Electron Distribution in 1-Organo-1H-tetrazole-5-thiols. Crystal and Molecular Structure of 1-methyl-1H-tetrazole-5-thiol* and Its Potassium(18-Crown-6) Salt

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ABSTRACT

The crystal and molecular structures of both neutral and anionic 1-methyl-1H-tetrazole-5-thiol, as its potassium(18-crown-6) salt, are reported. In the solid state, the molecular thiotetrazole adopts a planar, dimeric arrangement, in which two neighboring molecules are hydrogen bridged. Each monomeric unit exhibits considerable π electron delocalization over the CN₂S fragment. The anionic form displays extensive, but not uniform, π electron delocalization within the ring, which also extends to the exocyclic carbon-sulfur bond, the structure being best described as a hybrid. The potassium cation is coordinated to the macrocyclic 18-crown-6 ether as expected, but it also interacts with the NCS fragment of the tetrazolethiolate ring.

INTRODUCTION

Tetrazoles, 1, are compounds that have been structurally well characterized [1]. X-ray crystal struc-

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Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday, with appreciation to a great chemist and globe trotter.

*Current nomenclature in *Chem. Abstr.*: 1,2-Dihydro-1-methyl 5H-tetrazole-5-thione.

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tures of several tetrazole systems and molecular and metallic derivatives show the tetrazole ring to be a planar resonance hybrid [2,3]. For instance, the tetrazolate anion has been characterized as a stable 6π-aromatic system, with the electron density distributed uniformly over the five-membered ring [4].

In contrast, the sulfur-containing related compounds, 1-organo-1H-tetrazoline-5-thiones, 2, where exocyclic conjugation may play an important role, are poorly depicted in the literature in regard to their π-electron distribution, which therefore has remained unclear.

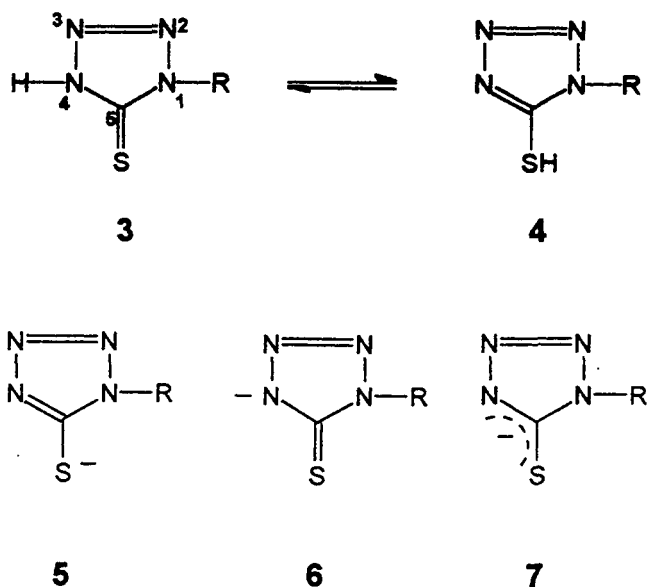**1**   **2**
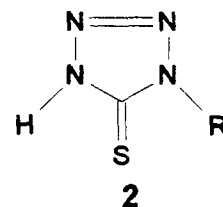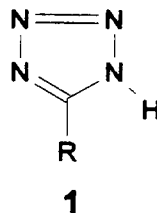
1-Alkyl- or 1-aryl-1H-tetrazoline-5-thiones, 2, can display thione-thiol tautomerism (3 ⇌ 4), and, when deprotonated, the localization of the negative charge at either sulfur (as in 5) or nitrogen (as in 6) is, in principle, possible; but, more likely, the charge will be delocalized at least over an S–C–N fragment (as in 7), a more extended delocalization over all the heterocycle also being feasible.

Structures 3, 4, 5, 6, 7

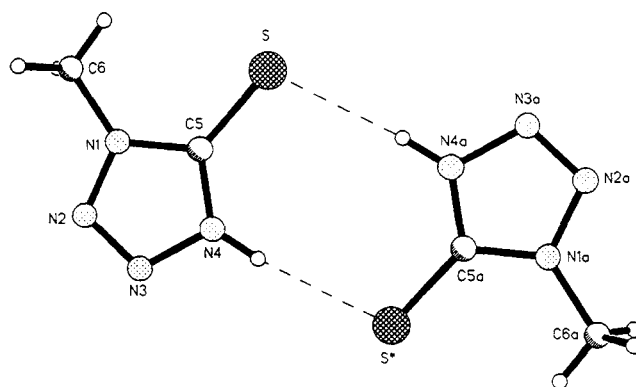**FIGURE 1** Molecular structure of 1-methyl-1H-tetrazole-5-thiol.

An X-ray structural determination of the related 1,3-dimethyl-2(3H)-imidazolethione indicated lengthening of the C=S bond and shortening of the adjacent C–N bonds, as well as absence of significant lengthening of the olefinic moiety, in agreement with a resonance hybrid **8a–8c**, in which structure **8b** is the major contributor [5].

