Heteroatom Chemistry
Volume 8, Number 4, 1997

Structural Studies of Tetrazoles. Crystal and Molecular Structure and Ab Initio Calculations of 1-Phenyl-1H-tetrazole-5-thiolate, as Its [Diaqua(18-crown-6)sodium] Salt: An Anionic Tetrazole Free of Direct Metal Interactions

Omar Jiménez-Sandoval,* Raymundo Cea-Olivares, Simón Hernández-Ortega, and Ioan Silaghi-Dumitrescu

Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, México, D.F., 04510, Mexico

Received 6 March 1997

ABSTRACT

The structure of the anionic heterocycle obtained by deprotonation of 1-phenyl-1H-tetrazole-5-thione was determined by X-ray diffractometry. The counterion is $[Na(18\text{-crown-}6)(H_2O)_2]^+$. *There are no direct interactions between the metal and the tetrazole, while hydrogen bonds between sodium ion coordinated water molecules and neighboring azole anions give cohesion to the crystal. The thiotetrazolato ion displays extensive π-delocalization, with all members of the ring and the exocyclic sulfur contributing to it; however, no interannular conjugation between the phenyl and azole rings is found. The structure of the heterocycle is best described as a resonance hybrid. The geometric parameters of the metal-free tetrazole could be used as the input of ab initio MO calculations at the 6-31G*//3-21G* level, which supported the proposal that the negative charge is mainly concentrated on the* N_4-C_5-S *portion of the tetrazolate. Some small but significant and consistent bond length differences are found in the uncoordinated tetrazole with respect to metal-bonded analogues. The coordination behavior of the crown ether, with five oxygens bonded to sodium in the complex cation, is rare.*

INTRODUCTION

Tetrazoles, **1**, are the formal nitrogen analogs of carboxylic acids and, as a class, represent the highest stable azoles. These compounds have raised great interest, mainly due to their varied applications in fields such as analytical chemistry, photography, and agriculture. The pharmacological activity, for example, analeptic, anti-inflammatory, antiallergic, antilipemic, and antimicrobial, as well as other medicinal properties discovered in several tetrazole derivatives has also triggered the development of the chemistry of these heterocycles in the last decades [1]. Comparatively, however, the number of X-ray structures of tetrazoles registered in the earlier literature [2] seems limited, given the great number of such rings known at present and the rich variety of structural possibilities these compounds have been identified to pose, for example, aromatic, nonaromatic, meso-ionic [1], etc. Moreover, if the fundamentals of the chemical and biological behavior of

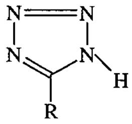
---

*To whom correspondence should be addressed.

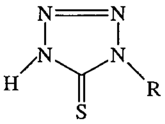
1042-7163/97/040351-09

this interesting family of heterocycles are to be understood, further crystallographic studies of tetrazole systems are certainly desired.

With a view to contributing to fill up this gap, we have initiated a systematic study of substituted tetrazoles in the solid state and have published the X-ray structure of a ring of the type represented in **2**, namely, 1-methyl-1H-tetrazole-5-thione, in both its neutral and anionic forms, the latter with K(18-crown-6)$^+$ as the accompanying counterion [3].



1



2

Although both exhibit extensive but not uniform (nonaromatic) π delocalization, with all members of the ring and the exocyclic sulfur contributing to it, the bond distances are significantly different. In the case of the metal salt, however, the potassium ion binds to the thiotetrazole through the N_4-C_5-S portion, affecting, consequently, the electron density distribution of the ring. Clearly, if the structural parameters of the negatively charged tetrazole are to be evaluated, it is necessary to avoid its coordinative interaction with the metal ion. To achieve this, the Na^+ ion constitutes a suitable candidate, in view of its smaller coordination numbers and higher degree of hydration, in comparison with K^+ [4]. Hence, such metal ion—in the cavity of a crown ether, for instance—would be expected to complete its coordination sphere with water molecules and *not* with tetrazolate anions, precluding direct metal–tetrazole interactions. Thus persuaded, we decided to synthesize (in an aqueous medium) and crystallographically characterize the [Na(18-crown-6)]$^+$ salt of a related tetrazole, namely, 1-phenyl-1H-tetrazole-5-thione, in order to study the structural features of this heterocyclic system, so extensively applied [5–10]. The results on the charge-separated species thus obtained, featuring a rare coordinative behavior of the [Na(18-crown-6)(H_2O)$_2$]$^+$ cation as well, are presented in this work. Additionally, some molecular orbital calculations of the ab initio type were performed with a view to gaining further information in the present effort to elucidate the structure of the thiotetrazole system.

RESULTS AND DISCUSSION

The title compound was prepared by in situ reaction of 1-phenyl-1H-tetrazole-5-thione (in its acid form, abbreviated here as Tz), 1,4,7,10,13,16-hexaoxacyclooactadecane (or 18-crown-6), and NaOH in aqueous solution, at ambient temperature. Evaporation of the solvent afforded white crystals of [diaqua(18-crown-6)sodium] 1-phenyl-1H-tetrazole-5-thiolate.

The infrared spectrum of the compound shows the absence of the N–H stretching vibration band [11] at 3040 cm^{-1} (observed for the neutral thiotetrazole), thus indicating the presence of the azole ring in its deprotonated (anionic) form. The cationic polyether-Na moiety is mainly evidenced by a strong band at 1107 cm^{-1}, assigned to asymmetric C–O–C stretchings [11]. Bands are also observed in the region 3200–3550 cm^{-1} and at 1670 cm^{-1}, which indicate the presence of water molecules in the compound [12], a common feature of 18-crown-6 sodium complexes [13].

