Formulation of an Unprecedented Potassium Thiadiazolate Framework Via In-Situ Ligand Synthesis

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Summary: The development of extended structures using s-block metal centres is fairly rare because of the predominance of ionic forces at metal center. The in-situ formation of 1,3,5-thiadiazole-2,5-dithiol ligand and its coordination to potassium metal ions results in the form of air stable green crystals of a novel framework [$C_2HKN_2OS_3$]. The two-dimensional framework is characterized as $P2_1$ space group with the potassium ion, being heptacoordinated. The compound, showed distorted pentagonal bipyramidal coordination geometry due to the larger cationic radius of the potassium. The potassium metal ion is forming a bond with a nitrogen atom of azine nitrogens, two bonds with the oxygen atoms of the two hydroxyl ions and four bonds with the four sulfide ions of thiol moieties of four different thiadiazole rings. The C-S bond distances are in the range of 1.687(4) to 1.760(4) slightly shorter than the ideal value of 1.77 Å for a C(sp^2)-S single bond. The thermogravimetric analysis indicates that a successive loss of the ligand occurs in the range of 253.06 ºC to 357.53 ºC that infers the stability of the compound.

Keywords: 1,3,5-thiadiazole-2,5-dithiol, Novel potassium framework, Mechanism, Infrared spectroscopy, Single crystal X-ray diffraction studies, Thermogravimetric analysis.

Introduction

A careful selection of ligands with suitable functional groups and metals for the formulation of extended networks has been a fascinating and appealing topic for inorganic chemists. These extended networks find ultimate applications in the areas of ion exchange [1,2] thin film devices [3,4], drug delivery [5,6], gas storage and separation [7-10], catalysis [11-13], magnetism [14] and nanoparticles [15].

The selection of multifunctional ligands especially those containing N-, S- and O- is extremely decisive to the synthesis of the desired compounds with a wide range of applications and exciting framework structures [16,17]. The multifunctional thiadiazole especially 1,3,4-thiadiazole is a flexible ligand and can bridge a wide range of metal centers as it contains more than one coordination sites [18]. These ligands find enormous applications in the field of pharmaceutical, and pharmacology industries [19].

The development of first and second group metals based organic frameworks is of utmost interest of the chemists nowadays as the MOF chemistry of these metals is less studied [20, 21]. In the past, mostly first row transition metal centers have been chosen because of their well-known coordination behaviors with different secondary building units. On the contrary, the coordination behavior of s-block metal centres is rarely studied because the interaction of these metal atoms with -S and -O donor ligands is ionic due to the large differences in the electronegativity of the atoms which results in a little room for prediction and control over geometry.

Despite facing problems in evaluating the coordination geometry of s-block metal-organic frameworks, there are several advantages of synthesizing these coordination polymers:

a) The s-block metals (Na, K, Mg and Ca) are among the ten most abundant elements, b) these frameworks could provide gravimetric advantages for gas adsorption due to their low-atomic weights, c) higher charge density of these metal ions leads to strong bonding interactions with donor atoms, d) they are cheap and non-toxic.

Here, we have synthesized a novel potassium based thiadiazolate network with in-situ ligand formation. The newly synthesized low-dimensional network is unique in the sense that the potassium metal ion is forming seven bonds through coordination with the four sulfide ions of thiol moieties of four different thiadiazole rings, one bond with nitrogen atom of azine nitrogens and two bonds with oxygen atoms of two hydroxyl ions observing a

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distorted pentagonal bipyramidal geometry. Such types of networks are interesting for the synthesis of heterometallic metal-organic frameworks [22].

In this article, we report the synthesis, mechanism, infra red spectroscopy, elemental analysis, thermogravimetric analysis and single crystal X-ray diffraction studies of potassium 1,3,4-thiadiazole-2,5-bis(thiolate) network.

