Synthesis and Crystal Structure of a Chloro-Bridged Dinuclear Germanium(IV) Heterocoordinate Complex with 5,14-Dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine

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A novel chloro-bridged dinuclear germanium(IV) complex with 5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*]-[1,4,8,11]tetraazacyclotetradecine has been synthesized and its crystal structure shows an unsymmetrical heterocoordinate dimer which has a five-coordinate square pyramid and a six-coordinate octahedron.

5,14-Dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]-tetraazacyclotetradecine (H_2tmtaa), a versatile ligand environment for transition and main group metal chemistry, has stimulated continuing interest in a wide range of chemical areas for nearly thirty years.[1] Because of its non-planar and saddle-shaped conformation, a limited number of investigations on its macromolecular characteristics were reported. On the other hand, not only dimers,[2] but also polymers[3] of other analogous macrocyclic ligands, porphyrin and phthalocyanine, were investigated widely due to their bigger N_4 coordination cavity 'hole size' and planar conformations compared with H_2tmtaa. However, several types of tmtaa dimers were studied till now. They indicate metal–metal bonded conformation (I),[4] N_4 plane–metal–N_4 plane octacoordinate sandwich conformation (II)[5] and metal–X–metal (X=O, S, CH_2, N) bridged conformation (III)[6–9] (Figure 1). Although germanium(II) complexes of H_2tmtaa were investigated,[10] no further structure characteristics relating to germanium(IV) tmtaa complexes were described in the literature. In this paper, we describe the synthesis and structural characterization of a Ge(IV)–Cl–Ge(IV)–Cl tmtaa dimer containing five- and six-coordinate configurations (Figure 1, **IV**). Its structural characteristics inspire us to attempt to do some investigation into macromolecule of H_2tmtaa in future.

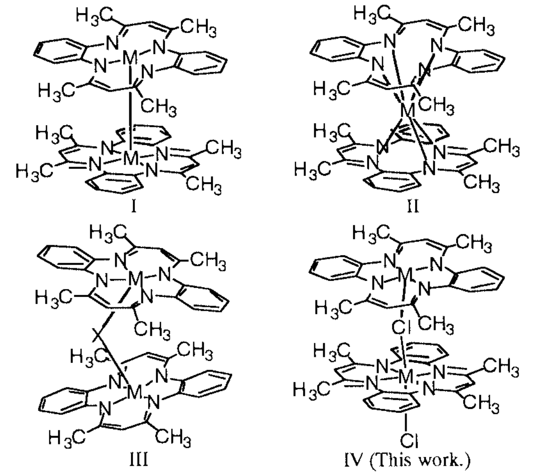

Figure 1. Type I, II, III, and IV tmtaa dimers. M: metal; X=O, S, CH_2, N.

The Ge(tmtaa)Cl_2 **1** was prepared as reported earlier.[11] The reaction between **1** and 3-nitrobenzyl alcohol was carried out in chloroform containing a small amount of triethylamine under a nitrogen atmosphere. Red powder was collected after evaporating the reaction solution. Red crystals of [{Ge(tmtaa)}(μ-Cl){Ge(tmtaa)Cl}](Cl)[$C_6H_4(NO_2)CH_2O$]·CH_3CN **2** were obtained by recrystallization from acetonitrile.[12] The crystals were air- and moisture-stable. After being put in air for about two weeks, one single crystal was selected for X-ray crystal structure analysis.[13] The crystals contain one [{Ge(tmtaa)}(μ-Cl){Ge(tmtaa)Cl}]$^{2+}$ cation, one chloro anion (near to five-coordinate unit, the nearest atom-to-atom distance to the cation is 3.46 Å), one 3-nitrobenzyloxy anion (facing to five-coordinate Ge, the nearest atom-to-atom distance to the cation is 3.35 Å) and one acetonitrile molecule. Figure 2 shows the crystal structure of [{Ge(tmtaa)}(μ-Cl){Ge(tmtaa)Cl}]$^{2+}$ cation.

