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Electronic Supplementary Information

Coordination networks derived from germanium(II) thioether macrocyclic ccomplexes – the first authenticated chalcogenoether complexes of Ge(II)

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Experimental

MeCN and CH_2Cl_2 were dried by distillation from CaH_2. Ligands were obtained from Aldrich and used as received. All reactions were conducted using Schlenk, vacuum line and glove-box techniques and under a dry dinitrogen atmosphere. IR spectra were recorded from Nujol mulls between CsI plates over the range 4000−180 cm^{-1} on a Perkin Elmer PE 983G spectrometer, Raman spectra using a Perkin Elmer FT Raman 2000R with a Nd:YAG laser. ^1H NMR spectra were recorded in CD_2Cl_2 solution on a Bruker AV300 spectrometer. Microanalytical measurements on new complexes were performed by the microanalytical service at Strathclyde University. [$GeCl_2$(dioxan)] was made as described.[1]

[$GeCl_2$([9]aneS$_3$)]: 1,4,7-Trithiacyclononane (0.090 g, 0.50 mmol) was added to a solution of [$GeCl_2$(1,4-dioxane)] (0.115 g, 0.50 mmol) in CH_2Cl_2 (15 mL) at room temperature with stirring which leads to the slow formation of white precipitate. After stirring for 30 min, the solvent was removed *in vacuo* to leave a white solid which was washed with diethyl ether and dried *in vacuo*. Yield: >95%. ^1H NMR of the bulk sample (CD_2Cl_2, 298 K): $\delta = 3.14$ (s), CH_2, [9]aneS$_3$ (no residual dioxan). Colourless crystals were obtained redissolving the bulk powder in CH_2Cl_2 and allowing this to evaporate slowly in the glove box. $C_6H_{12}Cl_2GeS_3$ (323.8): calcd. C, 22.2; H, 3.7. Found: C, 22.0; H, 3.7%. IR (Nujol, cm^{-1}): 290br υ(Ge–Cl). Raman (cm^{-1}): 308br υ(Ge–Cl).

[GeCl$_2$([14]aneS$_4$)]: was made analogously to [GeCl$_2$([9]aneS$_3$)] giving a white solid. The same 1:1 compound was obtained from MeCN solution using either a 1:1 or 2:1 mol. ratio of [GeCl$_2$(dioxan)] : [14]aneS$_4$. Colourless crystals were obtained by slow evaporation of the solvent from a CH$_2$Cl$_2$ solution. $C_{10}H_{20}Cl_2GeS_4 \cdot 0.5CH_2Cl_2$ (454.5): calcd. C, 27.7; H, 4.7. Found: C, 27.4; H, 4.7%. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): $\delta = 2.78$ (s) SC*H*$_2$ [8H], 2.66 (m) SC*H*$_2$ [8H], 1.84 (m) C*H*$_2$ [4H] (no residual dioxan, some residual CH$_2$Cl$_2$ evident). IR (Nujol, cm^{-1}): 340, 295 υ(Ge–Cl). Raman (cm^{-1}): 343, 297 υ(Ge–Cl).

[GeCl$_2$)$_2$([14]aneS$_4$)]: a small number of crystals of this 2:1 species were obtained by slow concentration of the CH$_2$Cl$_2$ from the filtrate (after removal of the bulk [GeCl$_2$([14]aneS$_4$)]) in the above reaction. Attempts to prepare the 2:1 complex directly using a 2:1 ratio of [GeCl$_2$(dioxan)]:thiacrown in MeCN solution also yielded the 1:1 complex (microanalytical evidence).

[GeBr$_2$([14]aneS$_4$)]: [14]aneS$_4$ (0.053 g, 0.20 mmol) was added to a solution of GeBr$_2$ (0.046 g, 0.20 mmol) in MeCN (5 mL) at room temperature with stirring, which led to the slow formation of white precipitate. After stirring for 30 min, the solvent was removed *in vacuo* to leave a white solid which was dried *in vacuo*. Colourless crystals were obtained by redissolving the bulk powder in MeCN and allowing the solvent to evaporate slowly in the glove box. $C_{10}H_{20}Br_2GeS_4$ (500.9): calcd. C, 24.0; H, 4.0. Found: C, 23.5; H, 3.9%. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): $\delta = 2.73$ (s) SC*H*$_2$ [8H], 2.61 (m) SC*H*$_2$ [8H], 1.86(m) C*H*$_2$ [4H]. IR (Nujol, cm^{-1}): 236m, 213m υ(Ge–Br). Raman (cm^{-1}): 224s, 209s υ(Ge–Br).