Structures 8a, 8b, 8c
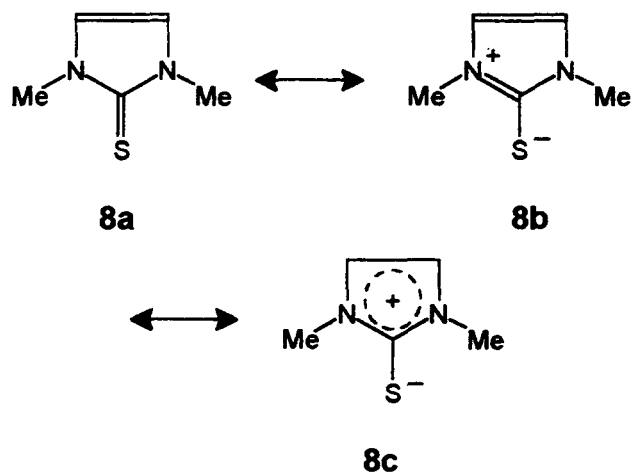
Thus, interested in the electron density distribution in tetrazoline-5-thione systems, on account of the different patterns they may display, we herein report the crystal and molecular structures of 1-methyl-1H-tetrazole-5-thiol and of its corresponding anion (as a potassium-crown ether salt).

Our studies are also in connection with the reactivity of such heterocyclic systems toward main group organometallic derivatives; e.g., some X-ray crystal structure investigations of organotin derivatives [6–8] revealed that the tin atom is primarily bonded to sulfur, with additional intra- or intermolecular coordination from nitrogen also being observed.

RESULTS AND DISCUSSION

Spectroscopic Characterization

The assignment of the infrared spectra of nitrogen-containing thio-carbonyl heterocycles is a rather difficult matter, since the observed bands bear a mixed character, due to the extensive vibrational coupling effects among C–S, C–N, and N–H vibrations that seem to occur in these systems [9,10]. Yet, the IR spectrum of 1-methyl-1H-tetrazoline-5-thione was useful to arrive at a conclusion on the thiol-thione tautomerism issue, since the presence of the N–H group in the neutral heterocycle was evidenced by two strong absorption bands (which disappeared upon deprotonation of the compound) at 3060 and 1510 cm^{-1} that corresponded to N–H stretching and bending vibrations, respectively [10].

Moreover, the S–H stretching vibration, usually observed in the 2590–2540 cm^{-1} range and reported to be weak in the infrared but strong in the Raman spectra [10], does not appear in the Raman spectrum of the compound in its acid form. These facts strongly support the presence of the thiotetrazole in the thione form, **3**, rather than as the thiol tautomer, **4**, in the solid state, a fact that was confirmed by an X-ray structure determination (see subsequent discussion).

Structure of 1-Methyl-1H-tetrazoline-5-thione

The molecular structure of the compound, established by single crystal X-ray diffraction, is shown in Figure 1, and the structure determination summary is presented in Table 1. Interatomic distances and bond angles are given in Table 2. Non-hydrogen atom coordinates are listed in Table 3.

In the solid state, 1-methyl-1H-tetrazoline-5-thione is a dimer, in which two planar neighboring molecules are connected by hydrogen bonds (N(4)–H(4) 1.063, N(4)–H(4)---S(1) 2.243 Å) and deviated 9.7° from coplanarity (symmetry code: 1-X, 1-Y, 2-Z). The N–H and S–H distances clearly point to
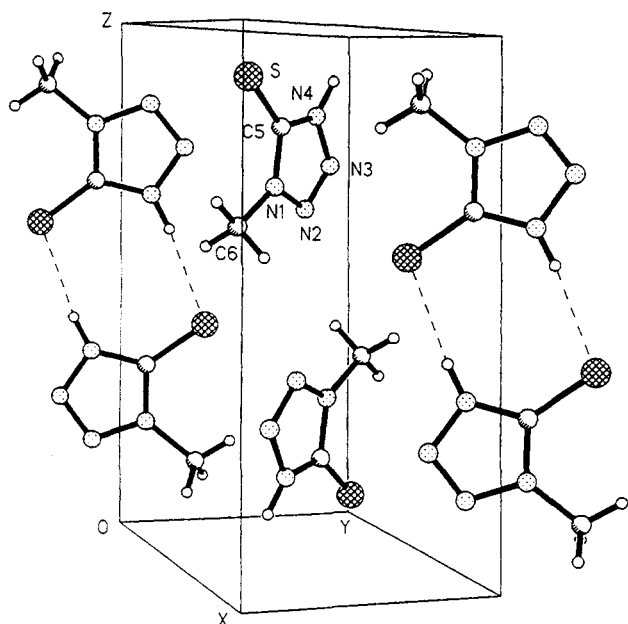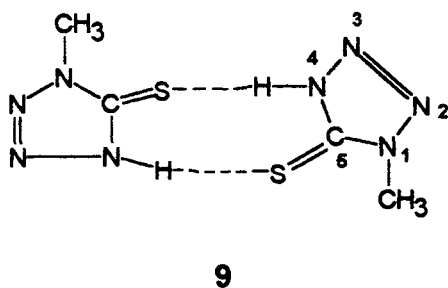
FIGURE 2 Unit cell of 1-methyl-1H-tetrazole-5-thiol, as viewed along the x-axis.

the existence of the compound in the thione form, as represented in **9**. In each monomeric unit, the deviation of the exocyclic sulfur atom from the CN₄ ring plane (0.107°) is negligible. The unit cell is shown in Figure 2.


