research communications

Synthesis and crystal structure of diaquabis(hexamethylenetramine-*κN*)bis(thiocyanato-*κN*)-cobalt(II)–hexamethylenetetramine–acetonitrile (1/2/2)

Christoph Krebs,[a]* Magdalena Ceglarska[b] and Christian Näther[a]

[a]Institut für Anorganische Chemie, Christian-Albrechts-Universität zu Kiel, Max-Eyth-Str. 2, D-24118 Kiel, Germany, and [b]Institute of Physics, Jagiellonian University, Lojasiewicza 11, 30-348 Kraków, Poland. *Correspondence e-mail: ckrebs@ac.uni-kiel.de

The crystal structure of the title solvated coordination compound, $[Co(NCS)_2(C_6H_{12}N_4)_2(H_2O)_2]\cdot 2C_6H_{12}N_4\cdot 2C_2H_3N$, consists of discrete complexes in which the Co^{2+} cations (site symmetry $\bar{1}$) are sixfold coordinated by two N-bonded thiocyanate anions, two water molecules and two hexamethylenetetramine (HMT) molecules to generate distorted *trans*-CoN_4O_2 octahedra. The discrete complexes are each connected by two HMT solvate molecules into chains *via* strong O—H···N hydrogen bonds. These chains are further linked by additional O—H···N and C—H···N and C—H···S hydrogen bonds into a three-dimensional network. Within this network, channels are formed that propagate along the *c*-axis direction and in which additional acetonitrile solvent molecules are embedded, which are hydrogen bonded to the network. The CN stretching vibration of the thiocyanate ion occurs at $2062\ cm^{-1}$, which is in agreement with the presence of N-bonded anionic ligands. XRPD investigations prove the formation of the title compound as the major phase accompanied by a small amount of a second unknown phase.

1. Chemical context

For several years, we have been interested in the synthesis of coordination compounds based on cobalt thiocyanate and additional co-ligands that in most cases consist of N-donor ligands. As is the case for, *e.g.* cyanides and azides, even this anionic ligand is able to mediate reasonable magnetic exchange (Mekuimemba *et al.*, 2018; Mousavi *et al.*, 2020; Palion-Gazda *et al.*, 2015). Therefore, we have focused especially on compounds in which the metal cations are linked by anionic ligands into coordination polymers. Most of the compounds with monocoordinating co-ligands consist of linear chains and show antiferromagnetic or ferromagnetic ordering or are single-chain magnets (Shi *et al.*, 2006; Jin *et al.*, 2007; Prananto *et al.*, 2017; Mautner *et al.*, 2018; Rams *et al.*, 2020; Ceglarska *et al.*, 2021; Werner *et al.*, 2014, 2015), whereas in compounds with non-linear chains the magnetic exchange is completely suppressed (Böhme *et al.*, 2020). In some cases, layered compounds are obtained, that are exclusively ferro-magnets (Suckert *et al.*, 2016; Wellm *et al.*, 2020). All these compounds have in common that only monocoordinating co-ligands are used, which means that the thiocyanate substructures are not additionally connected into structures of higher dimensionality. We have therefore tried to link the $Co(NCS)_2$ chains or layers by bridging co-ligands.
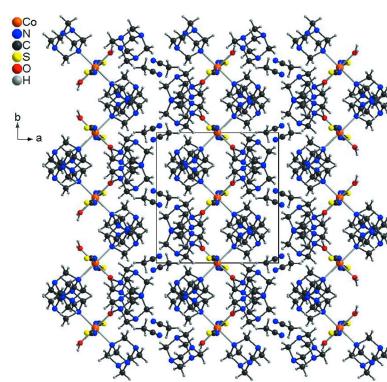
In this context, we became interested in urotropine, $C_6H_{12}N_4$ (also called hexamethylenetetramine or 1,3,5,7-tetraazaadamantane), as a co-ligand. On one hand, this ligand is magnetically silent and on the other hand it is able to form tetrahedral networks and some examples have been reported in the literature (Czubacka *et al.*, 2012; Li *et al.*, 2012). It is noted that some compounds with this ligand and Co(NCS)$_2$ have already been reported in the literature. In all cases, discrete complexes are formed in which the cobalt cations are octahedrally coordinated by two thiocyanate anions and some water, methanol or urotropine ligands (see *Database survey*). Compounds with urotropine in which the cobalt cations are linked by bridging thiocyanate anions have not been reported.
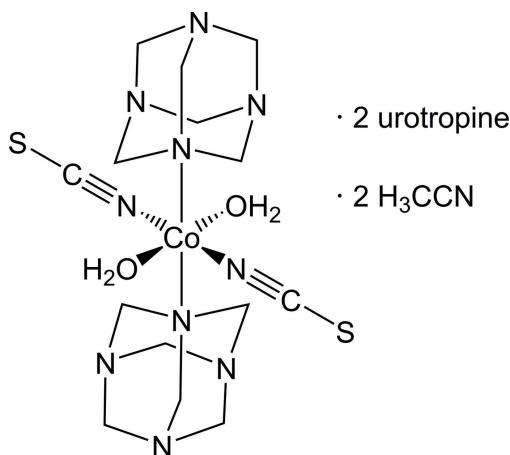
In the course of this project, we reacted Co(NCS)$_2$ with urotropine in acetonitrile, resulting in the formation of a light-yellow-colored crystalline phase, for which IR spectroscopic
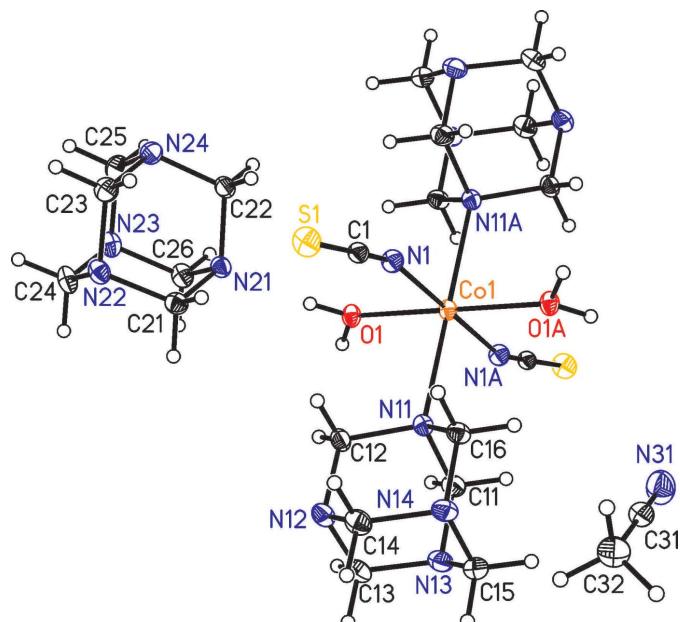
Table 1
Selected geometric parameters (Å, °).

