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

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Exocyclic coordination of macrocyclic thioethers to germanium(II) halides leads to infinite chains (with weak Ge···X bridges between the chains) or sheet structures containing distorted octahedral Ge(II) with [S_2X_2 + X_2] coordination and bridging thiacrowns.

Although the chemistry of germanium with neutral, soft donor ligands has been extended significantly recently, this work has focused on tetravalent germanium, yielding the first [GeF_4(diphosphine)] and [GeF_4(dithioether)] complexes.[1,2] Investigations of the lower valent Ge(II) ion have focused mainly on germylenes (Ge analogues of carbenes) and for applications in organic chemistry.[3–5] Further interest in complexes of Ge(II) arises from the presence of a lone pair of electrons which is expected to have significant stereochemical consequences. However, reports of the coordination chemistry of Ge(II) with neutral ligands are few—structural data available are for [$GeCl_2$(dioxan)],[6] the very unstable [$GeCl_2(thf)_2$][7] and a single diphosphine complex, [$GeCl_2\{Ph_2P(CH_2)_2PPh_2\}$][8]—each of which contains Ge(II) in a highly distorted tetrahedral environment. Two structurally characterised complexes, [$GeX_2(PPh_3)$] (X = Cl or I), involving pyramidal Ge(II) are also known,[9] while Ge(II) halide complexes incorporating diimine ligands have been reported albeit without structural data.[10]

While $GeBr_2$ itself is a convenient synthon for complex formation, [$GeCl_2$(dioxan)][5] presents a soluble source of $GeCl_2$ *via* substitution of the dioxan by the incoming ligand. Initial experiments aimed at introducing thioether coordination through reaction of [$GeCl_2$(dioxan)] with $RS(CH_2)_2SR$ in CH_2Cl_2 solution failed. However, stirring an equimolar solution of [$GeCl_2$(dioxan)] and the macrocyclic thioethers [9]aneS_3 (1,4,7-trithiacyclononane) or [14]aneS_4 (1,4,8,11-tetrathiacyclotetradecane) in anhydrous CH_2Cl_2 (and also MeCN for the latter) led to formation of white solids of composition [$GeCl_2$([9]aneS_3)] and [$GeCl_2$([14]aneS_4)] in excellent yield.‡ These compounds are moisture sensitive, but may be handled briefly in air. However, the samples were stored and handled in a dry, N_2-filled glove box. Single crystals of [$GeCl_2$([9]aneS_3)] came from CH_2Cl_2 solution, while slow concentration of the CH_2Cl_2 from the filtrate (after removal of the bulk [$GeCl_2$([14]aneS_4)]) gave single crystals of the 2 : 1 compound [$(GeCl_2)_2$([14]aneS_4)]·0.7CH_2Cl_2.

Confirmation of the Ge–S coordination in these species follows from single crystal structure determinations.§ The structure of [$GeCl_2$([9]aneS_3)] shows (Fig. 1a and b) the trithia macrocycle coordinated in a μ_2-κ^1 mode forming infinite zig-zag chains of $GeCl_2$ units bridged by [9]aneS_3 ligands. The coordination at each Ge(II) is therefore *via* two primary Ge–Cl bonds (*ca.* 2.29 Å, angle Cl–Ge–Cl *ca.* 99°) and two long, mutually *trans* Ge–S bonds (*ca.* 2.74 Å), giving a saw-horse environment at Ge, with the lone pair of electrons assumed to occupy the vacant equatorial site of a distorted pseudo-trigonal bipyramid. Two further long-range (secondary) Ge···Cl interactions (*ca.* 3.7 Å) from the Cl ligands on a Ge atom in an adjacent chain lead to an alternative description of the coordination environment as a highly distorted octahedron, based upon a [S_2Cl_2 + Cl_2] donor set. The chains

