Electronic Supplementary Information for Dalton Transactions

# Synthesis and structural characterisation of germanium(II) halide complexes with neutral N-donor ligands

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## Supplementary Data

**Table S1** Comparison of some selected bond lengths (Å) and angles (°) of [$GeCl_2\{Me_2N(CH_2)_2NMe_2\}$] computed for the molecular unit and measured for the crystal structure in this work (in brackets)

| | | | |
|---|---|---|---|
| Ge–N1 | 2.333 (2.157) | N1–Ge–N2 | 71.2 (78.5) |
| Ge–N2 | 3.003 (2.458) | Cl1–Ge–Cl2 | 99.2 (89.9) |
| Ge–Cl1 | 2.322 (2.526) | Cl1–Ge–N1 | 91.2 (89.1) |
| Ge–Cl2 | 2.289 (2.260) | Cl2–Ge–N1 | 92.0 (94.9) |

Computed charges

| Atom | Mulliken Charge | Natural Charge |
|---|---|---|
| Ge | 0.501 (0.535)* | 0.796 (0.874)* |
| Cl1 | –0.419 (0.268)* | –0.522 (–0.437)* |
| Cl2 | –0.395 | –0.507 |
| N1 | –0.177 | –0.561 |
| N2 | –0.171 | –0.534 |

* computed values in isolated $GeCl_2$

**Table S2** Comparison of some selected bond lengths (Å) and angles ($^o$) of [$GeCl_2$(2,2′-bipy)] computed for the global minimum monomer unit and measured for the crystal structure in this work (in brackets)

| | | | |
|---|---|---|---|
| Ge–N1 | 2.315[a] / 2.346[b] (2.074) | N1–Ge–N2 | 64.6 / 65.5 (77.5) |
| Ge–N2 | 2.816 / 2.690 (2.067) | Cl1–Ge–Cl2 | 98.4 / 98.1 (191.1[c]) |
| Ge–Cl1 | 2.274 / 2.285 (2.453) | Cl1–Ge–N1 | 93.8 / 91.0 (86.6) |
| Ge–Cl2 | 2.326 / 2.352 (2.719) | Cl2–Ge–N1 | 90.1 / 91.2 (82.9) |

[a] opt B3LYP/cc-pvTZ; [b] opt B3LYP/cc-pvDZ. Frequencies are those of the B3LYP/cc-pvTZ optimized geometry; [c] The angle in the crystal structure is 168.9$^o$, corresponding to 360 – 168.9 = 191.1$^o$.

Computed Charges

| **Atom** | **Mulliken Charge** | **Natural charge**[c] |
|---|---|---|
| Ge | 0.517[a] / 0.538[b] | 0.822 |
| Cl1 | –0.391 / –0.381 | –0.491 |
| Cl2 | –0.427 / –0.420 | –0.533 |
| N1 | –0.164 / –0.225 | –0.521 |
| N2 | –0.186 / –0.298 | –0.480 |

[a]opt B3LYP/cc-pvTZ; [b]opt B3LYP/cc-pvDZ; [c]Computed from Natural Orbital Analysis on ridft optimized geometry.

**Table S3** Comparison of some selected bond lengths (Å) and angles (°) of the higher energy conformation of the [$GeCl_2$(2,2′-bipy)] monomer and measured from the crystal structure in this work (in brackets). This conformation has a $C_{2v}$ structure.

| | | | |
|---|---|---|---|
| Ge–N | 2.139[a] / 2.174[b]<br>(2.074, 2.067) | N–Ge–N | 75.3 / 74.4<br>(77.5) |
| Ge–Cl | 2.520 / 2.509<br>(2.453, 2.719) | Cl–Ge–Cl | 198.4 / 198.6[d]<br>(191.1[c]) |
| | | Cl–Ge–N | 82.7 / 82.6<br>(86.6, 82.9, 89.6, 84.6) |
| | | | |
| | Mulliken charge | Natural charge[e] | |
| Ge | 0.441 / 0.583 | 0.923 | |
| N | −0.072 / −0.297 | −0.538 | |
| Cl | −0.571 / −0.551 | −0.602 | |

[a] opt B3LYP/cc-pvTZ; [b] opt B3LYP/cc-pvDZ; [c] The angle in the crystal structure is 168.9°, corresponding to 360 – 168.9 = 191.1°; [d] These angles correspond to the Cl–Ge–Cl angle in the input monomer model increasing progressively beyond 180°; [e] Computed from Natural Orbital Analysis on ridft optimized geometry.