Co1—N1	2.0744 (10)	Co1—N11	2.3112 (9)
Co1—O1	2.0661 (8)		
C1—N1—Co1	161.53 (9)		

investigations revealed the CN stretching vibration to be 2062 cm^{-1}. This indicates the presence of only N-bonded thiocyanate anions (see Fig. S1 in the supporting information). To identify this compound, a single-crystal structure analysis was performed, which proves that a discrete complex has formed. Comparison of the X-ray powder pattern of this crystalline phase with that calculated from single-crystal data reveals that the title compound has formed as the major phase, but that there are still some reflections indicating the formation of an additional and unknown crystalline phase (Fig. S2).

2. Structural commentary

In the crystal structure of the title compound, [Co(NCS)$_2$(H$_2$O)$_2$(C$_6$H$_{12}$N$_4$)$_2$]·(C$_6$H$_{12}$N$_4$)$_2$(C$_2$H$_3$N)$_2$, the cobalt cations are each octahedrally coordinated by two N-bonded thiocyanate anions, two urotropine molecules and two water molecules to form discrete complexes that are located on centers of inversion (Fig. 1). The Co1—O1 and the thiocyanate Co1—N1 bond lengths are similar, whereas the Co1—N11 bond length to the neutral co-ligand is significantly longer (Table 1). The *cis*-angles around the Co centers deviate from ideal values, showing that the octahedra are slightly distorted [range of *cis* bond angles = 87.51 (4)–92.49 (4)°]. This is also apparent from the value of the octahedral angle variance of 2.540°^{2} and the mean octahedral quadratic elongation of 1.006 calculated by the method of Robinson *et al.* (1971).

Figure 1
Crystal structure of the title compound with atom labeling and displacement ellipsoids drawn at the 50% probability level. Symmetry operation for the generation of equivalent atoms: (A) −x + 1, −y + 1, −z + 1.
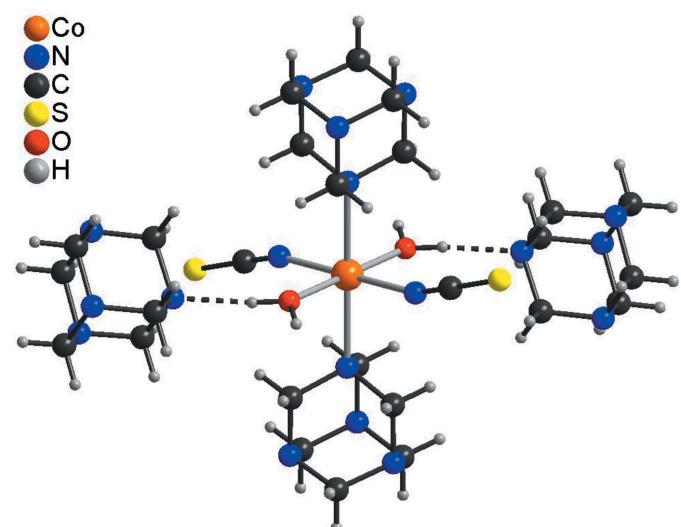
Figure 2
View of a discrete complex that is connected to two hexamethylenetetramine solvent molecules *via* O—H⋯N hydrogen bonds (dashed lines).
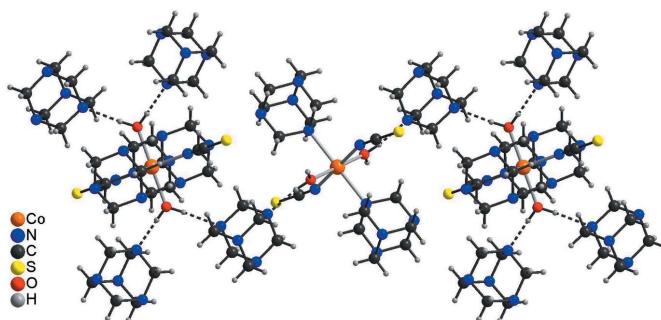
Figure 3
Part of the crystal structure of the title compound showing the connection of discrete complexes by hexamethylenetetramine solvate molecules *via* O—H···N hydrogen bonds (dashed lines).

