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Crystal structure of triaqua(2,6-dimethylpyrazine-κN^4)bis(thiocyanato-κN)manganese(II) 2,5-dimethylpyrazine disolvate

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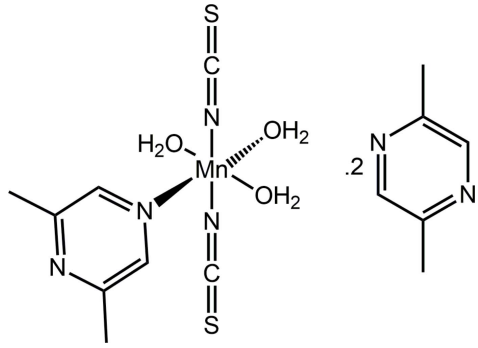
In the crystal structure of the title complex, $[Mn(NCS)_2(C_6H_8N_2)(H_2O)_3]\cdot 2C_6H_8N_2$, the Mn^{II} cation is coordinated by two terminally *N*-bonded thiocyanate anions, three water molecules and one 2,6-dimethylpyrazine ligand within a slightly distorted N_3O_3 octahedral geometry; the entire complex molecule is generated by the application of a twofold rotation axis. The asymmetric unit also contains an uncoordinating 2,5-dimethylpyrazine ligand in a general position. Obviously, the coordination to the 2,6-dimethylpyrazine ligand is preferred because coordination to the 2,5-dimethylpyrazine is hindered due to the bulky methyl group proximate to the N atom. The discrete complexes are linked by water-O—H···N(2,6-dimethylpyzazine/2,5-dimethylpyzazine) hydrogen bonding, forming a three-dimensional network. In the crystal, molecules are arranged in a way that cavities are formed in which unspecified, disordered solvent molecules reside. These were modelled employing the SQUEEZE routine in *PLATON* [Spek (2015). *Acta Cryst.* C**71**, 9–18]. The composition of the unit cell does not take into account the presence of the unspecified solvent.

Keywords: crystal structure; coordination complex; manganese(II); hydrogen bonding.

CCDC reference: 1434562

1. Related literature

For structures with metal thiocyanates and 2,5-dimethylpyrazine or 2,6-dimethylpyrazine, see: Otieno *et al.* (2003); Mahmoudi & Morsali (2009).



2. Experimental

2.1. Crystal data

$[Mn(NCS)_2(C_6H_8N_2)(H_2O)_3]\cdot 2C_6H_8N_2$
M_r = 549.58
Monoclinic, $C2/c$
a = 15.365 (1) Å
b = 27.9630 (14) Å
c = 7.0816 (5) Å
β = 93.59 (3)°
V = 3036.6 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.60 mm^{-1}
T = 200 K
0.30 × 0.23 × 0.13 mm

2.2. Data collection

Stoe IPDS-1 diffractometer
Absorption correction: numerical (*X-SHAPE* and *X-RED32*; Stoe, 2008)
T_{min} = 0.839, T_{max} = 0.921
12096 measured reflections
3674 independent reflections
2928 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.137
S = 1.07
3674 reflections
160 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*O1*···N20^{i}	0.82	1.97	2.790 (2)	177
O2—H1*O2*···N21	0.82	1.95	2.769 (2)	179
O2—H2*O2*···N11^{ii}	0.82	2.33	3.138 (3)	170

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

Data collection: *X-AREA* (Stoe, 2008); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Acknowledgements

We thank Professor Dr Wolfgang Bensch for access to his experimental facilities.

Supporting information for this paper is available from the IUCr electronic archives (Reference: TK5403).

