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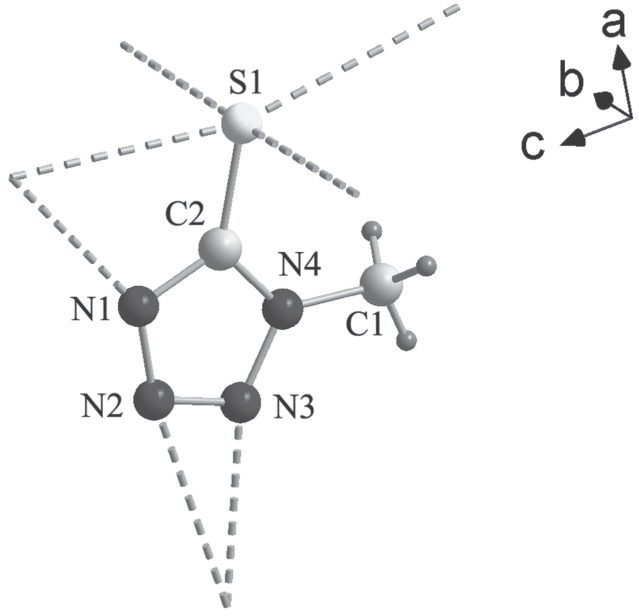
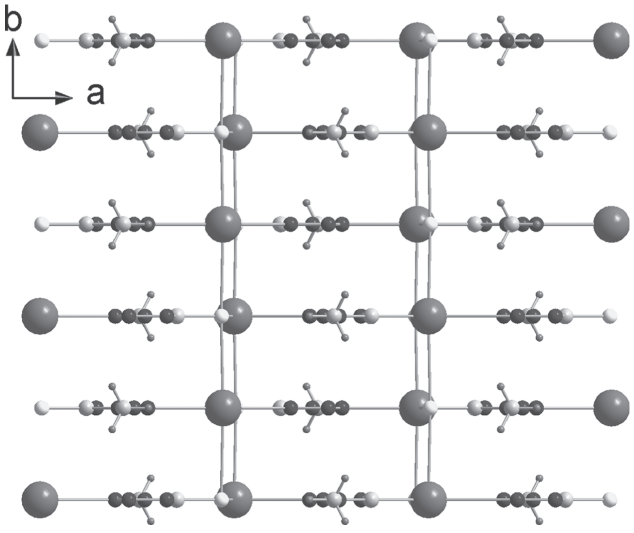
Crystal structure of potassium 1-methyl-1*H*-1,2,3,4-tetrazole-5-thiolate, $C_2H_3N_4SK$





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Abstract

$C_2H_3N_4SK$, orthorhombic, *Pnma* (no. 62), $a = 13.874(2)$ Å, $b = 6.5644(11)$ Å, $c = 6.6911(11)$ Å, $V = 609.39(17)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.02345$, $wR_{ref}(F^2) = 0.0594$, $T = 296$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	light yellow block
Size:	0.36 × 0.32 × 0.30 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	1.11 mm^{-1}
Diffractometer, scan mode:	CCD area detector, *φ* & *ω*
θ_{max}, completeness:	27.5°, 98.6%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	3239, 749, 0.056
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 693
$N(param)_{refined}$:	57
Programs:	Apex2, SAINT [13], SHELX [14, 15]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
K1	0.23565(3)	0.750000	0.39021(7)	0.03978(17)
S1	0.23112(4)	0.250000	0.38805(8)	0.03736(17)
N1	0.03416(12)	0.250000	0.3761(2)	0.0328(4)
N2	−0.04166(12)	0.250000	0.5012(3)	0.0398(4)
N3	−0.00662(13)	0.250000	0.6805(3)	0.0420(4)
N4	0.09076(12)	0.250000	0.6760(3)	0.0379(4)
C1	0.11639(13)	0.250000	0.4830(3)	0.0294(4)
C2	0.0210(2)	0.250000	0.1606(3)	0.0500(6)
H1	0.0496(16)	0.367(3)	0.109(3)	0.077(7)*
H2	−0.043(2)	0.250000	0.130(4)	0.070(9)*