[GeBr$_2$([16]aneS$_4$)] : 1,5,9,13-tetrathiacyclohexadecane (0.059 g, 0.20 mmol) was added to a solution of GeBr$_2$ (0.046 g, 0.20 mmol) in CH$_3$CN (5 mL) at room temperature with stirring. After stirring for 30 min, the solvent was removed *in vacuo* to leave a white solid which was dried *in vacuo*. Colourless crystals were obtained by redissolving the bulk solid in MeCN and allowing the solvent to evaporate slowly in the glove box. $C_{12}H_{24}Br_2GeS_4$ (733.4): calcd. C, 27.2; H, 4.6. Found: C, 26.8; H, 4.4%. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): 2.65(t) SC*H*$_2$ [16H], 1.88 (qn) C*H*$_2$ [8H]. IR (Nujol, cm^{-1}): 217m υ(Ge–Cl). Raman (cm^{-1}): 229s, 213s υ(Ge–Cl).

1. S. P. Kolesnikov, I. S. Rogozhin and O. M. Nefedov, *Seriya Khim.*, 1974, **10**, 2379.

Selected bond lengths (Å) and angles (°) for [$GeCl_2$([9]aneS_3)]

Ge1–Cl1	2.308(2)	Ge1–Cl2	2.299(2)
Ge1–S1	2.721(3)	Ge1–S2a	2.741(3)
Ge1···Cl3	3.796(3)	Ge1···Cl4	3.671(3)
Ge2–Cl3	2.285(2)	Ge2–Cl4	2.315(2)
Ge2–S4	2.721(2)	Ge2–S5a	2.744(3)
Ge3–Cl5	2.288(3)	Ge3–Cl6	2.305(3)
Ge3–S7	2.782(3)	Ge3–S8a	2.697(3)
S–C(min)	1.789(9)	S–C(max)	1.844(9)
Cl1–Ge1–Cl2	99.77(10)	S1–Ge1–S2a	164.58(8)
Cl3–Ge2–Cl4	99.54(9)	S4–Ge1–S5a	165.91(7)
Cl5–Ge3–Cl6	98.88(10)	S7–Ge1–S8a	165.17(8)

Symmetry operation: a = 1/2 – x, y, –1/2 + z.

Selected bond lengths (Å) and angles (°) for [$(GeCl_2)_2$([14]aneS_4)]$\cdot 0.7CH_2Cl_2$

Ge1–Cl1	2.272(3)	Ge1–Cl2	2.278(3)
Ge1–S1	2.7602(15)	Ge2–Cl3a	2.2850(17)
Ge2–Cl3	2.2850(17)	Ge2–S2	2.7719(15)
Cl1–Ge1–Cl2	97.22(12)	Cl1–Ge1–S1	88.38(4)
Cl2–Ge1–S1	88.06(4)	Cl3–Ge2–Cl3a	98.81(9)
Cl3a–Ge2–S2	87.53(5)	Cl3–Ge2–S2	90.07(5)

Symmetry operation: a = x, 1/2 – y, 1–z.

Selected bond lengths (Å) and angles (°) for [GeBr$_2$([14]aneS$_4$)]

Ge1–Br1	2.4656(5)	Ge1–S1	2.7498(8)
Br1–Ge1–Br1a	100.08(2)	Br1a–Ge1–S1	87.34(2)
Br1–Ge1–S1	85.79(2)	S1–Ge1–S1a	169.31(3)

Symmetry operation: a = 3/2 – x, y, 1/2 – z.

Selected bond lengths (Å) and angles (°) for [GeBr$_2$([16]aneS$_4$)]

Ge1–Br1	2.4497(4)	Ge1–S1	2.7316(6)
Br1–Ge1–Br1b	101.473(18)	Br1b–Ge1–S1	87.817(15)
Br1–Ge1–S1	86.896(15)	S1–Ge1–S1b	171.64(3)

Symmetry operation: b = – x, y, 3/2 – z.