The fast-atom bombardment (FAB) mass spectra (positive and negative) of the compound also show both the expected ionic species, [Na(18-crown-6)]$^+$ and (Tz-H)$^-$, while the unequivocal structure of the complex in the solid state came out only on the basis of X-ray diffraction studies. Further preparative details, physical properties, and the complete spectroscopic characterization results are given in the Experimental section.

The molecular structure of the compound, determined by single-crystal X-ray diffractometry at room temperature, is shown in Figure 1, along with the atom labeling scheme. A summary of crystallographic data is presented in Table 1, while atomic coordinates and thermal parameters are enlisted in

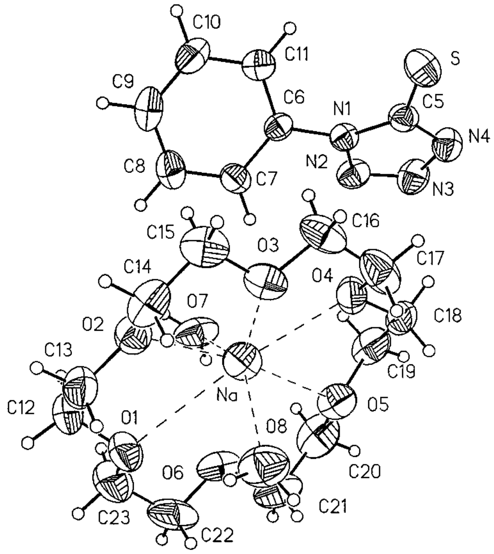


FIGURE 1 Structure of [Na(18-crown-6)(H_2O)$_2$][$C_7H_5N_4S$], with the atom-labeling scheme. Thermal ellipsoids are scaled to the 40% probability level.

TABLE 1 Summary of Crystallographic Data for [Na(18-crown-6)$(H_2O)_2$][$C_7H_5N_4S$]

Empirical formula	$C_{19}H_{33}N_4NaO_8S$
Formula weight	500.5
Color; habit	colorless; prism irregular
Crystal size (mm)	0.36 × 0.32 × 0.20
Crystal system	monoclinic
Space group	$P2_1$
Unit cell dimensions	
a (Å)	9.911(1)
b (Å)	12.625(1)
c (Å)	11.133(2)
β (°)	114.42(1)
Volume (Å^3)	1268.5(3)
D_{calc} (Mg/m^3)	1.310
Absorption coefficient (mm^{-1})	1.729
F(000)	532
2θ range	3.0–110.0°
Scan type	$\theta/2\theta$
Scan speed	variable; 4.00–100.00°/min in θ
Standard reflections	3 measured every 97 reflections
Reflections collected	1759
Independent reflections	1656 (R_{int} = 10.99%)
Observed reflections	1600 [$E > 3.0\sigma(F)$]
Extinction correction	$\chi = 0.013(3)$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0015F^2$
Number of parameters refined	310
Final *R* indices (obs. data), %	$R = 4.45$, $wR = 6.42$
Goodness-of-fit	1.35
Largest and mean Δ/σ	0.008, 0.002
Max/Min $\Delta\rho$ (e Å^{-3})	0.25/−0.19

TABLE 2 Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for [Na(18-crown-6)$(H_2O)_2$][$C_7H_5N_4S$]

	x	*y*	*z*	*U*(*eq*)^a
S	5487(2)	2610	3695(1)	65(1)
Na	714(3)	4104(2)	−2438(2)	72(1)
O(1)	−1599(5)	5330(4)	−4509(5)	79(2)
O(2)	−1390(4)	4981(4)	−1912(4)	71(2)
O(3)	358(4)	3342(4)	−489(4)	69(2)
O(4)	2823(4)	2947(3)	−884(4)	67(2)
O(5)	2816(4)	3350(4)	−3374(4)	75(2)
O(6)	873(6)	4877(5)	−5127(4)	83(2)
O(7)	1975(7)	5654(4)	−2504(4)	83(2)
O(8)	−1010(6)	2980(6)	−4006(6)	102(3)
N(1)	5567(4)	4147(4)	1947(3)	44(1)
N(2)	6249(5)	4308(4)	1103(4)	56(2)
N(3)	7050(5)	3479(5)	1223(5)	65(2)
N(4)	6947(5)	2781(4)	2088(4)	58(2)
C(5)	6019(5)	3201(4)	2569(4)	48(2)
C(6)	4529(5)	4923(4)	1990(4)	43(2)
C(7)	3583(5)	5387(4)	826(5)	52(2)
C(8)	2580(7)	6130(5)	852(6)	65(2)
C(9)	2506(7)	6390(5)	2033(7)	71(3)
C(10)	3488(7)	5946(5)	3187(6)	68(3)
C(11)	4496(7)	5193(5)	3179(5)	61(2)
C(12)	−2224(9)	5996(6)	−3825(7)	89(3)
C(13)	−2679(8)	5362(6)	−2969(8)	81(3)
C(14)	−1775(8)	4372(6)	−1038(8)	79(3)
C(15)	−408(7)	3989(7)	59(7)	78(3)
C(16)	1591(7)	2836(7)	507(6)	77(3)
C(17)	2392(8)	2224(7)	−130(8)	90(3)
C(18)	3841(7)	2485(7)	−1334(7)	83(3)
C(19)	4124(6)	3203(7)	−2236(8)	86(3)
C(20)	3044(9)	3876(8)	−4417(8)	97(4)
C(21)	1591(9)	4080(8)	−5532(7)	90(4)
C(22)	−597(10)	5127(8)	−6074(6)	98(4)
C(23)	−1302(12)	5866(8)	−5459(8)	105(4)

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

Table 2. Selected interatomic bond distances and angles have been assembled in Table 3.

