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Synthesis and Characterization of Sodium 5-Chlorotetrazolate Dihydrate by Chlorination of 1H-Tetrazole

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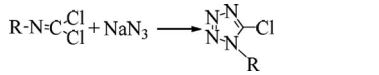
Keywords: Heterocycles; Tetrazole derivative; Chlorination; Halogenation

Abstract. A convenient, simple work-up procedure and low-cost chlorination method was developed to prepare sodium 5-chlorotetrazolate dihydrate by chlorination of self-prepared 1H-tetrazole with sodium hypochlorite solution. Several organic extracting solvents and factors (raw material ratio, reaction temperature, and reaction time) were investigated to optimize the operating conditions of the chlorination procedure. These products were characterized by ^{1}H and ^{13}C NMR spectroscopy, vibrational spectroscopy (IR), mass spectroscopy (MS), and single-crystal X-ray diffraction. In addition, the thermal behaviors of the resulting sodium 5-chlorotetrazolate dihydrate and sodium tetrazolate monohydrate were investigated and compared by differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). The results indicated that the optimum chlorination conditions were a stoichiometric raw materials ratio of 1:12:12 (1H-tetralzole : sodium hypochlorite solution : acetic acid solution), a reaction temperature of 55 °C, a reaction time of 6 h, affording a 92.76% yield; moreover, acetone was determined to be the best extraction solvent in terms of yield and toxicity. Crystal data: sodium tetrazolate, orthorhombic, *Pmc*2(1), a = 5.847(4), b = 5.605(3), c = 6.387(4) Å, V = 209.3(2) Å^3, Z = 2, ρ = 1.746 Mg·m^{-3}; sodium 5-chlorotetrazolate, orthorhombic, *Pnma*, a = 6.8611(19), b = 6.9243(19), c = 12.281(4) Å, V = 583.5(3) Å^3, Z = 8, ρ = 1.850 Mg·m^{-3}. Sodium tetrazolate has a melting point at 275.97 °C and an exothermic decomposition peak at 319.45 °C, whereas sodium 5-chlorotetrazolate shows only a sharp exothermic peak at 237.33 °C due to violent decomposition without melting.

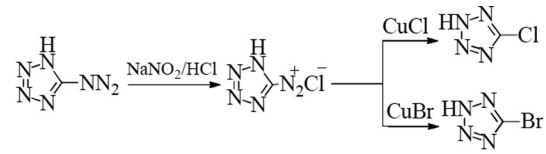
Introduction

Tetrazoles are a special class of five-membered heterocyclic compounds with many C–N, N–N, and N=N bonds that possess excellent thermal stability, high density and enthalpy of formation, good chemical reactivity, which have attracted great interest as pharmaceuticals,[1–3] photographic materials,[4] polydentate linker,[5,6] and energy materials.[7] The halogenating reaction of tetrazoles is of utmost importance for increasing the activity and halogen compounds are promising chemical intermediates for synthesizing many excellent materials that are used in medicines, agricultural agents, and even energy materials.[8,9]

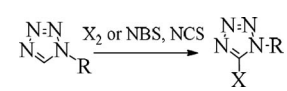
To date, the traditional methods for introducing halogen elements have included the following: (1) the [3+2] dipolar cycloaddition of dichloroisocyanide compounds with sodium azide[10–12] (Scheme 1); (2) Sandmeyer reaction of amino tetrazole derivatives with sodium nitrite and cuprous halides[13] (Scheme 2); (3) direct halogenation of tetrazole derivatives by elemental halogen, NBS or NCS[8,9,14] (Scheme 3); (4) halogenating reaction of nitro compounds[15,16] (Scheme 4). However, the four approaches suffer from drawbacks such as high toxicity, high raw materials cost, a complex reaction procedure, harsh reaction conditions, and the formation of sensitive intermediates and by-products that are difficult to separate.



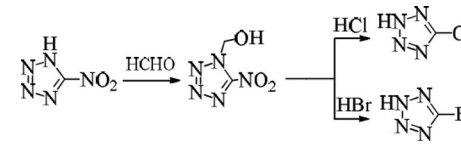
Scheme 1. [3+2] Dipolar cycloaddition of dichloroisocyanide compounds.



Scheme 2. Sandmeyer reaction of amino tetrazole derivatives.



Scheme 3. Direct halogenation of elemental halogen, NBS or NCS.



Scheme 4. Halogenating reaction of nitro compounds.

