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CS_2N_3, A Novel Pseudohalogen

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The $CS_2N_3^{\bullet}$ radical has been shown to fulfill all the criteria for being classified as a pseudohalogen. It is a strongly bound planar univalent radical ($CS_2N_3^{\bullet}$), which can form anions ($[CS_2N_3]^-$, **1**), hydracids (HNNNSC═S, **2**), neutral dipseudohalogen species ($(CS_2N_3)_2$, **3**), and the interpseudohalogen compound (CS_2N_3−CN, **4**).

The term *pseudohalogen* was introduced in 1925 for strongly bound, linear or planar univalent radicals (Y•, e.g., Y = CN, OCN, N_3, $SCSN_3$), which can form anions (Y^-), hydracids (H−Y), and neutral species (Y−Y, dipseudohalogens) as well as the interpseudohalogens (X−Y, X = halogen or pseudohalogen)[1a−c] and has remained a widely used concept ever since. However, while many pseudohalogens (e.g., CN, N_3, OCN etc.) are known, often the corresponding pseudohalide acids, dipseudohalogens, and interpseudohalogens are thermally highly unstable (e.g., HN_3, OCN−NCO, N_3SCS−$SCSN_3$)[2−4] or elusive species (e.g., N_3−N_3, OCN−N_3).[5,6] The structures of dipseudohalogens, pseudohalide acids, and interpseudohalogens attract great interest as structural determinations of such species in the solid state by X-ray crystallography are extremely rare. Moreover, few species actually fulfill all the original and necessary criteria outlined 75 years ago.

We report here the preparation, characterization (IR, Raman ^{13}C NMR, ^{14}N NMR), and X-ray structure determination of four molecular pseudohalogen compounds formally derived from the CS_2N_3 pseudohalogen radical (Scheme 1): (i) the pseudohalide anion $[CS_2N_3]^-$ (**1**) in the salt $[Na]^+[CS_2N_3]^-\cdot 4H_2O$, (ii) the pseudohalide acid HNNNS−C═S (**2**), (iii) the neutral dipseudohalogen (CS_2N_3)−(CS_2N_3) (**3**) and (iv) the interspeudohalogen compound CS_2N_3−CN (**4**).

The synthesis of sodium azidodithiocarbonate ($[Na]^+[\mathbf{1}]^-$) was first reported in 1915 by Sommer from the cycloaddition reaction between CS_2 and NaN_3.[7] However, it was not until 1991 that the structure of the $[CS_2N_3]^-$ anion was preliminary determined by X-ray diffraction to be that of a five-membered ring (**1**).[8] In the present study we found a new solvate and the salt to contain four molecules of water coordinated (Figure 1, Scheme 2).[9]

The corresponding free pseudohalide acid, HNNNSC═S (**2**), however, has so far not been conclusively identified. In an early paper on this topic, the authors claimed to have prepared a compound of the composition HCS_2N_3.[12] While IR spectrum was reported, the essential question as to whether this species contains S−H or N−H connectivity remained unanswered. We reacted sodium azidodithiocarbonate, $[Na]^+[CS_2N_3]^-\cdot 4H_2O$ with HCl (Scheme 1)[13] and obtained HCS_2N_3 (**2**) as a temperature-sensitive, white solid. Single crystals suitable for X-ray diffraction were obtained by recrystallization from methanol at low temperature. The ^{14}N NMR spectrum showed the presence of three peaks which correspond to the three ring nitrogen atoms, (40, 2, −118 ppm, rel. to $MeNO_2$); however, it was observed that one of the ring nitrogen peaks was dramatically shifted upfield with respect to the $[CS_2N_3]^-$ starting material (70, 9, −20 ppm, i.e., $-20 \rightarrow -118$ ppm). This indicated the presence of an N−H connectivity. This conclusion was confirmed for the solid state by X-ray structure determination (Figure 2).

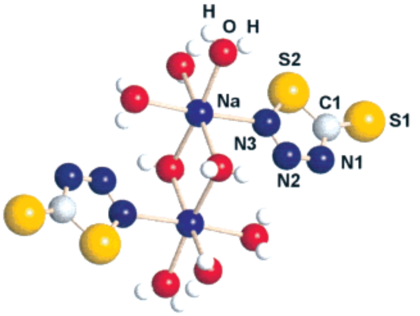
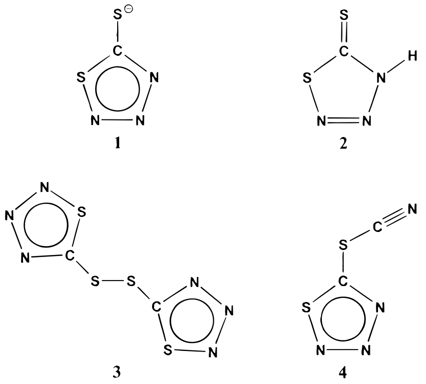