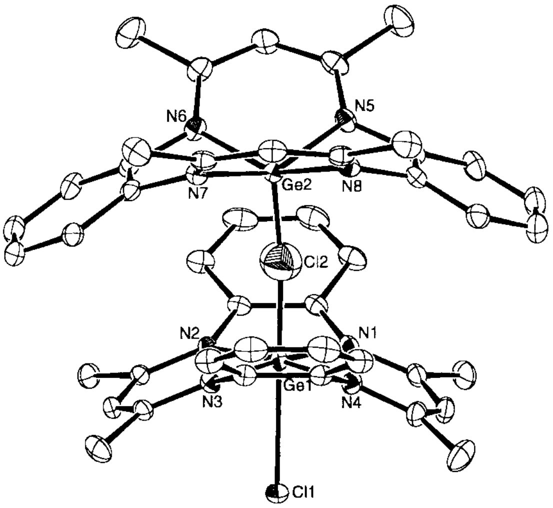

Figure 2. ORTEP view of [{Ge(tmtaa)}(μ-Cl){Ge(tmtaa)Cl}]$^{2+}$ cation with thermal ellipsoids shown at the 20% probability level. Selected bond distances (Å) and angles (°): Ge(1)-Cl(1) 2.433(1), Ge(1)-Cl(2) 1.810(3), Ge(1)-N(1) 1.944(3), Ge(1)-N(2) 1.935(3), Ge(1)-N(3) 1.931(3), Ge(1)-N(4) 1.942(3), Ge(2)-Cl(2) 1.686(3), Ge(2)-N(5) 1.939(3), Ge(2)-N(6) 1.936(4), Ge(2)-N(7) 1.941(3), Ge(2)-N(8) 1.935(3); Cl(1)-Ge(1)-Cl(2) 177.5(1), Ge(1)-Cl(2)-Ge(2) 171.0(2), Cl(1)-Ge(1)-N(1) 88.0(1), Cl(1)-Ge(1)-N(2) 87.0(1), Cl(1)-Ge(1)-N(3) 87.5(1), Cl(1)-Ge(1)-N(4) 87.9(1), Cl(2)-Ge(1)-N(1) 90.1(1), Cl(2)-Ge(1)-N(2) 91.2(1), Cl(2)-Ge(1)-N(3) 94.4(1), Cl(2)-Ge(1)-N(4) 93.9(1), Cl(2)-Ge(2)-N(5) 103.3(2), Cl(2)-Ge(2)-N(6) 106.2(2), Cl(2)-Ge(2)-N(7) 104.8(1), Cl(2)-Ge(2)-N(8) 101.6(2), N(1)-Ge(1)-N(3) 175.5(1), N(2)-Ge(1)-N(4) 174.9(1), N(6)-Ge(2)-N(8) 152.1(2), N(5)-Ge(2)-N(7) 151.8(2).

3-Nitrobenzyl alcohol was selected to react with six-coordinate dichloro germanium complex **1** to form a chloro-bridged heterocoordinate dinuclear complex **2**. This is very different from those oxidative addition reactions in which two four-coordinate complexes were connected by an oxidative agent to form a dinuclear complex.[6–8]

It is very interesting that the structure of [{Ge(tmtaa)}(μ-Cl){Ge(tmtaa)Cl}]$^{2+}$ cation has no symmetry, revealing one five- and one six-coordinate macrocyclic units. This is also different from O, S, CH_2-bridged tmtaa dimers which have two five-coordinate configurations and C_2 symmetry, with the C_2 axis passing through the bridged atoms.[6–8]

The distance between bridged chloro and five-coordinate germanium (1.686(3) Å) is about 0.124 Å shorter than that between bridged chloro and six-coordinate germanium (1.810(3) Å). Both of them are much shorter than bond length of six-coordinate germanium atom and the mono chloro atom (2.433(1) Å) in the cation. Two germanium atoms are all displaced from the N_4 planes toward the benzenoid faces of the saddle-shaped tmtaa ligands, as commonly observed in other six- and five-coordinate tmtaa complexes. However, because of the steric influence, the displacements are 0.468(2) Å in the five-coordinate unit and 0.082(2) Å in the six-coordinate unit. The average Ge–N bond lengths in two units are all about 1.938 Å and do not depend on coordination numbers and displacements of germanium atoms from the N_4 planes. This suggests that two germanium atoms are in the same oxidation states (+4) and that Ge dπ and N pπ orbital interaction are analogous. Parameters characterizing the Ge(IV)–Cl–Ge(IV) bridge are of considerable interest. The angle of Ge–Cl–Ge is 171.0(2)° and is significantly bigger than that of other analogous tmtaa bridging configurations (155.0(8)° in Ti–O–Ti,[6] 142.75° in Fe–O–Fe,[6] 126.3(1)° in Fe–S–Fe[7] and 122.5(3)° in Sn–CH_2–Sn[8]). This enhances the linear configuration of the three atoms and makes two tmtaa ligands in the complex orientation at an angle of 6.534(0.110)° between the two N_4 planes which are almost parallel to each other. Furthermore, two tmtaa ligands are rotated with respect to each other by about 90° and two groups of benzenoid rings in two tmtaa ligands are in the face-to-face configuration, which are similar to Type I and II dinuclear complexes.[4,5] It is clear that the dimer is in the most stable state when it adopts this configuration.

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References and Notes

1 P. Mountford, *Chem. Soc. Rev.*, **27**, 105 (1998).

2 D. A. Summerville and I. A. Cohen, *J. Am. Chem. Soc.*, **98**, 1747 (1976); A. D. Cian, M. Moussavi, J. Fischer, and R. Weiss, *Inorg. Chem.*, **24**, 3162 (1985); M. Moussavi, A. D. Cian, J. Fischer, and R. Weiss, *Inorg. Chem.*, **27**, 1287 (1988).