3. Supramolecular features

The crystal structure of the title compound is dominated by a variety of intermolecular O—H···N, C—H···N and C—H···S hydrogen bonds (Table 2). Each complex molecule is connected to two adjacent non-coordinating urotropine solvate molecules *via* O—H···N hydrogen bonds from one of the water H atoms. The O—H···N angle is close to linear and the N···H distance amounts to 1.85 (2) Å, which indicates a very strong interaction (Fig. 2). The complex molecules are linked by the urotropine solvate molecules into chains (Fig. 3). The chains are further connected by an O—H···N hydrogen bond arising from the second water hydrogen atom into layers, and these layers are further linked into a three-dimensional network by a number of weak C—H···N and C—H···S hydrogen bonds. In this way, channels are formed along the crystallographic *c*-axis direction in which additional aceto-nitrile molecules are located (Fig. 4). These molecules are

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···N21	0.88 (2)	1.85 (2)	2.7298 (13)	171.8 (18)
O1—H1B···N22^i	0.88 (2)	2.01 (2)	2.8759 (13)	167.7 (19)
C12—H12B···O1	0.97	2.60	3.0752 (14)	111
C13—H13A···S1^i	0.97	2.95	3.8089 (12)	148
C13—H13B···N24^{ii}	0.97	2.66	3.5045 (16)	146
C16—H16A···O1^{iii}	0.97	2.52	3.0571 (14)	115
C16—H16B···N1	0.97	2.70	3.2713 (15)	118
C21—H21A···S1	0.97	3.00	3.9471 (12)	165
C23—H23B···S1^{iv}	0.97	2.89	3.6683 (12)	138
C26—H26A···N31^{iii}	0.97	2.56	3.4794 (17)	158
C32—H32A···S1^v	0.96	3.02	3.9560 (15)	166
C32—H32B···N23^{vi}	0.96	2.58	3.4685 (16)	154
C32—H32C···N14^v	0.96	2.61	3.4750 (17)	149

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

linked to the main network *via* C—H···N interactions (Table 2).

4. Database survey

Some crystal structures have already been deposited in the Cambridge Structure Database (CSD version 5.42, last update November 2020; Groom *et al.*, 2016) that contain cobalt cations, thiocyanate anions and urotropine molecules. These include [Co(NCS)$_2$(C$_6$H$_{12}$N$_4$)(CH$_3$OH)$_2$(H$_2$O)] (refcode: POFGAT; Shang *et al.*, 2008), which consists of neutral complexes in which the cobalt cations are octahedrally coordinated by the N atoms of two thiocyanate anions, two methanol, one water and one urotropine ligand to generate a *mer*-CoN$_3$O$_3$ coordination polyhedron. [Co(NCS)$_2$(H$_2$O)$_4$]·2C$_6$H$_{12}$N$_4$ (XILXOG; Li *et al.*, 2007) is a discrete complex with a cobalt cation coordinated octahedrally by two thiocyanate anions and four water ligands (as a *trans*-CoN$_2$O$_4$ octahedron) with two additional urotropine solvent molecules. The structure of [Co(NCS)$_2$(C$_6$H$_{12}$N$_4$)$_2$(H$_2$O)$_2$][Co(NCS)$_2$(H$_2$O)$_4$]·2H$_2$O has been determined several times (MOTNIS; Liu *et al.*, 2002; MOTNIS01; Zhang *et al.*, 1999; MOTNIS02; Chakraborty *et al.*, 2006; MOTNIS03; Lu *et al.*, 2010) and contains two discrete octahedral cobalt complexes: one metal ion is coordinated by two thiocyanate anions, two water molecules and two urotropine molecules (*trans*-CoN$_4$O$_2$ octahedron) and the other by two thiocyanate anions and four water molecules (*trans*-CoO$_4$N$_2$ octahedron); two water molecules of crystallization complete the structure.

5. Synthesis and crystallization

Synthesis

Co(NCS)$_2$ and urotropine were purchased from Merck. All chemicals were used without further purification.

Light-yellow-colored single crystals suitable for single crystal X-ray analysis were obtained after heating 0.15 mmol Co(NCS)$_2$ (26.3 mg) and 0.30 mmol urotropine (42.1 mg) in
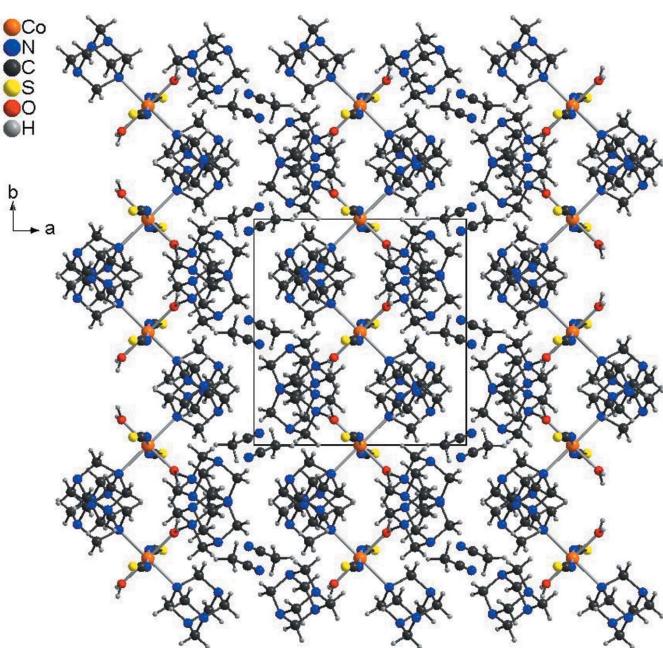
Figure 4
Crystal structure of the title compound viewed along the *c*-axis.

0.5 ml MeCN up to 353 K and then storing the mixture at 333 K overnight.

Since it was not possible to obtain a crystalline powder of the title component from solution, a sample was taken from the single crystal batch, crushed and measured.

IR: ν = 2967 (*w*), 2958 (*sh*), 2930 (*sh*), 2920 (*w*), 2881 (*w*), 2309 (*vw*), 2281 (*w*), 2252 (*vw*), 2234 (*vw*), 2185 (*vw*), 2168 (*vw*), 2062 (*s*), 1952 (*vw*), 1684–1560 (*vw*), 1461 (*m*), 1417 (*sh*), 1378 (*w*), 1372 (*w*), 1363 (*w*), 1325 (*vw*), 1231 (*s*), 1049 (*w*), 994 (*vs*), 935 (*w*), 917 (*m*), 825 (*m*), 800 (*m*), 782 (*m*), 770 (*m*), 731 (*sh*), 690 (*s*), 662 (*s*), 506 (*m*) cm^{-1}.