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supporting information

Acta Cryst. (2015). E**71**, m223–m224 [https://doi.org/10.1107/S2056989015020769]

Crystal structure of triaqua(2,6-dimethylpyrazine-κN^4)bis(thiocyanato-κN)manganese(II) 2,5-dimethylpyrazine disolvate

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S1. Synthesis and crystallization

$MnSO_4.H_2O$ was purchased from Merck and 2,5-dimethylpyrazine (97%) and $Ba(NCS)_2.3H_2O$ were purchased from Alfa Aesar. $Mn(NCS)_2$ was synthesized by stirring 17.97 g (58.44 mmol) $Ba(NCS)_2.3H_2O$ and 9.88 g (58.44 mmol) $MnSO_4.H_2O$ in H_2O (300 mL) at RT for 3 h. The white residue of $BaSO_4$ was filtered off and the solvent removed with a rotary evaporator. The title compound was prepared by the reaction of $Mn(NCS)_2$. H_2O (60.1 mg, 0.25 mmol) and 2,5-dimethylpyrazine (108.0 μL, 1.00 mmol) in water (1.0 mL) at RT. After few days, yellow blocks of the title compound were obtained, that contains 2,6-dimethylpyrazine in addition anothe rmaterial. Later, it was found that the commercially available 2,5-dimethylpyrazine contains about 3% of 2,6-dimethylpyrazine as a contamination.

S2. Refinement

The C—H H atoms were positioned with idealized geometry and were refined isotropically with U_{eq}(H) = 1.2 U_{eq}(C) using a riding model with C—H = 0.95 Å for aromatic H atoms and U_{eq}(H) = 1.5 U_{eq}(C) and C—H = 0.98 Å for methyl H atoms. The methyl H atoms were allowed to rotate but not to tip. After refinement there is some residual electron density indicating a disordered N-donor ligand that is located on a center of inversion. As no reasonabe model was found and the identity of this moelcule is unknown the data were modelled for disordered solvent using the SQUEEZE routine in PLATON (Spek, 2015).