Energy difference between the axial and the angular form, calculated as E(axial) – E(angular); energy values are zero point corrected:

+50.1 kJ/mol at B3LYP/cc-pvDZ level
+41.6 kJ/mol at B3LYP/cc-pvTZ level

**Table S4** Comparison of some selected bond lengths [Å] and angles [°] of $[GeCl_2(2,2'\text{-bipy})]_2$ and measured for the crystal structure in this work (in brackets). Comparison has been made between the Cl–Ge–Cl ‘linear’ part in the computed structure and the monomer unit in the crystal structure (see text).

| | | | |
|---|---|---|---|
| 1–2 (Ge–Cl) | 2.42 (2.45) | 2–1–6 (Cl–Ge···Ge) | 141.3 |
| 1–3 (Ge–Cl) | 2.75 (2.72) | 1–6–7 (Ge···Ge–Cl) | 50.6 |
| 1–4 (Ge–N) | 2.17 (2.07) | 7–6–8 (Cl–Ge–Cl) | 93.3 |
| 1–5 (Ge–N) | 2.19 (2.07) | 9–6–10 (N–Ge···N) | 66.0 |
| 3–6 (Ge···Cl) | 3.12 | 2–1–3 (Cl–Ge–Cl) | 197.6[b] (191.1[a]) |
| 6–7 (Ge–Cl) | 2.35 | 4–1–5 (N–Ge–N) | 74.4 (77.5) |
| 1–7 (Ge···Cl) | 3.42 | | |
| 1–6 ( Ge···Ge) | 4.39 | | |
| 6–8 ( Ge–Cl) | 2.48 | | |
| 6–10 (Ge–N) | 2.54 | | |
| 6–9 (Ge–N) | 2.41 | | |

[a] The angle in the crystal structure is 168.9°, corresponding to 360 – 168.9 = 191.1°; [b] These angles correspond to the Cl–Ge–Cl angle in the input monomer model increasing progressively beyond 180°.

Mulliken charges:

| | | | | |
|---|---|---|---|---|
| 1: 0.627 | 2: –0.494 | 3: –0.581 | 4: –0.318 | 5: –0.300 |
| 6: 0.636 | 7: –0.416 | 8: –0.513 | 9: –0.289 | 10: –0.260 |

**Fig. S1**. Computed B3LYP/cc-pvDZ structure of [$GeCl_2$(2,2´-bipy)]$_3$

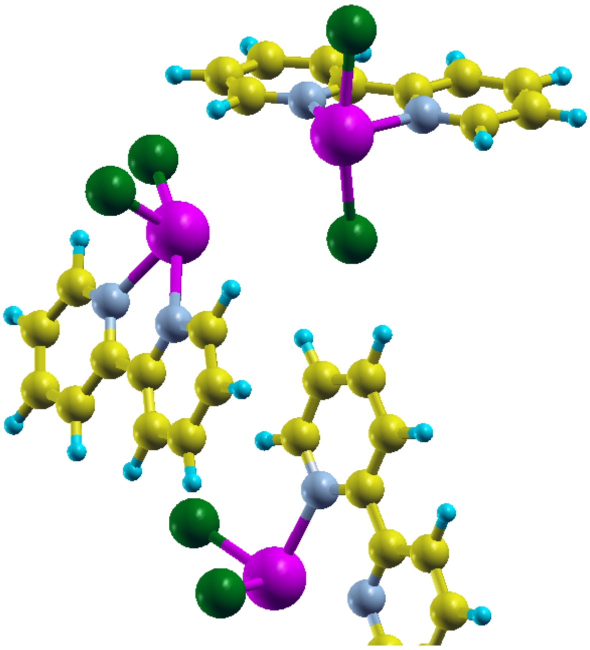


**Table S5** Comparison of some selected bond lengths (Å) and angles (°) of [$GeCl_2$(2,2´-bipy)]$_3$ and measured for the crystal structure in this work (in brackets). Comparison has been made between the Cl–Ge–Cl 'linear' part in the computed structure and the monomer unit in the crystal structure (see text).