9

With regard to the nature of the carbon–sulfur bond, the determined value of 1.695(9) Å lies practically in the middle of the range between the values for single (1.82 Å) and double (1.56 Å) C–S bonds and corresponds to ca. 50% π-bond character, according to experimental data and SCF calculations [11].

The value found can be compared with those of some thione derivatives of saturated and unsaturated N-heterocycles, as illustrated in Figure 3. The values are listed in Table 4. It can be seen that the C–S bond length in our compound is close to that observed in imidazoline-2-thiones **12** and **13** (1.698(2) and 1.685(2) Å, respectively) and in **15**, namely, anhydro-5-mercapto-2,3-diphenyltetrazolium hydroxide (or dehydrodithizone), in all of which π-electron delocalization within the ring
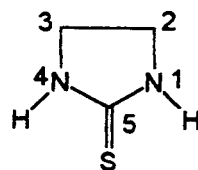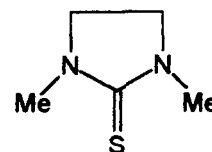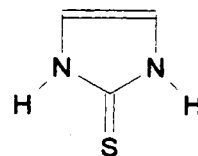
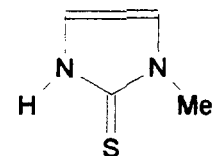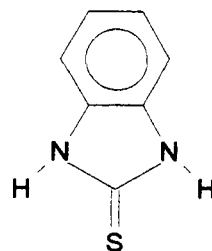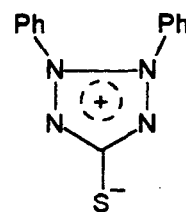**FIGURE 3** Some sulfur-containing nitrogen heterocycles related to the title compounds.

takes place [14,15,17]. The C–S distance in **9** also approaches very closely that in saturated cyclic thiourea **10** (1.708 Å) [12], where electronic conjugation has been reported to occur between the π-electron system of the C=S bond and the non-bonding electron pairs of the adjacent nitrogen atoms.

Comparison of structures **10–15** also leads to the conclusion that the presence of a C=C bond in the five-membered ring (increasing unsaturation or possibly the aromatic character) or the presence of a benzene ring fused to the heterocycle as in benz-1,3-imidazoline-2-thione, **14**, does not seem to influence dramatically the π-electron distribution in the carbon–sulfur bond.

The C–N bond lengths within the ring (1.340(11) and 1.314(12) Å) are shorter than the value expected for a single bond (1.47 Å) [18], but longer than that calculated for a double bond (1.27 Å) [19], as observed in π-delocalized tetrazoles and sulfur derivatives of imidazole-type compounds [15].

The slightly longer C(5)–N(1) bond distance in

TABLE 1 Structure Determination Summary for **9** and **16**, at 20°C

Formula	$C_2H_4N_4S$	$C_{14}H_{27}KN_4O_6S$
Color, habit	colorless, prismatic	colorless, prismatic
Crystal size (mm)	0.24 × 0.22 × 0.20	0.58 × 0.50 × 0.18
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions	$a = 7.811(2)$ Å	$a = 10.520(4)$ Å
	$b = 5.696(1)$ Å	$b = 8.872(4)$ Å
	$c = 11.672(2)$ Å	$c = 22.429(6)$ Å
	$B = 97.04(3)°$	$B = 98.68(3)°$
Volume	515.9(3) Å^3	2069.4(10) Å^3
Z	4	4
Formula weight	116.2	418.6
Density (calcd)	1.495 g/cm^3	1.343 g/cm^3
Absorption coefficient	4.531 mm^{-1}	0.393 mm^{-1}
F(000)	240	888
Diffractometer used	Nicolet P3/f	Siemens P4/PC
Radiation	Cu (K_α, 1.54178 Å)	Mo (K_α, 0.71073 Å)
2θ range	3–100°	3–50°
Scan type	2θ:θ	
Scan speed	variable (4.00–29.30°/min)	
Scan range	2.00°	2.00° + K_α separation
Standard reflections	3 every 100 reflections	2 every 50 reflections
Index range	0/h/7, 0/k/5/,−11/l/11	0/h/12, 0/k/10/,−26/l/26
Reflections collected	663	3883
Independent reflections	533 (R_{int} = 7.60%)	3672 (R_{int} = 10.30%)
Observed reflections ($F > 3.0\sigma(F)$)	452	2662
Number of variables	68	236
Goodness of fit	1.45	1.23
Final R indices	$R = 0.073$, $R_w = 0.092$	$R = 0.062$, $R_w = 0.089$
Δ/σ(max)	0.051	0.909
$\Delta\rho$(max)	0.37 eA^{-3}	0.65 eA^{-3}
$\Delta\rho$(min)	−0.44 eA^{-3}	−0.39 eA^{-3}

our compound (1.340(11) Å) may be accounted for by the presence of the methyl group attached to N(1), in contrast with the C(5)–N(4) bond length (1.314(12) Å), where N(4) is unsubstituted.