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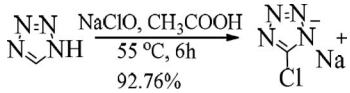
Table 1. The extraction effect of eight organic solvents.

Solvent	Boiling point /°C	Polarity	Content of extract /g	Color	FT-IR spectrogram
Et_2O	34.6	2.9	–	–	–
CH_2Cl_2	39.8	3.4	–	–	–
THF	66	4.2	0.03	yellow	Product
EtOH	78.4	4.3	0.36	white	Mixture
EtOAc	77	4.3	0.01	white	Product
Acetone	56.05	5.4	0.05	white	Product
Acetonitrile	81.1	6.2	0.05	yellow	Product
MeOH	64.5	6.6	0.62	white	Mixture

In this work, we developed a convenient, simple work-up process and low-cost chlorination protocol (Scheme 5) that can address the shortcomings of the abovementioned methods for the formation of sodium 5-chlorotetrazolate dihydrate using 1H-tetrazole as a raw material, sodium hypochlorite (NaClO) solution as a halogenating reagent and acetic acid as a solvent. Several organic extracting solvents and factors (raw material ratio, reaction temperature, and reaction time) were investigated to optimize the operating conditions. At the same time, sodium tetrazolate and sodium 5-chlorotetrazolate were fully characterized with IR and NMR (^1H, ^{13}C) spectroscopy, mass spectroscopy (MS), differential scanning calorimetry (DSC), thermogravimetric analysis (TG), and single-crystal X-ray diffraction.



Scheme 5. Chlorination of 1H-tetrazole with NaClO solution.

Results and Discussion

Process Optimization

Eight types of solvents (80 mL) were chosen to extract the same amount of mixture containing sodium 5-chlorotetrazolate dihydrate (0.80 g). The IR spectra and contents of filter and extract were measured and analyzed. The experimental results presented in Table 1 demonstrated the effect of extraction. It should be noted that the weak polarity of the solvents (diethyl ether and dichloromethane) adversely affected the extraction procedure, whereas the strong polarity of the solvents (particularly that of methyl alcohol) made it difficult to separate the product from the inorganic salt. Ethanol also led to poor extraction due to high solubility of the inorganic salt in ethanol. The final compound could easily be isolated by extraction using THF, ethyl acetate, acetone, and acetonitrile, among which acetone was the best extraction solvent in terms of yield and toxicity.

A orthogonal design experiment (Table 2) was carried out to test the effects of reaction temperature (25 °C, 35 °C, 45 °C), reaction time (6 h, 8 h, 12 h) and raw material molar ratio (1H-tetralzole: sodium hypochlorite solution: acetic acid solution = 1:3:3, 1:6:6, 1:12:12) on the product yield. The average values ($\bar{K}$) associated with the optimal reaction conditions and range analysis (R) confirming the degrees of influence of the various parameters were analyzed. The results showed that the reaction temperature and raw material ratio produced a greater effect on the yield than did the reaction time. Table 3 also thoroughly describes the effects of reaction temperatures on the yield at a raw material ratio of 1:12:12 and reaction time of 6 h and showed that 55 °C was the best reaction temperature because chlorine gas could escape rapidly at high temperature. In summary, the optimal reaction conditions were a raw material ratio of 1:12:12, a reaction temperature of 55 °C, and a reaction time 6 h, affording a 92.76% yield.

Table 2. Orthogonal design experiment of sodium 5-chlorotetrazolate dihydrate.

Entry	Reaction temperature /°C	Reaction time /h	Molar ratio	Yield /%
1	25	6	1:3:3	14.90
2	25	8	1:6:6	59.06
3	25	12	1:12:12	91.95
4	35	6	1:6:6	82.92
5	35	8	1:12:12	57.76
6	35	12	1:3:3	31.13
7	45	6	1:12:12	81.73
8	45	8	1:3:3	61.53
9	45	12	1:6:6	47.43
$\bar{K}1$	55.303	59.85	35.853	
$\bar{K}2$	57.270	59.450	63.137	
$\bar{K}3$	63.563	56.837	77.147	
R	8.26	3.013	38.77	

Table 3. The effect of reaction temperature on the yield.