Packing Arrangement

The structure consists of tetrazolate anions and complex cations made up of sodium atoms coordinated to the crown ether and to two water molecules (Figure 2). In satisfaction of the primary aim of the work, direct interactions between the metal ion and the tetrazolate moiety are absent, as the shortest distance between Na^+ and the heterocycle azole plane is 4.723(3) Å, ca. 0.9 Å larger than the corresponding sum of van der Waals radii [14]. The packing scheme of the compound, however, features a system of hydrogen bonds between the two water molecules bonded to sodium in the cation and a sulfur or nitrogen atom (N_4) of two distinct tetrazolate rings. This results in an arrangement of pseudohelicoidal chains of ionic units built along the *y* axis. The geometric parameters of such bonds are given in Table 4, and their role here is, undoubtedly, as stabilizing tools of the crystal structure. It should be noted that hydrogen bonding patterns of this kind are commonly observed in tetrazole(acceptor)–water(donor) systems [15,16].

There are two interatomic distances that represent the closest approaches between adjacent chains of ions, both of them involving methylene groups of the crown ether and a nitrogen atom of a tetrazole ring in a neighboring chain: (C_{15}-)H_{15c}—N_3 2.59(1) Å, C_{15}—N_3 3.34(2) Å and (C_{18}-)H_{18c}—N_3 2.740(8) Å, C_{18}—N_3 3.50(1) Å. These interatomic distances, however, may be regarded as the result of packing forces.

Structure of the Ionic Moieties

The interatomic bond distances and angles of the tetrazolate ring (Table 3) are, to the best of our knowl-

TABLE 3 Selected Interatomic Bond Distances (Å) and Angles (°) for [Na(18-crown-6) $(H_2O)_2$] [$C_7H_5N_4S$]

N(1)–N(2)	1.380(8)	N(4)–C(5)	1.349(8)
N(2)–N(3)	1.286(8)	C(5)–N(1)	1.360(7)
N(3)–N(4)	1.340(8)	N(1)–C(6)	1.435(7)
C(5)–S	1.719(6)*	C(6)–C(7)	1.378(6)
C(7)–C(8)	1.374(9)	C(9)–C(10)	1.370(8)
C(6)–C(11)	1.380(8)	C(8)–C(9)	1.387(12)
C(10)–C(11)	1.382(10)	Na–O(1)	2.932(5)
Na–O(2)	2.632(6)	Na–O(3)	2.528(6)
Na–O(4)	2.550(4)	Na–O(5)	2.850(6)
Na–O(6)	3.214(6)		
N(2)–N(1)–C(6)	118.8(4)	C(5)–N(1)–C(6)	132.2(5)
N(1)–N(2)–N(3)	105.3(5)	N(2)–N(3)–N(4)	112.4(6)
N(3)–N(4)–C(5)	107.1(5)	S–C(5)–N(1)	128.1(5)
S–C(5)–N(4)	125.7(4)	N(1)–C(5)–N(4)	106.2(5)
N(1)–C(6)–C(7)	118.5(5)	N(1)–C(6)–C(11)	120.1(4)
N(2)–N(1)–C(5)	108.9(5)	O(1)–Na–O(2)	61.2(2)
O(1)–Na–O(3)	122.3(2)	O(2)–Na–O(3)	64.2(2)
O(1)–Na–O(4)	172.2(2)	O(2)–Na–O(4)	126.4(2)
O(3)–Na–O(4)	64.3(2)	O(1)–Na–O(5)	109.9(2)
O(2)–Na–O(5)	171.0(2)	O(3)–Na–O(5)	124.7(2)
O(4)–Na–O(5)	62.5(2)	O(1)–Na–O(7)	77.7(2)
O(2)–Na–O(7)	97.9(2)	O(3)–Na–O(7)	127.7(2)
O(4)–Na–O(7)	101.6(2)	O(5)–Na–O(7)	77.7(2)
O(1)–Na–O(8)	69.0(2)	O(2)–Na–O(8)	91.1(2)
O(3)–Na–O(8)	95.2(2)	O(4)–Na–O(8)	107.4(2)
O(5)–Na–O(8)	86.8(2)	O(7)–NaO(8)	135.7(2)

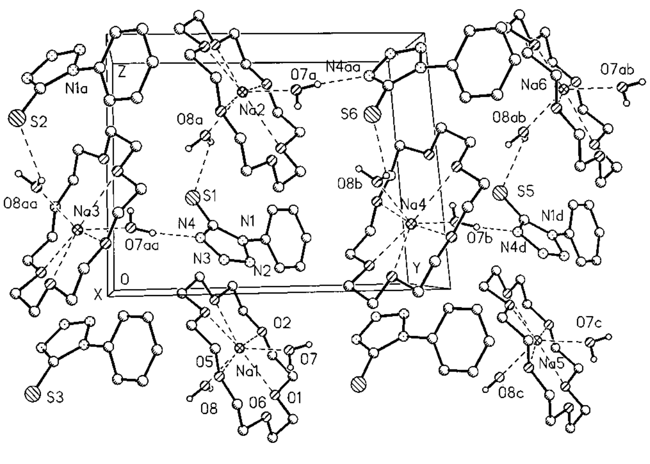


FIGURE 2 Unit cell view of [Na(18-crown-6)$(H_2O)_2$][$C_7H_5N_4S$], showing the hydrogen bonding system.