Figure 1. Structure of $[Na]^+[CS_2N_3]^-\cdot 4\ H_2O$ ($[Na]^+[\mathbf{1}]\cdot 4\ H_2O$). Bond lengths (Å): S1−C1 1.6964, S2−N3 1.6816(7), C1−N1 1.3403(9), N2−N3 1.286(1), N3−Na 2.5054(7), Na−O 2.4247(7); bond angles (deg): C1−S2−N3 91.69(3), S1−C1−S2 124.30(4), S1−C1−N1 126.57(5), S2−C1−N1 109.11(5), C1−N1−N2 112.27(6), N1−N2−N3 116.91(7)-S2−N3−N2 110.03(5).

Scheme 1



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§ X-ray structure determination

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(9) *$[Na][CS_2N_3]\cdot 4\ H_2O$*: $[Na][CS_2N_3]\cdot 4\ H_2O$ was prepared according to the literature.[7] Suitable crystals for X-ray structure determination were obtained by recrystallization from water. Crystal structure of $[Na][CS_2N_3]\cdot 4\ H_2O$ ($S_2CN_3NaO_4H_8$):[10,11] $M_r = 213.20$, monoclinic $P2_1/c$; $a = 11.3522(3)$ Å, $b = 11.0527(3)$ Å, $c = 7.1717(2)$ Å, $\beta = 100.245(1)°$, $V = 885.50(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.599$ g cm^{-3}, μ(Mo Kα) = 0.63 mm^{-1}, $F(000) = 441.4$, 33339 reflections measured, 7109 unique reflections, 5159 reflections with $I_{net} > 2.5\sigma(I_{net})$, $2\theta_{max} = 90.0°$, for 5159 significant reflections: $R_f = 0.032$, $R_w = 0.034$, for all 7109 reflections: $R_f = 0.051$, $R_w = 0.037$, GoF = 1.4171. Correction was made for absorption using SADABS.[11]

(10) Bruker SMART 1K diffractometer, Ω scan mode, $T = -120$ °C, $\lambda = 0.71073$ Å.

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(13) *HNNNSC═S (**2**)*: HNNNSC═S (**2**) was prepared at 0 °C from the reaction of $[Na][CS_2N_3]\cdot 4\ H_2O$ dissolved in water and concentrated hydrochloric acid, with the resultant HNNNSC═S precipitating as a white solid which was found to be stable at ≤− 25 °C but to decompose at rt within less than 1 h. Single crystals suitable for X-ray diffraction were obtained by recrystallization from CH_3OH.[14]

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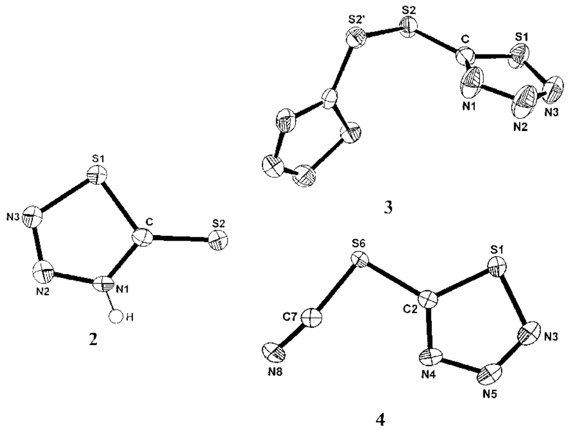
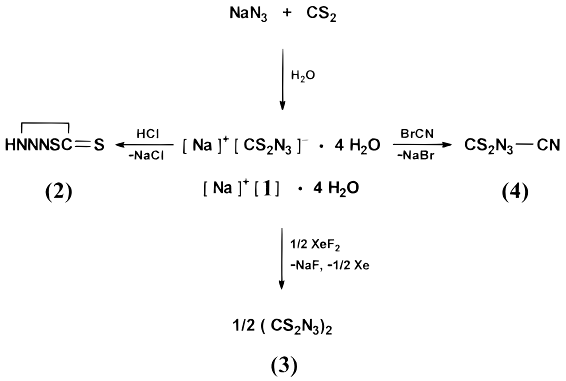


