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$CS_2N_3^-$-Containing Pseudohalide Species: An Experimental and Theoretical Study[†,‡]

Margaret-Jane Crawford,* Thomas M. Klapötke,* Peter Mayer,[§] and Martin Vogt[§]

Department of Chemistry, Ludwig-Maximilians University, Butenandtstrasse 5-13 (Haus D),
D-81377 Munich, Germany

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The first structural reports of anhydrous salts containing the CS_2N_3 moiety are presented. The new $M^+CS_2N_3^-$ species (M = NH_4 (**1**), $(CH_3)_4N$ (**2**), Cs (**3**), K (**4**)) were characterized by vibrational spectroscopy (IR, Raman), as well as multinuclear NMR spectroscopy (^1H, ^{13}C, ^{14}N NMR). Moreover, the solid-state structures of $NH_4CS_2N_3$ (**1**) [orthorhombic, *Pbca*, $a = 10.6787(1)$ Å, $b = 6.8762(1)$ Å, $c = 15.2174(2)$ Å, $V = 1117.40(2)$ Å^3, $Z = 8$] and $(H_3C)_4NCS_2N_3$ (**2**) [monoclinic, $P2_1/m$, $a = 5.9011(1)$ Å, $b = 7.3565(2)$ Å, $c = 10.9474(3)$ Å, $\beta = 91.428(1)°$, $V = 475.09(2)$ Å^3, $Z = 2$] were determined using X-ray diffraction techniques. The covalent compound $CH_3CS_2N_3$ (**5**) was prepared by the reaction of methyl iodide with sodium azidodithiocarbonate and was characterized by vibrational spectroscopy (IR, Raman), multinuclear NMR spectroscopy (^1H, ^{13}C, ^{14}N), and X-ray diffraction techniques [monoclinic, $P2_1/m$, $a = 5.544(1)$ Å, $b = 6.4792(7)$ Å, $c = 7.629(1)$ Å, $\beta = 105.53(2)°$, $V = 264.06(7)$ Å^3, $Z = 2$]. Furthermore, the gas-phase structure of **5** was calculated (MPW1PW91/cc-pVTZ) and found to be in very good agreement with the experimentally determined structure. Improved synthetic routes for the recently reported dipseudohalogen $(CS_2N_3)_2$ and interpseudohalogen CS_2N_3CN (**6**) are described, and the calculated gas-phase structure of **6** was compared with the experimentally determined structure (X-ray). The vibrational spectra of **6** and HCS_2N_3 (**7**) are also reported. Furthermore, several plausible isomers for **7** were calculated in an attempt to rationalize the experimentally observed structure which has N–H and not S–H connectivity. The lowest energy isomer for **7** is in agreement with the experimentally observed structure, and the Brønsted acidity was calculated at the MPW1PW91/cc-pVTZ level of theory. The unknown $CSe_2N_3^-$ anion (**8**) was also investigated both theoretically and experimentally, and the structure and vibrational data for the unknown $CTe_2N_3^-$ anion (**9**) were investigated by quantum-chemical calculations using a quasi-relativistic pseudopotential for Te (ECP46MWB) and a cc-pVTZ basis set for C and N. The gas-phase structure of **9** is predicted to be that of a five-membered ring in analogy to the sulfur and selenium analogues.

Introduction

The synthesis and reactivity of pseudohalides has been of interest to nonmetal chemists for many years. Due to the similarities between the halides and the pseudohalides, the pseudohalide family of compounds is of fundamental interest.[1−3] First introduced by Birkenbach in 1925,[4] the pseudohalide concept has been shown to be very useful in understanding the chemistry of many such moieties.[1−3] While several well-known examples have been thoroughly investigated in a variety of compounds, e.g. CN^-, OCN^-, CNO^-, SCN^-, $SeCN^-$, $TeCN^-$, and N_3^-,[5] very little has been reported about the $CS_2N_3^-$ moiety.

Structural investigations and detailed spectroscopic examinations of the azide, N_3^-, pseudohalide are often experimentally difficult, because its derivatives are often explosive.[6−9] Moreover, while the dihalogens have considerable thermal

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* To whom correspondence should be addressed. E-mail: mjc@cup.uni-muenchen.de.

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[§] X-ray structure determination.

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stability, many of the dipseudohalogens are either thermally highly unstable or have yet to be unequivocally established (e.g. OCN−NCO,[10,11] NCNC,[12] NCO−OCN,[10] N_6[13−15]). Since its introduction, the pseudohalide principle has been used extensively in nonmetal chemistry to predict the structure and stability of many species, and therefore, any new additional member to this series is of great interest. The so-called "azidodithiocarbonate" anion, more properly referred to as the 1,2,3,4-thiatriazole-5-thiolate anion, $CS_2N_3^-$, is of particular interest, as it is formed by the 1,3-dipolar cycloaddition reaction between two valence isoelectronic species, i.e. CS_2 and the azide anion, N_3^- (eq 1).

$$CS_2 + Na^+N_3^- \xrightarrow{H_2O,\ RT} Na^+CS_2N_3^-{\cdot}4H_2O \qquad (1)$$

First described and isolated in 1918 by Sommer,[16] it was not until 1991 that the structure of the $CS_2N_3^-$ anion in the form of its $NaCS_2N_3{\cdot}2H_2O$ salt was determined experimentally using X-ray diffraction techniques to be a five-membered ring,[17] in contrast to the previously postulated chain structure.[16] While early reports suggested the formation of several derivatives of this anion, little or no data were given to support these claims.[18−21] The limited thermal stability of many compounds containing the $CS_2N_3^-$ anion also poses experimental difficulties. These compounds often readily decompose forming the corresponding thiocyanate, elemental sulfur and dinitrogen (eq 2).[16]

$$Na^+CS_2N_3^-{\cdot}4H_2O \xrightarrow{\Delta T} Na^+SCN^- + 1/8S_8 + N_2 + 4H_2O \qquad (2)$$

Thus, the precise structures of many of these compounds are unknown and their existence remains unclear. Organic derivatives containing 2 equiv of the $CS_2N_3^-$ group have been reported (eq 3) and shown to be both thermally unstable and explosive and, therefore, not fully characterized.[22]

$$CH_2I_2 + 2NaCS_2N_3 \xrightarrow{H_2O/acetone} CH_2(CS_2N_3)_2 + 2NaI \qquad (3)$$