Source of material

To the solution of 10 mmol (1.161 g) 1-methyl-1*H*-tetrazole-5-thione in 60 mL bidistilled water, a solution of equimolar amount (10 mmol, 0.561 g) of potassium hydroxide in 40 mL

bidistilled water was added dropwise at room temperature. After vigorous stirring for 4 h, the resulting solution was evaporated to a volume of 20 mL in vacuum and filtered hot. The filtrate was set aside for crystallization at room temperature. Half a month later, light yellow crystals of the title compound were isolated.

Experimental details

H atoms were placed in calculated positions and were refined using the riding model.

Discussion

In the past two decades, 1-organyl-1*H*-1,2,3,4-tetrazole-5-thiones have attracted tremendous attention upon their coordination behaviors. Early research mainly focused on their transition metal complexes and it was found that the ligand anion tends to coordinate through the exocyclic S atom [1–9]. It was not until 2004 that a crystallographic investigation on alkaline 1-phenyl-1*H*-1,2,3,4-tetrazole-5-thiolate compounds had been addressed [10]. It was found that in case of alkaline 1-phenyl-1*H*-1,2,3,4-tetrazole-5-thiolate, the ligand coordinates through both the exocyclic S atom and the N atoms. In 2007 we first synthesized catena-Poly[[di-μ-aqua-aqua(1-methyl-1*H*-1,2,3,4-tetrazole-5-thiolato-κ*S*) sodium]-di-μ-aqua-κ^4O:O] [11]. Crystallographic analysis revealed that it is a one-dimensional chain constructed mainly by μ_2-bridging water molecules, in which the organic ligand is monodentate through the S atom. The coordination behavior is quite different from that of sodium 1-phenyl-1*H*-1,2,3,4-tetrazole-5-thiolate monohydrate $[Na(C_6H_5N_4CS)_2{\cdot}H_2O]_2$, which is a 2D polymer. Cesium 1-methyl-1*H*-1,2,3,4-tetrazole-5-thiolate and cesium 1-phenyl-1*H*-1,2,3,4-tetrazole-5-thiolate were quite different in respect to their structures and coordination behavior [10, 12]. To get deeper insight into coordination behavior of 1-methyl-1*H*-1,2,3,4-tetrazole-5-thiono anion, herein we report the crystal structure of potassium 1-methyl-1*H*-1,2,3,4-tetrazole-5-thiolate.

The asymmetric unit of the title compound comprises a potassium cation and a 1-methyl-1*H*-1,2,3,4-tetrazole-5-thiono anion. The K^+ cation is 7-coordinated, which is also true for the tetrazolethiolate ligand anion coordinates to seven adjacent K^+ cations by its μ_4-S atom and three N atoms (figure, upper part) with K-S distances from 3.2828(5) Å to 3.3915(9) Å and K-N distances from 2.7877(18) Å to 3.213(2) Å. The μ_4-S atoms bridge the K^+ to give (4,4) topological inorganic layers parallel to *bc* plane, which are further linked by the interlayer tetrazolethiolate ligand anions to form an organic and inorganic alternatingly arranged three-dimensional framework (lower part of the figure).