The C(6)–N(1) bond distance (1.453(13) Å), corresponding to the substituent methyl group, is close to that expected for a C–N single bond (1.47 Å) [19].

The N–N bond lengths display a pattern of one short (N(2)–N(3) 1.270(12) Å) and two long (N(1)–N(2) 1.349(11) and N(3)–N(4) 1.363(11) Å) bonds, in agreement with formulation **9**. Both are shorter than the sum of covalent radii (1.46 Å) of nitrogen (r_N = 0.73 Å) [18]. The short N(2)–N(3) distance is only slightly longer than 1.25 Å estimated for a N=N double bond [19].

Therefore, it can be concluded that, in the compound 1-methyl-1H-tetrazoline-5-thione, there is some electron delocalization in the CN$_2$S system, although the bond-shortening pattern throughout the heterocycle suggests that all the atoms contribute to the ring π-electron density, thus modifying the picture of a clean pattern and double bonds, as shown in **9**.

This result contrasts somewhat with that of the dehydrodithizone structure, **15**, in which the C–N

and N–N bond distances within the ring are all identical and indicative of the aromatic character of the molecule, the compound being described as a meso-ionic sydnone [17].

Structure of Potassium-(18-crown-6)-1-methyl-1H-tetrazole-5-thiolate

The single-crystal X-ray structure of the anion derived by deprotonation of **9**, obtained with potassium-18-crown-6 as the accompanying cation, is shown in Figure 4, and the interatomic distances and bond angles are listed in Table 5. Coordinates of non-hydrogen atoms are listed in Table 6.

The interatomic distances suggest that extensive, but not uniform, π-electron delocalization is present in the ring and extends over the exocyclic C–S bond (1.708(4) Å), which is, however, slightly longer than in the parent neutral molecule **9**.

The C–N bonds are symmetrically disposed within the ring (C(5)–N(1) 1.325(5) Å, C(5)–N(4) 1.330(5) Å).

The N(2)–N(3) bond length (1.233(7) Å) can clearly be regarded as that of a true double bond, but surprisingly, the N(3)–N(4) bond is also very

TABLE 2 Interatomic Distances (Å) and Bond Angles (°) for **9**

S(1)–C(5)	1.695(9)	N(2)–N(3)	1.270(12)
C(5)–N(1)	1.340(11)	N(3)–N(4)	1.363(11)
N(1)–N(2)	1.349(11)	N(4)–C(5)	1.318(12)
		N(1)–C(6)	1.453(13)
N(1)–C(5)–N(4)	103.6(7)	N(3)–N(4)–C(5)	110.7(8)
C(5)–N(1)–N(2)	110.5(7)	S–C(5)–N(4)	129.8(7)
N(1)–N(2)–N(3)	107.6(7)	S–C(5)–N(1)	126.5(7)
N(2)–N(3)–N(4)	107.5(8)	C(6)–N(1)–C(5)	127.8(7)
		C(6)–N(1)–N(2)	121.6(7)

TABLE 3 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($A^2 \times 10^3$) for **9**

	x	y	z	$U(eq)^a$
S	6314(3)	2103(4)	9072(2)	48(1)
N(1)	4958(9)	3910(13)	7005(6)	34(3)
N(2)	3993(10)	5733(16)	6558(7)	46(3)
N(3)	3648(10)	7004(15)	7394(8)	50(3)
N(4)	4382(10)	5971(15)	8388(7)	40(3)
C(5)	5189(10)	4026(16)	8160(7)	30(3)
C(6)	5559(14)	2099(18)	6273(8)	50(4)

^{a}Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

short (1.289(6) Å), which may be due to the presence of some of the negative charge that resulted from deprotonation at the N(4) site. The enlarged N(2)–N(3)–N(4) bond angle (115.2(4)°) is in agreement with the apparent π interaction in the N(2)–N(3)–N(4) fragment. By contrast, the N(1)–N(2) bond (1.390(6) Å) is nearly as long as expected for a single N–N bond (1.45 Å). These values suggest that the π-electron delocalization may be somewhat interrupted (or diminished) along the N(1)–N(2) bond, in accordance with the reduction of the N(3)–N(2)–N(1) angle (104.5(4)° vs. 107.6(7)° in the neutral molecule). Thus, the structure of the anion can grossly be represented as a resonance hybrid **16a–16d**.

It is also worth mentioning that the interatomic distances in the anion described here are surprisingly similar to those observed in the neutral molecule 1,3-imidazolidine-2-thione (**10**).