Entry	Reaction temperature /°C	Yield /%
1	45	81.73
2	55	92.76
3	65	73.57

Crystal Structures

Single crystals of sodium 5-chlorotetrazolate and sodium tetrazolate suitable for X-ray diffraction analysis were obtained by recrystallization from acetone and ethanol, respectively. Selected crystallographic data and parameters from X-ray collection and refinement for sodium 5-chlorotetrazolate and sodium tetrazolate are summarized in Table 4. Sodium 5-chlorotetrazolate containing two crystal water, crystallizes in the orthorhombic space group *Pnma* with a cell volume of 583.5(3) $Å^3$,

Table 4. Crystallographic data of sodium 5-chlorotetrazolate and sodium tetrazolate.

	Sodium 5-chlorotetrazolate	Sodium tetrazolate
Empirical formula	$C_{0.5}H_2Cl_{0.5}N_2Na_{0.5}O$	CH_3N_4NaO
Formula weight /g·mol^{-1}	81.26	110.06
Temperature /K	293(2)	153(2)
Wavelength /Å	0.71073	0.71073
θ range for data collection /°	3.32 to 31.52	3.48 to 31.52
Crystal system	orthorhombic	orthorhombic
Space group	*Pnma*	*Pmc*2(1)
a /Å	6.8611(19)	5.847(4)
b /Å	6.9243(19)	5.605(3)
c /Å	12.281(4)	6.387(4)
α /°	90	90
β /°	90	90
γ /°	90	90
Volume /Å^3	583.5(3)	209.3(2)
Z	8	2
Calculated density /Mg·m^{-3}	1.850	1.746
Absorption coefficient /mm^{-1}	0.652	0.230
F(000)	328	112
Crystal size /mm	0.48 × 0.35 × 0.28	0.67 × 0.20 × 0.08
R(int)	0.0243	0.0311
Goodness-of-fit on F^2	1.001	1.002
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0277, wR_2 = 0.0773	R_1 = 0.0302, wR_2 = 0.0651
R indices (all data)	R_1 = 0.0283, wR_2 = 0.0780	R_1 = 0.0328, wR_2 = 0.0666

while sodium tetrazolate containing one crystal water, crystallizes in the orthorhombic space group *Pmc*2(1) with a cell volume of 209.3(2) Å^3. The ORTEP plots of the two crystal structures are shown in Figure 1. Selected bond lengths and bond angles are listed in Table 5. The crystal structure of sodium 5-chlorotetrazolate dihydrate possesses laminar structure with non-overlapping and each layer contains intersecting channels viewed along *c* axis and *b* axis (Figure 2 and Figure 3).

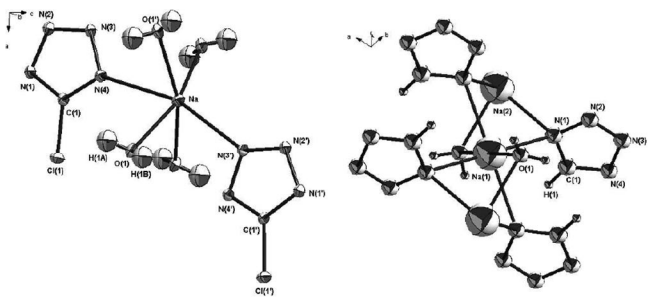


Figure 1. The ORTEP plots of the structures of crystal sodium 5-chlorotetrazolate dihydrate (left) and sodium tetrazolate monohydrate (right).

Table 5. Selected bond lengths /Å and angles /° for sodium 5-chlorotetrazolate and sodium tetrazolate.

Sodium 5-chlorotetrazolate		Sodium tetrazolate	
Na[1]–O(1)[2]	2.4211(9)	Na(1)[4]–O(1)	2.386(9)
Na–O(1′)	2.4107(10)	Na(1)–N(1)	2.536(6)
Na–N(4)[3]	2.5665(14)	Na(2)[5]–N(1)	2.544(6)
N(1)–C(1)	1.3286(16)	N(1)–C(1)	1.3312(13)
N(1)–N(2)	1.3520(17)	N(1)–N(2)	1.3539(13)
N(2)–N(3)	1.3173(15)	N(2)–N(3)[6]	1.3056(18)
N(3)–N(4)	1.3499(17)	N(3)–N(4)	1.3539(13)
C(1)–N(4)	1.3269(17)	C(1)–N(4)	1.3312(13)
C(1)–Cl(1)	1.7018(14)	C(1)–H(1)	0.9500
Na–N(3′)	2.5494(14)		
N(4)–Na–(O1)	84.85(3)	O(1)– Na(1)–N(1)	101.3(2)
N(4)–Na–O(1′)	77.13(3)	Na(1)–N(1)–N(2)	122.1(4)
Na–N(4)–N(3)	122.64(8)	Na(1)–N(1)–C(1)	114.5(5)
Na–N(4)–C(1)	133.66(9)	C(1)–N(1)–N(2)	104.13(9)
C(1)–N(1)–N(2)	103.69(10)	N(1)–N(2)–N(3)	109.60(5)
N(1)–N(2)–N(3)	109.43(11)	N(2)–N(3)–N(4)	109.60(5)
N(2)–N(3)–N(4)	109.66(11)	N(3)–N(4)–C(1)	104.13(9)
N(3)–N(4)–C(1)	103.70(10)	N(1)–C(1)–N(4)	112.52(14)
N(4)–C(1)–N(1)	113.52(12)	H(1)–C(1)–N(1)	123.7
Cl(1)–C(1)–N(4)	123.80(10)	H(1)–C(1)–N(4)	123.7
Cl(1)–C(1)–N(1)	122.67(10)		