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References

1. Cea-Olivares, R.; Jiménez-Sandoval, O.; Espinosa-Pérez, G.; Silvestru, C.: Crystal and molecular structure of 1-phenyl-l*H*-tetrazole + thiolato-trimethyltin(IV), Me_3SnSCN_4Ph, exhibiting unusual trimeric associations through intermolecular N→Sn bonds. J. Organomet. Chem. **484** (1994) 33–36.
2. Ortner, K.; Abram, U.: Gold(III) complexes with diphenylthiocarbazonate. Synthesis and structures of [Au(Hdamp-C1){PhNNC(S)NNPh}Cl]Cl × H_2O and [Au(Hdamp-C1){PhNNC(S)NNPh}(Smetetraz)] (Hdamp-C1 = 2-(dimethylammonium-methyl)phenyl); -Smetetraz = 2-methylmercaptotetrazolate). Polyhedron **18** (1999) 749–754.
3. Kim, Y. J.; Han, J. T.; Kang, S.; Han, W. S.; Lee, S. W.: Reactivity of di(azido)bis(phosphine) complexes of Ni(II), Pd(II) and Pt(II) toward organic isothiocyanates: synthesis, structures, and properties of bis(tetrazole-thiolato) and bis(isothiocyanato) complexes. Dalton Trans. **17** (2003) 3357–3364.
4. Chang, X.; Han, J. T.; Lim, M. S.: Cyclometallated Pd(II) azido complexes containing 6-phenyl-2,2′-bipyridyl or 2-phenylpyridyl derivatives: synthesis and reactivity toward organic isocyanides and isothiocyanates. Dalton Trans. **21** (2004) 3699–3708.
5. Kim, Y. J.; Lee, S. H.; Lee, S. H.; Jeon, S. I.; Lim, M. S.; Lee, S. W.: Reactivity of alkynyl Pd(II) azido complexes toward organic isocyanides, isothiocyanates, and nitriles. Inorg. Chim. Acta **358** (2005) 650–658.
6. Sanina, N. A.; Kozub, G. I.; Kondrat'eva, T. A.; Shilov, G. V.; Korchagin, D. V.; Emel'yanova, N. S.; Poleshchuk, O. K.; Chernyak, A. V.; Kulikov, A. V.; Mushenok, F. B.; Ovanesyan, N. S.; Aldoshin, S. M.: Structure and properties of bis(1-phenyl-1h-tetrazole-5-thiolate)diiron tetranitrosyl. J. Mol. Struct. **1041** (2013) 183–189.
7. Hu, H.; Zhang, W.; Gong, J.; Dong, H.; Zhao, F.; Huang, H.; Liu, Y.; Zhang, G.; Kang, Z.: Can tetrazole-functionalized ligands realize the role-control of Keggin-type POMs in hybrid frameworks? CrystEngComm **16** (2014) 5642–5649.
8. Liu, G.; Zhang, S.: Crystal structure of bis(1-methyl-1H-tetrazole-5-thiolato)mercury(II). Z. Kristallogr. NCS. **231** (2016) 479–480.
9. Liu, G.; Zhang, S.: Crystal structure of poly[(μ_4-1-methyl-1*H*-tetrazole-5-thiolato-κ^4S:S:N:N′)copper(I)], $C_2H_3CuN_4S$. Z. Kristallogr. NCS. **231** (2016) 791–792.
10. Hernández-Arganis, M.; Toscano, R. A.; Moya-Cabrera, M.; García-Montalvo, V.; Cea-Olivares, R.: Structural study of alkaline 1-phenyl-1*H*-1,2,3,4-tetrazole-5-thiolate salts: an example of periodicity in alkaline cations. Z. Anorg. Allg. Chem. **630** (2004) 1627–1631.

11. Wang, X. H.; Hu, M. C.; Yang, Z. Q.: Catena-Poly[[aqua(1-methyl-1*H*-1,2,3,4-tetrazole-5-thiolato-κS)sodium]di-μ-aqua-κ^4O:*O*]. Acta Crystallogr. **E63** (2007) m1527–m1529.
12. Chen, S. J.: Crystal structure of catena-(-μ_4-1-methyl-1*H*-1,2,3,4-tetrazole-5-thiolato)cesium(I), $Cs(C_2H_{3.5}N_4S)_2$. Z. Kristallogr. NCS. **227** (2016) 213–214.
13. Bruker. APEX2, SAINT. Bruker AXS Inc., Madison, Wisconsin, USA (2006).
14. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
15. Bruker Nonius. XSHELL. Version 4.02. Bruker Nonius AXS Inc., Madison, Wisconsin, USA (2004).