Comparison of structure **16** with that of the
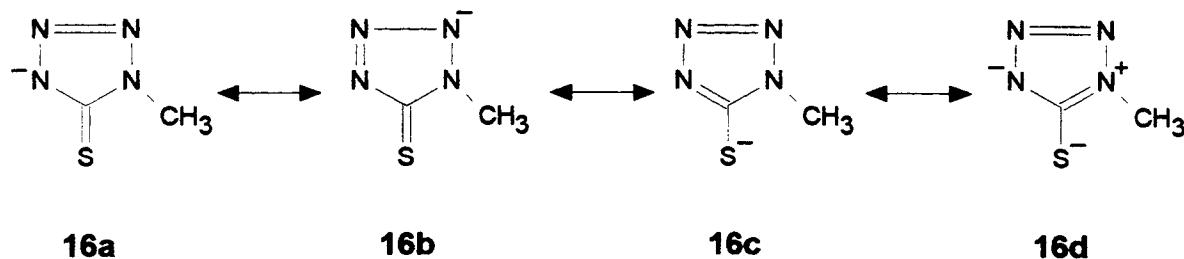
sydnone **15** illustrates the presence of extensive π-electron delocalization in both tetrazolethiolate systems. The π-electron density, however, appears to be more uniformly distributed over the N–N–N–N system in **15** than in **16**.

The potassium ion is coordinated by the thiotetrazole heterocycle and the 18-crown-6-macrocyclic ether as well.

The K–S distance in the compound, 3.373 (2) Å, fits well within the range found for sulfur-coordinated potassium in various other thiocarbonylic complexes, i.e., 3.316–3.576 Å [20–22].

The K–N(4) distance, 2.934(4) Å, is also very close to the sum of covalent radii, Σr_{cov} K, N = 2.71 Å [18], indicating bonding of the K^+ ion to the tetrazolethiolate ring, also through N(4).

Although it is difficult to compare the K–C(13) distance found in our compound (3.469(4) Å) with other structures, due to the scarcity of reports on analogous systems, it is approximately 1 Å shorter than the sum of the van der Waals radii of carbon and potassium (Σr_{vdw} K, C = 4.5 Å) [18] and it is close to those found in the range 3.003–3.276 Å for carbon-bonded potassium in organopotassium complexes [23–28]. Hence, the possibility of an interaction of the K^+ ion with the carbon atom of the heterocycle thiocarbonyl fragment cannot be ruled out, in which case the interaction of the metal with the thiotetrazolate anion would be through the whole NCS system. Accordingly, lengthening of both N(4)–C(5) (1.330(5) Å) and C(5)–S (1.708(4) Å) bond distances, relative to the uncoordinated parent molecule (1.314(12) and 1.695(9) Å, respectively) is observed. The small deviation (0.3 Å) of the potassium ion from the tetrazolethiolate moiety indicates that they lie practically in the same plane.

The structure found is in contrast with that of [K(18-crown-6)][NCS] wherein the thiocyanate anions interact only weakly with the potassium cations [29].

The coordination of potassium by the polyether ring presents no unusual features and is essentially similar to that observed in other compounds studied by us, e.g., in [K(18-crown-6)][Ph₂P(S)NPPh₂(S)] [30] and [K(18-crown-6)][Ph₂P(O)NPPh₂(O)]H₂O [31], and by other authors, e.g., [K(18-crown-6)][NCS] [29]. The crystal pack-

16a   **16b**   **16c**   **16d**
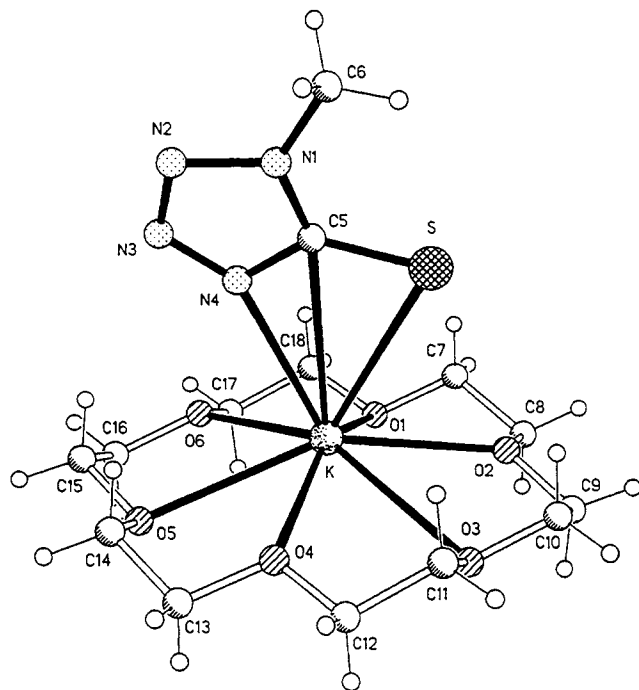
FIGURE 4 Molecular structure of potassium-(18-crown-6)-1-methyl-1H-tetrazole-5-thiolate.

ing in the unit cell, as shown in Figure 5, is entirely due to van der Waals forces.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 283B spectrometer, as KBr pellets.

The Raman experiments were carried out at room temperature, in a computer-controlled experimental setup with a double grating monochromator. The samples were excited with the 488 nm line of an Ar^+ laser, at near back scattering configuration.