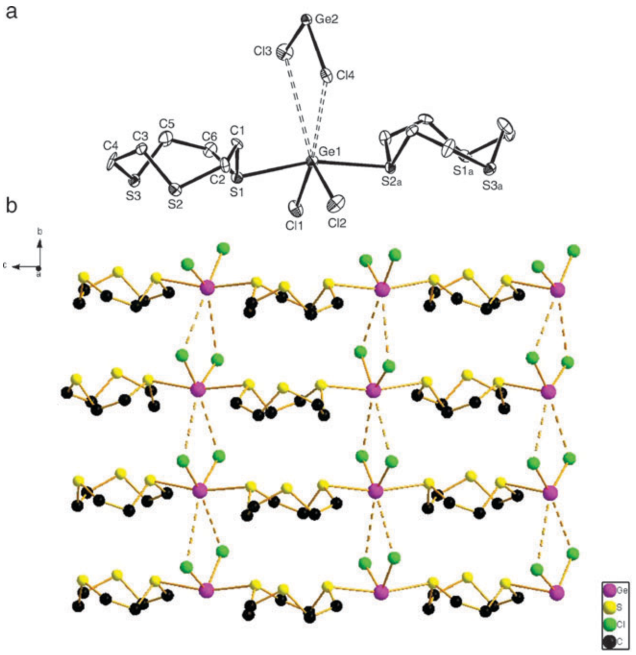

Fig. 1 (a) View of the coordination environment at Ge1 in the [$GeCl_2$([9]aneS_3)] polymer with numbering scheme adopted. Ellipsoids are shown at the 50% probability level. H atoms are omitted for clarity. Symmetry operation: a = 1/2 − *x*, *y*, *z* − 1/2. The environments about Ge2 and Ge3 are very similar. Selected bond lengths (Å) and angles (°): 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), 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). (b) View of a section of the [$GeCl_2$([9]aneS_3)] polymer showing the weak Ge···Cl interactions between the chains.

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are aligned along the *z* direction with adjacent Ge atoms in each chain related by a glide plane.

The 2 : 1 complex [$(GeCl_2)_2$([14]aneS_4)] shows (Fig. 2a and b) a $GeCl_2$ unit bound weakly to each of the four S-donor atoms of an exocyclic [14]aneS_4 molecule, and the μ_4-κ^1-coordinated tetrathiacrown units bridge $GeCl_2$ units to form infinite sheets. The coordination environment and bond lengths at each Ge are very similar to those for [$GeCl_2$([9]aneS_3)] above, based upon saw-horse S_2Cl_2 coordination (*trans* S atoms) with secondary, weak Ge···Cl interactions between the 2-D sheets. Ge1 is positioned on a mirror plane (4d site) and Ge2 on a 2-fold axis (site 4c). The sulfur ligand [14]aneS_4 has a centre of symmetry.

Direct reaction of $GeBr_2$ with 1 mol. equiv. of either [14]aneS_4 or the larger ring [16]aneS_4 (1,5,9,13-tetrathiacyclohexadecane) in anhydrous MeCN solution yields white powdered solids of composition [$GeBr_2$([14]aneS_4)] or [$GeBr_2$([16]aneS_4)], respectively, in excellent yields. Using a 2 : 1 $GeBr_2$: [14]aneS_4 ratio also gave the 1 : 1 product. Crystal structures show (Fig. 3a and b, 4a and b) that both compounds adopt infinite chain structures through exocyclic μ_2-κ^1 coordination of the macrocycles to distinct $GeBr_2$ units. However, since only alternate S atoms from each macrocycle are coordinated, these species form linear chain structures. The coordination environment at Ge is *via* two primary (*cis*) Ge–Br bonds (*ca.* 2.46 Å), and two long, mutually *trans* Ge–S bonds of *ca.* 2.74 Å, giving a saw-horse geometry with the Ge-based lone pair assumed to occupy an equatorial site of a pseudo-trigonal bipyramid (angle Br–Ge–Br *ca.* 100°).