| | | | |
|---|---|---|---|
| 1–2 (Ge–Cl) | 2.42 (2.45) | 2–1–6 (Cl–Ge···Ge) | 127.7 |
| 1–3 (Ge–Cl) | 2.69 (2.72) | 1–6–7 (Ge···Ge–Cl) | 76.4 |
| 1–4 (Ge–N) | 2.14 (2.07) | 7–6–8 (Cl–Ge–Cl) | 94.7 |
| 1–5 (Ge–N) | 2.16 (2.07) | 9–6–10 (N–Ge···N) | 69.2 |
| 3–6 (Ge···Cl) | 4.75 | 2–1–3 (Cl–Ge–Cl) | 196.3[b] (191.1[a]) |
| 6–7 (Ge–Cl) | 2.31 | 4–1–5 (N–Ge–N) | 75.1 (77.5) |
| 1–7 (Ge···Cl) | 5.86 | | |
| 1–6 ( Ge···Ge) | 5.96 | | |
| 6–8 ( Ge–Cl) | 2.45 | | |
| 6–10 (Ge···N) | 2.45 | | |
| 6–9 (Ge–N) | 2.25 | | |

[a] The angle in the crystal structure is 168.9°, corresponding to 360 – 168.9 = 191.1°; [b] These angles correspond to the Cl–Ge–Cl angle in the input monomer model increasing progressively beyond 180°.

Mulliken charges:

| | | | | |
|---|---|---|---|---|
| 1: 0.598 | 2: –0.489 | 3: –0.608 | 4: –0.314 | 5: –0.303 |
| 6: 0.560 | 7: –0.410 | 8: –0.496 | 9: –0.318 | 10: –0.276 |

**Fig. S2** Computed RIDFT/BP86 structure of [$GeCl_2$(2,2´-bipy)]$_4$

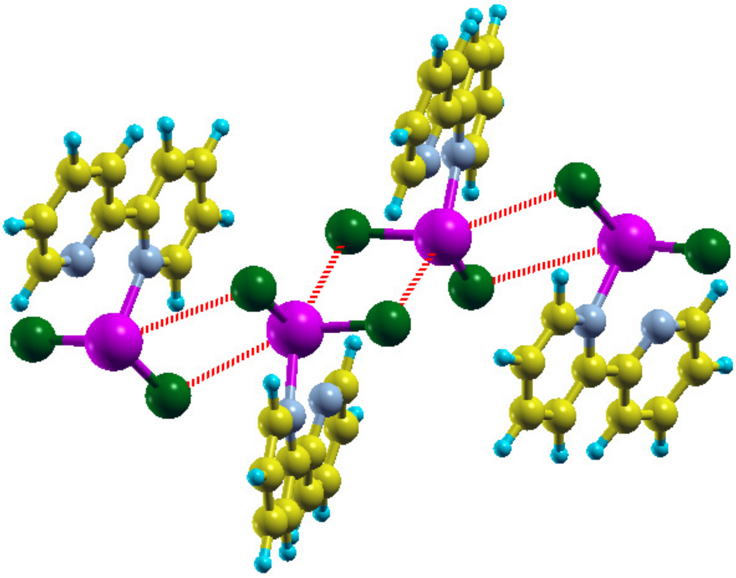
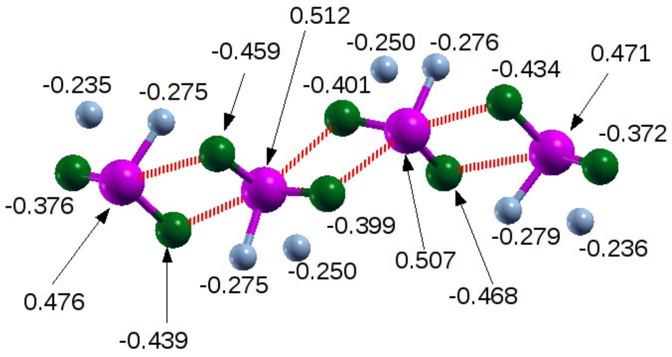


