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Tetraaquabis(thiocyanato-κN)cobalt(II) hexamethylenetetramine (1/2) cocrystal

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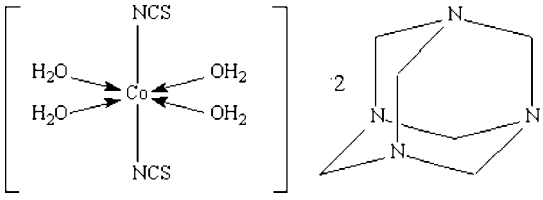
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(N–C) = 0.004 Å; R factor = 0.034; wR factor = 0.100; data-to-parameter ratio = 10.8.

In the crystal structure of the title compound, $[Co(H_2O)_4(NCS)_2]\cdot 2C_6H_{12}N_4$, the six-coordinated Co^{II} atom lies on a special position of *mmm* site symmetry and the hexamethylenetetramine molecule about a special position of $\overline{4}$ site symmetry. The two entities interact through an O—H···N hydrogen bond to form a three-dimensional network.

Related literature

For related compounds, see Li, Tong *et al.* (2004); Li, Zhao *et al.* (2004).



Experimental

Crystal data

$[Co(H_2O)_4(NCS)_2]\cdot 2C_6H_{12}N_4$
M_r = 527.55
Tetragonal, $P4_2/mnm$
a = 9.4846 (4) Å
c = 13.7339 (6) Å
V = 1235.47 (7) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.90 mm^{-1}
T = 293 (2) K
0.43 × 0.40 × 0.25 mm

Data collection

Siemens SMART diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.685, T_{max} = 0.798
2871 measured reflections
625 independent reflections
554 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.100
S = 1.06
626 reflections
58 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}

Table 1
Selected bond angles (°).

O1W^{i}—Co—O1W	90.6 (3)	C1—N1—Co	180.0
O1W—Co—O1W^{ii}	89.4 (3)	N1—C1—S1	179.999 (1)

Symmetry codes: (i) $-x+1, -y+1, z$; (ii) $x, y, -z+1$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1···N2^{iii}	0.98	1.94	2.867 (3)	157.1

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

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2324).

References

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supplementary materials

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Tetraaquabis(thiocyanato-*κN*)cobalt(II) hexamethylenetetramine (1/2) cocrystal

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Comment

Thiocyanate ion has played an important role in constructing heteronuclear complexes in our systems. (Li, Tong *et al.*,2004; Li, Zhao *et al.*, 2004). Herein is described a crystal structure of thiocyanate complex, $[Co(NCS)_2(H_2O)_4]\cdot 2(C_6H_{12}N_4)$. The cell contains two same units of the title compound. A perspective drawing of the complex with atomic numbering scheme is depicted in Fig. 1 and selected bonding parameters are presented in Table 1.

The cobalt atom locates in a slightly disordered CoN_2O_4 octahedral coordination geometry. Each hmt connects with four $[Co(NCS)_2(H_2O)_4]$ units and each $[Co(NCS)_2(H_2O)_4]$ unit connects with eight hmt molecules through O—H···N hydrogen bonds leading to 3-D network.

Experimental

$AgNO_3$ (0.68 g, 4.0 mmol), NH_4SCN (0.61 g, 4.0 mmol) and hmt (1.4 g, 10 mmol) were added to a stired $CoCl_2\cdot 6H_2O$ (0.47 g, 2.0 mmol) solution in acetonitrile, respectively. The mixture was stirred in r.t. for 12 h. After filtration, the filtrate was disposed to stand in the air. A few days later, purple-red single crystals suitable for X-ray diffraction were obtained.

Refinement

The positions of hydrogen atoms were generated geometrically (C—H bond fixed at 0.96 Å) expect those connected to O1w atoms which are generated according to the fourier map, assigned isotropic thermal parameters and allowed to ride on their respective parent C atoms before the final cycle of least-squares refinement.

Figures

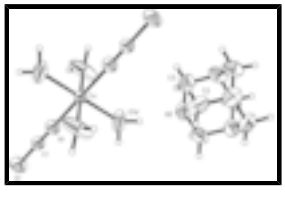

Fig. 1. A view of the complex with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

Tetraaquabis(thiocyanato-κ*N*)cobalt(II) hexamethylenetetramine (1/2) cocrystal

Crystal data

$[Co(H_2O)_4(NCS)_2]\cdot 2C_6H_{12}N_4$	$Z = 2$
$M_r = 527.55$	$F_{000} = 554$
Tetragonal, $P4_2/mnm$	$D_x = 1.418$ Mg m^{-3}

Hall symbol: -P 4n 2n	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 9.4846$ (4) Å	Cell parameters from 200 reflections
$b = 9.4846$ Å	$\theta = 2.6–25.1^\circ$
$c = 13.7339$ (6) Å	$\mu = 0.90$ mm^{-1}
$\alpha = 90^\circ$	$T = 293$ (2) K
$\beta = 90^\circ$	Prism, purple-red
$\gamma = 90^\circ$	0.43 × 0.40 × 0.25 mm
$V = 1235.47$ (7) Å^3	