TABLE 4 Geometric Parameters of the Hydrogen Bonds in the Crystal Structure of [Na(18-crown-6)$(H_2O)_2$][$C_7H_5N_4S$][a]

Bond	*D-H*	*H—A*	*D—A*	*D-H—A*
O_8-H_{8c}—S^b	0.85(2)	2.775(5)	3.388(7)	130.6(1)
O_7-H_{7c}—N_4^c	0.85(2)	2.094(7)	2.856(7)	148.5(2)

[a] Bond distances in angstroms and angles in degrees.
[b] Symmetry operation: X, Y, Z → 1 − X, Y, 1 + Z.
[c] Symmetry operation: − X, 0.5 + Y, − Z → 1 − X, Y − 0.5, − Z.

edge, the first to be reported for an anionic tetrazole, free of direct interactions with metal counterions [17]. The shortest Na–N distance is that between a sodium ion and the N(4) of a neighboring tetrazole in the same chain, whose value of 5.132(6) Å is far larger than the sum of the van der Waals radii (3.85 Å). The shortest Na–S distance [5.522(2) Å] is equally large. By contrast, the structure of the monohydrated sodium salt of tetrazole **1** displays close Na–N(heterocycle) interactions of 2.560(2) Å. [15].

The thiotetrazolate ring is essentially planar. The average deviation of the atoms from the calculated least-squares plane (CN_4) is 0.004 Å, and the largest deviation is 0.007 Å. Likewise, the deviation of the exocyclic sulfur atom from the azole plane (0.029 Å) is negligible.

All the interatomic distances in the thiotetrazole ring are, to a different extent, shorter than the accepted values for single bond lengths. This is indicative of considerable π-electron resonance within the ring, a feature common to practically all tetrazole systems [1]. The only bond length that approaches that of a single bond is N_1–C_6 [1.435(7) Å], that is, that connecting the tetrazole and the phenyl ring systems (Figure 1). Although this distance is slightly shorter than the expected value of 1.47 Å [18], the dihedral angle between the two ring planes, namely, C_5-N_1-C_6-C_{11} = 42.09°, indicates that interannular

TABLE 5 Experimental *vs.* 6-31G* *Ab Initio* Calculated Geometric Parameters[a] and Bond Orders for 1-Phenyl-1H-tetrazole-5-thiolate (Tz-Ph⁻) and 1-Methyl-1H-tetrazole-5-thiolate (Tz-Me⁻)

	Tz-Ph⁻			Tz-Me⁻		
Geometric Parameter	Calcd.	Exptl.	Bond Order	Calcd.	Exptl.[b]	Bond Order
C_5–S	1.724	1.719(6)	1.225	1.730	1.708(4)	1.172
C_5–N_1	1.363	1.360(7)	1.022	1.348	1.325(5)	1.086
N_1–N_2	1.349	1.380(8)	1.030	1.337	1.390(6)	1.066
N_2–N_3	1.248	1.286(8)	1.560	1.253	1.233(7)	1.523
N_3–N_4	1.331	1.340(8)	1.175	1.331	1.289(6)	1.225
N_4–C_5	1.319	1.349(8)	1.357	1.321	1.330(5)	1.365
N_1–C_6	1.411	1.435(7)	0.823	1.435	1.440(6)	0.870
C_5–N_4–N_3	107.42	107.1(5)		106.98	105.9(4)	
N_4–N_3–N_2	112.27	112.4(6)			112.01	115.2(4)
N_3–N_2–N_1	106.39	105.3(5)		106.21	104.5(4)	
N_2–N_1–C_5	108.48	108.9(5)		109.19	107.1(4)	
N_1–C_5–N_4	105.44	106.2(5)		105.60	107.3(4)	
S–C_5–N_1	127.03	128.1(5)		125.02	124.7(3)	
C_6–N_1–C_5	132.77	132.2(5)		130.21	130.4(4)	

[a] Bond lengths in angstroms and angles in degrees.

[b] From Ref. [3].

conjugation is very little or nil. Due to the scarcity of reports on aryl-tetrazoles in the solid state, it is difficult to compare this behavior with those of similar systems; nevertheless, the crystal structure of the aromatic compound anhydro-5-mercapto-2,3-diphenyltetrazolium hydroxide (commonly known as dehydrodithizone) [19] also reveals the absence of interannular conjugation. HF/6-31G*//HF/3-21G* Ab initio molecular orbital calculations performed by us on the present system point out that even in the gas phase there is little tendency for conjugation between both rings, since the computed C_5-N_1-C_6-C_{11} torsional angle is 39.46°. The calculated Mulliken N_1–C_6 bond order of 0.823 (Table 5) also gives support to this statement.