**Fig. S3** Mullikan (top) and Natural (bottom) charges computed for the $[GeCl_2(2,2'\text{-bipy})]_4$ tetramer unit.

Mulliken charges



Natural charges

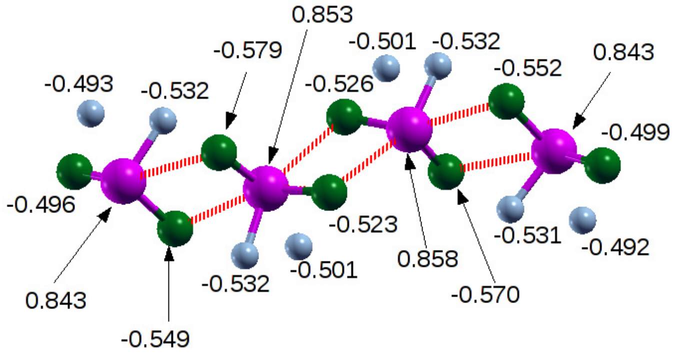
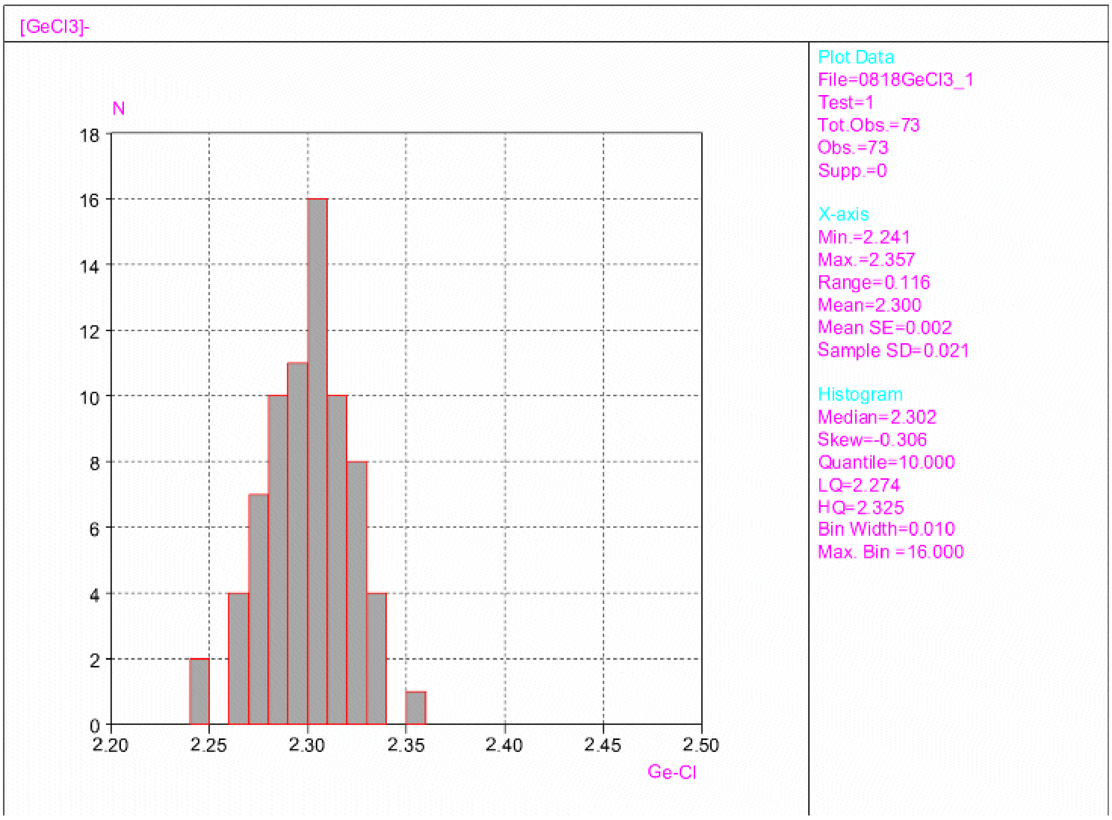


**Table S6** [GeBr(pmdta)][$GeBr_3$] crystallographic data

| Compound | [GeBr(pmdta)][$GeBr_3$] |
|---|---|
| Formula | $C_9H_{23}Br_4Ge_2N_3$ |
| *M* | 638.12 |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ (no. 14) |
| *a* /Å | 6.6108(5) |
| *b* /Å | 14.143(3) |
| *c* /Å | 20.132(4) |
| α /° | 90 |
| β /° | 91.332(10) |
| γ /° | 90 |
| $U$ /Å$^3$ | 1881.8(6) |
| *Z* | 4 |
| μ(Mo-Kα) /mm$^{-1}$ | 11.678 |
| Total no. reflections | 17148 |
| $R_{int}$ | 0.0 |
| Unique reflections | 17148 |
| No. of parameters | 169 |
| $R_1$ [$I_o > 2\sigma(I_o)$] | 0.096 |
| $R_1$[all data] | 0.166 |
| $wR_2$ [$I_o > 2\sigma(I_o)$] | 0.185 |
| w$R_2$ [all data] | 0.225 |