Data collection

Siemens SMART diffractometer	625 independent reflections
Radiation source: fine-focus sealed tube	554 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.024$
$T = 293(2)$ K	$\theta_{max} = 25.1^\circ$
φ and ω scans	$\theta_{min} = 2.6^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -7\rightarrow11$
$T_{min} = 0.685$, $T_{max} = 0.798$	$k = -11\rightarrow11$
2871 measured reflections	$l = -16\rightarrow10$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.034$	$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2 + 0.8126P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.100$	$(\Delta/\sigma)_{max} = 0.01$
$S = 1.06$	$\Delta\rho_{max} = 0.33$ e Å^{-3}
626 reflections	$\Delta\rho_{min} = -0.46$ e Å^{-3}
58 parameters	Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.052 (5)
Secondary atom site location: difference Fourier map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-

factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Co	0.5000	0.5000	0.5000	0.0295 (4)
S1	0.86349 (9)	0.86349 (9)	0.5000	0.0606 (5)
O1W	0.3901 (3)	0.6099 (3)	0.3938 (3)	0.0960 (13)
H1	0.3990	0.7114	0.3810	0.115*
N1	0.6560 (3)	0.6560 (3)	0.5000	0.0413 (9)
C1	0.7427 (3)	0.7427 (3)	0.5000	0.0348 (10)
N2	0.1198 (3)	0.5440 (3)	0.31207 (17)	0.0558 (7)
C2	0.0000	0.5000	0.3713 (3)	0.0637 (13)
H2	−0.023 (4)	0.572 (4)	0.409 (2)	0.081 (11)*
C3	0.1598 (3)	0.4253 (4)	0.2505 (3)	0.0632 (9)
H3A	0.179 (4)	0.350 (4)	0.293 (3)	0.078 (11)*
H3B	0.243 (4)	0.457 (4)	0.212 (3)	0.079 (10)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co	0.0285 (4)	0.0285 (4)	0.0315 (5)	−0.0055 (3)	0.000	0.000
S1	0.0445 (6)	0.0445 (6)	0.0930 (11)	−0.0205 (6)	0.000	0.000
O1W	0.0788 (14)	0.0788 (14)	0.131 (3)	−0.0392 (18)	−0.0664 (18)	0.0664 (18)
N1	0.0391 (14)	0.0391 (14)	0.046 (2)	−0.0050 (18)	0.000	0.000
C1	0.0322 (15)	0.0322 (15)	0.040 (2)	−0.0018 (19)	0.000	0.000
N2	0.0523 (14)	0.0631 (15)	0.0520 (13)	0.0067 (11)	−0.0179 (11)	−0.0131 (11)
C2	0.095 (4)	0.065 (3)	0.0310 (18)	0.031 (2)	0.000	0.000
C3	0.0467 (17)	0.071 (2)	0.072 (2)	0.0158 (15)	0.0021 (14)	−0.0125 (17)

Geometric parameters (Å, °)

Co—O1W^{i}	2.074 (3)	N2—C2	1.459 (3)
Co—O1W^{ii}	2.074 (3)	N2—C3^{iv}	1.459 (4)
Co—O1W	2.074 (3)	N2—C3	1.458 (4)
Co—O1W^{iii}	2.074 (3)	C2—N2^{v}	1.459 (3)
Co—N1^{ii}	2.092 (4)	C2—H2	0.88 (3)
Co—N1	2.092 (4)	C3—N2^{vi}	1.459 (4)
S1—C1	1.621 (5)	C3—H3A	0.94 (4)
O1W—H1	0.9821	C3—H3B	0.99 (4)
N1—C1	1.163 (6)		
O1W^{i}—Co—O1W^{ii}	89.4 (3)	Co—O1W—H1	125.1
O1W^{i}—Co—O1W	90.6 (3)	C1—N1—Co	180.0
O1W^{ii}—Co—O1W	180.0	N1—C1—S1	179.999 (1)
O1W^{i}—Co—O1W^{iii}	180.0	C2—N2—C3^{iv}	108.4 (2)

O1W^{ii}—Co—O1W^{iii}	90.6 (3)	C2—N2—C3	107.8 (2)
O1W—Co—O1W^{iii}	89.4 (3)	C3^{iv}—N2—C3	108.44 (18)
O1W^{i}—Co—N1^{ii}	90.0	N2—C2—N2^{v}	112.2 (3)
O1W^{ii}—Co—N1^{ii}	90.0	N2—C2—H2	107 (2)
O1W—Co—N1^{ii}	90.0	N2^{v}—C2—H2	111 (2)
O1W^{iii}—Co—N1^{ii}	90.0	N2^{vi}—C3—N2	111.8 (3)
O1W^{i}—Co—N1	90.0	N2^{vi}—C3—H3A	107 (2)
O1W^{ii}—Co—N1	90.0	N2—C3—H3A	106 (2)
O1W—Co—N1	90.0	N2^{vi}—C3—H3B	112 (2)
O1W^{iii}—Co—N1	90.0	N2—C3—H3B	106 (2)
N1^{ii}—Co—N1	180.0	H3A—C3—H3B	114 (3)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H1···N2^{vii}	0.98	1.94	2.867 (3)	157.1

Symmetry codes: (vii) −*y*+1, −*x*+1, *z*.

Fig. 1