Symmetry transformations used to generate equivalent atoms: [1] 1 –*x*, 0.5+*y*, –*z* + 1; [2] –0.5+*x*, 1.5–*y*, 0.5–*z*; [3] 0.5–*x*, 2 –*y*, –0.5+*z*; [4] *x*, *y*, *z*; [5] 2 –*x*, 1 –*y*, 0.5+*z*; [6] 1 –*x*, *y*, *z*.

Thermal Behavior

The thermal behaviors of sodium 5-chlorotetrazolate dihydrate and sodium tetrazolate monohydrate were investigated by TG/DSC at a heating rate of 10 °C·min^{-1} in the temperature range from 35–450 °C with an amount of 1.6088 mg and 3.4073 mg, respectively. The curves of TG and DSC are shown in Figure 4 and Figure 5.

In the curves, it can be seen that the two products loose crystal water at 100 °C; sodium tetrazolate monohydrate was melting at 275.97 °C and had an exothermic decomposition peak at 319.45 °C, whereas sodium 5-chlorotetrazolate dihydrate only decomposed at 237.33 °C without melting; the two products released nitrogen in the stage of decomposition resulting in a shock for the specimen holder and an increase of weight, but sodium 5-chlorotetrazolate dihydrate produced more gas and was more powerful than sodium tetrazolate monohydrate. The result indicated that sodium 5-chlorotet-

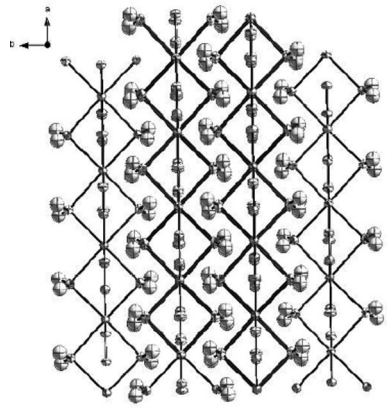


Figure 2. View along *c* axis in the structure of sodium 5-chlorotetrazolate dihydrate.

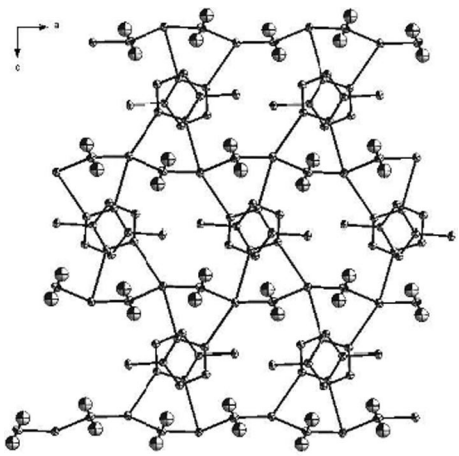


Figure 3. View along *b* axis in the structure of sodium 5-chlorotetrazolate dihydrate.