Experimental details

The data collection for the single-crystal structure analysis was performed using an XtaLAB Synergy, Dualflex, HyPix diffractometer from Rigaku with Cu $K\alpha$ radiation.

The PXRD measurement was performed with Cu $K\alpha_1$ radiation (λ = 1.540598 Å) using a Stoe transmission powder diffraction system (STADI P) equipped with a MYTHEN 1K detector and a Johansson-type Ge(111) monochromator.

The IR spectrum was measured using an ATI Mattson Genesis Series FTIR spectrometer, control software: WINFIRST, from ATI Mattson.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All non-hydrogen atoms were refined anisotropically. Water O atoms were freely refined. The C-bound H atoms were located in a difference map but positioned with idealized geometry (C—H = 0.96–0.97 Å, methyl H atoms allowed to rotate but not to tip) and were refined isotropically with $U_{iso}(H) = 1.2U_{eq}(C)$ (1.5 for methyl H atoms) using a riding model.

Funding information

Table 3
Experimental details.

Crystal data	
Chemical formula	[Co(NCS)₂(C₆H₁₂N₄)₂(H₂O)₂]·2C₆H₁₂N₄·2C₂H₃N
M_r	854.01
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	13.0008 (2), 12.5903 (2), 12.9988 (2)
β (°)	114.899 (2)
V (Å³)	1929.93 (6)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	4.99
Crystal size (mm)	0.20 × 0.04 × 0.03
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2021)
T_{min}, T_{max}	0.779, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25388, 4088, 3972
R_{int}	0.021
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.635
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.025, 0.071, 1.09
No. of reflections	4088
No. of parameters	259
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.20, −0.39

Computer programs: *CrysAlis PRO* (Rigaku OD, 2021), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2016/6* (Sheldrick, 2015b), *DIAMOND* (Brandenburg & Putz, 1999) and *publCIF* (Westrip, 2010).

References

Li, J., Meng, S., Zhang, J., Song, Y., Huang, Z., Zhao, H., Wei, H., Huang, W., Cifuentes, M. P., Humphrey, M. G. & Zhang, C. (2012). *CrystEngComm*, **14**, 2787–2796.

Li, X.-L., Niu, D.-Z. & Lu, Z.-S. (2007). *Acta Cryst.* E**63**, m2478.

Liu, Q., Xi, H.-T., Sun, X.-Q., Zhu, J.-F. & Yu, K.-B. (2002). *Chin. J. Struct. Chem.* **21**, 355–359.

Lu, J., Liu, H.-T., Zhang, X.-X., Wang, D.-Q. & Niu, M.-J. (2010). *Z. Anorg. Allg. Chem.* **636**, 641–647.

Mautner, F. A., Traber, M., Fischer, R. C., Torvisco, A., Reichmann, K., Speed, S., Vicente, R. & Massoud, S. S. (2018). *Polyhedron*, **154**, 436–442.

Mekuimemba, C. D., Conan, F., Mota, A. J., Palacios, M. A., Colacio, E. & Triki, S. (2018). *Inorg. Chem.* **57**, 2184–2192.

Mousavi, M., Duhayon, C., Bretosh, K., Béreau, V. & Sutter, J. P. (2020). *Inorg. Chem.* **59**, 7603–7613.

Palion-Gazda, J., Machura, B., Lloret, F. & Julve, M. (2015). *Cryst. Growth Des.* **15**, 2380–2388.

Prananto, Y. P., Urbatsch, A., Moubaraki, B., Murray, K. S., Turner, D. R., Deacon, G. B. & Batten, S. R. (2017). *Aust. J. Chem.* **70**, 516–528.

Rams, M., Jochim, A., Böhme, M., Lohmiller, T., Ceglarska, M., Rams, M. M., Schnegg, A., Plass, W. & Näther, C. (2020). *Chem. Eur. J.* **26**, 2837–2851.

Rigaku OD (2021). *CrysAlis PRO*. Rigaku Oxford Diffraction.

Robinson, K., Gibbs, G. V. & Ribbe, P. H. (1971). *Science*, **172**, 567–570.

Shang, W.-L., Bai, Y., Ma, C.-Z. & Li, Z.-M. (2008). *Acta Cryst.* E**64**, m1184–m1185.

Sheldrick, G. M. (2015a). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015b). *Acta Cryst.* C**71**, 3–8.

Böhme, M., Jochim, A., Rams, M., Lohmiller, T., Suckert, S., Schnegg, A., Plass, W. & Näther, C. (2020). *Inorg. Chem.* **59**, 5325–5338.

Brandenburg, K. & Putz, H. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Ceglarska, M., Böhme, M., Neumann, T., Plass, W., Näther, C. & Rams, M. (2021). *Phys. Chem. Chem. Phys.* **23**, 10281–10289.

Chakraborty, J., Samanta, B., Rosair, G., Gramlich, V., Salah El Fallah, M., Ribas, J., Matsushita, T. & Mitra, S. (2006). *Polyhedron*, **25**, 3006–3016.

Czubacka, E., Kruszynski, R. & Sieranski, T. (2012). *Struct. Chem.* **23**, 451–459.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Jin, Y., Che, Y. X. & Zheng, J. M. (2007). *J. Coord. Chem.* **60**, 2067–2074.

research communications

Shi, J.-M., Chen, J.-N. & Liu, L.-D. (2006). *Pol. J. Chem.* **80**, 1909–1913.