Experimental

Materials and Measurements

All the starting reagents were purchased commercially and used without further purification. Melting points were determined on Gallen Kamp apparatus. Infrared measurements (4000-400 cm^{-1}) were taken on Thermo scientific NICOLET 6700 FTIR spectrophotometer. Elemental analyses were performed with a Thermo Scientific FLASH 2000 CHNS/O analyzer. The TGA curve was recorded using a METTLER TOLEDO(SWITZERLAND) Model TGA/SDTA 851 equipment under air. The sample was heated from 0 ºC to 750 ºC. Diffraction data of the network was collected at 100(2) K on beam line MX1 at the Australian Synchrotron (λ = 0.71703 Å) [23]. The data reduction and indexing of diffraction pattern was performed by XDS software. The structures were solved by direct methods and refined by full matrix least squares against F2 of data using SHELXL97 (Sheldrick, 1997) software [24]. All non-hydrogen atoms were refined with anisotropic displacement parameters.

Synthesis of ligand and potassium framework

The thiadiazolate containing potassium based framework was synthesized by adding 2-(2-fluorobiphenyl-4-yl) propanoic acid hydrazide (1 mmol, 0.258 g) to an ice cooled alcoholic potassium hydroxide solution containing 2 mmoles (0.112 g) of KOH. To the reaction mixture, CS_2 (2 mmoles, 0.12 mL) was added dropwise under constant stirring. The reaction mixture was stirred further for 12 hours at room temperature and left in open air for slow evaporation of solvent. Air stable greenish yellow colored crystals of the title compound were isolated from deposit after 10 days with a yield of 65%.

Mechanism

The nucleophilic attack of the base on the electrophilic carbon atom of the hydrazide molecule results in the formation of a hydrazine moiety. This hydrazine molecule reacts with carbon disulphide leading to the synthesis of 1,3,4-thiadiazole-2,5-dithiol ligand. The in-situ synthesized ligand reacts with KOH to give potassium 1,3,4-thiadiazole-2,5-bis(thiolate) framework (Mechanism).

Infrared Spectroscopy

The IR spectrum shows absorptions due to stretching modes of O-H (3389 cm^{-1}), C=N (1540 cm^{-1}), C-S (763 cm^{-1}) and N-N (1064 cm^{-1}) confirming the formation of the framework. The absence of absorption band for the

-SH moiety shows that the thiol protons have been removed completely upon reaction with KOH.

Elemental Analysis

The elemental analysis shows a good agreement between the calculated and observed values for elements.

Calculated for [$C_2HKN_2OS_3$]: C, 11.76; N, 13.71; H, 0.49, Found: C, 11.96; N, 13.53; H, 0.62.

Thermogravimetric Analysis

The thermal stability of the compound was checked by thermogravimetric analysis. The TGA curve shows a loss of hydroxyl moiety (Observed 7.60 %, Calculated: 8.3%) in the temperature range of 96.50 ºC to 162.87 ºC. A successive loss of the ligand occurs in the range of 253.06 ºC to 357.53 ºC (Observed 53.55 %, Calculated: 60.0%) that indicates the stability of the compound (Fig. 1).

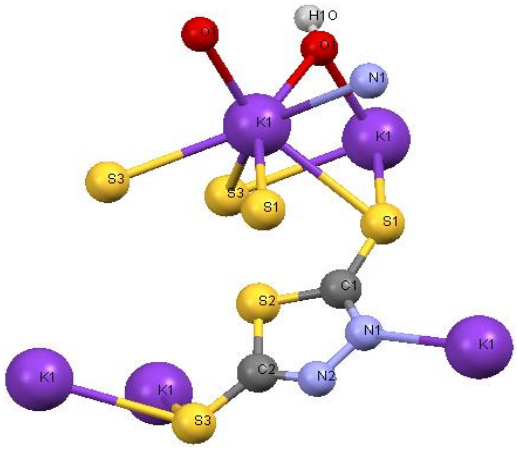
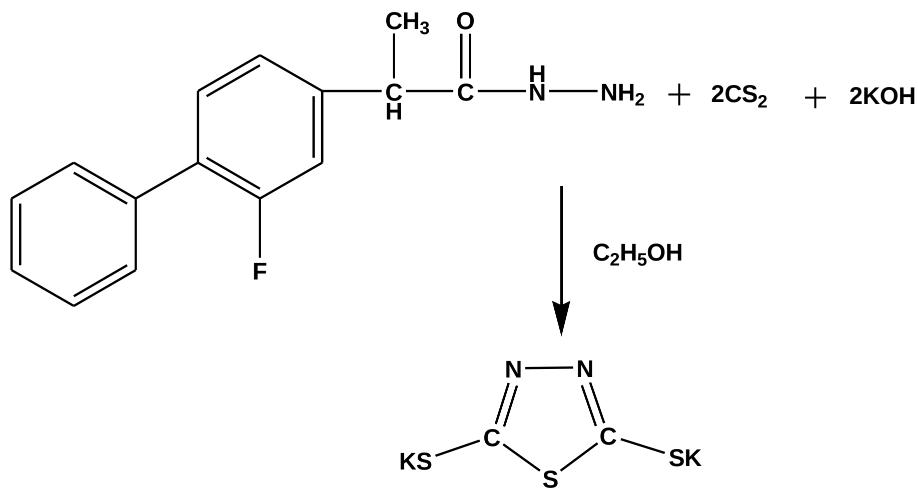