In a short communication we have recently reported the characterization of several CS_2N_3-containing species.[23] In a previous investigation, we also reported the first quantum-chemical calculations on the $CS_2N_3^-$ moiety which not only supported the formation of the five-membered ring (in contrast to the also possible chain structure) but were also in very good agreement with the experimentally determined structure.[17] Previous reports on this compound included UV−vis studies and IR spectroscopy;[24−26] however, the precise structure of this anion was unknown until the X-ray structure determination of $NaCS_2N_3{\cdot}2H_2O$ was reported by Perman and Gleason.[17] To our knowledge, the only other experimentally determined structure containing the CS_2N_3 moiety in the form of a simple derivative was that of the benzoyl species, $C_6H_5COCS_2N_3$,[17] which showed that in covalent derivatives, not only does the ring remain intact but also the site of attachment of the R group is most likely at the exocyclic sulfur atom in contrast to the previously suggested N−R connectivity.[27] However, full characterization was not reported for this compound and, therefore, characteristic spectroscopic trends for CS_2N_3 containing compounds could not be determined. With no other structure determinations having been reported, the question as to the possible attachment of an R group to a ring nitrogen atom preferentially over the exocyclic sulfur atom remained unanswered. Therefore, the structure and bonding of derivatives of the $CS_2N_3^-$ moiety was clearly an important and unanswered question. It is interesting that while the $CS_2N_3^-$ species and heavier homologues of OCN^-, i.e., SCN^-, $SeCN^-$, and $TeCN^-$ are known, no reports are available on the existence $CSe_2N_3^-$ or $CTe_2N_3^-$.

The synthesis of various ionic salts MCS_2N_3 (M = NH_4 (**1**), $(H_3C)_4N$ (**2**), Cs (**3**), K (**4**)) was important to establish the five-membered ring as the standard form for the $CS_2N_3^-$ anion, and also, the preparation of the first anhydrous $CS_2N_3^-$ salt greatly increases the number of possible synthetic applications. Moreover, the synthesis of a simple derivative of this anion, methyl azidodithiocarbonate, $H_3CCS_2N_3$ (**5**), is important in establishing the basic chemistry of this pseudohalide.

Experimental Section

Caution! *Sodium azidodithiocarbonate and other compounds containing the azidodithiocarbonate group are potentially explosive, and appropriate safety precautions should be taken, in particular the use of plastic beakers and spatulas as well as wearing ear protectors, a thick leather jacket, face shield, and Kevlar/steel gloves. Only small quantities of compounds were handled, and in particular, electrostatic shock should be avoided.*

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Materials. The syntheses and spectroscopic characterization of $NaCS_2N_3{\cdot}4H_2O$, HCS_2N_3, and $(CS_2N_3)_2$ have been previously described.[16,18−21,26−28] The syntheses of CSe_2 and ICN were carried out as described in the literature.[29] All other starting materials and solvents were obtained commercially and used as supplied. All IR spectra were recorded as solids between KBr plates at 20 °C using a Perkin-Elmer 983G spectrometer. All Raman spectra were recorded using a Perkin-Elmer R2000 spectrometer fitted with a Nd:YAG laser (1064 nm). Multinuclear NMR spectra were recorded using a JEOL EX 400 FT-NMR spectrometer. The X-ray diffraction studies for $H_3CCS_2N_3$, $NH_4CS_2N_3$, and $(H_3C)_4NCS_2N_3$ were carried out using a STOE IPDS diffractometer (**5**) and a Nonius Kappa CCD diffractometer (**1**, **2**) with graphite-monochromated Mo−Kα radiation (λ = 0.0710 73 Å), the SHELX97 program, direct methods, and least-squares refinement (F^2).[30] Further details of the crystal structure determination are available upon request from the Cambridge Crystallographic Data Center, on quoting the depository numbers CCDC 206073 (**1**), 206072 (**2**), and 206071 (**5**), the names of the authors, and the journal citation.

Synthesis of $M^+CS_2N_3^-$ (M = $(H_3C)_4N$, K, Cs). The syntheses of the $M^+CS_2N_3^-$ species were achieved by the following general route: 1.0 mmol of the corresponding hydroxide, MOH, was dissolved in 2 mL of distilled H_2O, to which 1.0 mmol of HCS_2N_3 was added. Stirring of the colorless solution at room temperature for 1 h, followed by evaporation of the solvent by leaving the solution over P_4O_{10} in a desiccator under vacuum for 48 h in the dark, resulted in the desired MCS_2N_3. Decomposition of these compounds at −25 °C was observed over several weeks. Redissolving the salts in D_2O yielded solutions suitable for multinuclear NMR spectroscopy.

(a) M = $(H_3C)_4N$ (2): IR (KBr plates, RT (room temperature), ν/cm^{-1}) 3018 m, 2960 w, 1473 vs, 1450 w, 1405 s, 1260 s, 1190 s, br, 1138 w, 1100 w, 1058 m, 948 vs, 900 w, 865 w, 818 w, 790 w, 683 w, 660 vw; Raman (4 mm sample tube, 1064 nm, RT, ν/cm^{-1}) 3026 (3), 3007 (2), 2946 (1), 2801 (1), 1454 (1), 1410 (1), 1265 (1), 1202 (3), 1192 (10), 1063 (3), 1043 (5), 948 (2), 751 (2), 687 (1), 637 (4), 467 (1), 454 (1), 268 (5);

^{13}C NMR (297 K, D_2O, TMS, 100.52 MHz, δ in ppm) 195.0 ($CS_2N_3^-$), 56.0 t ($(H_3C)_4N^+$);

^{14}N NMR (297 K, D_2O, $MeNO_2$, 28.89 MHz, δ in ppm) 69, 5, −28 ($CS_2N_3^-$), −340 ($(H_3C)_4N^+$).

(b) M = Cs (3): IR (KBr plates, RT, ν/cm^{-1}) 2030 m, 1269 m, 1195 s, 1140 w, 1063 m, 1045 w, 950 vw, 900 s, 870 w, 819 w, 790 w, 682 s, 662 s; Raman (4 mm sample tube, 1064 nm, RT, ν/cm^{-1}) 2052 (1), 2042 (1) (Cs^+SCN^-), 1346 (1), 1240 (3), 1209 (2), 1193 (6), 1088 (1), 1048 (5), 746 (1), 684 (1), 634 (10), 472 (5) (S_8), 430 (1) (S_8), 293 (9), 277 (4), 219 (6) (S_8), 152 (7) (S_8), 136 (5), 118 (5), 90 (10);

^{14}N NMR (297 K, D_2O, $MeNO_2$, 28.89 MHz, δ in ppm) 60, 4, −48 ($CS_2N_3^-$), −175 (NCS^-).