Suckert, S., Rams, M., Böhme, M., Germann, L. S., Dinnebier, R. E., Plass, W., Werner, J. & Näther, C. (2016). *Dalton Trans.* **45**, 18190–18201.

Wellm, C., Majcher-Fitas, A., Rams, M. & Näther, C. (2020). *Dalton Trans.* **49**, 16707–16714.

Werner, J., Rams, M., Tomkowicz, Z. & Näther, C. (2014). *Dalton Trans.* **43**, 17333–17342.

Werner, J., Tomkowicz, Z., Rams, M., Ebbinghaus, S. G., Neumann, T. & Näther, C. (2015). *Dalton Trans.* **44**, 14149–14158.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Zhang, Y., Li, J., Xu, H., Hou, H., Nishiura, M. & Imamoto, T. (1999). *J. Mol. Struct.* **510**, 191–196.

supporting information

Synthesis and crystal structure of diaquabis(hexamethylenetramine-*κN*)bis(thio-cyanato-*κN*)cobalt(II)–hexamethylenetetramine–acetonitrile (1/2/2)

Christoph Krebs, Magdalena Ceglarska and Christian Näther

Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2021); cell refinement: *CrysAlis PRO* (Rigaku OD, 2021); data reduction: *CrysAlis PRO* (Rigaku OD, 2021); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016/6* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg & Putz, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Diaquabis(hexamethylenetramine-*κN*)bis(thiocyanato-*κN*)cobalt(II)–hexamethylenetetramine–acetonitrile (1/2/2)

Crystal data
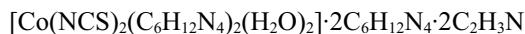
$[Co(NCS)_2(C_6H_{12}N_4)_2(H_2O)_2] \cdot 2C_6H_{12}N_4 \cdot 2C_2H_3N$	$F(000) = 906$
$M_r = 854.01$	$D_x = 1.470$ Mg m^{-3}
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
$a = 13.0008$ (2) Å	Cell parameters from 20611 reflections
$b = 12.5903$ (2) Å	$\theta = 3.7$–77.9°
$c = 12.9988$ (2) Å	$\mu = 4.99$ mm^{-1}
$\beta = 114.899$ (2)°	$T = 100$ K
$V = 1929.93$ (6) Å^3	Needle, light yellow
$Z = 2$	$0.20 \times 0.04 \times 0.03$ mm

Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer	$T_{min} = 0.779$, $T_{max} = 1.000$
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source	25388 measured reflections
	4088 independent reflections
	3972 reflections with $I > 2\sigma(I)$
Mirror monochromator	$R_{int} = 0.021$
Detector resolution: 10.0000 pixels mm^{-1}	$\theta_{max} = 78.0°$, $\theta_{min} = 3.8°$
ω scans	$h = -12 \rightarrow 16$
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2021)	$k = -15 \rightarrow 15$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	Primary atom site location: dual
$R[F^2 > 2\sigma(F^2)] = 0.025$	Hydrogen site location: mixed
$wR(F^2) = 0.071$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.09$	$w = 1/[\sigma^2(F_o^2) + (0.0427P)^2 + 0.5759P]$
4088 reflections	where $P = (F_o^2 + 2F_c^2)/3$
259 parameters	

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{min} = -0.39$ e Å^{-3}

$\Delta\rho_{max} = 0.20$ e Å^{-3}

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.500000	0.500000	0.500000	0.01162 (8)
N1	0.49434 (8)	0.46285 (8)	0.65301 (8)	0.01532 (19)
C1	0.46823 (9)	0.46250 (9)	0.72848 (10)	0.0135 (2)
S1	0.43052 (3)	0.46382 (2)	0.83365 (3)	0.02096 (8)
O1	0.62345 (7)	0.61232 (7)	0.58179 (7)	0.01480 (16)
H1A	0.6441 (16)	0.6265 (15)	0.6543 (17)	0.034 (5)*
H1B	0.6416 (17)	0.6677 (18)	0.5509 (18)	0.046 (6)*
N11	0.36295 (8)	0.62692 (8)	0.47457 (8)	0.01335 (19)
N12	0.31137 (9)	0.78613 (8)	0.55340 (9)	0.0178 (2)
N13	0.23595 (9)	0.76282 (8)	0.34775 (9)	0.0188 (2)
C11	0.32652 (10)	0.68571 (9)	0.36510 (10)	0.0175 (2)
H11A	0.391355	0.722732	0.363717	0.021*
H11B	0.300127	0.635132	0.303039	0.021*
C12	0.40035 (10)	0.70880 (9)	0.56706 (10)	0.0163 (2)
H12A	0.423172	0.673366	0.639612	0.020*
H12B	0.465940	0.746048	0.567719	0.020*
C13	0.27803 (11)	0.83883 (9)	0.44318 (11)	0.0194 (2)
H13A	0.342809	0.876660	0.442661	0.023*
H13B	0.219187	0.890515	0.432994	0.023*
C14	0.21257 (10)	0.72912 (10)	0.55236 (11)	0.0194 (2)
H14A	0.153212	0.779834	0.543355	0.023*
H14B	0.233623	0.693517	0.624588	0.023*
C15	0.13874 (10)	0.70598 (10)	0.35186 (10)	0.0196 (2)
H15A	0.110306	0.654944	0.290289	0.023*
H15B	0.078532	0.756406	0.340611	0.023*
C16	0.25985 (9)	0.57494 (9)	0.47493 (10)	0.0156 (2)
H16A	0.231942	0.522809	0.414419	0.019*
H16B	0.280830	0.537541	0.546167	0.019*
N14	0.16833 (8)	0.64994 (8)	0.46020 (9)	0.0173 (2)
N21	0.70755 (8)	0.64919 (8)	0.80957 (8)	0.01507 (19)
N22	0.71117 (9)	0.72608 (8)	0.98413 (9)	0.0167 (2)
N23	0.87597 (9)	0.74634 (8)	0.93941 (9)	0.0184 (2)
N24	0.83066 (8)	0.57193 (8)	0.99309 (8)	0.0165 (2)
C21	0.64056 (10)	0.70037 (9)	0.86374 (10)	0.0166 (2)
H21A	0.579657	0.653203	0.858804	0.020*
H21B	0.606714	0.765088	0.823090	0.020*
C22	0.75820 (10)	0.55052 (9)	0.87319 (10)	0.0159 (2)