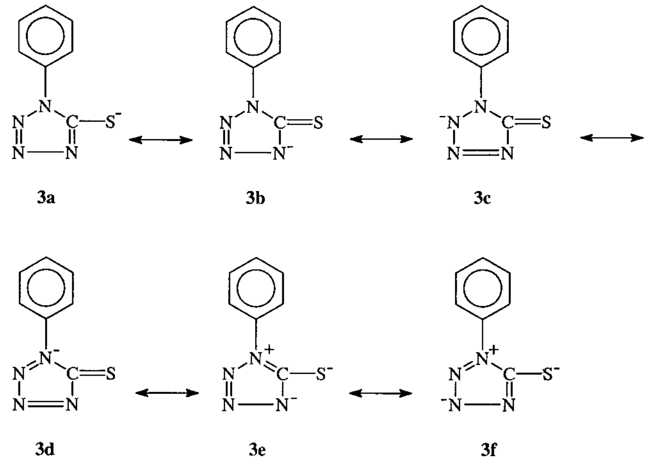
The crystallographic C–S bond distance [1.719(6) Å] is intermediate between the accepted single (1.81 Å) and double (1.61 Å) bond length values, an evidence, together with the position of the sulfur in the tetrazole plane, of important electronic conjugation with the exocyclic atom. Likewise, the two carbon–nitrogen distances within the ring [C_5–N_1 1.360(7) Å and C_5–N_4 1.349(8) Å] are ca. halfway in the range for single and double bonds.

The N_2–N_3 distance [1.286(8) Å] is virtually that of a true double bond [18] and is significantly shorter than the other nitrogen–nitrogen distances within the ring [N_1–N_2 1.380(8) Å and N_3–N_4 1.340(8) Å], which in turn are shorter than the expected single bond length (1.45 Å), but longer than that for a double one (1.25 Å). This pattern of one short and two longer N–N distances is a feature observed in several tetrazole systems [2]. Different arrangements, however, can be found in, for example, the meso-ionic compounds dehydrodithizone [19] and 1,3-dimethyl-5-iminotetrazole [20] (as its hydrochloride and hydrobromide salts), where the nitrogen–nitrogen bond lengths are all equal within experimental error and present a pattern of one long and two short distances, respectively. Hence, the present tetrazolate system may be best described as a resonance hybrid, as shown in **3a**–**3f**. The bond length scheme observed indicates that probably structures **3a** and **3b** have a more important contribution to the overall structure than the rest.

In Table 5, we have collected the calculated geometric parameters and bond orders of the anionic phenyl-tetrazole under study and its methyl analogue; for the sake of comparison, the X-ray experimental results obtained for both rings have also been included. The net atomic charges resulting from a Mulliken population analysis appear in Figure 3.

FIGURE 3 Mulliken atomic charges, calculated by 6-31G*//3-21G* *ab initio* methods, for 1-phenyl-1H-tetrazole-5-thiolate and 1-methyl-1H-tetrazole-5-thiolate.

The notable agreement between the calculated and the experimental geometric parameters allows us to suppose that similar atomic charges are present in the phenyl-tetrazole in the solid state. It may be easily observed that the greatest negative charges lie on N_1 and N_4, as semiempirical methods also indicated for the parent 1H-tetrazole [21], although in the present system, a large negative charge may be found in the exocyclic sulfur as well.



These data clearly point to a relatively large concentration of the negative charge on the N_4-C_5-S portion of the ring, in accord with the proposal of a large contribution of forms **3a** and **3b** to the resonance hybrid.

By contrast, a larger discrepancy is observed between the X-ray data of the metal coordinated methyl-tetrazolate [3] and the computed geometry of the anion in the gas phase; for instance, the calculations predict a N_3–N_4 distance of 1.331 Å, in fact, the same as that calculated for the *metal-free* phenyl-tetrazolate, while the bond length observed is considerably shorter, 1.289(6) Å. This observation should be mainly ascribed, keeping in mind the difference in aggregation states, to the strong bonding of the potassium ion to the N_4-C_5-S moiety of the heterocycle [K–N_4 2.934(4), K–C_5 3.469(4), K–S 3.373(2) Å]. Table 6 provides a comparison of the present ring bond lengths with those found in metal complexes of 1-phenyl-1H-tetrazole-5-thiolate, namely, tin(IV) derivatives [22–25], which exhibit primary Sn–S bonds as well as some Sn–N interactions in the 2.617–3.285(12) Å range (cf. Sn,N $\Sigma r_{\text{cov}} = 2.15$; $\Sigma r_{\text{vdW}} = 3.75$ Å). Inspection of the dimensions collected reveals several interesting features. First, the C_5–N_4 distance in the metal-free tetrazolate [1.349(8) Å] is considerably larger than in all its metal complexes [1.314(5)–1.322(7) Å]. The C–S bond length, on the other hand, is slightly longer in the metal compounds than in the uncoordinated tetrazole, as expected from the establishment of a covalent bond between the exocyclic sulfur and the tin atom. This could be observed in spite of the hydrogen bond involving the sulfur atom of the metal-free tetrazolate (O—H···S—C, 2.775 Å), probably due to its relative weakness (cf. Σr_{vdW} H,S = 2.8 Å). Somewhat surprisingly, however, the C–S distance of the dimethylin derivative [25] is practically identical to that of the present structure.

In summary, it can be seen from Table 6 that, although small, there are some significant and consistent bond length differences between the metal-free and the metal-coordinated tetrazole and that these changes are mainly concentrated on the thioamide N_4-C_5-S moiety, where most of the anionic charge has been found to reside.

