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Crystal structure of tetraaquabis(1,3-dimethyl-2,6-dioxo-7*H*-purin-7-ido-κN^7)cobalt(II)

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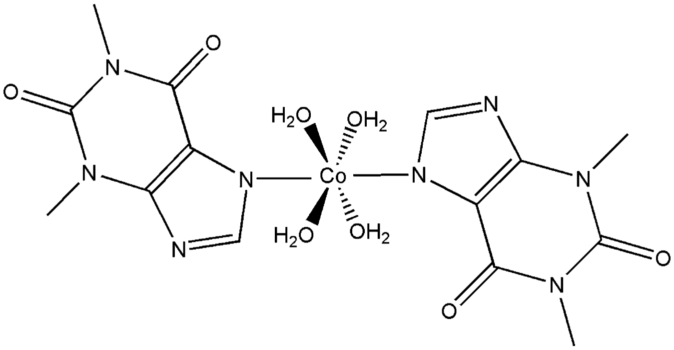
The title complex, $[Co(C_7H_7N_4O_2)_2(H_2O)_4]$, comprises mononuclear molecules consisting of a Co^{II} ion, two deprotonated theophylline ligands (systematic name: 1,3-dimethyl-7*H*-purine-2,6-dione) and four coordinating water molecules. The Co^{II} atom lies on an inversion centre and has a slightly distorted octahedral coordination environment, with two N atoms of two *trans*-oriented theophylline ligands and the O atoms of four water molecules. An intramolecular hydrogen bond stabilizes this conformation. A three-dimensional supramolecular network structure is formed by intermolecular O—H⋯O and O—H⋯N hydrogen bonds.

1. Chemical context

Theophylline (systematic name: 1,3-dimethyl-7*H*-purine-2,6-dione) belongs to the family of xanthines, which are purine derivatives. It is related to dietary xanthines caffeine and theobromine and is an important pharmacologic compound (Shukla & Mishra, 1994). Usually, synthetic drugs of theophylline are used for the treatment of disorder in the physiological functions of the pulmonary system (Childs, 2004) because theophylline is a bronchodilator that is given against asthma and bronchospasm in adults (Chen *et al.*, 2007).



The complexing ability of theophylline has been studied towards modelling metal interactions with the guanine base of nucleic acids (Orbell *et al.*, 1988). Theophylline can be deprotonated in basic or neutral media. In the majority of cases, the resulting anionic ligand is monodentate and coordinates through the N7 atom of theophylline (Marzilli *et al.*, 1973; Begum & Manohar, 1994; Bombicz *et al.*, 1997; Buncel *et al.*, 1985), while only in a few cases has a different coordination behaviour been reported, *e.g.* through the N9 atom of the imidazole ring (Aoki & Yamazaki, 1980). In addition, deprotonated theophylline may act as a bidentate ligand, where the

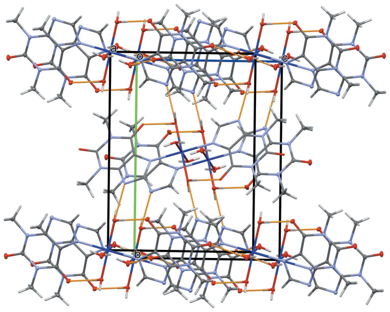


Table 1
Selected geometric parameters (Å, °).

N1—Co1	2.1847 (12)	O15—Co1	2.0756 (10)
O14—Co1	2.1022 (11)		
N1—Co1—N1^{i}	180	O14—Co1—O15^{i}	91.42 (4)
N1—Co1—O14	88.00 (4)	N1—Co1—O15	90.47 (4)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O14—H142···O11^{ii}	0.81	1.99	2.773 (2)	164
O15—H151···O13	0.83	1.82	2.638 (2)	173
O14—H141···O11^{iii}	0.81	2.01	2.817 (2)	174
O15—H152···N3^{iv}	0.82	2.01	2.799 (2)	162

Symmetry codes: (ii) $-x+1, -y+1, -z+2$; (iii) $x, y, z-1$; (iv) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$.

initial metal bonding to N7 is supplemented by coordination to the O6 atom, forming an N7/O6 chelate (Cozak *et al.*, 1986).