(c) M = K (4): IR (KBr plates, RT, ν/cm^{-1}) 3446 br (H_2O), 2064 s (KSCN), 1626 m, br (H_2O), 1309 w, 1270 s, 1204 vs, 1191 vs, 1157 m, 1104 w, 1075 vs, 1050 sh, w, 916 s, 907 w, 747 w, 702 m, 667 w, 654 w, 644 vw, 552 w, 484 w, 454 w; Raman (4 mm sample tube, 1064 nm, RT, ν/cm^{-1}) 1309 (1), 1269 (2), 1206 (4), 1193 (10), 1074 (4), 1052 (5), 916 (1), 703 (2), 645 (10), 456 (1), 280 (6).

Synthesis of $NH_4^+CS_2N_3^-$ (1). A 1.0 mmol amount of HCS_2N_3 was suspended in 2 mL of distilled H_2O. A 10-fold excess of concentrated NH_3 was then slowly added using a pipet. The reaction mixture was then allowed to stand at room temperature in the dark for 1 h, followed by evaporation of the solvent by leaving the solution over P_4O_{10} in a desiccator under vacuum for 48 h in the dark. Decomposition of this compound at −25 °C was observed over several weeks. Redissolving the salt in D_2O yielded a solution which was suitable for multinuclear NMR spectroscopy.

IR (KBr plates, RT, ν/cm^{-1}): 3108 m, br, 2987 m, br, 2854 w, 2811 w, 2072 w (NH_4SCN), 1652 w, 1448 w, 1423 m, 1397 s, 1311 w, 1282 m, 1210 s, 1106 w, 1074 s, 911 m, 699 w, 655 w, 649 w. Raman (4 mm sample tube, 1064 nm, RT, ν/cm^{-1}): 3016 (1), 1411 (1), 1309 (1), 1284 (2), 1214 (10), 1074 (3), 1061 (5), 911 (1), 702 (2), 657 (4), 649 (8), 278 (5), 109 (7).

^{13}C NMR (297 K, D_2O, TMS, 100.52 MHz, δ in ppm): 194.7 ($CS_2N_3^-$).

^{14}N NMR (297 K, D_2O, $MeNO_2$, 28.89 MHz, δ in ppm): 73, 6, −22 ($CS_2N_3^-$), −361 (NH_4^+).

Synthesis of $CH_3CS_2N_3$ (5). A 1.0 mmol amount of $Na^+CS_2N_3^-$ was dissolved in H_2O at room temperature followed by cooling to 0 °C using an ice bath. To this solution, 1.0 mmol of CH_3I dissolved in 2 mL of acetone was added. After being left for 2 h at 0 °C, colorless, crystalline $CH_3CS_2N_3$ was obtained as a crystalline precipitate which was then filtered off. $CH_3CS_2N_3$ was dissolved in CD_2Cl_2 for recording the multinuclear NMR spectra. This compound was stable for weeks if maintained in the dark at 0 °C.

IR (KBr plates, RT, ν/cm^{-1}): 3010 w, 2930 w, 2057 w,br (H_3CSCN), 1438 m, 1419 m, 1406 m, 1330 m, 1304 s, 1238 s, 1213 m, 1098 s, 1094 s, 1072 sh, 1012 m, 984 m, 963 m, 909 s, 701 m, 642 w, 548 w. Raman (4 mm sample tube, 1064 nm, RT, ν/cm^{-1}): 3013 (3), 2930 (8), 1421 (3), 1407 (2), 1334 (3), 1311 (4), 1289 (1), 1237 (9), 1095 (2), 1013 (3), 986 (1), 914 (1), 702 (5), 633 (10), 473 (1), 448 (1), 310 (9), 299 (2), 114 (7).

^{13}C NMR (297 K, CD_2Cl_2, TMS, 100.40 MHz, δ in ppm): 181.2 ($H_3COS_2N_3^-$); 17.9 ($H_3CCS_2N_3$).

^{14}N NMR (297 K, CD_2Cl_2, $MeNO_2$, 28.904 MHz, δ in ppm): 74, 10, −17 ($CS_2N_3^-$).

Improved Synthesis of $(CS_2N_3)_2$. This compound can be made by either the previously described route using XeF_2[23] or the following improved route: To a solution of $Na^+CS_2N_3^-{\cdot}4H_2O$ (1.0 mmol) in 5 mL of H_2O cooled to 0 °C using an ice bath, XeF_2 (0.5 mmol) in 5 mL acetone was added dropwise. A highly vigorous reaction occurred resulting in the precipitation of a thermally unstable white solid. Following rapid separation of this precipitate using a Buchner funnel, $(CS_2N_3)_2$ could be obtained in reasonable yields which were significantly higher than that of our original preparation.

Alternate Synthesis of CS_2N_3CN (6). A 1.0 mmol amount of $Na^+CS_2N_3^-{\cdot}4H_2O$ was dissolved in 5 mL of distilled H_2O and cooled using an ice bath. To this solution, 1.0 mmol of ICN dissolved in acetone was added dropwise using a pipet. Immediately, a white precipitate formed and was filtered off quickly at room temperature and stored at −25 °C, at which temperature the isolated solid was found to be stable for several weeks.

Attempted Synthesis of $NaCSe_2N_3$ (8). A suspension of 14.7 mmol of NaN_3 in 25 mL of thf was stirred, while being maintained at −40 °C using a dichloromethane/liquid-nitrogen cold slush. On the dropwise addition of 14.7 mmol of CSe_2 a reaction was observed to occur immediately with the generation of gas (N_2) and elemental red selenium solid. A Raman spectrum was recorded of the reaction mixture which showed only thf solvent, elemental selenium, and

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Na^+SeCN^- indicating that decomposition of the possible $NaCSe_2N_3$ intermediate may have occurred at temperatures below −40 °C.

Raman (4 mm sample tube, 1064 nm, RT, ν/cm^{-1}): 2972 (2), 2874 (2) thf, 2079 (3) Na^+SeCN^-, 1361 (10) $Na^+N_3^-$, 1270 (1), 913 (0.5), 869 (0.5) thf, 366 (1), 283 (1), 258 (2) 200 (0.5) Se, 191 (1).

Computational Aspects. The structures of all compounds were preoptimized using semiempirical calculations. All semiempirical calculations were carried out using the program package HYPERCHEM[31] at the semiempirical PM3 level of theory using a VSTO-3G basis set. Finally, the structures, energies, vibrational frequencies, and zero-point energies were computed at several levels of theory using the program package Gaussian 98.[32] In this paper the results from MPW1PW91 calculations are presented. For H, C, N, and S a correlation consistent cc-pVTZ basis was used. For Se and Te we applied quasi-relativistic pseudopotentials (Se, ECP28MWB; Te, ECP46MWB) and the following valence basis sets: Se, (14s10p2d1f)/[3s3p2d1f]; Te, (16s12p4d2f)/[4s4p3d2f]. NBO analyses[33] were performed using the resonance keyword implemented in G98 at the MPW1PW91 level of theory.