The coordination of sodium in the complex cation is unusual. The Na–O(ether) bond lengths, Table 3, can clearly be divided into two sets, one of three short, 2.528(6)–2.632(6) Å, and one of three long distances, 2.850(6)–3.214(6) Å. The latter lies in the long end of the range usually found in $[Na(18\text{-crown-}6)]^+$ complexes (2.3–2.9 Å); however, the Na–O_6 distance of 3.214(6) Å is too long to be considered a coordinative interaction. Thus, the sodium ion coordinates to only five of the six oxygens of the crown ether, being only slightly deviated from the ring plane of best fit, (−0.067 Å), as well as to two axial water molecules at usual Na–O distances of 2.340(7) Å, O_7, and 2.348(6) Å, O_8. The O_7-Na-O_8 angle [135.7(2)°], however, indicates that this axis is far from being perpendicular to the ether mean plane, and hence, the geometry about the metal center can best be described as a highly distorted pentagonal bipyramid, with four of the O_{eq}-Na-O'_{eq} angles (61°–64°) smaller than the expected value of 72° and the remaining one [109.9(2)°] much larger. The equatorial section of the bipyramid may thus be viewed as a nonregular pentagon with four edges (O_{eq}–O'_{eq} vectors) in the range 2.7–2.85 Å and a longer one (O_1–O_5) of 4.734(7) Å.

The fact that the two water molecules are "bent" toward one-half of the ether ring, namely, that where the oxygen atoms make the longer contacts with the metal center, leads us to suggest that electronic repulsions between the water lone pairs and those of the oxygens of that part of the ether (O_1, O_5, and O_6) may be responsible for the coordination mode of the sodium. Comparatively, the Na–O bond lengths in the cation $[Na(\text{dibenzo-18-crown-6})(H_2O)_2]^+$, where the $O_{ax}(H_2O)$-Na-$O'_{ax}(H_2O)$ angle is 173.6°, are in the much less spread range 2.63–2.82 Å [26], supporting the above-proposed explanation.

The coordination behavior observed in the pres-

TABLE 6 Interatomic Bond Distances (Å) of the Phenylthiotetrazolate Ring (Tz-Ph$^-$), as Compared to those of its Tin(IV) Complexes (**3**–**7**)

Bond	*Tz$^-$*	*3*	*4^b*	*5*	*6*	*7*
C_5–S	1.719(6)	1.733(4)	1.726	1.727(18)	1.728(4)	1.719(5)
C_5–N_1	1.360(7)	1.335(4)	1.362	1.344(15)	1.347(5)	1.354(6)
N_1–N_2	1.380(8)	1.363(4)	1.35	1.351(25)	1.365(4)	1.366(6)
N_2–N_3	1.286(8)	1.285(5)	1.287	1.295(19)	1.288(4)	1.288(6)
N_3–N_4	1.340(8)	1.368(5)	1.351	1.345(21)	1.358(4)	1.360(6)
N_4–C_5	1.349(8)	1.314(5)	1.317	1.321(16)	1.314(5)	1.322(7)
N_1–$C_6{}^c$	1.435(7)	1.431(5)	1.46	1.441(22)	1.426(5)	1.443(6)

[a] Complexes **3**–**7** are: (*n*-Bu)$_2$SnTz$_2$, **3** [22]; Bz$_3$SnTz, **4** [22]; Me$_3$SnTz, **5** [23]; Ph$_3$SnTz, **6** [24]; Me$_2$SnTz$_2$, **7** [25].

[b] Average distance of two independent molecules in the unit cell.

[c] C_6 represents the *ipso* carbon of the phenyl substituent.

ent complex is unusual in the sense that, unless stronger metal–ligand interactions preclude it [27], the Na$^+$ tends to coordinate to *all* six oxygen atoms of 18-crown-6 and its substituted analogs. This can be attained with the sodium cation positioned at [28] or off [26,29,30] the center of the ether ring cavity, with no appreciable distortion of the host conformation. Moreover, the 18-crown-6 in particular is flexible enough to adapt itself to the coordination needs of the metal [31] and the examples of sodium complexes with distorted crown-ether frameworks, given in order to optimize the host–guest interactions, are numerous [30,32,33].

The case of the sodium complex of 2,3,11,12-tetracarboxyl-(18-crown-6), where only four of the six ether oxygens are coordinated to the metal, is rather different from ours, since in the former, the Na$^+$ is considerably deviated [0.4371(4) Å] from the ring best plane, and, given the flattened twist-boat arrangement that the macrocycle adopts, two of the cycle oxygens are left outside of the bonding distance to the metal [34]. In the present case, by contrast, the coordination behavior observed in the complex cation seems to arise primarily from the position of the water molecules, determined in turn by the hydrogen bonding scheme in which they are involved, probably given mainly as a packing strategy of the solid. In other words, the current one appears to be a structure where hydrogen bonding exerts a direct effect on the host–guest interaction.

The macrocyclic ether adopts a typical "crown" conformation (approximate D_{3d} symmetry) with the C and O atoms lying alternately about 0.13–0.29 Å below and above the mean plane of the ring. The C–C and C–O average bond distances (1.475 and 1.417 Å, respectively) correspond closely to those observed previously for this conformation, and the ring angles are also as expected [31].

EXPERIMENTAL

Materials and Physical Measurements

1-Phenyl-1H-tetrazole-5-thione was obtained according to the literature procedure [35], while all other starting materials were purchased from Aldrich Chemical Co. and used without additional purification.

The infrared spectra were recorded as KBr pellets on a Nicolet FT-IR Magna 750 spectrometer.