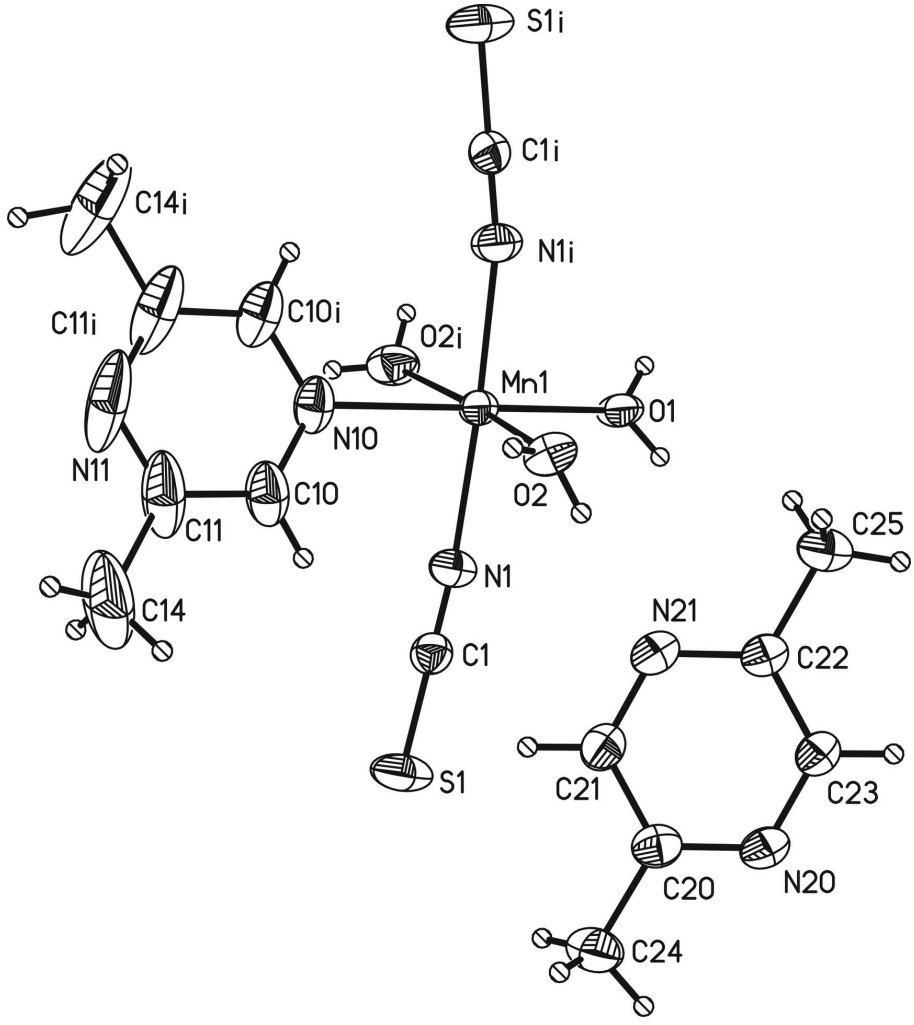

Figure 1

The molecule structures of the complex molecule (located on a 2-fold axis) and solvent molecule (full weight) in the title compound with labelling and displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (i) = -*x* + 1, *y*, -*z* + 3/2].

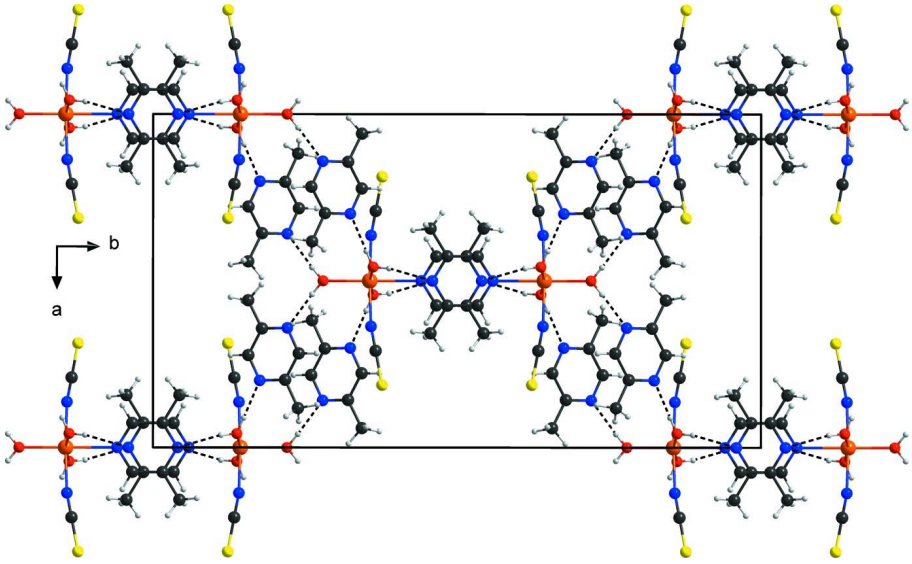

Figure 2

Part of the crystal structure of the title compound viewed along the *c* axis. Hydrogen bonding is shown as dashed lines.

Triaqua(2,6-dimethylpyrazine-κN^4)bis(thiocyanato-κN)manganese(II) 2,5-dimethylpyrazine disolvate

Crystal data

$[Mn(NCS)_2(C_6H_8N_2)(H_2O)_3]\cdot 2C_6H_8N_2$
$M_r = 549.58$
Monoclinic, $C2/c$
$a = 15.365\ (1)$ Å
$b = 27.9630\ (14)$ Å
$c = 7.0816\ (5)$ Å
$\beta = 93.59\ (3)°$
$V = 3036.6\ (3)$ Å^3
$Z = 4$
$F(000) = 1148$
$D_x = 1.202$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 12096 reflections
$\theta = 2.9–28.1°$
$\mu = 0.60$ mm^{-1}
$T = 200$ K
Block, yellow
0.30 × 0.23 × 0.13 mm

Data collection

Stoe IPDS-1 diffractometer
Radiation source: fine-focus sealed tube
phi–scans
Absorption correction: numerical (*X-SHAPE* and *X-RED32*; Stoe, 2008)
$T_{min} = 0.839$, $T_{max} = 0.921$
12096 measured reflections
3674 independent reflections
2928 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 28.1°$, $\theta_{min} = 2.9°$
$h = -20\rightarrow20$
$k = -36\rightarrow33$
$l = -9\rightarrow9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.137$
$S = 1.07$
3674 reflections
160 parameters
0 restraints
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0893P)^2 + 0.7561P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}
Extinction correction: *SHELXL2013* (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0112 (14)