^1H and ^{13}C NMR spectra were obtained for

$CDCl_3$ solutions on a Varian Gemini 200 spectrometer, operating at 200 MHz for ^1H and 50 MHz for ^{13}C. The experiments were carried out at room temperature and TMS was used as an internal reference.

For both compounds, suitable crystals for X-ray diffractometry were obtained by solvent diffusion in a CH_2Cl_2/n-hexane mixture, at room temperature. The crystals were glued on the top of a glass fiber and mounted on the diffractometer. Cell constants for both compounds were obtained by least-squares refinement of the setting angles of 25 carefully centered reflections, and the space group was determined from systematic absences ($h0l$; h + l: $2n$ + 1, $0k0$; k: $2n$ + 1). For 9, the correction for Lorentz and polarization effects as well as the absorption correction were performed by the DIFABS method [32] applied to reflection data (max/min: 0.979/0.748), after isotropic refinement. No absorption correction was applied for 16.

Both structures were solved by the direct methods technique, using the Siemens SHELXTL package [33]. All position and anisotropic thermal parameters for nonhydrogen atoms were refined by the full-matrix least-squares technique. With the exception of the nitrogen-attached H atom of dimer 9, which was localized and its coordinates refined, all other hydrogen atom positions were calculated using the riding model with a fixed isotropic U value (U = 0.06 $Å^2$) and added to the structure factor calculations, without being refined. The function minimized was $\Sigma w(F_o - F_c)^2$, with a weighting scheme $w^{-1} = \sigma^2 F_c + GF_o^2$, where G = 0.008 for 9 and 0.0034 for 16. No secondary extinction was observed in the latter compound, while an isotropic extinction parameter x = 0.019(6), with $F_c^* = F[1 + 0.002 \times F_c^2/\sin 2\theta]^{-1/4}$, was applied for 9. The final R values are given in Table 1. Further details of the crystal structure determination can be obtained from the Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, United Kingdom.

TABLE 4 Some Important Bond Distances in the Title Compounds as Compared with Analogous Heterocyclic Systems

Compound	Structure	Bond Lengths (Å)			Reference
		C(5)–S	C(5)–N(4)	C(5)–N(1)	
1,3-Imidazolidine-2-thione	10	1.708	1.322	1.322	[12]
1,3-Dimethyl-1,3-imidazolidine-2-thione	11	1.673(5)	1.342(5)	1.334(5)	[13]
1,3-Imidazoline-2-thione	12	1.698(2)	1.346(3)	1.344(3)	[14]
1-Methyl-1,3-imidazoline-2-thione	13	1.685(2)	1.351(4)	1.344(3)	[15]
Benz-1,3-imidazoline-2-thione	14	1.671(8)	1.362(6)	1.362(6)	[16]
Anhydro-5-mercapto-2,3-diphenyltetrazolium hydroxide	15	1.687(5)	1.360(4)	1.360(4)	[17]
1-Methyl-1H-tetrazoline-5-thione	9	1.695(9)	1.314(12)	1.340(11)	this work
Potassium-18-crown(6)-1-methyl-1-H-tetrazole-5-thiolate	16	1.708(4)	1.329(5)	1.325(5)	this work