Fig. 1: Crystal structure of the framework.



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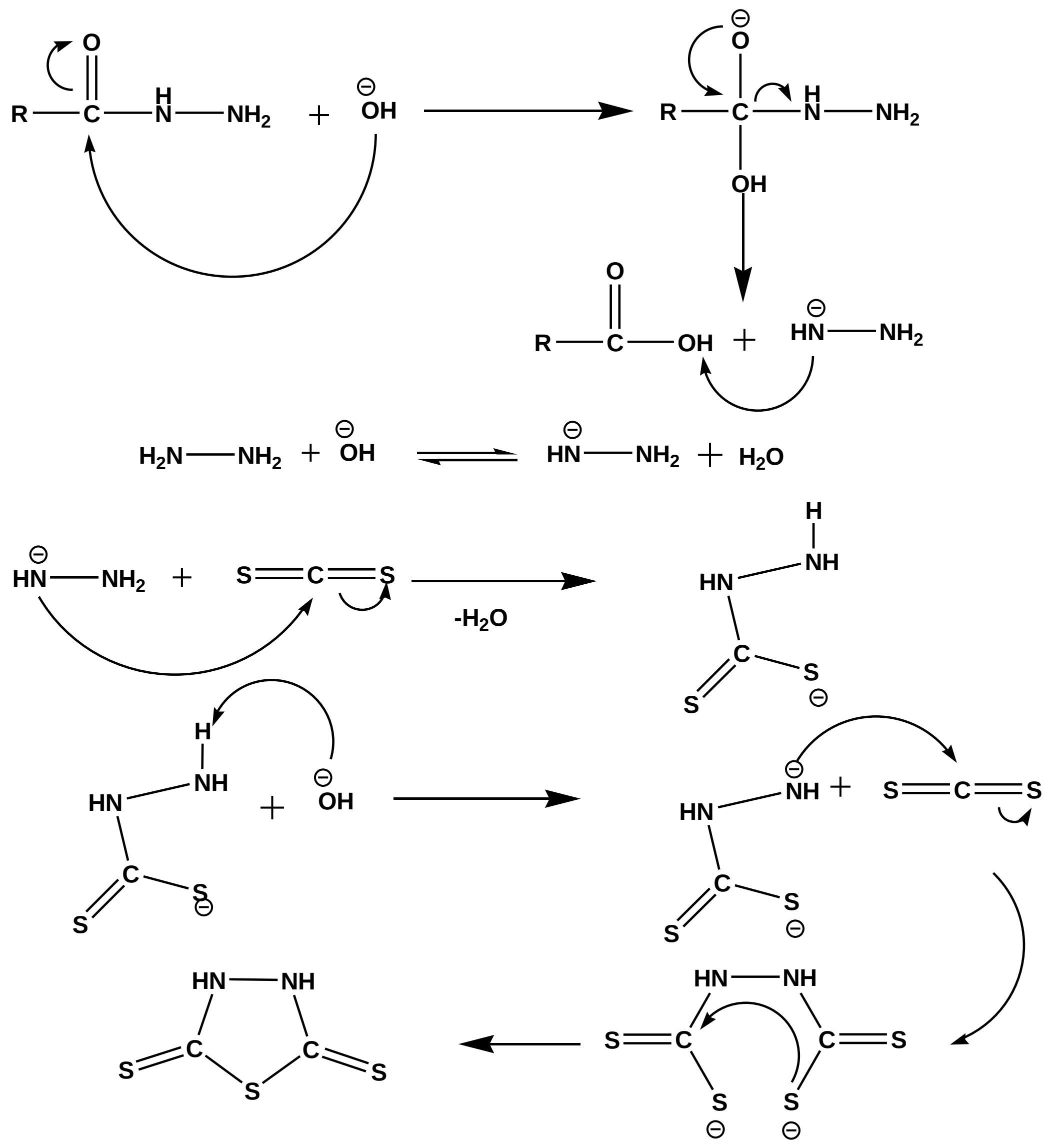