H22A	0.697996	0.502245	0.867830	0.019*
H22B	0.802836	0.516073	0.838924	0.019*
C23	0.76143 (11)	0.62520 (10)	1.04253 (10)	0.0184 (2)
H23A	0.808248	0.639798	1.121947	0.022*
H23B	0.700979	0.577825	1.038421	0.022*
C24	0.80542 (11)	0.79507 (10)	0.98977 (11)	0.0195 (2)
H24A	0.774373	0.861136	0.950611	0.023*
H24B	0.852716	0.811921	1.068513	0.023*
C25	0.92101 (10)	0.64522 (10)	0.99882 (10)	0.0197 (2)
H25A	0.966605	0.611322	0.965300	0.024*
H25B	0.969896	0.659937	1.077698	0.024*
C26	0.80131 (10)	0.72159 (10)	0.82069 (10)	0.0180 (2)
H26A	0.845870	0.689137	0.785169	0.022*
H26B	0.769710	0.787150	0.780642	0.022*
N31	0.02532 (10)	0.44658 (10)	0.24906 (11)	0.0297 (3)
C31	−0.03061 (10)	0.46842 (10)	0.29362 (11)	0.0198 (2)
C32	−0.10137 (13)	0.49834 (10)	0.35086 (13)	0.0242 (3)
H32A	−0.179624	0.497188	0.297589	0.036*
H32B	−0.081381	0.568548	0.381669	0.036*
H32C	−0.089767	0.449026	0.411080	0.036*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.01283 (13)	0.01259 (14)	0.01083 (13)	−0.00162 (9)	0.00635 (10)	−0.00092 (9)
N1	0.0171 (5)	0.0161 (5)	0.0139 (5)	−0.0003 (4)	0.0077 (4)	0.0002 (4)
C1	0.0131 (5)	0.0120 (5)	0.0148 (5)	−0.0004 (4)	0.0052 (4)	−0.0002 (4)
S1	0.02595 (16)	0.02425 (17)	0.01980 (15)	0.00071 (11)	0.01660 (12)	−0.00011 (11)
O1	0.0176 (4)	0.0156 (4)	0.0124 (4)	−0.0034 (3)	0.0074 (3)	−0.0018 (3)
N11	0.0151 (4)	0.0126 (4)	0.0136 (4)	−0.0011 (3)	0.0072 (4)	−0.0004 (4)
N12	0.0189 (5)	0.0153 (5)	0.0207 (5)	0.0013 (4)	0.0099 (4)	−0.0024 (4)
N13	0.0229 (5)	0.0147 (5)	0.0199 (5)	0.0035 (4)	0.0099 (4)	0.0022 (4)
C11	0.0226 (6)	0.0159 (5)	0.0164 (5)	0.0025 (4)	0.0104 (5)	0.0022 (4)
C12	0.0164 (5)	0.0145 (5)	0.0178 (5)	0.0002 (4)	0.0071 (4)	−0.0040 (4)
C13	0.0232 (6)	0.0125 (5)	0.0245 (6)	0.0008 (4)	0.0120 (5)	0.0004 (4)
C14	0.0208 (6)	0.0197 (6)	0.0220 (6)	0.0026 (5)	0.0133 (5)	−0.0008 (5)
C15	0.0186 (5)	0.0175 (6)	0.0197 (6)	0.0023 (4)	0.0051 (5)	0.0012 (4)
C16	0.0140 (5)	0.0133 (5)	0.0201 (5)	0.0002 (4)	0.0078 (4)	0.0008 (4)
N14	0.0157 (5)	0.0156 (5)	0.0216 (5)	0.0024 (4)	0.0088 (4)	0.0013 (4)
N21	0.0186 (5)	0.0135 (4)	0.0142 (4)	0.0001 (4)	0.0080 (4)	−0.0003 (4)
N22	0.0219 (5)	0.0151 (5)	0.0170 (5)	−0.0011 (4)	0.0119 (4)	−0.0011 (4)
N23	0.0202 (5)	0.0178 (5)	0.0195 (5)	−0.0041 (4)	0.0107 (4)	−0.0024 (4)
N24	0.0174 (5)	0.0173 (5)	0.0153 (5)	−0.0001 (4)	0.0074 (4)	0.0009 (4)
C21	0.0172 (5)	0.0160 (5)	0.0178 (6)	0.0015 (4)	0.0084 (4)	0.0002 (4)
C22	0.0194 (5)	0.0129 (5)	0.0159 (5)	−0.0001 (4)	0.0079 (4)	−0.0011 (4)
C23	0.0240 (6)	0.0190 (6)	0.0159 (5)	0.0006 (5)	0.0120 (5)	0.0017 (4)
C24	0.0252 (6)	0.0159 (5)	0.0203 (6)	−0.0051 (5)	0.0124 (5)	−0.0059 (4)
C25	0.0162 (5)	0.0235 (6)	0.0189 (6)	−0.0017 (5)	0.0067 (4)	−0.0007 (5)