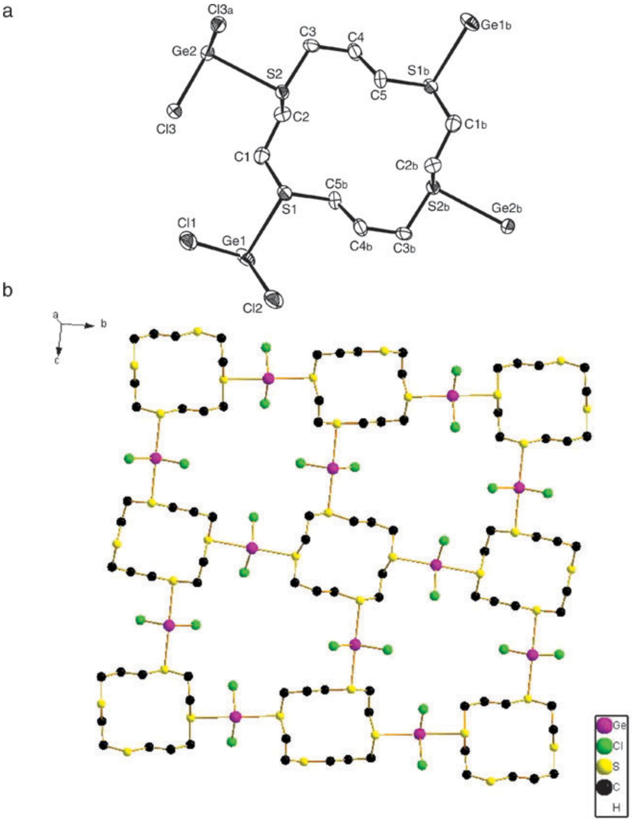

Fig. 2 (a) View of the structure of the core in [$(GeCl_2)_2$([14]aneS_4)] with numbering scheme adopted. Ellipsoids are shown at the 50% probability level and H atoms are omitted for clarity. Symmetry operations: a = *x*, 1/2 − *y*, 1 − *z*; b = −*x*, 1 − *y*, 1 − *z*. Selected bond lengths (Å) and angles (°): 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). (b) View of a section of the sheet structure observed for [$(GeCl_2)_2$([14]aneS_4)]. Weak Ge···Cl interactions also occur between the sheets.

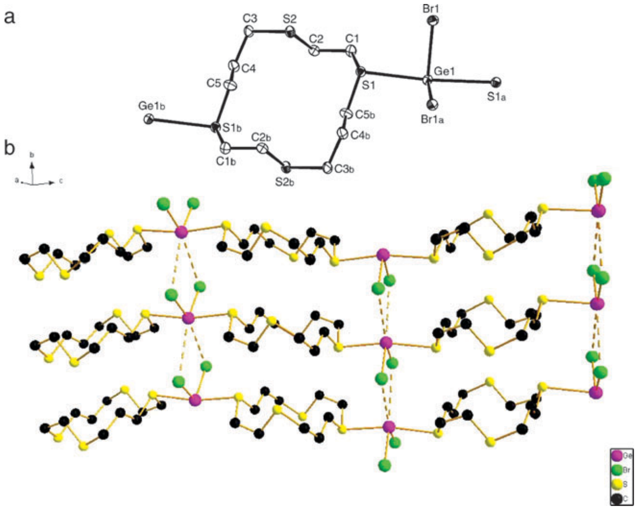

Fig. 3 (a) View of the structure of a section of the [$GeBr_2$([14]aneS_4)] polymer with numbering scheme adopted. Ellipsoids are shown at the 50% probability level and H atoms are omitted for clarity. Symmetry operations: a = 3/2 − *x*, *y*, 1/2 − *z*; b = 1 − *x*, −*y*, 1 − *z*. Selected bond lengths (Å) and angles (°): 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). (b) View of a section of the [$GeBr_2$([14]aneS_4)] polymer showing the infinite chains; weak Ge···Br interactions link adjacent chains.

