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Aqua(azido)(dimethylglyoximato)(dimethylglyoxime)cobalt(III) monohydrate

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Key indicators

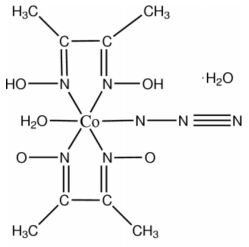
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.042
wR factor = 0.100
Data-to-parameter ratio = 13.2

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

A new mononuclear Co^{III} complex, $[Co(N_3)(dmg)(H_2dmg)(H_2O)]\cdot H_2O$ or $[Co(N_3)(C_2H_6N_2O_2)(C_2H_8N_2O_2)(H_2O)]\cdot H_2O$, has been synthesized and characterized by single-crystal X-ray diffraction analysis. In the complex, the Co^{III} ion is six-coordinated in a distorted octahedral configuration. The compound was also studied by means of room-temperature magnetic susceptibility measurements and IR spectroscopy.

Comment

Supramolecular polymer chemistry is an important developing branch of modern chemical science (Lehn, 1995, 1999; Kholbystov *et al.*, 2001). The first and essential problem of supramolecular polymer chemistry is to ensure that the polymer structure is controllable and predictable. According to the basic principles of the engineering of supramolecular polymers (Desiraju, 1995), it is very important for supramolecular polymer researchers to start from simple systems and do further research on more complicated systems through modeling and investigation of simple systems. It is well known that the oximate group (═N—O—) can function as a bridge in binding one metal atom, through the imine N atom, to generate bi- or trinuclear complexes (Zhan & Dai, 1999; Zhan *et al.*, 1999; Xu & Gu, 1998; Chaudhuri & Winter, 1991). At the same time, the deprotonated O atom can also coordinate in diverse ways with metal ions (Cervera *et al.*, 1997; Ruiz *et al.*, 1993; Ruiz *et al.*, 1993; Ruiz *et al.*, 1998; Kubiak *et al.*, 1995). Dimethylglyoxime, H_2dmg, is a potentially tetradentate ligand and can also act as a mono-, bi- or tridentate ligand. Framework molecular models show that it is more likely to bond to different metal ions and thus act as a bridging ligand rather than as a terminal ligand. Previously, we have synthesized some one-dimensional chain-like complex polymers, but in this study we have found a new polymer which is not linked through H_2dmg but by intermolecular hydrogen bonding.



(I)

A perspective view of the complex, with the atom-numbering scheme, is depicted in Fig. 1 and a packing view along the *a* direction is shown in Fig. 2. The title compound consists of a mononuclear complex $[Co(H_2O)(dmg)(H_2dmg)(N_3)]$ and a solvate water molecule. The cobalt(III) ion is

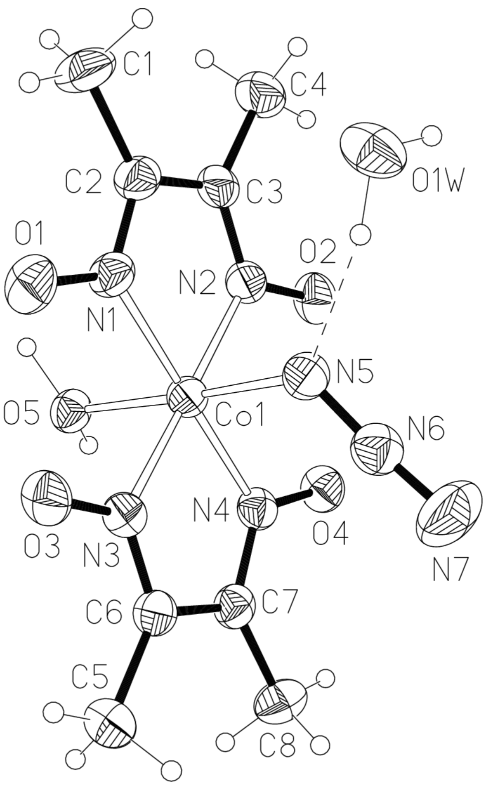


Figure 1
The structure of the title complex, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 35% probability level. H atoms attached to non-water O atoms have been omitted.

coordinated by five N atoms and one O atom to form a distorted octahedral configuration. The four N atoms (N1, N2, N3 and N4) and Co1 are approximately coplanar. Atom N5 of the azido group and O5 of the coordinated water molecule occupy the axial positions. The Co1—N1 and Co1—N2 bond lengths are longer than those of Co1—N3 and Co1—N4. The angles C2—N1—O1 and C3—N2—O2 are smaller than C6—N3—O3 and C7—N4—O4.

The H_2dmg and dmg^{2-} groups are linked by two hydrogen bonds (Table 2). An intermolecular hydrogen-bond network is also present, involving atoms O3 and O4 of the dmg group, atom N5 of the azido group, and O1*W* of the water of crystallization; *via* this network, the molecules of the complex are stacked to form a one-dimensional structure, with the Co atoms arranged in a zigzag fashion.

The magnetic susceptibility measurement performed at room temperature clearly confirms the cobalt ion to be trivalent and low spin. This means that the Co^{II} ion was oxidized to Co^{III} by oxygen in the solution. The IR spectrum shows the characteristic C═N stretching vibration of dmg^{2-} at 1570 cm^{-1}, N—O at 1237 cm^{-1}, and the characteristic N═N stretching vibration of $(N_3)^-$ at 2036 cm^{-1}.