Figure 2. Structures of HNNNSC═S (**2**), $(CS_2N_3)_2$ (**3**) and $CS_2N_3{-}CN$ (**4**) (ORTEP plots). **2**: bond lengths (Å): S1−N3 1.706(3), S2−C 1.661(3), N1−C 1.346(4), N2−N3 1.260(4), C−S1 1.722(3), N1−N2 1.351(4); bond angles (deg): C−N1−N2 117.8(3), N1−N2−N3 112.7(3), S1−N3−N2 112.2(2), N1−C−S2 127.1(2); **3**: bond lengths (Å): S2−S2’ 2.041(1), S2−C 1.741(3), S1−N3 1.674(3), S1−C 1.692(3), N3−N2 1.278(4), N2−N1 1.358(4), N1−C 1.310(4); bond angles (deg): C−S2−S2′ 100.5(1), C−S1−N3 89.8(1), S1−N3−N2 111.6(2), N1−N2−N3 115.6(3), C−N1−N2 110.7(3). **4**: bond lengths (Å): S1−C2 1.699(2), C2−N4 1.305(2), N4−N5 1.364(3), N3−N5 1.276(3), S1−N3 1.670(2), C2−S6 1.756(2), S6−C7 1.697(2), C7−N8 1.139(3); bond angles (deg): S1−C2−S6 122.7(1), N4−C2−S6 124.6(1), C2−N4−N5 110.2(2), N3−N5−N4 115.9(2), S1−N3−N5 111.8(2), C2−S1−N3 89.5(1), C2−S6−C7 97.5(1), S1−C2−N4 112.7(2), S6−C7−N8 172.6(2).

Scheme 2



The dipseudohalogen **3** was first reported by Sommer, Browne et al. as the oxidation product of $[Na]^+[\mathbf{1}]^-$ with either permanganate or H_2O_2 as a white solid which is highly explosive even when kept under water.[7,17] We found that **3** can best be obtained from oxidation of $[Na]^+[\mathbf{1}]^-$ in H_2O with XeF_2 in acetone (Scheme 2) and recrystallization from cold acetone.[18] The molecular structure of this dipseudohalogen is shown in Figure 2.

The new interpseudohalogen $CS_2N_3{-}CN$ (**4**) can be obtained from the reaction of $[Na]^+[CS_2N_3]^- \cdot 4\ H_2O$ and cyanogen bromide, BrCN (Scheme 1).[20] The unstable $CS_2N_3{-}CN$ species was unambiguously identified by low-temperature NMR (^{13}C, ^{14}N), Raman, and FT-IR spectroscopy. The low-temperature ^{13}C NMR spectrum shows two singlet resonances, one at +171 ppm (cf. $[CS_2N_3]^-$, δ ^{13}C +194.8 ppm),[22] and the other at +106 ppm (cf. Et-SCN, δ ^{13}C +112 ppm).[23] In the ^{14}N NMR spectrum four well-resolved peaks are observed. The three peaks at +82, +23, and −5 ppm are attributed to the three ring nitrogen atoms and compare with those of the starting material ($[Na]^+[CS_2N_3]^-$, +70, +8, −21 ppm).[22] The peak at −90 ppm is assigned to the SCN moiety (cf. Et-SCN, δ ^{14}N −103 ppm).[24a,b] Crystals suitable for an X-ray diffraction study were grown by the rapid evaporation of acetone from a saturated solution, with the crystals obtained being stable for several days if at −25 °C. The X-ray structure shows the presence of the exocyclic sulfur−cyanide bond (Figure 2).

As the $CS_2N_3\bullet$ radical fulfills all of the requirements outlined by Birkenbach [1c] for a species to be considered a pseudohalogen (see above), the reported species $[CS_2N_3]^-$ (**1**), HNNNS−C═S (**2**), $(CS_2N_3){-}(CS_2N_3)$ (**3**), and CS_2N_3CN (**4**) can be classified conclusively as a pseudohalide (**1**), a pseudohalide acid (**2**), a dipseudohalogen, and an interpseudohalogen (**4**). The calculated absolute electronegativity of $\chi(CS_2N_3) = 7.0$ eV [25,26] lies between that of iodine and bromine ($\chi(I) = 6.8$ eV, $\chi(Br) = 7.6$)[27] and therefore the more familiar analogues to **1**, **2**, **3**, and **4** would be either $[I]^-$, HI, I_2, and I−CN or $[Br]^-$, HBr, Br_2, and BrCN.

Caution: $[Na][CS_2N_3] \cdot 4\ H_2O$ and (CS_2N_3) are explosive and thermally unstable species, BrCN is highly toxic and appropriate safety precautions should be taken.

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Supporting Information Available: Tables of crystal data, structure solutions and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1**, **2**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Crystal structure of HNNNSC═S (**2**) (CHN_3S_2):[15, 16] $M_r = 119.17$, monoclinic $P2_1/n$; $a = 3.9676(8)$ Å, $b = 15.278(2)$ Å, $c = 7.078(1)$ Å, $\beta = 96.95(2)°$, $V = 425.9(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.859$ g cm^{-3}, μ(Mo Kα) = 1.07 mm^{-1}, $F(000) = 240.0$, 2224 reflections measured, 766 unique reflections, 571 reflections with $I_{net} > 4\sigma(I_{net})$, $2\theta_{max} = 51.6°$, for all unique 766 reflections: $R_f = 0.0488$, $R_w = 0.0774$. GoF = 0.949. Empirical correction was made for absorption using SHELX97.[16]

(15) STOE IPDS diffractometer, $T = -73$ °C, $\lambda = 0.71073$ Å.