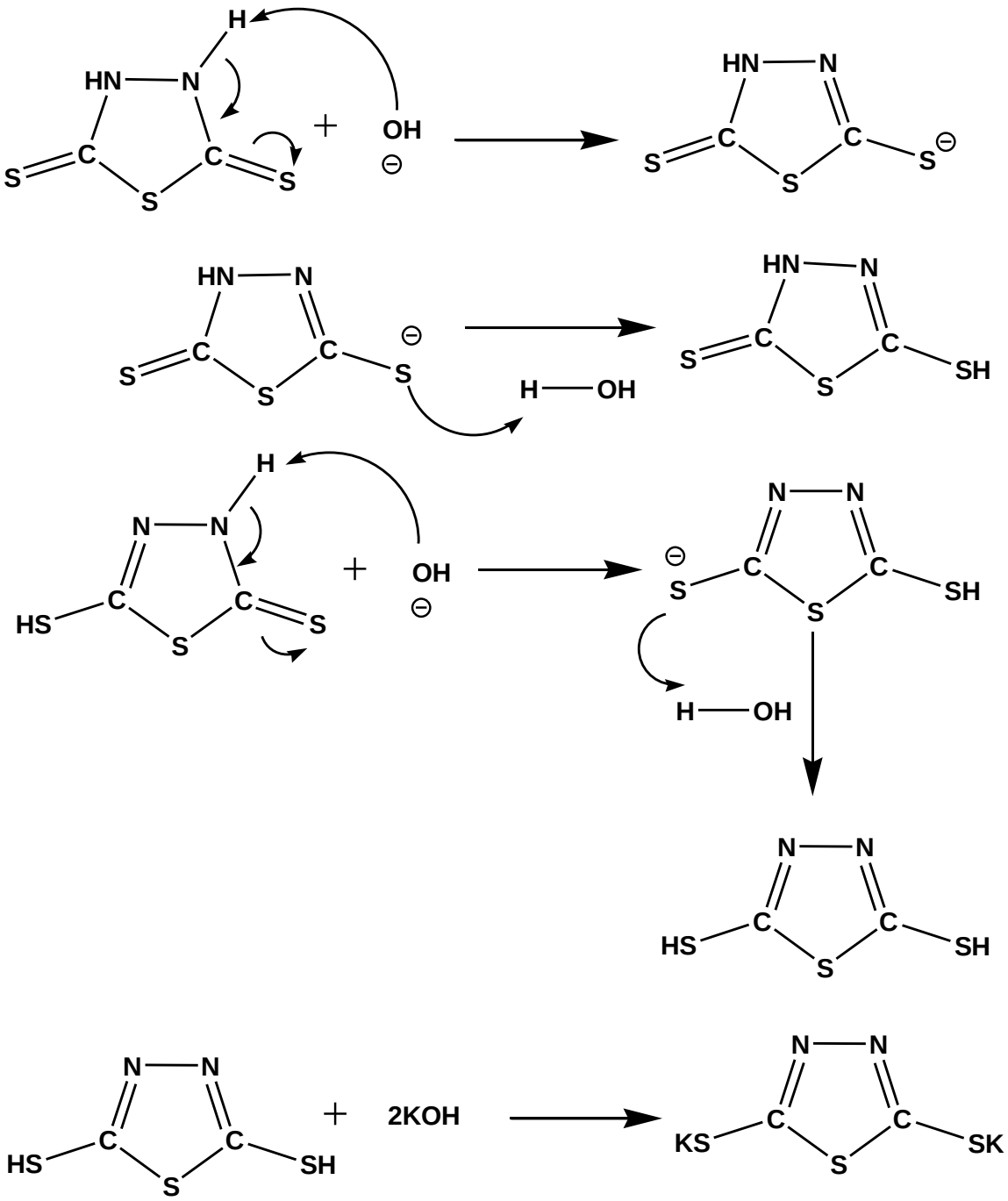

Mechanism: Synthesis of 1,3,4-thiadiazole-2,5-dithiol and potassium 1,3,4-thiadiazole-2,5-bis(thiolate) network.

X-ray crystallography

Crystal data and structure refinement parameters for the framework are given in Table-1 while selected bond lengths (Å) and bond angles (°) are given in Table-2. The N-N bond length in the given thiadiazolate framework is 1.381(5) Å, which is in close agreement to the distance described in the literature [18], but slightly smaller than the single bond distance of 1.40 Å. The C-N bond lengths range from 1.308(5) to 1.326(5) Å which can be assigned a double bond character. The C-S bond distances are in the range of 1.687(4) to 1.760(4) slightly shorter than the ideal value of 1.77 Å for a C(sp^2)-S single bond.

Thus thiadiazole ring remains as a non-conjugate system or has a very little conjugation**.** In the given molecular structure of network, the potassium ion is heptacoordinated forming distorted pentagonal bipyramidal geometry (Fig. 2). The two oxygen donor atoms and four sulfur donor atoms are bridged between two potassium ions. In addition to this, a nitrogen atom from a second thiadiazole ring is also coordinating to