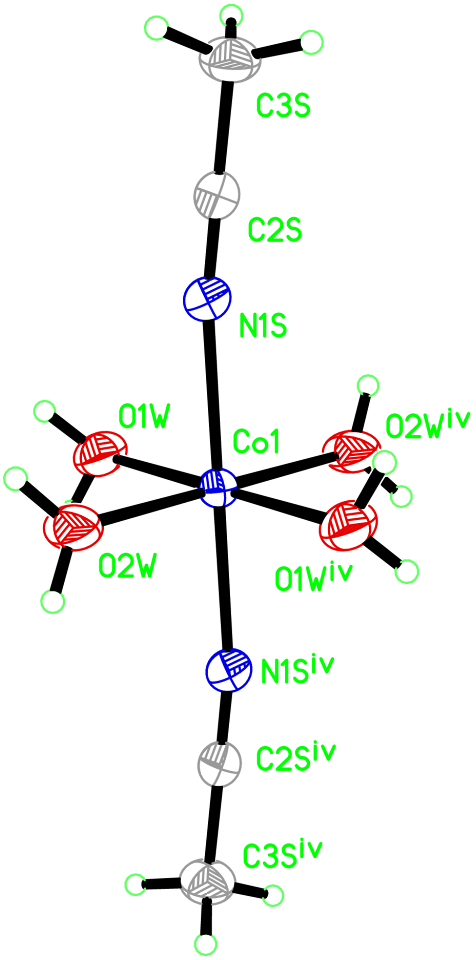


Figure 1
View of the $[Co(CH_3CN)_2(H_2O)_4]^{2+}$ cation. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (iv) $2-x$, $-y$, $2-z$.]

reported structure, one of the aqua ligands is disordered over two sites, resulting in O—Co—O angles of 83.5 (4) and 98.7 (6)°. In the current report, no disorder is observed and an O—Co—O angle of 89.00 (8)° is found. Subtle differences in the hydrogen-bonding arrangement are also observed. Most noticeably, at 293 K, only two of the nitrate O atoms act as hydrogen-bond acceptors, in contrast to the current study where all three O atoms accept hydrogen bonds from water molecules coordinated to cobalt centres.

Experimental

Orange block-shaped crystals of the title compound were grown by cooling a heated solution of $Co(NO_3)_2 \cdot 6H_2O$ in MeCN/toluene.

Crystal data

$[Co(C_2H_3N)_2(H_2O)_4](NO_3)_2$
$M_r = 337.12$
Monoclinic, $P2_1/c$
$a = 7.7375$ (15) Å
$b = 13.029$ (3) Å
$c = 7.7605$ (15) Å
$\beta = 119.744$ (3)°
$V = 679.3$ (2) Å^3
$Z = 2$

$D_x = 1.648$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 2057 reflections
$\theta = 3.0$–26.3°
$\mu = 1.32$ mm^{-1}
$T = 150$ (2) K
Block, orange
0.19 × 0.17 × 0.10 mm

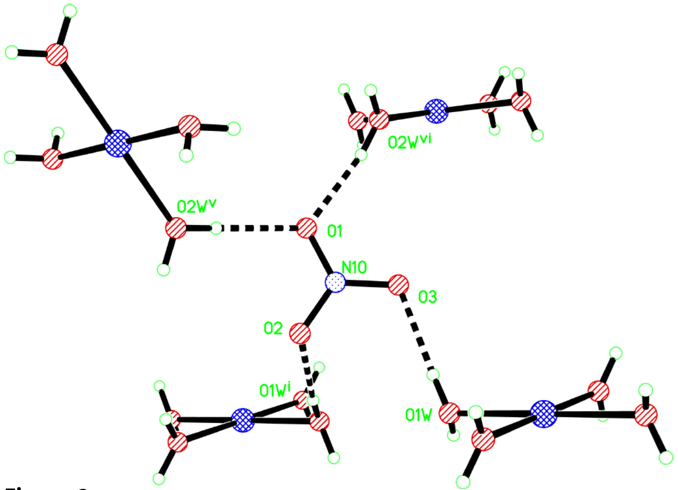


Figure 2
View of the hydrogen-bonding arrangement around the nitrate anion. MeCN molecules have been removed for clarity and hydrogen-bonding interactions are represented by dashed lines. Key: Co cross-hatch, N dotted and O left-hatch. [Symmetry codes: (i) $1-x$, $-y$, $2-z$; (v) $x-1$, $\frac{1}{2}-y$, $-\frac{1}{2}+z$; (vi) $x-1$, y, $z-1$.]

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.712$, $T_{max} = 0.877$
5625 measured reflections

1552 independent reflections
1345 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 28.0°$
$h = -9 \rightarrow 10$
$k = -17 \rightarrow 16$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.082$
$S = 1.07$
1552 reflections
105 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 0.255P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—O1*W*	2.0780 (18)	Co1—N1*S*	2.1182 (15)
Co1—O2*W*	2.0423 (16)		
O1*W*—Co1—O2*W*	89.00 (8)	O2*W*—Co1—N1*S*	89.05 (6)
O1*W*—Co1—N1*S*	91.09 (8)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1W-H1A\cdots O2^{i}$	0.826 (10)	1.953 (10)	2.769 (2)	169 (2)
$O1W-H1B\cdots O3$	0.835 (10)	1.932 (10)	2.765 (2)	176 (3)
$O2W-H2A\cdots O1^{ii}$	0.834 (10)	1.917 (10)	2.751 (2)	178 (3)
$O2W-H2B\cdots O1^{iii}$	0.834 (10)	1.898 (11)	2.724 (2)	171 (3)

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

All H atoms were located from a ΔF synthesis; these were then refined either as a rigid H_2O group [O—H 0.85 (1) Å and H···H

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1.34 (2) Å] or using a rigid-rotor model in the case of the MeCN H atoms. Displacement parameters for the MeCN H atoms were constrained such that $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$, while those of the water H atoms were refined freely.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT* and *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2002).

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