Fast Atom Bombardment (FAB) mass spectra were obtained as acetone solutions on a Jeol JMS SX102A spectrometer, operated at an accelerating voltage of 10 Kv. Samples were desorbed from a nitrobenzyl alcohol matrix, using 6 Kev xenon atoms.

NMR spectra were recorded in deuterated water on a Varian Unity 300, operating at 300 and 75 MHz for ^{1}H and ^{13}C, respectively. The spectra were measured at ambient temperature.

RHF ab initio molecular orbital calculations were carried out employing the 3-21G* basis set, with full geometry optimization, and performing subsequent single-point calculations at the 6-31G* level on the parameters obtained, by using the Spartan 4.0 package of programs [36]. Such calculations are denoted as HF/6-31G*//HF/3-21G*. The input consisted of geometrical parameters (bond lengths and angles) obtained from the crystal structure determinations presented here and in Ref. [3]. The structures of the anions were subjected to full geometry optimizations, until the changes in energy and density were less than 10–8 and 10–5, respectively. The nature of the stationary points thus obtained was checked by calculating the numerical second derivatives.

Single-crystal X-ray diffraction studies were performed on a Siemens P4/PC diffractometer with CuK$_\alpha$ radiation, λ = 1.54178 Å (parallel-graphite monochromator), at 298 K. The data were corrected for Lorentz and polarization effects. A semiempirical absorption correction was also applied, with min/max transmission factor 0.6764/0.8755. The structure was solved by direct methods, using Siemens SHELXTL-PC software (1992). A number of 310 parameters were refined by the full-matrix least-squares technique, with positional and anisotropic thermal parameter factors for non-H atoms. All hydrogens were located in difference Fourier maps and refined isotropically ($U = 0.06$ Å) with C–H = 0.96 Å, except for hydrogens on O_7 and O_8, which were refined as non-H atoms.

Preparation of [Na(18-crown-6)$(H_2O)_2$][$C_7H_5N_4S$]

The title compound was obtained from 1-phenyl-1H-tetrazole-5-thione (0.27 g, 1.5 mmol), 1, 4, 7, 10, 13, 16-hexaoxacyclooctadecane (0.4 g, 1.5 mmol), and sodium hydroxide (0.06 g, 1.51 mmol) in aqueous solution (16.5 mL), on stirring for 4 hours, at room temperature. The resulting solution was evaporated until white microcrystals of the compound deposited (0.64 g, 84% yield). Mp = 151–152°C (softening occurs at 60°C). Single crystals suitable for X-ray diffraction could be obtained by the solvent-diffusion method, from an acetone/*n*-hexane mixture at ambient temperature.

Spectroscopic characterization: IR (KBr) cm^{-1}: 3448, 3246 (w-m, νOH), 2900 (m, $\nu C\text{–}H_{arom}$), 1670 (w, δHOH), 1600 (w, Ph nucleus), 1107 (s, νC-O-C). ^{1}H-NMR (D_2O): δ 3.6 (s, 24H, O-CH_2-CH_2-O), 7.57 (m, 5H, C_6H_5). ^{13}C-NMR (D_2O): δ 69.46 (O-CH_2-CH_2-O), 125.55 (C_0), 129.50, 129.58 (C_m and C_p), 135.04 (C_i), 165.74 (C=S). MS: FAB^+m/e 287 (Na-18-crown-6)$^+$; FAB^-m/e 177 (Tz − H)$^-$.

ACKNOWLEDGMENTS

Financial support from the National Council of Science and Technology (CONACYT-México), through Grant 0109-E, is gratefully acknowledged. We also wish to express our gratitude to L. Velasco-Ibarra and R. L. Gaviño-Ramírez for their work in recording the spectra.

REFERENCES

[1] R. N. Butler: "Tetrazoles," in A. R. Katritzky, C. W. Rees (eds): *Comprehensive Heterocyclic Chemistry,* Pergamon Press, Oxford, vol. 5, p. 791 (1984).

[2] G. B. Ansell, *J. Chem. Soc., Perkin Trans. II,* 1973, 2036, and references therein.

[3] R. Cea-Olivares, O. Jiménez-Sandoval, S. Hernández-Ortega, M. Sánchez, R. A. Toscano, I. Haiduc, *Heteroatom Chem., 6,* 1995, 89.

[4] D. E. Fenton: "Alkali Metals and Group II Metals," in G. Wilkinson (ed): *Comprehensive Coordination Chemistry,* Pergamon Press, Oxford, vol. 3, p. 4 (1987).

[5] H. Seneca, P. Peer, *Antimicrobial Agents Chemother.,* 1964, 470.

[6] C. E. Moore, T. A. Robinson, *Anal. Chim. Acta, 23,* 1960, 533.

[7] E. E. Schweizer, B. J. Rogers, *Weeds, 12,* 1964, 7; *Chem. Abstr., 60,* 1964, 11305g.

[8] (a) A. N. Chechneva, A. V. Radushev, *Zh. Anal. Khim., 23,* 1968, 1059; *Chem. Abstr., 69,* 1968, 92675z. (b) A. V. Radushev, A. N. Chechneva, *Zh. Anal. Khim., 26,* 1971, 2410; *Chem. Abstr., 76,* 1972, 80577a. (c) A. V. Radushev, L. A. Statina, *Zh. Anal. Khim., 27,* 1972, 1344; *Chem. Abstr., 77,* 1972, 159755m.

[9] J. M. Grasshoff, J. L. Reid, L. D. Taylor, *J. Polym. Sci., Polym. Chem. Ed., 16,* 1978, 2403.