Results and Discussion

The synthesis and characterization of $M^+CS_2N_3^-$ salts (M = NH_4, $(H_3C)_4N$, K, Cs) by the reaction of the corresponding MOH with HCS_2N_3 (eqs 4 and 5) is the first general synthetic route to $CS_2N_3^-$ salts and is analogous to that applicable for azide salts.[34] All of these salts were found to have only limited thermal stability, with the sodium salt decomposing slowly at room temperature, in contrast to the related azide species, whereby NaN_3 is indefinitely stable at room temperature.[1] The cesium salt, $Cs^+CS_2N_3^-$, decomposes at room temperature within a few hours, forming the corresponding thiocyanate species, Cs^+SCN^-, dinitrogen, and elemental sulfur according to eq 6. The $Cs^+CS_2N_3^-$ decomposition products were identified using ^{14}N NMR spectroscopy, vibrational spectroscopy (IR, Raman) (Cs^+SCN^-), and Raman spectroscopy (S_8).

$$MOH + HCS_2N_3 \xrightarrow{H_2O,\ RT} M^+CS_2N_3^- + H_2O \qquad (4)$$

$$M = Na, K, Cs, (H_3C)_4N$$

$$NH_3 + HCS_2N_3 \xrightarrow{H_2O,\ RT} NH_4^+CS_2N_3^- \qquad (5)$$

$$Cs^+CS_2N_3^- \xrightarrow{\Delta T} Cs^+SCN^- + N_2 + 1/8S_8 \qquad (6)$$

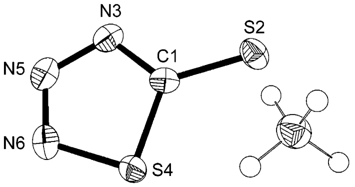

Figure 1. Molecular structure of $NH_4CS_2N_3$ (**1**) in the crystalline state. (Thermal ellipsoids represent 50% probability.)

The Raman, ^{13}C and ^{14}N multinuclear NMR spectra of the ionic species **1**−**4** are all very similar, and the presence of three peaks in the ^{14}N NMR spectrum is consistent with the presence of three ring nitrogen atoms. The chain isomer of the anion would constitute a covalent azide, and therefore, three peaks in the ^{14}N NMR spectrum would be expected. In particular, one very broad peak would be expected to be observed at ∼−300 ppm corresponding to N_α of the covalent azide moiety ($X-N_\alpha-N_\beta-N_\gamma$) which was not observed in the spectra for compounds **1**−**4** [6,35] Due to the high concentrations and long measurement times required to obtain ^{15}N NMR spectra, only the ^{15}N NMR spectrum of the most stable salt, $NaCS_2N_3$, was obtained. The ^{15}N NMR spectrum shows 3 very well resolved, sharp peaks at +69, +4, and −25 ppm, which correspond to the 3 ring nitrogen atoms in the $CS_2N_3^-$ moiety. A determination of the solid-state structure of the sodium salt (which was briefly mentioned in our prior communication on parts of this work[23]) revealed the presence of four coordinated water molecules, $Na^+CS_2N_3^-\cdot 4H_2O$, as opposed to two coordinated water molecules found in the earlier structure determination.[17] In the previously determined structure of $Na^+CS_2N_3^-\cdot 2H_2O$,[17] sodium−exocyclic sulfur contacts were observed to be present with the five-membered ring being slightly bowed. The structure of $Na^+CS_2N_3^-\cdot 4H_2O$ exhibited sodium−nitrogen contacts with the sodium in an octahedral arrangement with four water molecules coordinated. It has proven useful to be able to prepare anhydrous MCS_2N_3 derivatives as starting materials for further reactions with moisture sensitive compounds. The synthesis of two such compounds $NH_4CS_2N_3$ (**1**) and $Me_4NCS_2N_3$ (**2**) was achieved. Moreover, from the synthesis of a range of salts containing the $CS_2N_3^-$ anion, peaks characteristic for the $CS_2N_3^-$ moiety could be identified from the vibrational spectra (IR, Raman).

Whereas the structures of the ionic azides, e.g. $(H_3C)_4NN_3$, NaN_3, KN_3, CsN_3, NH_4N_3, etc., have been determined by X-ray diffraction techniques to comprise linear ($D_{\infty h}$) azide ions,[3,6,36,37] the structures of the analogous ionic $CS_2N_3^-$ salts have not been established. Therefore, the structure determinations of two salts were undertaken. It was shown that in both $NH_4CS_2N_3$ (Figure 1; Tables 1 and 2) and $(H_3C)_4NCS_2N_3$ (Figure 2; Tables 1 and 2), the $CS_2N_3^-$ anion is a planar five-membered ring within standard deviations. The planarity of the $CS_2N_3^-$ anions is a further indication for

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Table 1. Selected Bond Lengths (Å) and Angles (deg) of $NH_4CS_2N_3$ (**1**) and $(H_3C)_4NCS_2N_3$ (**2**)

params: d, ∠	$NH_4CS_2N_3$ (**1**)	$(H_3C)_4NCS_2N_3$ (**2**)
C1−S2	1.701(2)	1.699(2)
C1−S4	1.722 (2)	1.720(2)
S4−N6	1.683(1)	1.680(2)
N5−N6	1.281(2)	1.284(3)
N3−N5	1.352(2)	1.354(3)
C1−N3	1.338(2)	1.332(3)
S2−C1−S4	125.2(1)	124.9(1)
C1−S4−N6	91.75(8)	91.78(9)
S4−N6−N5	110.0(1)	110.1(2)
N3−N5−N6	117.0(1)	116.6(2)
C1−N3−N5	112.4(1)	112.5(2)
S2−C1−N3	125.9(1)	126.1(2)

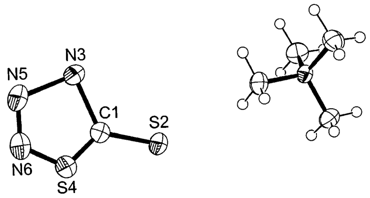

Figure 2. Molecular structure of $(H_3C)_4NCS_2N_3$ (**2**) in the crystalline state. (Thermal ellipsoids represent 50% probability.)

both the aromatic and the pseudohalide character of this species. Moreover, in both cases, the observed bond lengths and angles are similar to those observed for the $Na^+CS_2N_3^-{\cdot}4H_2O$ salt (Table 1).[23] Thus, not only the tetramethylammonium compound $(H_3C)_4NCS_2N_3$ (**2**) (Figure 2) but also the ammonium salt $NH_4CS_2N_3$ (**1**) exist as ionic compounds where some hydrogen bonding occurs in the latter case between the NH_4^+ protons and the azidodithiocarbonate anion.