the same potassium ion. In the given structure, different bond distances like K-N (2.952(4)) Å, K-O (2.681(3)) Å and K-S (3.3475(14)) Å lie in close agreement to the reported values in the literature [25]. The resulting extended structure shows two-dimensional network. The coordination of thiadiazolate ligand with potassium metal resulted in a geometry which is different from that of other potassium based MOFs [22] but is in close agreement to the geometry described for some other metal-organic frameworks of potassium [26]. The crystal packing diagram and 2D chain structure of the framework is given in Fig. 2).

Table-1: Crystal data and structure refinement parameters for the network.

CCDC #	1810827
Chemical Formula	$[C_2HKN_2OS_3]$
Formula weight	204.33
Crystal system	Monoclinic
Space group	P 2_1
Temperature	293(2) K
Wavelength	0.71073 Å
Unit cell dimensions (Å)	a = 4.1135(4) b = 10.5405(10) c = 8.5497(7)
(°)	α = 90 β = 95.494(8) γ= 90
Volume	369.00(6) $Å^3$
Z	2
Density (calculated)	1.839 Mg/m^3
Absorption coefficient	1.486 mm^{-1}
F(000)	204
Goodness-of-fit on F^2	1.109
Crystal size	? x ? x ? mm^3
Final R indices [I>2sigma(I)]	R1 = 0.0326, wR2 = 0.0778
R indices (all data)	R1 = 0.0361, wR2 = 0.0827