In this study, we reacted theophylline with the Co^{II} ion to yield the title complex, $[Co(C_7H_7N_4O_2)_2(H_2O)_4]$.

2. Structural commentary

The molecular structure of the title complex is shown in Fig. 1. The complex lies across an inversion centre, with the Co^{II} atom being coordinated in a slightly distorted octahedral environment by four aqua ligands in the equatorial sites and the imidazole ring N atoms of two 1,3-dimethyl-2,6-dioxo-7*H*-purin-7-ide ligands [N1 and N1^{i}; see Table 1 for symmetry code], in the axial sites. The Co—O bond lengths are shorter than the Co—N bond length (Table 1). The purine ring system is essentially planar, with a maximum deviation of 0.029 Å for N5; methyl atoms C10 and C12 deviate from this mean plane by −0.117 and 0.12 Å, respectively. The molecular conformation is stabilized by an intramolecular O—H···O hydrogen bond between a water molecule (O15) and a carbonyl O atom (O13) (Table 2), leading to an *S*(7) graph-set motif (Bernstein *et al.*, 1995).

3. Supramolecular features

In the crystal, the mononuclear units are connected into a layered arrangement parallel to (010). The coordinating water molecules are involved in various hydrogen-bonding interactions (Table 2), including $R_4^2(8)$ graph-set motifs that are formed through (O14···O11^{ii} = 2.817 (2) Å and O14···O11^{iii} = 2.773 (2) Å; see Table 2 for symmetry codes) between a coordinating water molecule and the carbonyl groups of symmetry-related theophylline ligands (Fig. 2). In addition, water molecule O15 is hydrogen bonded to the nonmethylated N atom of the imidazole group (O15···N3^{iv} = 2.799 (2) Å; see Table 2 for symmetry code), leading to an overall three-dimensional network.

4. Synthesis and crystallization

Theophylline (360 mg, 2 mmol) was dissolved in water (20 ml). An aqueous solution (10 ml) of NaOH (80 mg, 2 mmol) was added slowly. $CoCl_2·6H_2O$ (237 mg, 1 mmol) in water (10 ml) was then added. Pink single crystals of the title compound suitable for X-ray analysis were obtained after several months by slow evaporation of the solvent at room temperature.

5. Refinement

Details of data collection and structure refinement are summarized in Table 3. The calculated strategy was based on monoclinic chiral symmetry, with a completeness of 100%, an average multiplicity of 11.4 and no missing reflections. However, some reflections were still missing after data collection, thus reducing the completeness to less than 100%. All H atoms were located in a difference map, but those attached to C atoms were repositioned geometrically. The H atoms were refined with soft restraints on bond lengths and angles to regularize their geometry (C—H = 0.93–0.98 Å, N—H = 0.86–0.89 Å, N—H = 0.86 Å and O—H = 0.82 Å) and

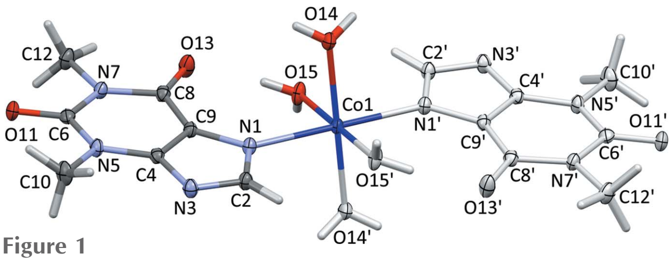


Figure 1
The molecular structure of the title complex. Primed atoms are related to the nonprimed atoms by the inversion centre of the title compound (symmetry code: $-x, -y+1, -z+1$). Displacement ellipsoids are drawn at the 50% probability level.

