Structure of 1-Isothiocyanato-2,8,9-trioxa-5-aza-1-germabicyclo[3.3.3]undecane: the First Metallatrane with a Direct Metal–NCS Bond

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A germatrane with a Ge–NCS bond has been isolated and characterised by X-ray crystallography and molecular spectroscopy; $\mathrm{Ge(NCS)(OCH_2CH_2)_3N}$ exhibits the shortest known Ge–N bond distance amongst germatranes and the first ^{13}C–^{14}N coupling [$J(^{13}C–^{14}N) = 21.0$ Hz] in a five-co-ordinate germanium compound.

Metallatranes† of Group 14 elements bearing a wide variety of side groups are known.[1–4] Recent reports on the reactivity of a few silatranes[5–8] have shown modified properties of these side groups. Although the chemical reactivity of a pseudohalogen group[9] in a metallatrane structural framework may thus afford novel derivatives, as yet there has been no report of a metallatrane binding such a functionality directly to the metal atom. Herein, we therefore report the preparation and X-ray crystal structure of 1-isothiocyanato-2,8,9-trioxa-5-aza-1-germabicyclo[3.3.3]undecane **1** as the first member of this class of compound.

Reaction of triethoxy(isothiocyanato)germane with triethanolamine leads to the formation of $\mathrm{Ge(NCS)(OCH_2CH_2)_3N}$ **1** ‡ in 80–85% yield. Its X-ray crystal structure § (Fig. 1) reveals that although the three oxygen atoms are positioned in the conventional equatorial fashion, the transannular nitrogen atom and the NCS group adopt apical positions in the least-distorted trigonal-bipyramidal geometry known amongst germatranes [O(1)–Ge–O(2) 120.5(3), O(1)–Ge–O(3) 120.8(2), O(2)–Ge–O(3) 118.0(3), N(1)–Ge–N(2) 179.4(3)°]. In addition the compound is the first example of a metallatrane of a Group 14 element to display an axial N–Ge–N moiety; also the Ge–N(1) bond length [2.081(5) Å] is the shortest reported in a germatrane.[11] In silatranes[12] the short transannular M–N bond is reported to influence the opposite apical M–X bond distance but this effect could not be ascertained in the present case because of a lack of relevant experimental structural data. However, taking into consideration the theoretical Ge–N bond distance[1] (1.92 Å), it is apparent that there is practically no effect on the Ge–N(2) [1.917(7) Å] bond length and therefore the difference between the dative Ge–N(1) and the covalent N(2)–Ge bond lengths (*ca.* 0.17 Å) is minimal. Another noteworthy feature is the strengthening of the N(2)–C(7) bond [1.133(8) Å] of the isothiocyanato group. In organic, organometallic and co-ordinatively complexed isothiocyanates[13–16] the N–C and C–S bond distances lie in the ranges 1.16–1.15 and 1.61–1.58 Å respectively. In compound **1**, although the C(7)–S(1) bond length observed [1.575(8) Å] is within the

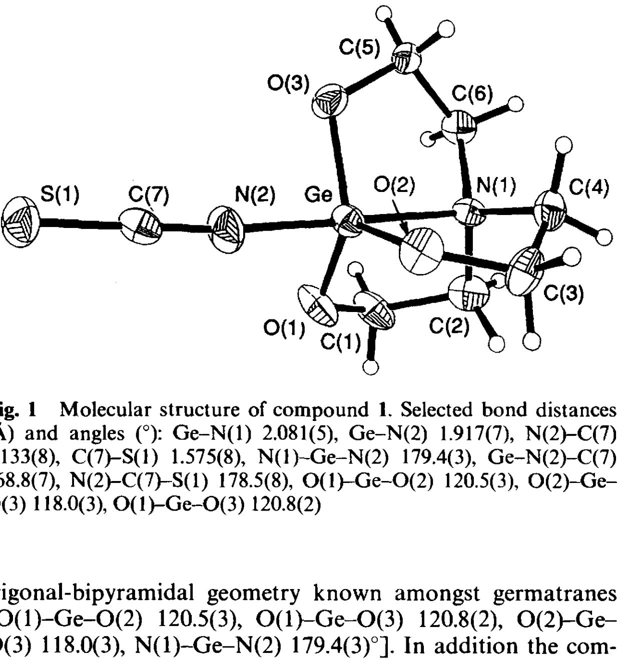

Fig. 1 Molecular structure of compound **1**. Selected bond distances (Å) and angles (°): Ge–N(1) 2.081(5), Ge–N(2) 1.917(7), N(2)–C(7) 1.133(8), C(7)–S(1) 1.575(8), N(1)–Ge–N(2) 179.4(3), Ge–N(2)–C(7) 168.8(7), N(2)–C(7)–S(1) 178.5(8), O(1)–Ge–O(2) 120.5(3), O(2)–Ge–O(3) 118.0(3), O(1)–Ge–O(3) 120.8(2)

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† Cyclic organometallic ethers of tris(2-oxyalkyl)amines.