C26	0.0247 (6)	0.0171 (5)	0.0167 (6)	−0.0022 (4)	0.0130 (5)	0.0000 (4)
N31	0.0242 (6)	0.0341 (6)	0.0311 (6)	−0.0005 (5)	0.0119 (5)	−0.0095 (5)
C31	0.0180 (6)	0.0164 (6)	0.0216 (6)	0.0005 (5)	0.0051 (5)	−0.0009 (5)
C32	0.0226 (7)	0.0262 (7)	0.0267 (7)	0.0014 (5)	0.0131 (6)	0.0011 (5)

Geometric parameters (Å, º)

Co1—N1^i	2.0744 (10)	C16—H16B	0.9700
Co1—N1	2.0744 (10)	C16—N14	1.4670 (14)
Co1—O1^i	2.0661 (8)	N21—C21	1.4786 (14)
Co1—O1	2.0661 (8)	N21—C22	1.4840 (14)
Co1—N11	2.3112 (9)	N21—C26	1.4797 (15)
Co1—N11^i	2.3112 (9)	N22—C21	1.4788 (15)
N1—C1	1.1654 (16)	N22—C23	1.4827 (15)
C1—S1	1.6352 (12)	N22—C24	1.4784 (15)
O1—H1A	0.88 (2)	N23—C24	1.4669 (15)
O1—H1B	0.88 (2)	N23—C25	1.4763 (16)
N11—C11	1.4931 (14)	N23—C26	1.4695 (15)
N11—C12	1.5008 (14)	N24—C22	1.4673 (15)
N11—C16	1.4934 (14)	N24—C23	1.4697 (15)
N12—C12	1.4645 (14)	N24—C25	1.4707 (15)
N12—C13	1.4690 (16)	C21—H21A	0.9700
N12—C14	1.4665 (15)	C21—H21B	0.9700
N13—C11	1.4685 (15)	C22—H22A	0.9700
N13—C13	1.4773 (16)	C22—H22B	0.9700
N13—C15	1.4727 (16)	C23—H23A	0.9700
C11—H11A	0.9700	C23—H23B	0.9700
C11—H11B	0.9700	C24—H24A	0.9700
C12—H12A	0.9700	C24—H24B	0.9700
C12—H12B	0.9700	C25—H25A	0.9700
C13—H13A	0.9700	C25—H25B	0.9700
C13—H13B	0.9700	C26—H26A	0.9700
C14—H14A	0.9700	C26—H26B	0.9700
C14—H14B	0.9700	N31—C31	1.1377 (18)
C14—N14	1.4764 (16)	C31—C32	1.4554 (18)
C15—H15A	0.9700	C32—H32A	0.9600
C15—H15B	0.9700	C32—H32B	0.9600
C15—N14	1.4740 (15)	C32—H32C	0.9600
C16—H16A	0.9700		
N1^i—Co1—N1	180.0	N11—C16—H16B	108.9
N1—Co1—N11^i	92.49 (4)	H16A—C16—H16B	107.7
N1^i—Co1—N11^i	87.51 (4)	N14—C16—N11	113.40 (9)
N1—Co1—N11	87.51 (4)	N14—C16—H16A	108.9
N1^i—Co1—N11	92.49 (4)	N14—C16—H16B	108.9
O1—Co1—N1^i	90.32 (4)	C15—N14—C14	107.93 (9)
O1^i—Co1—N1^i	89.68 (4)	C16—N14—C14	108.13 (9)
O1—Co1—N1	89.68 (4)	C16—N14—C15	107.69 (9)

O1ⁱ—Co1—N1	90.32 (4)	C21—N21—C22	108.15 (9)
O1ⁱ—Co1—O1	180.0	C21—N21—C26	108.13 (9)
O1—Co1—N11	89.16 (3)	C26—N21—C22	107.90 (9)
O1ⁱ—Co1—N11	90.84 (3)	C21—N22—C23	107.32 (9)
O1—Co1—N11ⁱ	90.84 (3)	C24—N22—C21	108.26 (9)
O1ⁱ—Co1—N11ⁱ	89.16 (3)	C24—N22—C23	107.49 (9)
N11ⁱ—Co1—N11	180.0	C24—N23—C25	108.18 (9)
C1—N1—Co1	161.53 (9)	C24—N23—C26	107.26 (9)
N1—C1—S1	179.08 (11)	C26—N23—C25	107.92 (9)
Co1—O1—H1A	120.6 (12)	C22—N24—C23	108.11 (9)
Co1—O1—H1B	127.1 (14)	C22—N24—C25	108.12 (9)
H1A—O1—H1B	107.8 (18)	C23—N24—C25	108.33 (9)
C11—N11—Co1	113.28 (7)	N21—C21—N22	111.82 (9)
C11—N11—C12	106.78 (9)	N21—C21—H21A	109.3
C11—N11—C16	107.17 (9)	N21—C21—H21B	109.3
C12—N11—Co1	112.96 (7)	N22—C21—H21A	109.3
C16—N11—Co1	109.60 (7)	N22—C21—H21B	109.3
C16—N11—C12	106.68 (8)	H21A—C21—H21B	107.9
C12—N12—C13	108.19 (9)	N21—C22—H22A	109.2
C12—N12—C14	108.65 (9)	N21—C22—H22B	109.2
C14—N12—C13	108.33 (10)	N24—C22—N21	111.96 (9)
C11—N13—C13	108.05 (9)	N24—C22—H22A	109.2
C11—N13—C15	108.54 (9)	N24—C22—H22B	109.2
C15—N13—C13	107.73 (9)	H22A—C22—H22B	107.9
N11—C11—H11A	109.0	N22—C23—H23A	109.1
N11—C11—H11B	109.0	N22—C23—H23B	109.1
N13—C11—N11	112.72 (9)	N24—C23—N22	112.71 (9)
N13—C11—H11A	109.0	N24—C23—H23A	109.1
N13—C11—H11B	109.0	N24—C23—H23B	109.1
H11A—C11—H11B	107.8	H23A—C23—H23B	107.8
N11—C12—H12A	109.0	N22—C24—H24A	108.9
N11—C12—H12B	109.0	N22—C24—H24B	108.9
N12—C12—N11	112.74 (9)	N23—C24—N22	113.15 (9)
N12—C12—H12A	109.0	N23—C24—H24A	108.9
N12—C12—H12B	109.0	N23—C24—H24B	108.9
H12A—C12—H12B	107.8	H24A—C24—H24B	107.8
N12—C13—N13	112.28 (10)	N23—C25—H25A	109.1
N12—C13—H13A	109.1	N23—C25—H25B	109.1
N12—C13—H13B	109.1	N24—C25—N23	112.47 (10)
N13—C13—H13A	109.1	N24—C25—H25A	109.1
N13—C13—H13B	109.1	N24—C25—H25B	109.1
H13A—C13—H13B	107.9	H25A—C25—H25B	107.8
N12—C14—H14A	109.2	N21—C26—H26A	109.1
N12—C14—H14B	109.2	N21—C26—H26B	109.1
N12—C14—N14	112.24 (9)	N23—C26—N21	112.70 (9)
H14A—C14—H14B	107.9	N23—C26—H26A	109.1
N14—C14—H14A	109.2	N23—C26—H26B	109.1
N14—C14—H14B	109.2	H26A—C26—H26B	107.8