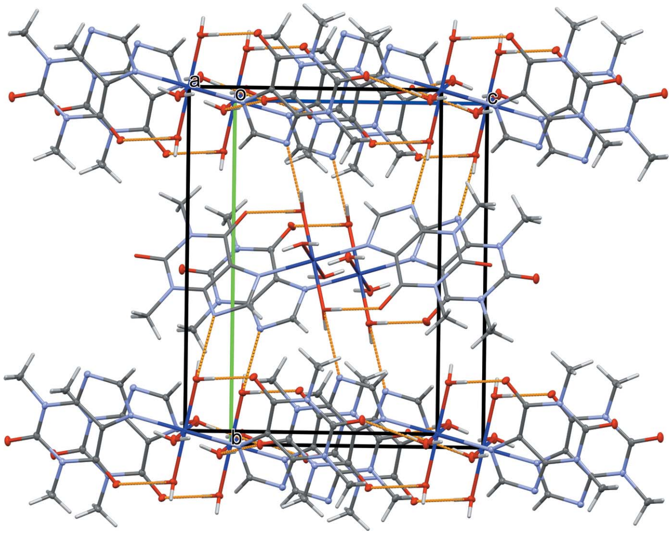


Figure 2
The crystal structure, showing the overall three-dimensional hydrogen-bonded network (hydrogen bonds as dashed lines).

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$U_{\rm iso}$(H) values (in the range 1.2–1.5 times $U_{\rm eq}$ of the parent atom), after which the positions were refined with riding constraints (Cooper *et al.*, 2010).

Acknowledgements

The authors would like to thank the LCC CNRS (Laboratory of Chemistry of Coordination) for their help.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Co(C_7H_7N_4O_2)_2(H_2O)_4]$
M_r	489.31
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	175
a, b, c (Å)	7.6304 (3), 13.1897 (6), 9.6670 (4)
β (°)	104.9744 (17)
V (Å^3)	939.87 (7)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.98
Crystal size (mm)	0.20 × 0.20 × 0.15
Data collection	
Diffractometer	Nonius KappaCCD
Absorption correction	Multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\rm min}$, $T_{\rm max}$	0.81, 0.86
No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections	41453, 1736, 1704
$R_{\rm int}$	0.028
(sin $\theta/\lambda)_{\rm max}$ (Å^{-1})	0.604
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.021, 0.023, 1.00
No. of reflections	1686
No. of parameters	142
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\rm max}$, $\Delta\rho_{\rm min}$ (e Å^{-3})	0.29, −0.22

Computer programs: *COLLECT* (Nonius, 2001)., *DENZO/SCALEPACK* (Otwinowski & Minor, 1997), *APEX2* (Bruker, 2006), *SUPERFLIP* (Palatinus & Chapuis, 2007), *CRYSTALS* (Betteridge *et al.*, 2003) and *CAMERON* (Watkin *et al.*, 1996).

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supporting information

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Crystal structure of tetraaquabis(1,3-dimethyl-2,6-dioxo-7*H*-purin-7-ido-κ*N*^{7})cobalt(II)

Hicham El Hamdani, Mohammed El Amane and Carine Duhayon

Computing details

Data collection: *COLLECT* (Nonius, 2001).; cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *APEX2* (Bruker, 2006); program(s) used to solve structure: SUPERFLIP (Palatinus & Chapuis, 2007); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS* (Betteridge *et al.*, 2003).

Tetraaquabis(1,3-dimethyl-2,6-dioxo-7*H*-purin-7-ido-κ*N*^{7})cobalt(II)

Crystal data

$[Co(C_7H_7N_4O_2)_2(H_2O)_4]$
$M_r = 489.31$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 7.6304$ (3) Å
$b = 13.1897$ (6) Å
$c = 9.6670$ (4) Å
$\beta = 104.9744$ (17)°
$V = 939.87$ (7) Å^3
$Z = 2$
$F(000) = 506$
$D_x = 1.729$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9823 reflections
$\theta = 3$–25°
$\mu = 0.98$ mm^{-1}
$T = 175$ K
Block, pale pink
0.20 × 0.20 × 0.15 mm

Data collection

Nonius KappaCCD
diffractometer
Graphite monochromator
φ & ω scans
Absorption correction: multi-scan
(DENZO/SCALEPACK; Otwinowski & Minor, 1997)
$T_{min} = 0.81$, $T_{max} = 0.86$
41453 measured reflections
1736 independent reflections
1704 reflections with $I > 2.0\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 25.4°$, $\theta_{min} = 2.7°$
$h = -9 \rightarrow 9$
$k = -15 \rightarrow 15$
$l = -11 \rightarrow 11$