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mn1	0.5000	0.35637 (2)	0.7500	0.02817 (16)
N1	0.63645 (12)	0.35855 (7)	0.8519 (3)	0.0392 (4)
C1	0.70974 (14)	0.36619 (7)	0.8897 (3)	0.0320 (4)
S1	0.81250 (4)	0.37677 (3)	0.94387 (10)	0.0516 (2)
N10	0.5000	0.44106 (9)	0.7500	0.0384 (6)
C10	0.57337 (19)	0.46610 (9)	0.7441 (4)	0.0466 (6)
H10	0.6271	0.4495	0.7390	0.056*
C11	0.5741 (3)	0.51597 (10)	0.7453 (5)	0.0701 (11)
N11	0.5000	0.54050 (11)	0.7500	0.0908 (18)
C14	0.6575 (3)	0.54330 (13)	0.7435 (7)	0.1057 (18)
H14A	0.6836	0.5460	0.8729	0.159*
H14B	0.6458	0.5753	0.6918	0.159*
H14C	0.6979	0.5265	0.6647	0.159*
N20	0.85869 (11)	0.27900 (7)	0.3202 (3)	0.0333 (4)
C20	0.85722 (13)	0.32096 (8)	0.4089 (3)	0.0328 (4)
C21	0.77715 (14)	0.34317 (8)	0.4339 (3)	0.0340 (4)
H21	0.7770	0.3729	0.4986	0.041*
C22	0.70304 (13)	0.28263 (7)	0.2784 (3)	0.0293 (4)
C23	0.78238 (13)	0.26022 (7)	0.2550 (3)	0.0317 (4)
H23	0.7825	0.2304	0.1905	0.038*
C24	0.94162 (15)	0.34348 (10)	0.4817 (4)	0.0481 (6)
H24A	0.9518	0.3727	0.4099	0.072*
H24B	0.9896	0.3210	0.4668	0.072*
H24C	0.9385	0.3514	0.6159	0.072*
C25	0.61833 (14)	0.26149 (9)	0.2047 (3)	0.0397 (5)
H25A	0.5932	0.2812	0.1006	0.060*
H25B	0.5780	0.2604	0.3064	0.060*
H25C	0.6282	0.2290	0.1588	0.060*
N21	0.70130 (11)	0.32445 (6)	0.3712 (3)	0.0327 (4)
O1	0.5000	0.27960 (7)	0.7500	0.0436 (6)
H1O1	0.5402	0.2616	0.7278	0.065*
O2	0.54166 (10)	0.36203 (6)	0.4560 (3)	0.0431 (4)
H1O2	0.5890	0.3508	0.4324	0.065*
H2O2	0.5375	0.3883	0.4048	0.065*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0211 (2)	0.0233 (2)	0.0402 (3)	0.000	0.00231 (16)	0.000

N1	0.0256 (8)	0.0395 (10)	0.0520 (12)	−0.0022 (7)	0.0000 (7)	−0.0025 (9)
C1	0.0309 (10)	0.0287 (9)	0.0366 (11)	0.0015 (7)	0.0034 (8)	0.0018 (8)
S1	0.0252 (3)	0.0799 (5)	0.0492 (4)	−0.0089 (3)	−0.0008 (2)	−0.0037 (3)
N10	0.0544 (16)	0.0242 (11)	0.0377 (14)	0.000	0.0107 (12)	0.000
C10	0.0690 (17)	0.0307 (11)	0.0419 (13)	−0.0106 (10)	0.0184 (12)	−0.0035 (9)
C11	0.120 (3)	0.0331 (13)	0.0631 (19)	−0.0243 (15)	0.053 (2)	−0.0122 (12)
N11	0.157 (4)	0.0227 (14)	0.103 (3)	0.000	0.095 (3)	0.000
C14	0.154 (4)	0.0514 (19)	0.121 (4)	−0.052 (2)	0.081 (3)	−0.029 (2)
N20	0.0268 (8)	0.0384 (9)	0.0348 (9)	0.0069 (7)	0.0023 (7)	0.0026 (7)
C20	0.0293 (9)	0.0389 (11)	0.0301 (10)	0.0024 (8)	0.0012 (7)	0.0045 (8)
C21	0.0346 (10)	0.0353 (10)	0.0322 (10)	0.0052 (8)	0.0030 (8)	−0.0023 (8)
C22	0.0280 (9)	0.0341 (10)	0.0260 (9)	0.0029 (7)	0.0036 (7)	0.0044 (8)
C23	0.0306 (9)	0.0320 (10)	0.0328 (10)	0.0051 (7)	0.0032 (7)	0.0004 (8)
C24	0.0314 (11)	0.0581 (15)	0.0543 (15)	−0.0061 (10)	−0.0010 (10)	−0.0051 (12)
C25	0.0289 (10)	0.0502 (13)	0.0396 (12)	−0.0025 (9)	−0.0009 (8)	0.0023 (10)
N21	0.0299 (8)	0.0384 (9)	0.0302 (9)	0.0072 (7)	0.0043 (6)	0.0019 (7)
O1	0.0194 (9)	0.0231 (10)	0.0887 (19)	0.000	0.0056 (10)	0.000
O2	0.0298 (8)	0.0495 (10)	0.0508 (10)	0.0038 (6)	0.0098 (7)	−0.0048 (8)