(16) (a) Sheldrick, G. M. *SHELXS-86, Structure Solving Program for Crystal Structure Determination*; University of Göttingen: Göttingen, 1986. (b) Sheldrick, G. M.; *SHELXS-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, 1997.

(17) Browne, A. W.; Hoel, A. B. *J. Am. Chem. Soc.* **1922**, *44*, 2106.

(18) *$(CS_2N_3)_2$ (**3**)*: A solution of 0.17 g (1.0 mmol) XeF_2 in 15 mL H_2O was reacted with a solution of 0.43 g (2.0 mmol) $[Na][CS_2N_3] \cdot 4\ H_2O$ in 10 mL H_2O. After a few minutes the white precipitate was filtered off at rt, and the reaction product (0.15 g, 63%) was dried at −25 °C overnight under vacuum. The compound is stable for days at −25 °C. Crystals suitable for X-ray diffraction were obtained by recrystallization from acetone at −25 °C.[19]

(19) Crystal structure of $(CS_2N_3)_2$ (**3**) ($C_2N_6S_4$):[15,16] $M_r = 236.32$, monoclinic $P2_1/c$; $a = 10.759(2)$ Å, $b = 5.576(6)$ Å, $c = 14.012(2)$ Å, $\beta = 106.47(2)°$, $V = 806.1(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.9476(5)$ g cm^{-3}, μ(Mo Kα) = 1.13 mm^{-1}, $F(000) = 472.0$, 3732 reflections measured, 1447 unique reflections, 997 reflections with $I_{net} > 4\sigma(I_{net})$, $2\theta_{max} = 51.7°$, for all unique 1447 reflections: $R_f = 0.0359$, $R_w = 0.0644$. GoF = 0.818. Empirical correction was made for absorption using SHELX97.[16]

(20) *CS_2N_3-CN (**4**)*: A solution of BrCN (0.106 g, 1.00 mmol) in acetone (2 mL) at 0 °C was added to an aqueous solution of $[Na][CS_2N_3] \cdot 4\ H_2O$ (0.213 g, 1.0 mmol). After the mixture was stirred at 0 °C for several minutes, the white solid precipitate formed was filtered at 0 °C and stored at −25 °C. Crystals suitable for X-ray diffraction studies[21] were obtained by the rapid evaporation of the acetone solvent, followed by storage at temperatures below −25 °C.

(21) Crystal structure of $CS_2N_3{-}CN$ (**4**) ($C_2N_4S_2$):[15,16] $M_r = 144.20$, orthorhombic *Pnma*; $a = 11.454(2)$ Å, $b = 6.4642(9)$ Å, $c = 6.9812(9)$ Å, $V = 516.9(1)$ Å^3, Z = 8, $\rho_{calcd} = 1.8530(5)$ g cm^{-3}, μ(Mo Kα) = 0.90 mm^{-1}, $F(000) = 288.0$, 3585 reflections measured, 544 unique reflections, 473 reflections with $I_{net} > 4\sigma(I_{net})$, $2\theta_{max} = 52.0°$, for 473 significant reflections: $R_1 = 0.021$, for all 544 reflections: $R_1 = 0.025$, $R_w = 0.051$, GoF = 1.040. Empirical correction was made for absorption using SHELX97.[16]

(22) IRIS-IX conference, Saarbrücken, Germany, July 23−28, 2000.

(23) Kalinowski, H. O.; Berger, S.; Braun, S. *^{13}C NMR-Spektroskopie*, S. Thieme: Stuttgart, 1984.

(24) (a) Witanowski, M. *J. Am. Chem. Soc.* **1968**, *90*, 5683. (b) Herbison-Evans, D.; Richards, R. E. *Mol. Phys.* **1964**, *8*, 19.

(25) MP2(FULL)/6-311G(d): $E([CS_2N_3]^-) = -997.537558$ au, $E([CS_2N_3]\bullet) = -997.416080$ au, $E([CS_2N_3]^+) = -997.022841$ au; $I([CS_2N_3]\bullet) = 10.7$ eV, $A([CS_2N_3]\bullet) = 3.3$ eV.; $\chi([CS_2N_3]\bullet) = (I + A)/2 = 7.0$ eV. For a definition and calculation of *I* (ionization energy) and *A* (electron affinity) see refs 26a−c.

(26) (a) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512. (b) Pearson, R. G. *Inorg. Chem.* **1988**, *27*, 734. (c) Pearson, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 7684.

(27) Klapötke, T. M.; Tornieporth-Oetting, I. C. *Nichtmetallchemie*; VCH: Weinheim, 1994; appendix.