Refinement

Refinement on F
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.023$
$S = 1.00$
1686 reflections
142 parameters
0 restraints
Primary atom site location: other
Hydrogen site location: difference Fourier map
H-atom parameters constrained
Method = Quasi-Unit *w*eights W = 1.0 or 1./4*F*sq
$(\Delta/\sigma)_{max} = 0.0003458$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems open-flow nitrogen cryostat (Cosier & Glazer, 1986) with a nominal stability of 0.1 K.
Cosier, J. & Glazer, A.M., 1986. J. Appl. Cryst. 105-107.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
N1	0.05846 (17)	0.45527 (9)	0.72491 (13)	0.0126
N3	0.04606 (18)	0.33836 (10)	0.89795 (13)	0.0151
N5	0.24314 (17)	0.42364 (10)	1.10036 (13)	0.0143
N7	0.34987 (17)	0.58201 (10)	1.04872 (13)	0.0139
C2	−0.0068 (2)	0.36737 (12)	0.75802 (16)	0.0143
C4	0.1522 (2)	0.41609 (11)	0.95762 (15)	0.0124
C6	0.3386 (2)	0.50912 (12)	1.14880 (16)	0.0145
C8	0.2695 (2)	0.57724 (11)	0.89958 (16)	0.0136
C9	0.16404 (19)	0.48879 (11)	0.85772 (15)	0.0119
C10	0.2355 (2)	0.34042 (13)	1.19853 (17)	0.0218
C12	0.4475 (2)	0.67528 (12)	1.10615 (17)	0.0196
O11	0.41386 (15)	0.52183 (9)	1.27770 (11)	0.0188
O13	0.29724 (16)	0.64754 (8)	0.82313 (12)	0.0206
O14	0.26896 (14)	0.46163 (9)	0.50496 (11)	0.0197
O15	0.08751 (15)	0.64646 (8)	0.55927 (11)	0.0172
Co1	0.0000	0.5000	0.5000	0.0103
H21	−0.0864	0.3279	0.6895	0.0161*
H103	0.3447	0.3423	1.2769	0.0336*
H101	0.1296	0.3467	1.2352	0.0345*
H102	0.2316	0.2770	1.1486	0.0330*
H121	0.4345	0.7242	1.0325	0.0318*
H122	0.4018	0.7025	1.1814	0.0314*
H123	0.5741	0.6614	1.1459	0.0311*
H142	0.3487	0.4654	0.5786	0.0298*
H151	0.1601	0.6467	0.6392	0.0273*
H141	0.3056	0.4824	0.4383	0.0306*
H152	0.0280	0.6987	0.5575	0.0275*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0148 (6)	0.0118 (6)	0.0100 (6)	−0.0004 (5)	0.0012 (5)	−0.0006 (5)
N3	0.0188 (7)	0.0135 (6)	0.0124 (6)	−0.0009 (5)	0.0031 (5)	0.0011 (5)
N5	0.0164 (6)	0.0158 (6)	0.0094 (6)	0.0006 (5)	0.0010 (5)	0.0024 (5)
N7	0.0138 (6)	0.0148 (6)	0.0114 (6)	−0.0019 (5)	0.0003 (5)	−0.0019 (5)
C2	0.0163 (7)	0.0135 (7)	0.0122 (7)	−0.0016 (6)	0.0019 (6)	−0.0014 (6)
C4	0.0125 (7)	0.0136 (7)	0.0109 (7)	0.0021 (6)	0.0026 (6)	0.0001 (6)
C6	0.0112 (7)	0.0191 (8)	0.0129 (7)	0.0028 (6)	0.0026 (6)	−0.0008 (6)
C8	0.0127 (7)	0.0150 (7)	0.0122 (7)	0.0020 (6)	0.0015 (6)	−0.0008 (6)
C9	0.0124 (7)	0.0129 (7)	0.0097 (7)	0.0015 (6)	0.0014 (5)	0.0002 (6)

C10	0.0312 (9)	0.0187 (8)	0.0139 (8)	0.0009 (7)	0.0030 (7)	0.0065 (6)
C12	0.0216 (8)	0.0177 (8)	0.0171 (8)	−0.0042 (7)	0.0004 (6)	−0.0049 (6)
O11	0.0170 (5)	0.0280 (6)	0.0089 (5)	−0.0012 (5)	−0.0008 (4)	−0.0012 (5)
O13	0.0272 (6)	0.0171 (6)	0.0141 (5)	−0.0082 (5)	−0.0008 (5)	0.0032 (5)
O14	0.0146 (5)	0.0329 (7)	0.0105 (5)	0.0010 (5)	0.0012 (4)	0.0005 (5)
O15	0.0236 (6)	0.0119 (5)	0.0125 (5)	0.0007 (5)	−0.0021 (4)	−0.0016 (4)
Co1	0.01218 (14)	0.00993 (14)	0.00793 (14)	−0.00056 (11)	0.00085 (10)	−0.00020 (11)