The synthesis and characterization of the methylated compound was attempted because the related CH_3CN and CH_3N_3 counterparts are well-known. $CH_3CS_2N_3$ would also be an interesting compound to compare the site of attachment of the R group with that in CS_2N_3CN and HCS_2N_3. Methyl azidodithiocarbonate, $CH_3CS_2N_3$ (**5**), was synthesized and characterized in a convenient and high yield route according to eq 7. This compound has been previously reported; however, only an IR spectrum was reported,[27] which makes it difficult to establish unambiguously the site of attachment of the R group. We have shown that spectroscopic characterization utilizing Raman and multinuclear NMR spectroscopy is much more informative.

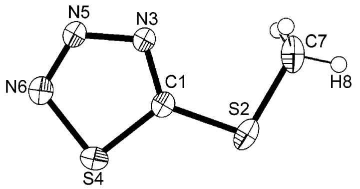

Figure 3. Molecular structure of $H_3CCS_2N_3$ (**5**) in the crystalline state. (Thermal ellipsoids represent 50% probability.)

$$CH_3I + Na^+CS_2N_3^-{\cdot}4H_2O \xrightarrow{H_2O/\text{acetone, ice bath}} CH_3CS_2N_3 + NaI + 4H_2O \quad (7)$$

Using X-ray diffraction, the structure of $CH_3CS_2N_3$ was determined to be covalent with a planar five-membered ring and exocyclic sulfur−methyl connectivity (Figure 3; Table 3). The planarity of the five-membered ring, as well as the internuclear distances, clearly indicate strong π delocalization within the ring system. No strong intermolecular hydrogen bonding is present in this structure. This structure closely resembles that of CS_2N_3CN in which the CN group is also coordinated to the CS_2N_3 moiety at the exocyclic sulfur atom (Figure 4). The Raman spectrum of the solid shows peaks in the 1000−1400 and 600−750 cm^{-1} regions which are characteristic for compounds containing the CS_2N_3 group;[23] however, the peaks are significantly shifted with respect to the starting material, thus excluding the possibility of these peaks corresponding to unreacted $Na^+CS_2N_3^-{\cdot}4H_2O$. In both the IR and Raman spectra, the peaks corresponding to the C−H stretching frequencies at 2930 and 3013 cm^{-1} can clearly be observed. The presence of very weak unassigned peaks at around 2000 and 1200 cm^{-1} in the IR and Raman spectra indicate that the five-membered ring of the CS_2N_3 moiety has been maintained and has not isomerized into the also possible chain structure and instead a very small amount of decomposition has already occurred resulting in the formation of the corresponding thiocyanate. This observation was confirmed by ^{14}N NMR spectroscopy, where the only

Table 2. Crystal Data and Structure Refinements for $NH_4CS_2N_3$ (**1**), $(H_3C)_4NCS_2N_3$ (**2**), and $H_3CCS_2N_3$ (**5**)

param	$NH_4CS_2N_3$ (**1**)	$(H_3C)_4NCS_2N_3$ (**2**)	$H_3CCS_2N_3$ (**5**)
chem formula	$CH_4N_4S_2$	$C_5H_{12}N_4S_2$	$C_2H_3N_3S_2$
fw	136.201	192.308	133.197
color, habit	colorless, prism	colorless, prism	colorless, irregular
temp (K)	200(2)	200(2)	200(3)
cryst size (mm)	0.335 × 0.145 × 0.099	0.172 × 0.137 × 0.083	0.20 × 0.18 × 0.15
cryst syst	orthorhombic	monoclinic	monoclinic
space group	Pbca	$P2_1/m$	$P2_1/m$
a (Å)	10.6787(1)	5.9011(1)	5.544(1)
b (Å)	6.8762(1)	7.3565(2)	6.4792(7)
c (Å)	15.2174(2)	10.9474(3)	7.629(1)
α (deg)	90	90	90
β (deg)	90	91.428(1)	105.53(2)
γ (deg)	90	90	90
V (Å^3)	1117.40(2)	475.09(2)	264.06(7)
Z	8	2	2
ρ(calcd) (g cm^{-3})	1.61927(3)	1.34433(6)	1.6752(4)
μ (mm^{-1})	0.828	0.508	0.869
R1, wR2 [$I > 2\sigma(I)$]	0.0298, 0.0747	0.0325, 0.0794	0.0231, 0.0583
R1, wR2 (all data)	0.0361, 0.0786	0.0479, 0.0858	0.0283, 0.0602

Table 3. Comparison of Selected Experimentally Determined (X-ray) and Calculated (MPW1PW91/cc-pVTZ) Structural Parameters (Å, deg) for H3CCS$_2$N$_3$ (**5**)

param: *d*, ∠	obsd (X-ray)	calcd (MPW1PW91/cc-pVTZ)
C1−S2	1.723 (2)	1.720
C1−N3	1.314 (2)	1.310
C1−S4	1.699 (2)	1.700
S2−C7	1.799 (2)	1.800
N3−N5	1.356 (2)	1.340
S4−N6	1.680 (2)	1.700
N5−N6	1.274 (2)	1.250
C7−H8	0.92 (3)	1.080
S2−C1−N3	125.9 (1)	120.2
S2−C1−S4	122.3 (1)	123.6
N3−N5−N6	116.6(1)	117.5
S4−N6−N5	110.8 (1)	110.5
C1−N3−N5	110.6 (1)	110.6

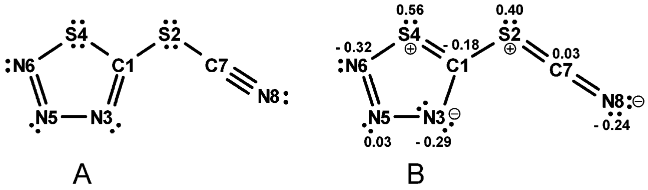

Figure 4. Lewis structures for CS$_2$N$_3$CN (**6**) according to an NBO analysis (MPW1PW91/cc-pVTZ).

Table 4. Calculated (MPW1PW91/cc-pVTZ) Vibrational Data for the Ring and Chain Isomers of H$_3$CCS$_2$N$_3$ (**5**) with Calculated IR Intensities in Parentheses

calcd (unscaled) (MPW1PW91/cc-pVTZ) ring isomer (ν in cm^{-1})	calcd (unscaled) (MPW1PW91/cc-pVTZ) chain isomer (ν in cm^{-1})
79 (3)	85 (0)
146 (0)	133 (0)
179 (4)	140 (0)
241 (1)	161 (0)
308 (1)	220 (1)
453 (1)	337 (0)
569 (0)	380 (0)
618 (7)	531 (0)
672 (0)	547 (0)
716 (5)	587 (1)
728 (2)	748 (2)
944 (11)	754 (1)
980 (2)	978 (1)
996 (4)	983 (4)
1077 (0)	1031 (38)
1139 (100)	1173 (37)
1346 (56)	1339 (77)
1366 (45)	1357 (3)
1417 (0)	1451 (2)
1455 (8)	1465 (3)
1473 (12)	2331 (100)
3083 (6)	3073 (1)
3181 (1)	3171 (0)
3188 (1)	3174 (0)

peak not assigned to H$_3$CCS$_2$N$_3$ corresponded to a thiocyanate group.