TABLE 5 Interatomic Distances (Å) and Bond Angles (°) for **16**

K–N(4)	2.934(4)	K–S	3.373(2)
K–C(5)	3.469(4)	K–O(1)	2.974(4)
K–O(2)	2.841(4)	K–O(3)	2.978(3)
K–O(4)	2.780(3)	K–O(5)	2.951(3)
K–O(6)	2.866(3)	N(1)–N(2)	1.390(6)
N(1)–C(5)	1.325(5)	N(1)–C(6)	1.440(6)
N(2)–N(3)	1.233(7)	N(3)–N(4)	1.289(6)
N(4)–C(5)	1.330(5)	S–C(5)	1.708(4)
O(1)–C(7)	1.401(8)	O(1)–C(18)	1.438(7)
C(7)–C(8)	1.502(11)	C(8)–O(2)	1.396(6)
O(2)–C(9)	1.414(6)	C(9)–C(10)	1.501(8)
C(10)–O(3)	1.410(6)	O(3)–C(11)	1.423(5)
C(11)–C(12)	1.483(7)	C(12)–O(4)	1.413(5)
O(4)–C(13)	1.400(6)	C(13)–C(14)	1.482(7)
C(14)–O(5)	1.415(5)	O(5)–C(15)	1.418(5)
C(15)–C(16)	1.484(8)	C(16)–O(6)	1.436(6)
O(6)–C(17)	1.384(6)	C(17)–C(18)	1.467(10)
N(4)–K–S	50.8(1)	N(4)–K–C(5)	22.0(1)
S–K–C(5)	28.9(1)	N(4)–K–O(1)	119.5(1)
S–K–O(1)	110.4(1)	C(5)–K–O(1)	119.5(1)
N(4)–K–O(2)	127.4(1)	S–K–O(2)	79.6(1)
C(5)–K–O(2)	107.3(1)	O(1)–K–O(2)	57.3(1)
N(4)–K–O(3)	119.6(1)	S–K–O(3)	81.7(1)
C(5)–K–O(3)	103.0(1)	O(1)–K–O(3)	109.9(1)
O(2)–K–O(3)	58.3(1)	N(4)–K–O(4)	88.2(1)
S–K–O(4)	95.6(1)	C(5)–K–O(4)	90.4(1)
O(1)–K–O(4)	150.1(1)	O(2)–K–O(4)	116.3(1)
O(3)–K–O(4)	58.2(1)	N(4)–K–O(5)	84.2(1)
S–K–O(5)	130.3(1)	C(5)–K–O(5)	104.0(1)
O(1)–K–O(5)	109.9(1)	O(2)–K–O(5)	148.4(1)
O(3)–K–O(5)	110.1(1)	O(4)–K–O(5)	58.5(1)
N(4)–K–O(6)	88.4(1)	S–K–O(6)	127.8(1)
C(5)–K–O(6)	106.8(1)	O(1)–K–O(6)	57.9(1)
O(2)–K–O(6)	115.1(1)	O(3)–K–O(6)	149.9(1)
O(4)–K–O(6)	116.8(1)	O(5)–K–O(6)	58.4(1)
N(2)–N(1)–C(5)	107.1(4)	N(2)–N(1)–C(6)	122.5(4)
C(5)–N(1)–C(6)	130.4(4)	N(1)–N(2)–N(3)	104.5(4)
N(2)–N(3)–N(4)	115.2(4)	K–N(4)–N(3)	151.2(3)
K–N(4)–C(5)	102.3(3)	N(3)–N(4)–C(5)	105.9(4)
K–S–C(5)	78.7(1)	K–C(5)–N(1)	162.3(3)
K–C(5)–N(4)	55.8(2)	N(1)–C(5)–N(4)	107.3(4)
K–C(5)–S	72.4(1)	N(1)–C(5)–S	124.7(3)
N(4)–C(5)–S	128.0(3)	K–O(1)–C(7)	106.0(3)
K–O(1)–C(18)	106.9(3)	C(7)–O(1)–C(18)	115.2(2)
O(1)–C(7)–C(8)	110.2(5)	C(7)–C(8)–O(2)	108.4(5)
K–O(2)–C(8)	122.2(3)	K–O(2)–C(9)	120.0(3)
C(8)–O(2)–C(9)	112.2(4)	O(2)–C(9)–C(10)	108.4(4)
C(9)–C(10)–O(3)	109.5(4)	K–O(3)–C(10)	106.2(2)
K–O(3)–C(11)	102.4(2)	C(10)–O(3)–C(11)	111.0(3)
O(3)–C(11)–C(12)	108.6(3)	C(11)–C(12)–O(4)	109.4(4)
K–O(4)–C(12)	121.2(3)	K–O(4)–C(13)	121.0(3)
C(12)–O(4)–C(13)	113.9(4)	O(4)–C(13)–C(14)	109.1(4)
C(13)–C(14)–O(5)	109.0(4)	K–O(5)–C(14)	105.3(2)
K–O(5)–C(15)	106.4(3)	C(14)–O(5)–C(15)	111.1(4)
O(5)–C(15)–C(16)	108.4(4)	C(15)–C(16)–O(6)	108.9(4)
K–O(6)–C(16)	118.1(3)	K–O(6)–C(17)	119.9(3)
C(16)–O(6)–C(17)	111.7(4)	O(6)–C(17)–C(18)	108.3(5)
O(1)–C(18)–C(17)	110.3(5)	—	—

TABLE 6 Atomic Coordinates (X 10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 X 10^3) for **16**

	x	y	z	$U(eq)^a$
K	−54(1)	1122(1)	3256(1)	49(1)
N(1)	3440(3)	2936(4)	4662(2)	63(1)
N(2)	2816(5)	4249(5)	4793(2)	86(2)
N(3)	1780(4)	4216(4)	4452(2)	65(1)
N(4)	1607(4)	3058(5)	4103(2)	69(2)
S	3001(1)	541(2)	3921(1)	75(1)
C(5)	2661(3)	2221(4)	4234(2)	45(1)
C(6)	4691(5)	2523(7)	4972(3)	95(2)
O(1)	−154(3)	1579(4)	1936(1)	73(1)
C(7)	896(6)	786(9)	1776(3)	98(3)
C(8)	734(6)	−875(8)	1871(2)	89(2)
O(2)	724(3)	−1128(4)	2485(1)	69(1)
C(9)	564(5)	−2669(6)	2615(2)	74(2)
C(10)	753(4)	−2862(5)	3288(2)	70(2)
O(3)	−261(3)	−2149(3)	3524(1)	58(1)
C(11)	−45(4)	−2176(5)	4165(2)	61(2)
C(12)	−1148(5)	−1437(5)	4388(2)	62(2)
O(4)	−1187(3)	102(3)	4224(1)	58(1)
C(13)	−2185(5)	910(5)	4424(2)	62(2)
C(14)	−2009(5)	2538(6)	4314(2)	65(2)
O(5)	−2166(3)	2796(3)	3684(1)	57(1)
C(15)	−1975(5)	4337(5)	3555(3)	72(2)
C(16)	−2154(4)	4532(5)	2891(3)	75(2)
O(6)	−1118(3)	3793(3)	2658(1)	69(1)
C(17)	−1255(7)	3892(6)	2036(2)	90(2)
C(18)	−134(7)	3179(7)	1836(2)	96(3)