Geometric parameters (Å, º)

Mn1—O1	2.147 (2)	C11—N11	1.331 (4)
Mn1—N1^{i}	2.175 (2)	C11—C14	1.493 (5)
Mn1—N1	2.175 (2)	N11—C11^{i}	1.331 (4)
Mn1—O2^{i}	2.2216 (18)	N20—C20	1.332 (3)
Mn1—O2	2.2216 (18)	N20—C23	1.340 (3)
Mn1—N10	2.368 (2)	C20—C21	1.399 (3)
N1—C1	1.161 (3)	C20—C24	1.504 (3)
C1—S1	1.628 (2)	C21—N21	1.328 (3)
N10—C10	1.330 (3)	C22—N21	1.343 (3)
N10—C10^{i}	1.330 (3)	C22—C23	1.390 (3)
C10—C11	1.395 (4)	C22—C25	1.493 (3)
O1—Mn1—N1^{i}	91.61 (5)	C10—N10—Mn1	121.76 (15)
O1—Mn1—N1	91.61 (5)	C10^{i}—N10—Mn1	121.77 (15)
N1^{i}—Mn1—N1	176.79 (10)	N10—C10—C11	122.2 (3)
O1—Mn1—O2^{i}	94.09 (5)	N11—C11—C10	120.6 (3)
N1^{i}—Mn1—O2^{i}	88.89 (8)	N11—C11—C14	118.2 (3)
N1—Mn1—O2^{i}	90.88 (8)	C10—C11—C14	121.2 (4)
O1—Mn1—O2	94.09 (5)	C11—N11—C11^{i}	118.0 (3)
N1^{i}—Mn1—O2	90.88 (8)	C20—N20—C23	117.86 (17)
N1—Mn1—O2	88.89 (8)	N20—C20—C21	119.46 (19)
O2^{i}—Mn1—O2	171.82 (9)	N20—C20—C24	119.41 (19)
O1—Mn1—N10	180.0	C21—C20—C24	121.1 (2)
N1^{i}—Mn1—N10	88.39 (5)	N21—C21—C20	122.9 (2)
N1—Mn1—N10	88.39 (5)	N21—C22—C23	119.70 (19)
O2^{i}—Mn1—N10	85.91 (5)	N21—C22—C25	118.18 (18)
O2—Mn1—N10	85.91 (5)	C23—C22—C25	122.12 (19)

C1—N1—Mn1	169.32 (19)	N20—C23—C22	122.52 (19)
N1—C1—S1	179.7 (2)	C21—N21—C22	117.57 (17)
C10—N10—C10^{i}	116.5 (3)		

Symmetry code: (i) −*x*+1, *y*, −*z*+3/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*1···N20^{ii}	0.82	1.97	2.790 (2)	177
O2—H1*O*2···N21	0.82	1.95	2.769 (2)	179
O2—H2*O*2···N11^{iii}	0.82	2.33	3.138 (3)	170

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