The ring and chain isomers containing an S−CH$_3$ group were calculated (MPW1PW91/cc-pVTZ), and both were found to represent true minima on the potential energy surface (Table 4). However, in the gas phase, the experimentally observed ring isomer was found to be 7.3 kcal mol^{-1} lower in energy than the chain structure (Figure 5). It is interesting to note that, to the best of our knowledge, the azidodithiocarbonate moiety has been shown (X-ray) only to adopt the ring isomer form. Furthermore, only the structure of one compound containing the azidodithiocarbonate moiety containing a ring N−R connectivity (R = H) has been determined using X-ray diffraction techniques. Further evidence to support the formation of the CH$_3$CS$_2$N$_3$ species with the exocyclic sulfur−methyl group connectivity comes form the ^{14}N NMR spectrum where, as expected, three broad peaks are observed (H$_3$CCS$_2$N$_3$; ^{14}N NMR δ 74, 10, −17 ppm), in the same region as those observed in the ^{14}N NMR spectrum for other compounds containing the CS$_2$N$_3$ moiety (MCS$_2$N$_3$, M = Na, NH$_4$, (CH$_3$)$_4$N, Cs; CS$_2$N$_3$CN), and are in sharp contrast to the ^{14}N NMR spectrum of HCS$_2$N$_3$ where one peak is dramatically shifted upfield (NaCS$_2$N$_3$, ^{14}N NMR δ 69, 4, −25 ppm; HCS$_2$N$_3$, ^{14}N NMR δ 40, 2, −118 ppm), thus indicating the presence of a nitrogen−hydrogen bond.[23] In the spectrum of CH$_3$CS$_2$N$_3$, no large upfield shift of any of the three peaks was observed, thus supporting exocyclic sulfur−methyl group connectivity. This compound is a small, simple derivative of the CS$_2$N$_3^-$ pseudohalide that can be compared to CH$_3$I (starting material) and the methylated pseudohalides, e.g. CH$_3$N$_3$ and CH$_3$CN.

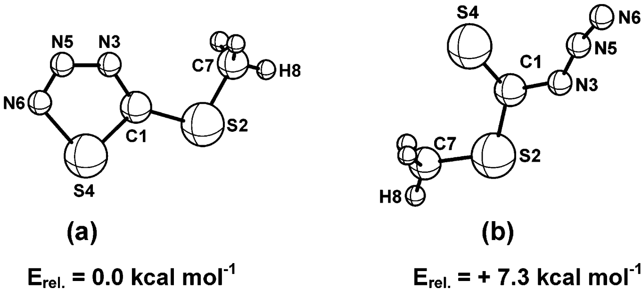

Figure 5. Calculated (MPW1PW91/cc-pVTZ) ring and chain isomers of H$_3$CCS$_2$N$_3$ (**5**).

With the synthesis and characterization of the dipseudohalogen species (CS$_2$N$_3$)$_2$ having been previously reported,[23] a better synthetic route to this fundamentally important derivative was desired. It is interesting to note that despite the large interest in dipseudohalogens, the structures of many such species, e.g. (OCN)$_2$[10,11] and (N$_3$)$_2$,[13−15] remain experimentally unknown in the solid state. The debate as to whether (CS$_2$N$_3$)$_2$ would consist of two covalent azide groups in a chain structure or whether the two five-membered rings would stay intact and dimerize through a disulfur bridge was answered both theoretically and experimentally. The chain structure was calculated to be 13 kcal mol^{-1} higher in energy than the experimentally observed C_1 symmetry structure, similar to hydrogen peroxide.[23] It was found that the yield of (CS$_2$N$_3$)$_2$ could be increased from our previously reported synthesis[23] by first dissolving the XeF$_2$ in acetone and adding this solution dropwise to the Na$^+$CS$_2$N$_3^-$·4H$_2$O dissolved in H$_2$O (eq 8) in a highly exothermic reaction.

$$\mathrm{XeF_2} + 2\mathrm{Na^+CS_2N_3^-{\cdot}4H_2O} \xrightarrow{\mathrm{H_2O/acetone,\ ice\ bath}} (\mathrm{CS_2N_3})_2 + 2\mathrm{NaF} + \mathrm{Xe} + 8\mathrm{H_2O} \quad (8)$$

A white precipitate was formed immediately in this reaction, and cooling of the reaction vessel was required to prevent instantaneous decomposition of the desired product.

Table 5. Experimental (X-ray) and Calculated (MPW1PW91/cc-pVTZ) Structural Parameters (Å, deg) for $NCCS_2N_3$ (**6**)

param: *d*, ∠	MPW1PW91/cc-pVTZ	obsd (X-ray)
C1−S4	1.700	1.699(2)
C1−N3	1.300	1.305(2)
N3−N5	1.340	1.364(3)
N5−N6	1.250	1.276(3)
S4−N6	1.700	1.670(2)
C1−S2	1.740	1.756(2)
S2-C7	1.680	1.697(2)
C7−N8	1.150	1.139(3)
S4−C1−S2	122.2	122.7(1)
N3−C1−S2	124.8	124.6(1)
C1−N3−N5	110.8	110.2(2)
N3−N5−N6	116.8	115.9(2)
S4−N6−N5	111.8	111.8(2)
C1−S4−N6	87.7	89.5(1)
C1−S2−C7	100.4	97.5(1)
S4−C1−N3	113.3	112.7(2)
S2−C7−N8	173.7	172.6(2)

Crystals of $(CS_2N_3)_2$ were obtained by redissolving the white solid obtained from the above reaction in a minimum amount of acetone and allowing the acetone to evaporate quickly. Evaporation of the solvent had to be complete within a few minutes otherwise decomposition of the $(CS_2N_3)_2$ was observed.