Geometric parameters (Å, º)

N1—C2	1.333 (2)	C8—C9	1.416 (2)
N1—C9	1.3994 (18)	C8—O13	1.2375 (19)
N1—Co1	2.1847 (12)	C10—H103	0.971
N3—C2	1.363 (2)	C10—H101	0.966
N3—C4	1.341 (2)	C10—H102	0.962
N5—C4	1.3786 (19)	C12—H121	0.947
N5—C6	1.358 (2)	C12—H122	0.955
N5—C10	1.4620 (19)	C12—H123	0.961
N7—C6	1.382 (2)	O14—Co1	2.1022 (11)
N7—C8	1.4149 (19)	O14—H142	0.810
N7—C12	1.4706 (19)	O14—H141	0.813
C2—H21	0.933	O15—Co1	2.0756 (10)
C4—C9	1.380 (2)	O15—H151	0.826
C6—O11	1.2414 (18)	O15—H152	0.823
C2—N1—C9	102.52 (12)	H103—C10—H102	108.8
C2—N1—Co1	118.74 (10)	H101—C10—H102	109.7
C9—N1—Co1	138.49 (10)	N7—C12—H121	110.0
C2—N3—C4	101.73 (12)	N7—C12—H122	110.7
C4—N5—C6	119.43 (13)	H121—C12—H122	109.2
C4—N5—C10	120.08 (13)	N7—C12—H123	110.6
C6—N5—C10	120.48 (13)	H121—C12—H123	109.2
C6—N7—C8	126.39 (13)	H122—C12—H123	107.1
C6—N7—C12	115.76 (12)	Co1—O14—H142	120.9
C8—N7—C12	117.76 (13)	Co1—O14—H141	115.7
N3—C2—N1	116.71 (13)	H142—O14—H141	110.0
N3—C2—H21	121.3	Co1—O15—H151	110.6
N1—C2—H21	122.0	Co1—O15—H152	129.6
N5—C4—N3	125.28 (14)	H151—O15—H152	104.5
N5—C4—C9	122.90 (14)	N1—Co1—N1^{i}	180
N3—C4—C9	111.81 (13)	N1—Co1—O14^{i}	92.00 (4)
N7—C6—N5	117.44 (13)	N1^{i}—Co1—O14^{i}	88.00 (4)
N7—C6—O11	120.82 (14)	N1—Co1—O14	88.00 (4)
N5—C6—O11	121.74 (14)	N1^{i}—Co1—O14	92.00 (4)
N7—C8—C9	113.12 (13)	O14^{i}—Co1—O14	180
N7—C8—O13	118.63 (13)	N1—Co1—O15^{i}	89.53 (4)
C9—C8—O13	128.25 (14)	N1^{i}—Co1—O15^{i}	90.47 (4)
C8—C9—N1	132.26 (13)	O14^{i}—Co1—O15^{i}	88.58 (4)

C8—C9—C4	120.50 (13)	O14—Co1—O15^{i}	91.42 (4)
N1—C9—C4	107.23 (13)	N1—Co1—O15	90.47 (4)
N5—C10—H103	108.5	N1^{i}—Co1—O15	89.53 (4)
N5—C10—H101	110.6	O14^{i}—Co1—O15	91.42 (4)
H103—C10—H101	110.0	O14—Co1—O15	88.58 (4)
N5—C10—H102	109.2	O15^{i}—Co1—O15	180

Symmetry code: (i) −*x*, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O14—H142···O11^{ii}	0.81	1.99	2.773 (2)	164
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O14—H141···O11^{iii}	0.81	2.01	2.817 (2)	174
O15—H152···N3^{iv}	0.82	2.01	2.799 (2)	162

Symmetry codes: (ii) −*x*+1, −*y*+1, −*z*+2; (iii) *x*, *y*, *z*−1; (iv) −*x*, *y*+1/2, −*z*+3/2.