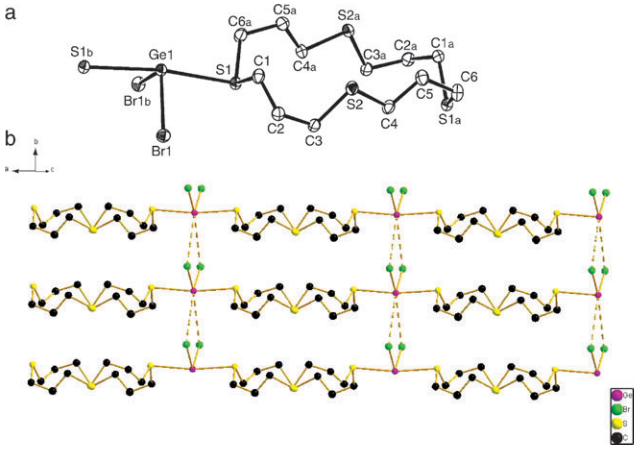

Fig. 4 (a) View of the structure of a section of [$GeBr_2$([16]aneS_4)] with numbering scheme adopted. Ellipsoids are shown at the 50% probability level and H atoms are omitted for clarity. Symmetry operations: a = 1 − *x*, *y*, 3/2 − *z*; b = −*x*, *y*, 3/2 − *z*. Selected bond lengths (Å) and angles (°): 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). (b) View of a section of the [$GeBr_2$([16]aneS_4)] polymer showing the infinite chains; weak Ge···Cl interactions link adjacent chains.

Table 1 Crystallographic parameters

	[GeCl$_2$-([9]aneS$_3$)]	[(GeCl$_2$)$_2$-([14]aneS$_4$)]·0.7CH$_2$Cl$_2$	[GeBr$_2$-([14]aneS$_4$)]	[GeBr$_2$-([16]aneS$_4$)]
Formula	C_6H_{12}-Cl_2GeS_3	$C_{10}H_{20}$-$Cl_4Ge_2S_4$·0.7CH_2Cl_2	$C_{10}H_{20}Br_2$-GeS_4	$C_{12}H_{24}$-Br_2GeS_4
M	323.83	615.14	500.91	528.96
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	$Pca2_1$ (no. 29)	$Pbcm$ (no. 57)	$P2/n$ (no. 13)	$P2/c$ (no. 13)
a/Å	15.025(3)	4.9051(10)	10.241(2)	13.0690(15)
b/Å	14.182(3)	22.596(3)	4.8585(10)	4.9527(5)
c/Å	16.401(2)	20.973(3)	17.778(4)	15.898(2)
α/°	90	90	90	90
β/°	90	90	102.475(10)	112.114(10)
γ/°	90	90	90	90
U/Å^3	3494.7(11)	2324.5(7)	863.7(3)	953.35(19)
Z	12	4	2	2
μ(Mo-Kα)/mm^{-1}	3.574	3.560	6.862	6.222
Total no. reflections	30 595	12 862	9076	10 369
R_{int}	0.068	0.060	0.046	0.031
Unique reflections	7868	2721	1958	2194
No. of parameters	326	118	78	87
R_1 [$I_0 > 2\sigma(I_o)$]	0.047	0.063	0.030	0.022
R_1 [all data]	0.069	0.088	0.038	0.028
wR_2 [$I_0 > 2\sigma(I_0)$]	0.087	0.140	0.058	0.043
wR_2 [all data]	0.097	0.157	0.060	0.046

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

As in the chloro complexes above, two additional weak, secondary Ge···halogen interactions (in this case Ge···Br around 3.9 Å) occur between the chains. Within both [GeBr$_2$([14]aneS$_4$)] and [GeBr$_2$([16]aneS$_4$)] the Ge1 atom occupies a crystallographic 2-fold site with the macrocycle ring having a centre of symmetry in the former and a 2-fold axis in the latter.