We also investigated an alternative synthesis for the interpseudohalogen CS_2N_3CN (**6**). Our initial communication reported the convenient synthesis of CS_2N_3CN from $NaCS_2N_3$ and BrCN. However, we have now found that BrCN can be replaced with ICN, which is more convenient to prepare,[29] and therefore this new method is advantageous (eq 9).

$$NaCS_2N_3{\cdot}4H_2O + ICN \xrightarrow{H_2O/acetone} CS_2N_3CN + NaI + 4H_2O \quad (9)$$

A comparison of the calculated (MPW1PW91/cc-pVTZ) and experimentally determined structures (X-ray) for CS_2N_3CN shows very good agreement (Table 5). Furthermore, good agreement was also found between the calculated (MPW1PW91/cc-pVTZ) and observed (IR, Raman) vibrational data (Table 6). Therefore, we undertook an NBO analysis (DFT density) to gain more insight into the bonding situation in **6**. The standard Lewis structure to which the NBO analysis corresponds is shown in Figure 4A. This resonance structure has reasonably well localized σ NBOs (1.976−1.993 electrons) but two severely depleted π lone pairs (π-LP(S1),1.617 and π-LP(S2), 1.811 electrons) and corresponding high occupancy in three π^* antibonds (π^*(C2−N4), 0.363, π^*(N3−N5), 0.293, and π^*(C7−N8), 0.087 electrons, respectively). The most significant types of donor−acceptor interaction (negative hyperconjugation) that are responsible for these non-Lewis contributions are π-LP(S4) ⇒ π^*(C1−N3) (66.2 kcal mol^{-1}), π-LP(S4) ⇒ π^*(N6−N5) (38.1 kcal mol^{-1}), π-LP(S2) ⇒ π^*(C1−N3) (36.8 kcal mol^{-1}), and π-LP(S2) ⇒ π^*(C7−N8) (36.9 kcal mol^{-1}). Figure 4B shows that the second most important standard Lewis structure and the computed (and observed) structural parameters as well as partial charges are in accord with resonance between the standard Lewis structures A and B (cf. Table 5, Figure 4).

Table 6. Experimentally Determined (IR, Raman) and Calculated (MPW1PW91/cc-pVTZ) Vibrational Data for $NCCS_2N_3$ (**6**) with Calculated IR Intensities in Parentheses

MPW1PW91/cc-pVTZ (cm^{-1})	MPW1PW91/cc-pVTZ, scaled with $F = 0.95$ (cm^{-1})	obsd (cm^{-1})	
		IR	Raman
42 (0)	40		
111 (2)	105		154 (5)
231 (0)	219		254 (2)
251 (3)	238		266 (8)
373 (2)	353		
394 (2)	374		376 (3)
497 (6)	472		498 (2)
561 (1)	533		
611 (7)	580	632 w	
667 (0)	634	648 m	645 (10)
711 (0)	675		686 (3)
733 (12)	696	710/720 m	717 (1)
939 (12)	892	903 m	903 (1)
1065 (3)	1012	1008 m	1003 (4)
1124 (100)	1068	1070/1080 s	1077 (2)
1362 (71)	1294	1237 m	1236 (7)
1426 (2)	1355	1335 sh	1334 (7)
2316 (5)	2200	2170 m	2179 (10)

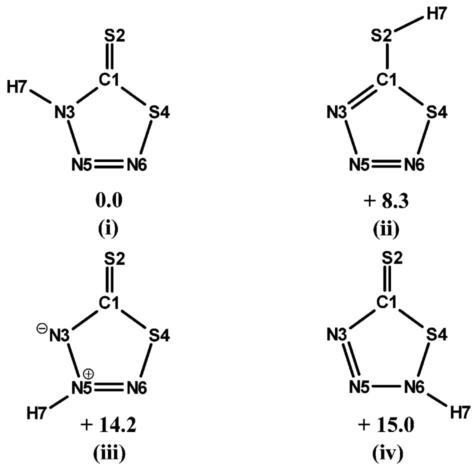

Figure 6. Calculated relative energies of HCS_2N_3 (**7**) isomers (MPW1PW91/cc-pVTZ).

Having successfully synthesized HCS_2N_3 and determined the solid-state structure of this acid using X-ray diffraction techniques, it was desirable to rationalize the site of protonation. While much speculation has occurred over the years as to whether the site of protonation was at the exocyclic sulfur atom or at one of the ring nitrogen atoms, quantum-chemical calculations of the four most likely isomers were undertaken, with the aim of finding the lowest energy isomer and calculating its Brønsted acidity.

The experimentally observed isomer i with H−N(3) connectivity (Figure 6) was found to be the lowest energy isomer for HCS_2N_3 in the gas phase (MPW1PW91/cc-pVTZ). A comparison of the computed and experimentally determined structural parameters shows very good agreement (Table 7). Interestingly, isomer ii with an exocyclic S−H bond was calculated to be the next higher energy isomer only 8.3 kcal mol^{-1} higher in energy than isomer i. Both isomers represented local minima on the potential energy surface (NIMAG = 0). The experimental data (vibrational spectroscopy, multinuclear NMR spectroscopy, X-ray) and quantum-chemical calculations all show that

Table 7. Comparison of Selected Experimentally Determined (X-ray) and Calculated (MPW1PW91/cc-pVTZ) Structural Parameters (Å, deg) for HCS_2N_3 (**7**)

param: d, ∠	obsd (X-ray)	calcd (MPW1PW91/cc-pVTZ)
C1−S2	1.661(3)	1.630
C1−N3	1.346(4)	1.360
C1−S4	1.722(3)	1.730
N3−N5	1.351(4)	1.330
S4−N6	1.706(3)	1.710
N5−N6	1.260(4)	1.240
N3−H7	0.80(1)	1.00
S2−C1−N3	127.1(2)	126.8
N3−N5−N6	112.7(3)	113.7
S4−N6−N5	112.2(2)	111.4
C1−N3−N5	117.8(3)	119.0

isomer i is the favored structure. To establish the relative energies, isomers iii and iv were also computed (MPW1PW91/cc-pVTZ) in C_s symmetry. Isomers iii and iv are both local minima (NIMAG = 0), higher in energy than isomer i by 14.2 and 15.0 kcal mol^{-1}, respectively (MPW1PW91/cc-pVTZ). To investigate the proton affinity of $CS_2N_3^-$, the total energies of the neutral Brønsted acid, HCS_2N_3, and the corresponding $CS_2N_3^-$ anion were calculated (999.381 596 and 998.853 094 au, respectively, at MPW1PW91/cc-pVTZ level of theory). Using these values, the gas-phase dissociation energy of HCS_2N_3 (eq 10) was calculated and converted into the room-temperature gas-phase acidity after corrections for zero point energies, rotational and translational degrees of freedom, and the work term.

$$HCS_2N_3(g) \rightarrow CS_2N_3^-(g) + H^+(g) \qquad (10)$$

$$\Delta H_{acid} = 327.0 \text{ kcal mol}^{-1}$$

This calculated value compares nicely with the calculated (MPW1PW91/cc-pVTZ) and experimentally determined gas-phase acidities for HCl and HCN (ΔH_{acid} HCl = 339.3 kcal mol^{-1} (calcd), 333.2 kcal mol^{-1} (exp.);[38] ΔH_{acid} HCN = 358. 5 kcal mol^{-1} (calcd), 351.5 kcal mol^{-1} (exp)[38]).