N13—C15—H15A	109.1	N31—C31—C32	178.95 (14)
N13—C15—H15B	109.1	C31—C32—H32A	109.5
N13—C15—N14	112.61 (10)	C31—C32—H32B	109.5
H15A—C15—H15B	107.8	C31—C32—H32C	109.5
N14—C15—H15A	109.1	H32A—C32—H32B	109.5
N14—C15—H15B	109.1	H32A—C32—H32C	109.5
N11—C16—H16A	108.9	H32B—C32—H32C	109.5
Co1—N11—C11—N13	177.50 (7)	C16—N11—C12—N12	−56.82 (12)
Co1—N11—C12—N12	−177.30 (7)	C21—N21—C22—N24	−58.62 (12)
Co1—N11—C16—N14	179.51 (7)	C21—N21—C26—N23	59.00 (12)
N11—C16—N14—C14	−58.13 (12)	C21—N22—C23—N24	58.82 (12)
N11—C16—N14—C15	58.26 (12)	C21—N22—C24—N23	−58.16 (13)
N12—C14—N14—C15	−58.00 (12)	C22—N21—C21—N22	58.99 (12)
N12—C14—N14—C16	58.24 (12)	C22—N21—C26—N23	−57.76 (12)
N13—C15—N14—C14	58.10 (12)	C22—N24—C23—N22	−58.82 (12)
N13—C15—N14—C16	−58.43 (12)	C22—N24—C25—N23	59.03 (12)
C11—N11—C12—N12	57.52 (12)	C23—N22—C21—N21	−58.65 (12)
C11—N11—C16—N14	−57.18 (12)	C23—N22—C24—N23	57.48 (12)
C11—N13—C13—N12	−58.92 (12)	C23—N24—C22—N21	58.22 (12)
C11—N13—C15—N14	58.66 (12)	C23—N24—C25—N23	−57.90 (12)
C12—N11—C11—N13	−57.52 (12)	C24—N22—C21—N21	57.10 (12)
C12—N11—C16—N14	56.90 (12)	C24—N22—C23—N24	−57.44 (12)
C12—N12—C13—N13	58.99 (12)	C24—N23—C25—N24	57.61 (12)
C12—N12—C14—N14	−58.86 (12)	C24—N23—C26—N21	−58.72 (12)
C13—N12—C12—N11	−58.73 (12)	C25—N23—C24—N22	−57.80 (13)
C13—N12—C14—N14	58.46 (12)	C25—N23—C26—N21	57.63 (12)
C13—N13—C11—N11	58.71 (12)	C25—N24—C22—N21	−58.86 (12)
C13—N13—C15—N14	−58.10 (12)	C25—N24—C23—N22	58.11 (12)
C14—N12—C12—N11	58.67 (12)	C26—N21—C21—N22	−57.60 (12)
C14—N12—C13—N13	−58.62 (12)	C26—N21—C22—N24	58.13 (11)
C15—N13—C11—N11	−57.84 (12)	C26—N23—C24—N22	58.38 (13)
C15—N13—C13—N12	58.16 (12)	C26—N23—C25—N24	−58.14 (12)
C16—N11—C11—N13	56.49 (12)		

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

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1—H1*A*⋯N21	0.88 (2)	1.85 (2)	2.7298 (13)	171.8 (18)
O1—H1*B*⋯N22ⁱⁱ	0.88 (2)	2.01 (2)	2.8759 (13)	167.7 (19)
C12—H12*B*⋯O1	0.97	2.60	3.0752 (14)	111
C13—H13*A*⋯S1ⁱⁱ	0.97	2.95	3.8089 (12)	148
C13—H13*B*⋯N24ⁱⁱⁱ	0.97	2.66	3.5045 (16)	146
C16—H16*A*⋯O1ⁱ	0.97	2.52	3.0571 (14)	115
C16—H16*B*⋯N1	0.97	2.70	3.2713 (15)	118
C21—H21*A*⋯S1	0.97	3.00	3.9471 (12)	165

C23—H23*B*···S1^{iv}	0.97	2.89	3.6683 (12)	138
C26—H26*A*···N31^{i}	0.97	2.56	3.4794 (17)	158
C32—H32*A*···S1^{v}	0.96	3.02	3.9560 (15)	166
C32—H32*B*···N23^{vi}	0.96	2.58	3.4685 (16)	154
C32—H32*C*···N14^{v}	0.96	2.61	3.4750 (17)	149

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