^{a}Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

1-Methyl-1H-tetrazoline-5-thione

The compound was synthesized from methyl isothiocyanate and sodium azide (Aldrich Chemical Co., Inc., Milwaukee, WI), according to published procedures [34]. Mp 122–124°C (lit. 125–126°C). IR (KBr) cm^{-1}: 3060-s (ν NH), 2960-s ($ν_{as}$ CH$_3$), 2860-s ($ν_s$ CH$_3$), 1510-s (δ NH), 1380-m ($δ_s$ CH$_3$). NMR (CDCl$_3$)δ: ^{1}H 3.95 (s, 3H, CH_3), 10 (bs, NH); ^{13}C 34 (s, CH_3), 164.142 (s, CS).

Potassium-(18-crown-6)-1-methyltetrazole-5-thiolate

The compound was prepared by the reaction of stoichiometric amounts of the thiotetrazole in its acid form, potassium hydroxide, and 18-crown-6 in aqueous ethanol at 40°C, for 3 hours. The reaction mixture was then evaporated with stirring, until white crystals of the compound deposited. The compound was dried in vacuum. IR (KBr) cm^{-1}: 2900-m,s ($ν_{as}$ CH$_2$), 2870-m ($ν_s$ CH$_3$, CH$_2$), 1455-m ($δ_{as}$ CH$_3$), 1360-s ($δ_s$ CH$_3$). NMR (CDCl$_3$)δ: ^{1}H 3.87
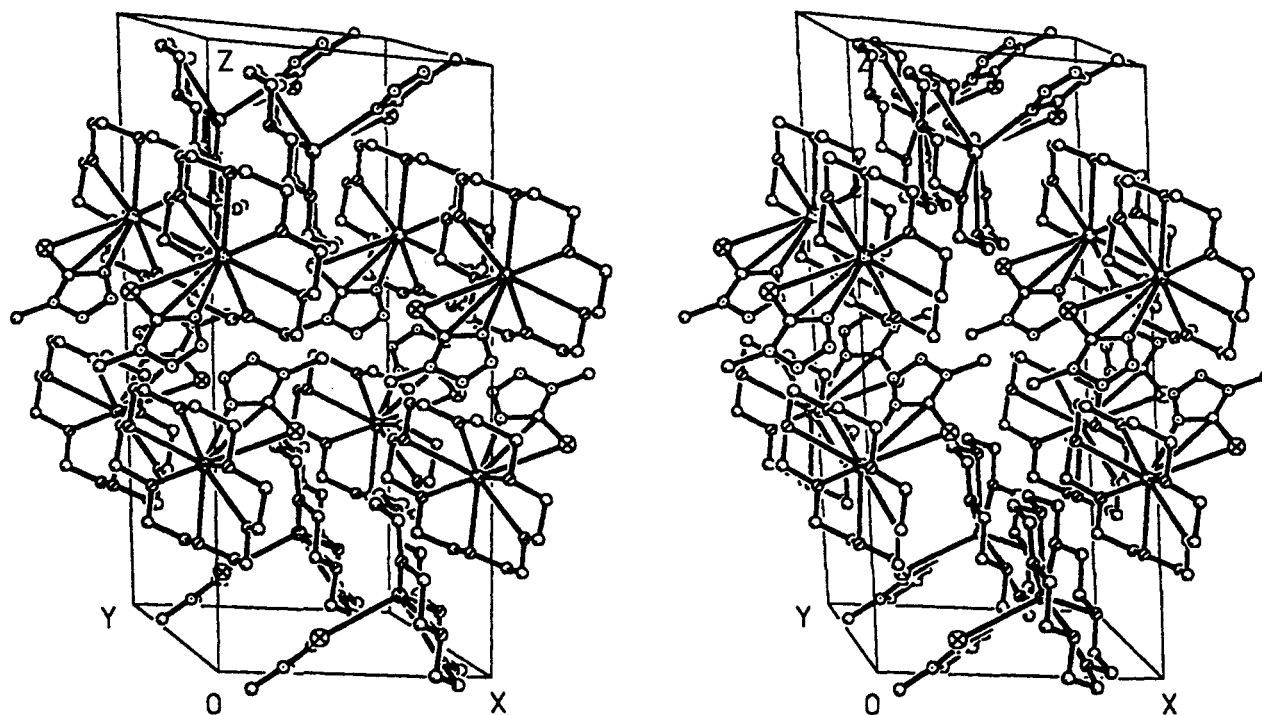
FIGURE 5   Stereoscopic view of the unit cell of potassium-(18-crown-6)-1-methyl-1H-tetrazole-5-thiolate.

(s, 3H, CH_3), 3.65 (s, 24H, CH_2); ^{13}C 70.09 (s, CH_2), 36.74 (s, CH_3).

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