The above-mentioned computational studies have shown that they are useful and effective tools for elucidating the structures of many CS_2N_3-containing compounds. We therefore decided to undertake an investigation of the heavier analogue, $NaCSe_2N_3$. We considered this a realistic synthetic target compound because, in contrast to CTe_2,[5] CSe_2 can be prepared under normal laboratory conditions[29] and, therefore, the reaction of CSe_2 with NaN_3 offered a sensible approach (eq 11).

$$NaN_3 + CSe_2 \rightarrow NaCSe_2N_3 \qquad (11)$$

On reaction of CSe_2 with NaN_3 at room temperature, the formation of elemental red selenium (Raman), NaSeCN (Raman), and dinitrogen (evolution of gas) was observed (eq 12). A low-temperature synthesis at −78 °C was attempted; however, the same decomposition products were obtained. The decomposition of $NaCS_2N_3$ is known to yield NaSCN, 1/8 S_8, and N_2; therefore, it may be postulated that the intermediate formation of $NaCSe_2N_3$ occurred but that this compound was unstable under the conditions applied and resulted in decomposition of the intermediately formed $NaCSe_2N_3$ into NaSeCN, Se, and N_2 in analogy to the aforementioned $NaCS_2N_3$ (eqs 2 and 12).

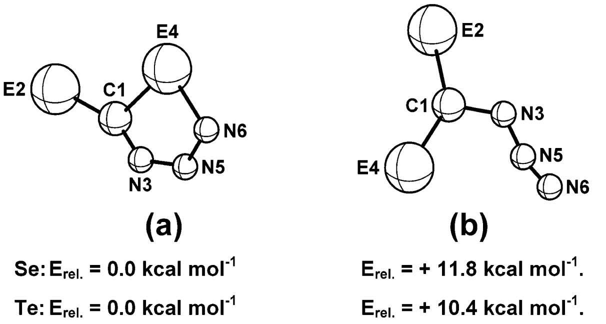

Figure 7. Calculated ring and chain isomers and relative energies for $CSe_2N_3^-$ (**8**) and $CTe_2N_3^-$ (**9**) (MPW1PW91/cc-pVTZ).

$$\{NaCSe_2N_3\} \rightarrow NaSeCN + Se + N_2 \qquad (12)$$

The synthesis of $NaCSe_2N_3$ would be particularly desirable because this compound would likely be a new member of the pseudohalide class of compounds. Furthermore, only one other well-established selenium containing pseudohalide is known, i.e. selenocyanate, $SeCN^-$.[1,2,5] However, when one considers how unstable many selenium−nitrogen anions and neutral compounds are, e.g. Se_4N_4,[39−43] the synthesis and isolation of $Na^+CSe_2N_3^-$ may be difficult, and so far, we have been unable to obtain any conclusive evidence for the $CSe_2N_3^-$ moiety. Therefore, we investigated the likely gas-phase structure for the anion using quantum-chemical calculations which had been successful in predicting the structure for the $CS_2N_3^-$ anion.

The ring isomer (**8a**) was found to be lower in energy than the chain isomer (**8b**), although both isomers represented minima on the potential energy surface ($\Delta E_{(ring-chain)}$ = 11.8 kcal mol^{-1}, NIMAG = 0) (Figure 7) at MPW1PW91 level of theory (ECP28MWB for Se and a (16s12p4d2f)/[4s4p3d2f] basis set), and the computed structural parameters (MPW1PW91 level of theory) were found to be within reasonable values for C−Se, Se−N, and N−N bond lengths. Finally, to complete the investigation of the $CE_2N_3^-$ (E = S, Se, Te) anions, we undertook a computational study of the likely structure of the hitherto unknown $CTe_2N_3^-$ anion (**9**) with the aim of establishing a trend for the $CE_2N_3^-$ (E = S, Se, Te) species. Due to the low stability of carbon ditelluride, CTe_2, the most obvious starting material,[5] the synthesis of **9** has not yet been achieved (eq 13).

$$CTe_2 + Na^+N_3^- \rightarrow Na^+CTe_2N_3^- \qquad (13)$$

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It was found that for $CTe_2N_3^-$, as for $CS_2N_3^-$ and $CSe_2N_3^-$, the ring isomer was the lower energy structure with $\Delta E_{(\mathrm{ring-chain})} = 10.4$ kcal mol^{-1} (Figure 7). We will report more detailed theoretical investigations regarding these and other related compounds in a future study.

Conclusions

The synthesis and spectroscopic characterization (IR, Raman, multinuclear NMR) of salts containing the $CS_2N_3^-$ moiety has been established, including the preparation of the first anhydrous salts containing the $CS_2N_3^-$ anion. The structure and bonding in the interpseudohalogen CS_2N_3CN and the acid HCS_2N_3 have been investigated using quantum-chemical calculations, and the gas-phase acidity of HCS_2N_3 has been calculated to be 327 kcal mol^{-1}. The methylated derivative, $H_3CCS_2N_3$, has been successfully synthesized and characterized and found to possess $S-CH_3$ connectivity in analogy to CS_2N_3CN using X-ray diffraction techniques. In this study, the chemistry of the CS_2N_3 moiety has been investigated with the focus being on small and simple derivatives. Thus, the understanding of the simplest members of this class of compounds might enable the synthesis and understanding of further more complex systems.

In an attempt to investigate the possible synthesis of the heavier members of the $CE_2N_3^-$ series, ($E = S$, Se, Te), a combined experimental and theoretical investigation of the $CSe_2N_3^-$ anion was undertaken. The attempted synthesis of $NaCSe_2N_3$ resulted only in identification of Na^+SeCN^-, Se, and N_2. As the analogous decomposition products were observed for the related sulfur system, the synthesis of the $CSe_2N_3^-$ anion in the form of its sodium salt may have been achieved as an unstable intermediate. Quantum-chemical calculations were used to predict the most likely structure for the $CSe_2N_3^-$ anion in the gas phase. The five-membered ring structure, analogous to that experimentally observed for $CS_2N_3^-$, was calculated to be lower in energy than the chain structure. Finally, calculation of the analogous tellurium species, $CTe_2N_3^-$, also predicted the ring isomer to be lower in energy than the chain isomer in the gas phase. Thus, it can be postulated that, for all of the $CE_2N_3^-$ species ($E = S$, Se, Te), the expected structures are those of five-membered rings with exocyclic chalcogen atoms.

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