3 C. W. Dirk, T. Inabe, K. F. Schoch, Jr., and T. J. Marks, *J. Am. Chem. Soc.*, **105**, 1539 (1983).

4 D. Mandon, J. Giraudon, L. Toupet, J. Sala-Pala, and J. E. Guerchais, *J. Am. Chem. Soc.*, **109**, 3490 (1987); J. J. H. Edema, S. Gambarotta, P. Sluis, W. J. J. Smeets, and A. L. Spek, *Inorg. Chem.*, **28**, 3784 (1989); F. A. Cotton, J. Czuchajowska, and X. Feng, *Inorg. Chem.*, **29**, 4329 (1990); F. A. Cotton, and J. Czuchajowska, *Polyhedron*, **9**, 2553 (1990); J. Hesschenbrouck, E. Solari, R. Scopelliti, C. Floriani, and N. Re, *J. Organomet. Chem.*, **596**, 77 (2000); J. Magull and A. Simon, *Z. Anorg. Allg. Chem.*, **615**, 81 (1992).

5 S. D. Angelis, E. Solari, E. Gallo, C. Floriani, A. Chiesi-Villa, and C. Rizzoli, *Inorg. Chem.*, **31**, 2520 (1992); Z. Wang, K. Sakata, and M. Hashimoto, *Polyhedron*, **17**, 4451 (1998); Z. Wang, N. Hu, K. Sakata, and M. Hashimoto, *J. Chem. Soc., Dalton Trans.*, **1999**, 1695; J. Magull and A. Simon, *Z. Anorg. Allg. Chem.*, **615**, 77 (1992).

6 M. C. Weiss, and V. L. Goedken, *Inorg. Chem.*, **18**, 819 (1979); C. E. Housmekerides, D. L. Ramage, C. M. Kretz, J. T. Shontz, R. S. Pilato, G. L. Geoffroy, A. L. Rheingold, and B. S. Haggerty, *Inorg. Chem.*, **31**, 4453 (1992).

7 P. Berno, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Chem. Soc., Dalton Trans.*, **1989**, 551.

8 W. J. Belcher, P. J. Brothers, A. P. Meredith, C. E. F. Rickard, and D. C. Ware, *J. Chem. Soc., Dalton Trans.*, **1999**, 2833.

9 V. L. Goedken and J. A. Ladd, *Chem. Commun.*, **1981**, 910.

10 D. A. Atwood, V. O. Atwood, A. H. Cowley, J. L. Atwood, and E. Roman, *Inorg. Chem.*, **31**, 3871 (1992); D. A. Atwood, V. O. Atwood, A. H. Cowley, H. R. Gobran, and J. L. Atwood, *Inorg. Chem.*, **32**, 4671 (1993).

11 W. J. Belcher, P. J. Brothers, M. V. Land, C. E. F. Rickard, and D. C. Ware, *J. Chem. Soc., Dalton Trans.*, **1993**, 2101.

12 The yield of [{Ge(tmtaa)}(μ-Cl){Ge(tmtaa)Cl}](Cl)[$C_6H_4(NO_2)CH_2O$]·CH_3CN is 28% (Found: C, 56.57; H, 5.00; N, 12.67%. Calcd for $C_{53}H_{53}Cl_3Ge_2N_{10}O_3$: C, 56.35; H, 4.73; N, 12.40%). λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1})($CHCl_3$) 272 (28100), 380 (48200), 431 (20700). ν_{max} (KBr)/cm^{-1} 1581s, 1548s, 1471s and 1416s (C=N, C=C), 1548s and 1372s (N=O). ^{1}H NMR ($CDCl_3$, 400 MHz, 293K) δ/ppm $C_6H_4(NO_2)CH_2O$: 8.23 (s, 1H, 2-H), 8.13 (d, J = 7.2 Hz, 1H, 4-H), 7.69 (d, J = 6.1 Hz, 1H, 6-H), 7.52 (dd, J = 7.2, 6.1 Hz, 1H, 5-H), 4.79 (s, 2H, CH_2); [{Ge(tmtaa)}(μ-Cl)-{Ge(tmtaa)Cl}]: 7.19, 7.15 (m, m, 8H, 8H, CH_4), 5.42 (br, s, 4H, CH), 2.53 (s, 24H, CH_3); 2.00 (s, 3H, CH_3CN). Λ_m(CH_3NO_2, 298 K): 135.6 s cm^2 mol^{-1}.

13 Crystal data: [{Ge(tmtaa)}(μ-Cl){Ge(tmtaa)Cl}](Cl)[$C_6H_4(NO_2)CH_2O$]·CH_3CN, $C_{53}H_{53}Cl_3Ge_2N_{10}O_3$, M_r = 1129.61; red prism, 0.40 × 0.80 × 0.80 mm, monoclinic, space group $P2_1$/n, a = 12.862(2), b = 21.089(3), c = 18.797(2) Å, β = 98.09(1)°, V = 5047(1) Å^3, Z = 4, D_c = 1.486 g/cm^3, μ = 1.404 mm^{-1}. Using Mo Kα radiation (λ = 0.71069 Å) at 293 K, a total of 12438 reflections was collected ($2\theta_{max}$ = 55.0°), of which 11591 were independent. Refinement converged to R_1 = 0.055 [$I > 2\sigma(I)$] and R = 0.095, R_w = 0.198 (all data).