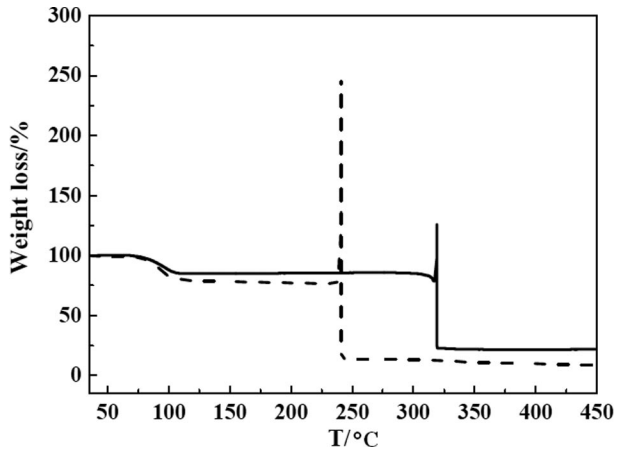


Figure 4. TG of sodium 5-chlorotetrazolate dihydrate (imaginary line) and sodium tetrazolate monohydrate (full line) at a heating rate of 10 °C·min^{-1}.

razolate dihydrate could be a potential candidate for a gas generating compound.

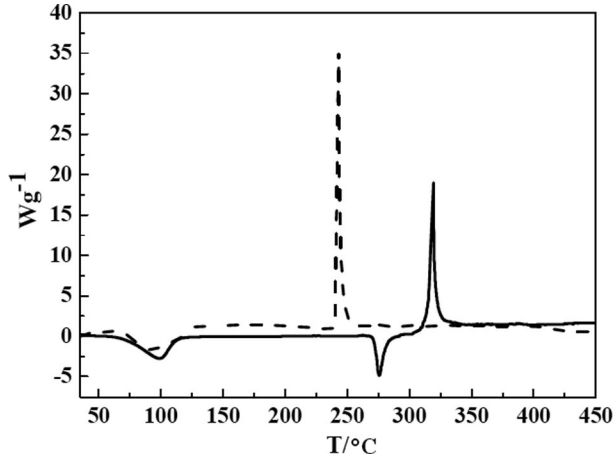


Figure 5. DSC of sodium 5-chlorotetrazolate dihydrate (imaginary line) and sodium tetrazolate monohydrate (full line) at a heating rate of 10 °C·min^{-1}.

Conclusions

A low-toxicity, convenient, simple work-up procedure and low-cost method for producing sodium 5-chlorotetrazolate dihydrate by the chlorination of 1H-tetrazole was developed. By optimizing the synthesis of sodium 5-chlorotetrazolate dehydrate, which is a stoichiometric ratio of raw materials of 1:12:12, a reaction temperature of 55 °C, a reaction time of 6 h, and acetone as the best extraction solvent in terms of yield and toxicity, affording a 92.76% yield, the results obtained in this study provide guidelines for the scaled-up halogenation of tetrazole derivatives. Owing to its violent decomposition without melting at 237.33 °C, sodium 5-chlorotetrazolate dihydrate would be a moderately potential gas generating compound with lower decomposition temperature compared with sodium tetrazolate monohydrate and release of nitrogen.

Experimental Section

General Methods: All other starting materials were of reagent quality and were obtained from commercial sources without further purification. Infrared spectra were recorded with a Bruker TENSOR 27 spectrophotometer (Germany) with KBr pellets in the 400–4000 cm^{-1} region. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker Aspect ARX400 spectrometer at room temperature in [D$_6$]DMSO solutions with an internal TMS reference. Elemental analyses for carbon, hydrogen, and nitrogen were performed with a Perkin-Elmer 2400 (II) analyzer. Mass spectra were recorded with an API 2000 LC/MS/MS apparatus. The thermal properties of the resulting materials were determined using a METTLER TOLEDO STAR^{e} Thermal Analysis System apparatus. Measurements were performed at a heating rate of 10 °C·min^{-1} in a nitrogen flow rate of 20 mL·min^{-1}.

Synthesis of 1H-Tetrazole: 1H-tetrazole was synthesized as reported in the literature.[17–19] Into a mixture of sodium azide (0.045 mol, 2.925 g), NH_4Cl (0.135 mol, 7.221 g), triethylorthoformate (0.135 mol, 20 mL), AcOH (0.18 mol, 11 mL) were added. The mixture was refluxed at 90 °C for 10 h. To the cooled solution, concentrated hydrochloric acid (2 mL) was added (the solution was acidified to pH 2–3 with concentrated hydrochloric acid). A precipitate of sodium chloride