[10] J. Ehrenfreund, E. Stamm, Eur. Pat. Appl. EP406163 (1991); A.-G. Ciba-Geigy, *Chem. Abstr., 115,* 1991, 8810c.

[11] N. B. Colthup, L. H. Daly, S. E. Wiberley: *Introduction to Infrared and Raman Spectroscopy,* Academic, San Diego (1990).

[12] K. Nakamoto: *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* Wiley, New York (1986).

[13] N. S. Poonia, *J. Am. Chem. Soc., 96,* 1974, 1012.

[14] J. E. Huheey: *Inorganic Chemistry,* Harper & Row, New York (1983).

[15] G. J. Palenik, *Acta Cryst., 16,* 1963, 596.

[16] K. Britts, I. L. Karle, *Acta Cryst., 22,* 1967, 308.

[17] The structure of another metal-free anionic tetrazole, namely, 5-aminotetrazole, has been reported by J. H. Bryden, *Acta Cryst., 11,* 1958, 31; however, no metal was used as counterion, the $NH_2\text{–}NH_3^+$ ion being used instead.

[18] M. Green: "Bonding in Nitrogen Compounds," in C. Colburn, (ed): *Developments in Inorganic Nitrogen Chemistry,* Elsevier, Amsterdam, vol. 1, p. 9 (1966).

[19] Y. Kushi, Q. Fernando, *J. Am. Chem. Soc., 92,* 1970, 1965.

[20] J. H. Bryden, *Acta Cryst., 8,* 1955, 211.

[21] O. A. Ivashkevich, P. N. Gaponik, A. O. Koren, O. N. Bubel, E. V. Fronchek, *Int. J. Quantum Chem., 43,* 1992, 813.

[22] R. Cea-Olivares, O. Jiménez-Sandoval, G. Espinosa-Pérez, C. Silvestru, *Polyhedron, 13,* 1994, 2809.

[23] R. Cea-Olivares, O. Jiménez-Sandoval, G. Espinosa-Pérez, C. Silvestru, *J. Organomet. Chem., 484,* 1994, 33.

[24] J. Bravo, M. B. Cordero, J. S. Casas, A. Sánchez, J. Sordo, E. E. Castellano, J. Zukerman-Schpector, *J. Organomet. Chem., 482,* 1994, 147.

[25] O. Jiménez-Sandoval, R. Cea-Olivares, S. Hernández-Ortega, unpublished work.

[26] M. A. Bush, M. R. Truter, *J. Chem. Soc. (B),* 1971, 1440.

[27] S. Gambarotta, F. Arena, C. Floriani, P. F. Zanazzi, *J. Am. Chem. Soc., 104,* 1982, 5082.

[28] D. J. Darensbourg, C. G. Bauch, A. L. Rheingold, *Inorg. Chem., 26,* 1987, 977; D. Bright, M. R. Truter, *J. Chem. Soc. (B),* 1970, 1544; J.-C. Berthet, C. Villiers, J.-F. Le-Marechal, B. Delavaux-Nicot, M. Lance, M. Nierlich, J. Vigner, M. Ephritikhine, *J. Organomet. Chem., 440,* 1992, 53; W. S. Sheldrick, J. Kroner, F.

Zwaschka, A. Schmidpeter, *Angew. Chem. Int. Ed. Engl., 18,* 1979, 934.

[29] G. Weber, G. M. Sheldrick, T. Burgemeister, F. Dietl, A. Mannschreck, A. Mertz, *Tetrahedron, 40,* 1984, 855.

[30] M. K. Cooper, P. A. Duckworth, K. Henrick, M. McPartlin, *J. Chem. Soc., Dalton Trans.,* 1981, 2357.

[31] I. Goldberg: "Geometry of the Ether, Sulphide and Hydroxyl Groups and Structural Chemistry of Macrocyclic and Non-cyclic Polyether Compounds," in S. Patai, Z. Rappoport, (eds): *Crown Ethers and Analogs,* Wiley, Chichester, pp. 373–376 (1989).

[32] M. Dobler, J. D. Dunitz, P. Seiler, *Acta Cryst., B30,* 1974, 2741; M. Mercer, M. R. Truter, *J. Chem. Soc., Dalton Trans.,* 1973, 2215.

[33] M. E. Fraser, S. Fortier, M. K. Markiewicz, A. Rodrigue, J. W. Bovenkamp, *Can. J. Chem., 67,* 1987, 2558; A. S. C. Chan, H.-S. Shieh, J. R. Hill, *J. Organomet. Chem., 279,* 1985, 171; M. E. Fraser, S. Fortier, A. Rodrigue, J. W. Bovenkamp, *Can. J. Chem., 64,* 1986, 816; S.-H. Han, J.-S. Song, P. D. Macklin, S. T. Nguyen, G. L. Geoffroy, A. L. Rheingold, *Organometallics, 8,* 1989, 2127; S.-H. Han, G. L. Geoffroy, B. D. Dombek, A. L. Rheingold, *Inorg. Chem., 27,* 1988, 4355.

[34] P. J. Dutton, T. M. Fyles, V. V. Suresh, F. R. Fronczek, R. D. Gandour, *Can. J. Chem., 71,* 1993, 239.

[35] E. Lieber, J. Ramachandran, *Can. J. Chem., 37,* 1959, 101.

[36] Spartan, Version 4.0, Wavefunction, Inc., Irvine, CA, ©Wavefunction, Inc., 1996.