A feature common to the three structures containing tetrathioether macrocycles is one cell axis of around 4 Å; this axis then governs the stacking distance between the polymeric chains or sheets, and the alignment of the GeX$_2$ units in the lattice gives rise to the long-range Ge···halogen linkages and also means that the macrocyclic units in individual chains (or sheets) are aligned. Thus both the coordination environment at Ge(II) and the extended structures in these, the first Ge(II) thioether complexes, show substantial similarities, and the Ge–S bond distances do not differ significantly, suggesting that the Lewis acidities of GeCl$_2$ and GeBr$_2$ are rather similar.

The only other thioether complexes of germanium are the distorted octahedral complexes of Ge(IV), [GeF$_4${RS(CH$_2$)$_2$SR}] (R = Me or Et), with chelating dithioethers.[2] The Ge–S bond distances in the present Ge(II) complexes (~2.74 Å) are significantly longer than those observed in the GeF$_4$ complexes (d(Ge–S) = 2.4334(7), 2.4728 and d(Ge–S) = 2.4611(8), 2.4903(8) Å for R = Me and Et, respectively), consistent with very weak thioether bonding in the new Ge(II) complexes.

Proton NMR studies of these compounds in CD$_2$Cl$_2$ showed resonances consistent with dissociated ligand even at −50 °C—not unexpected based upon the high lability anticipated for the Ge(II) species.

These results present the first experimental and structural evidence for chalcogenoether coordination to the weakly Lewis acidic GeX$_2$ fragments, revealing highly unexpected extended coordination networks. They suggest that a rich chemistry of Ge(II) may well be accessible under appropriate experimental conditions.

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Notes and references

‡ *Preparation.* The bulk compounds [GeCl$_2$([9]aneS$_3$)] and [GeCl$_2$([14]aneS$_4$)] were obtained by reaction of equimolar quantities of [GeCl$_2$(dioxan)] with the appropriate ligand in anhydrous CH$_2$Cl$_2$ solution and isolated as colourless solids by removing the solvents *in vacuo*. Crystalline samples were then obtained from CH$_2$Cl$_2$ solutions. Satisfactory microanalytical and ^{1}H NMR, IR and Raman spectroscopic data were obtained. The compounds [GeBr$_2$([14]aneS$_4$)] and [GeBr$_2$([16]aneS$_4$)] were obtained as colourless solids by direct reaction of equimolar quantities of GeBr$_2$ with the macrocycle in MeCN solution and crystals obtained from MeCN solution. See ESI† for full details and characterisation data.

§ *X-Ray crystallography*. Crystallographic parameters are given in Table 1. Data collections used a Bruker-Nonius Kappa CCD diffractometer fitted with monochromated (graphite or confocal mirrors) Mo-Kα radiation (λ = 0.71073 Å), with the crystals held at 120 K in a nitrogen gas stream. Structure solution and refinement were straightforward[11,12] except as described below, with H atoms introduced into the models in calculated positions using the default C–H distance. For [(GeCl$_2$)$_2$([14]aneS$_4$)] a disordered, partial (refined sof = 0.7) CH$_2$Cl$_2$ solvent molecule was located in the difference map. A residual peak (*ca.* 2.0 e Å^{-3}) approx. 2.0 Å from Cl4 and Cl5 remained but was not satisfactorily modelled. For [GeCl$_2$([9]aneS$_3$)] two space groups were consistent with the systematic absences ($Pca2_1$ and $Pbcm$ in standard settings) with our solution in $Pca2_1$. When run through the checkcif software[13] the output strongly suggested that the correct space group was the centrosymmetric $Pbcm$ and attempts were made to seek a solution here. A promising CFOM in SHELXS (but high RE value) lead to plausible Ge and Cl positions (Ge on the 4c sites with 2-fold symmetry and Cl in general positions), but attempts to develop the model and locate the S ligand were not successful. Looking at the unit cell packing diagram shows the close similarity in the location of the GeCl$_2$ fragments in the two models. Accordingly the structure is reported in the space group $Pca2_1$.

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