(NaCl) was filtered off, and all solvents were removed using a rotary evaporator. The remaining solid matter was dissolved in boiling EtOH (8 mL). The clear solution obtained was left overnight in a refrigerator. The crystalline product was filtered and purified by recrystallization from acetone (yield: 2.838 g, 91.55 %). M.p. 143.66 °C. CH_2N_4 (70 g·mol): C 16.23 (calcd. 17.13); H 3.311 (2.855); N 80.034 (79.94) %. **IR** (KBr): $\tilde{\nu}$ = (=C–H) 3158.51, ν(N–H) 3057.05, ν(C=N) 1658.26, ν(N=N) 1524.31, ν(C–N) 1401.98, ν(N–N) 1256.77, δ(C–H) 1145.02, δ(N–H) 937.83 cm^{-1}. **^{1}H NMR** (400 MHz, [D_6]DMSO): δ = 9.39 (s, C-H), 7.20 (s, N-H). **^{13}C NMR** (400 MHz, [D_6]DMSO): δ = 143.12 (s, C-1) ppm.

Synthesis of Sodium Tetrazolate Monohydrate: 1H-tetrazole (0.7 g, 0.01 mol) was dissolved in distilled water and sodium hydroxide solution (50 %, aqueous solution, 0.01 mol) was added slowly. Meanwhile, the pH of the solution was adjusted from 5 to 7. The reaction solvent was removed using a rotary evaporator; A colorless solid matter was dried by distillation of azeotrope with three 15 mL portions of EtOH and recrystallized from EtOH. The colorless acicular crystalline solid of sodium tetrazolate was obtained (yield: 0.856 g, 93 %). M.p. 275.97 °C. **IR** (KBr): $\tilde{\nu}$ = (–OH) 3296.12, ν(=C–H) 3114.54, δ(–OH) 1692.01, ν(N–N) 1286.42, δ(C–H) 1131.57 cm^{-1}. **^{1}H NMR** (400 MHz, [D_6]DMSO): δ = 8.10 (s, H-1). **^{13}C NMR** (400 MHz, [D_6]DMSO): δ = 148.41 (s, C-1) ppm. **ESI-MS**: *m/z* = 69.2 $[M]^-$; 41$[M\text{-}N_2]^-$.

Synthesis of Sodium 5-Chlorotetrazolate Dihydrate: A sodium hypochlorite solution (0.12 mol, 74.5 g) was added dropwise with vigorous stirring into 1H-tetrazole (0.01 mol, 0.70 g) dissolved in an AcOH solution (50 %, aqueous solution, 0.12 mol) at 55 °C over a period of 6 h. All of the reaction solvents were removed using a rotary evaporator; the solid matter was dried by distillation of azeotrope with three 20-mL portions of EtOH and extracted with acetone; after filtering the NaCl, the filtrate was dried with $MgSO_4$. Following the removal of acetone by purging with warm air, sodium 5-chlorotetrazolate dihydrate was obtained as a colorless crystal with a 92.76 % yield (1.3496 g). M.p. 237.33 °C (decomposition). **IR** (KBr): $\tilde{\nu}$ = (–OH) 3512.89 (m), δ(–OH) 1628.05, ν(C=N) 1376.12, ν(N=N) 1354.65, ν(N–N) 1195.19, ν(C–Cl) 724.49 cm^{-1}. **^{13}C NMR** (400 MHz, [D_6]DMSO): δ = 150.34 (s, C-1). **ESI-MS**: *m/z* = 102.8 $[M]^-$ (^{35}Cl), 104.8$[M]^-$ (^{37}Cl);75$[M\text{–}N_2]^-$; 76.8$[M\text{–}N_2]^-$; 42$[M\text{–}N_2\text{–Cl+2H}]^-$.

X-ray Data Collection and Structure Determination: X-ray single-crystal diffraction data were collected with a Rigaku RAXIS RAPID IP diffractometer equipped with a graphite at 298(2) K using Mo-K_α radiation (λ = 0.71073 Å). The program SAINT was used to integrate the diffraction profiles. Semi-empirical absorption corrections were performed using the program SADABS. All of the structures were solved by direct methods using the SHELXS 97 program of the SHELXTL package and refined by the full-matrix least-squares method with SHELXL 97.[20,21] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of organic groups were placed in calculated positions in a riding model approximation with a fixed temperature factor.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1028253 (sodium tetrazolate monohydrate) and CCDC-1028254 (sodium 5-chlorotetrazolate dihydrate) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): IR spectra of sodium tetrazolate monohydrate and sodium 5-chlorotetrazolate dihydrate; ^{1}H and ^{13}C NMR. ESI-MS of sodium tetrazolate and sodium 5-chlorotetrazolate.

Acknowledgements

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