‡ The addition of stoichiometric amounts of the reactants in CH_2Cl_2 at room temperature immediately yielded a white solid which dissolved after some time to give a clear pale yellow solution. After stirring the reaction mixture for 4–5 h followed by concentration, an air-stable white crystalline solid was obtained. Yield 80–85%, decomp. >210 °C [Found (Calc.): C, 30.3 (30.3); H, 4.2 (4.3); Ge, 25.7 (26.2); N, 10.1 (10.1); S, 11.2 (11.5%)]. Mass spectrum (70 eV): *m/z* 278, M^+; 220, $[M - NCS]^+$; 190, $[M - NCS - OCH_2]^+$; 160, $[M - NCS - O_2C_2H_4]^+$; 130, $[M - NCS - O_3C_3H_6]^+$. IR [Nujol, CH_2Cl_2 (solution)]: ν(NCS) at 2110 cm^{-1}. NMR (CD_3CN): ^1H(400 MHz), δ 3.88 (t, 6 H, OCH_2) and 3.06 (t, 6 H, NCH_2); ^{13}C (proton decoupled), δ 57.28 (OCH_2); 50.97 (NCH_2); 139.23, 139.02, 138.81 (NCS) [$J(^{13}C–^{14}N) = 21.0$ Hz].

‡ Crystal data: $C_7H_{12}GeN_2O_3S$, crystal dimensions 0.21 × 0.37 × 0.43 mm, $M = 276.8$, orthorhombic, space group *Pbca*, $a = 13.169(2)$, $b = 13.247(2)$, $c = 12.167(3)$ Å, $U = 2122.5(8)$ Å^3, $Z = 8$, $D_c = 1.733$ mg m^{-3}, λ(Mo-Kα) = 0.710 73 Å, $F(000) = 1120$; 2167 reflections collected with $4.0 < 2\theta < 50°$ at 296 K; 1618 unique, 1124 [$F > 4.0\sigma(F)$] used in structural analysis. The data were collected on a Rigaku AFC6S diffractometer. The structure was solved by Patterson methods and refined by full-matrix least squares (all non-hydrogen atoms anisotropic); $R(R') = 0.0446$ (0.0411), $w^{-1} = \sigma^2(F) + 0.0050F^2$. All calculations were performed using the TEXSAN crystallographic software package.[10a] Fig. 1 was drawn using ORTEP.[10b] Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

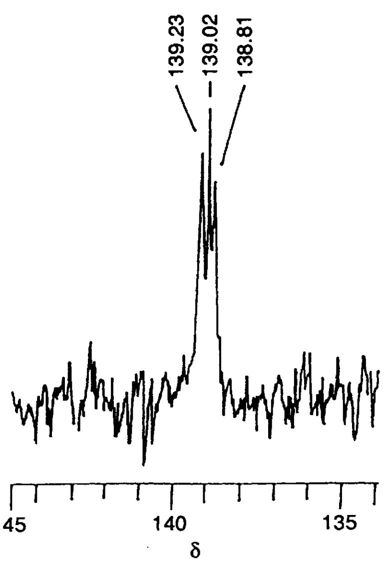

Fig. 2 Part of the ^{13}C NMR spectrum of compound **1** showing the $^{13}C-^{14}N$ coupling

reported range, the N(2)–C(7) distance is not and can be compared with C–N bond lengths [1.13(2) Å] encountered in four-co-ordinate organogermanium cyanides.[17,18]

The X-ray crystal structure of compound **1** is supported by IR, mass, ^{1}H and ^{13}C NMR spectral data. In addition, the ^{13}C NMR spectrum shows a triplet at δ 139.23, 139.02 and 138.81 (Fig. 2) attributable to the NCS group and depicts ^{13}C and ^{14}N coupling [$J(^{13}C-^{14}N) = 21.0$ Hz]. This coupling has not been reported so far in germanium compounds. However, its value compares favourably with that of the corresponding silatrane (26.1 Hz).[19]

Acknowledgements

Financial assistance from the University Grants Commission (to R. S.) and Council of Scientific and Industrial Research, Government of India (to S. S.) is gratefully acknowledged. We also thank the Tata Institute of Fundamental Research (Bombay) and Indian Institute of Science (Bangalore) for NMR facilities.

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Received 26*th June* 1992; *Communication* 2/03369K