Experimental

0.116 g (1.0 mmol) H_2dmg was dissolved in 20 ml ethanol, and 0.185 g (0.5 mmol) $Co(ClO_4)_2.6H_2O$ was added to yield a dark-brown solution. 0.032 g (0.5 mmol) sodium azide, dissolved in 10 ml water, was then added to the solution. The dark-red mixture was filtered to remove any solid particles and allowed to evaporate slowly at room temperature. After 12 d, brown plates of the title complex, suitable for X-ray analysis, were obtained. They were collected by suction filtration and air dried.

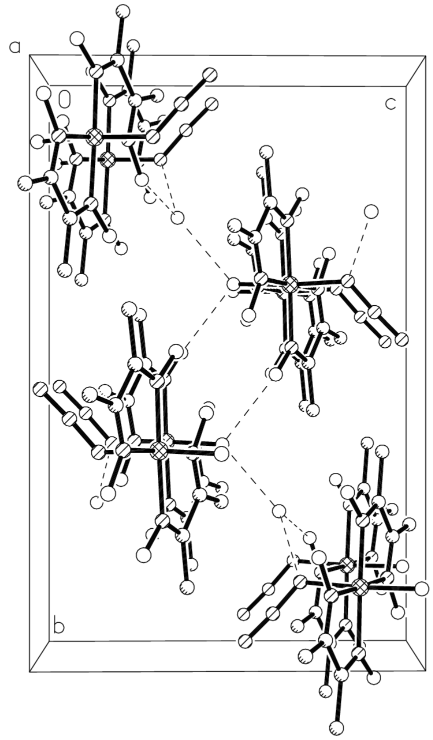


Figure 2
A view of the packing, along the *a* direction. Hydrogen bonds are indicated by dashed lines.

Crystal data

$[Co(N_3)(H_2O)(C_2H_6N_2O_2)$-
$(C_2H_8N_2O_2)]\cdot H_2O$
$M_r = 367.22$
Monoclinic, $P2_1/n$
$a = 7.6739$ (18) Å
$b = 17.515$ (4) Å
$c = 11.261$ (2) Å
$\beta = 91.243$ (14)°
$V = 1513.2$ (6) Å^3
$Z = 4$

$D_x = 1.612$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 31 reflections
$\theta = 5.0$–12.6°
$\mu = 1.18$ mm^{-1}
$T = 293$ (2) K
Plate, brown
0.40 × 0.20 × 0.04 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.225$, $T_{max} = 0.269$
3523 measured reflections
2635 independent reflections
1853 reflections with $I > 2\sigma(I)$

$R_{int} = 0.038$
$\theta_{max} = 25.0°$
$h = -9 \rightarrow 1$
$k = -1 \rightarrow 20$
$l = -13 \rightarrow 13$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.100$
$S = 1.02$
2635 reflections
200 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 2P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0018 (2)

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Table 1
Selected geometric parameters (Å, °).

Co1—N4	1.883 (3)	O3—N3	1.328 (4)
Co1—N3	1.891 (3)	O4—N4	1.342 (4)
Co1—N1	1.911 (3)	N1—C2	1.290 (5)
Co1—N5	1.919 (3)	N2—C3	1.288 (5)
Co1—N2	1.924 (3)	N3—C6	1.298 (5)
Co1—O5	1.945 (2)	N4—C7	1.309 (5)
O1—N1	1.354 (4)	N5—N6	1.210 (4)
O2—N2	1.362 (4)	N6—N7	1.139 (5)
N4—Co1—N3	82.49 (14)	C2—N1—O1	119.0 (3)
N4—Co1—N1	178.59 (14)	C2—N1—Co1	117.6 (3)
N3—Co1—N1	98.64 (14)	O1—N1—Co1	123.4 (3)
N4—Co1—N5	93.36 (13)	C3—N2—O2	119.0 (3)
N3—Co1—N5	91.10 (14)	C3—N2—Co1	117.3 (3)
N1—Co1—N5	87.47 (14)	O2—N2—Co1	123.7 (2)
N4—Co1—N2	98.91 (14)	C6—N3—O3	122.9 (3)
N3—Co1—N2	178.48 (14)	C6—N3—Co1	115.6 (3)
N1—Co1—N2	79.97 (14)	O3—N3—Co1	121.5 (2)
N5—Co1—N2	88.24 (14)	C7—N4—O4	122.4 (3)
N4—Co1—O5	90.13 (12)	C7—N4—Co1	115.7 (3)
N3—Co1—O5	88.39 (12)	O4—N4—Co1	121.9 (2)
N1—Co1—O5	89.06 (12)	N6—N5—Co1	122.1 (3)
N5—Co1—O5	176.37 (12)	N7—N6—N5	175.3 (5)
N2—Co1—O5	92.19 (12)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1F···O3	1.06	1.45	2.501 (4)	168
O2—H2A···O4	1.21	1.33	2.529 (4)	174
O1W—H1D···N5	0.97	1.93	2.862 (4)	161
O1W—H1E···O3$^{\rm i}$	0.99	1.81	2.769 (4)	161
O5—H5A···O4$^{\rm ii}$	1.08	1.57	2.631 (3)	167
O5—H5B···O1$W^{\rm iii}$	1.04	1.60	2.628 (4)	171

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

All H atoms were treated as riding on their parent atoms in the final refinement.

Data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1995); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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