The crystals of [GeBr(pmdta)][$GeBr_3$] were twinned. A structure solution was obtained ignoring the twinning problem that looked chemically correct but the difference electron-density map showed a few large peaks (ca. 6 e Å$^{-3}$) close (ca. 1 Å) to the heavy atoms. The diffractometer software was used to index the twin with two components allowing for overlapping and non-overlapping reflections to produce an HKLF 5 type file for use with SHELXL. Use of this and a BASF command gave a better fit to the data and much reduced peaks in the e/d map.

**Fig. S4.** Histogram summarising the Ge–Cl distances in crystallographically characterised compounds of $[GeCl_3]^-$ from the CSD



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HQ=2.325
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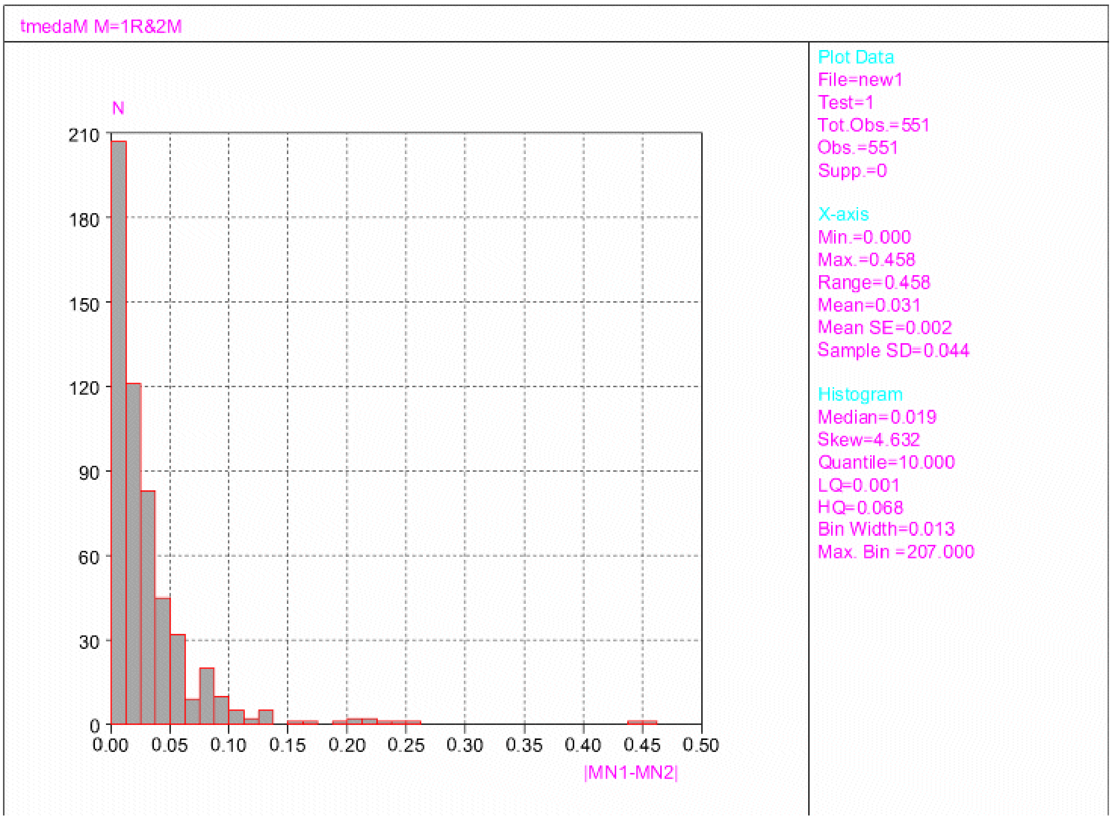
**Fig. S5.** Histogram summarising Δ(M–N) in structurally characterised complexes containing a 1st row transition metal or an element from Groups 13–15 with a chelating $Me_2N(CH_2)_2NMe_2$ ligand from the CSD



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Sample SD=0.044

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LQ=0.001
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