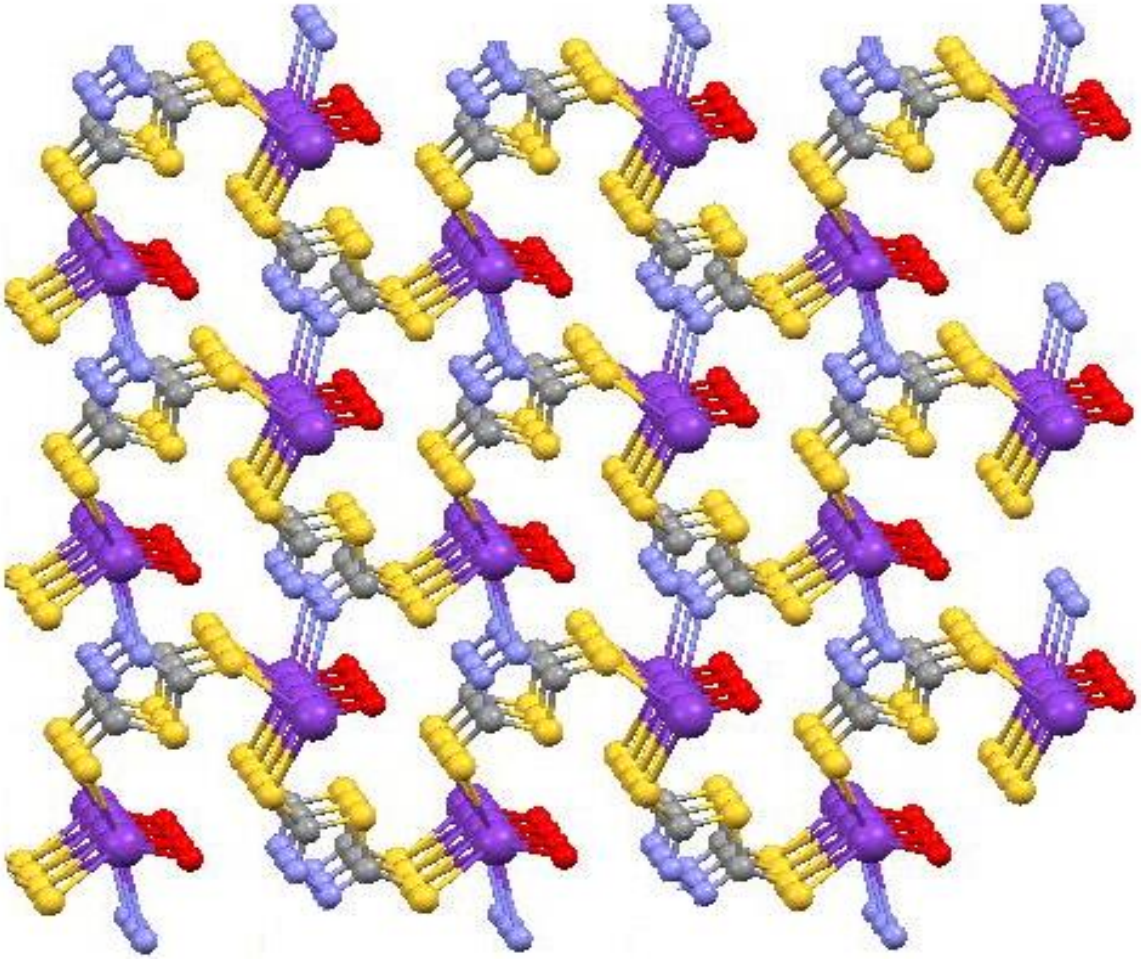

Fig. 2: Crystal packing diagram of the framework.

Table-2: Selected bond lengths (Å) and bond angles (°).

Selected Bond Lengths		Selected Bond Angles	
K(1)-O(1)	2.681(3)	O(1)-K(1)-O(1)#1	97.12(11)
K(1)-O(1)#1	2.805(4)	O(1)-K(1)-N(1)#2	78.30(11)
K(1)-N(1)#2	2.952(4)	O(1)-K(1)-S(3)#3	134.90(8)
K(1)-S(3)#3	3.2481(14)	N(1)#2-K(1)-S(3)#3	142.11(8)
K(1)-S(1)#1	3.3129(14)	O(1)-K(1)-S(1)#1	148.10(8)
K(1)-S(1)	3.3475(14)	C(1)-S(1)-K(1)	96.04(13)
K(1)-S(3)#4	3.5289(15)		
K(1)-S(2)#4	3.7076(14)		
K(1)-K(1)#1	4.1135(4)		
K(1)-K(1)#5	4.1135(4)		

Conclusions

The development of frameworks containing alkali metals is exceptional owing to the prevalence of ionic forces at metal atoms. A novel extended structure containing potassium metal ion was formulated by in-situ synthesis of 1,3,5-thiadiazole-2,5-dithiol ligand. The novel two-dimensional framework has a heptacoordinated potassium ion bearing distorted pentagonal bipyramidal geometry.

Disclosure

The authors confirm that this article content has no conflict of interest.

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