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Communications

Macrocyclic ($C_{22}H_{22}N_4$) Complexes of Germanium(II), Tin(II), Gallium(III), and Indium(III). Main Group Functionalities in Unusual Environments

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Main group moieties with unusual coordination numbers, oxidation states, and geometries have been stabilized both by the deployment of bulky ligands and also by incorporation into the coordination spheres of d- and f-block complexes. Interestingly, much less use has been made of macrocyclic ligands to achieve the foregoing objectives. Porphyrin and phthalocyanine complexes of the main group elements constitute well-recognized classes of compound. However, there is a paucity of information regarding the usefulness of other tetraaza macrocycles such as the dibenzotetramethyltetraaza[14]annulene (tmtaa) ligand.[1] Distinctive features of tmtaa include the modest core size (1.902 Å), the unusual saddle-shaped geometry, and the enforced cis disposition of reactive sites, X, in $M(tmtaa)X_2$ derivatives. We, therefore, reasoned that unusual reactivity patterns and coordination geometries might stem from the incorporation of main group fragments into this particular macrocycle.[2]

Treatment of the dilithium salt of tmtaa[1] with an equimolar quantity of $GeCl_2$·dioxane in Et_2O at −78 °C resulted, after workup and recrystallization from toluene, in a 68% yield of a red crystalline compound of composition Ge(tmtaa) (**1**).[5] ^1H NMR spectral data ($CDCl_3$ solution) suggested (a) that the Ge is bonded symmetrically to the four N atoms of the macrocycle and (b) that toluene is present in the crystal lattice. These indications were confirmed by an X-ray analysis.[6] Pairs of molecules of **1** (Figure 1) are separated by a disordered toluene molecule. The geometry of the GeN_4 subunit is square planar, and the Ge atom is situated 0.909 (4) Å above the N_4 plane; the tmtaa ligand adopts the customary saddle-type conformation. To our knowledge, **1** represents the first example of a square pyramidal Ge(II) complex. It is also noteworthy that unligated germanium(II) porphyrin and phthalocyanine compounds are not known.[7] The mean Ge–N bond distance in **1** is 2.107 (4) Å. We are aware of no precedents for M(II)–N bond distances in $M^{II}N_4$ systems (M = Ge, Sn).

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(1) For an excellent review, see: Cotton, F. A.; Czuchajowska, J. *Polyhedron* **1990**, *9*, 2553.

(2) Previous reports of main group/tmtaa complexes are confined to some interesting Al(III) derivatives[3] and one structurally uncharacterized Zn(II) compound.[4]

(3) Goedken, V. L.; Ito, H.; Ito, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1453.

(4) Neves, D. R.; Dabrawiak, J. C. *Inorg. Chem.* **1976**, *15*, 129.

(5) ^1H NMR (300.15 MHz, $CDCl_3$, 295 K, TMS external): **1**, δ 2.338 (s, 12 H, CH_3), 4.861 (s, 2 H, H), 6.972 (s, 8 H, C_6H_4); **5**, δ 2.242 (s, 12 H, CH_3), 4.902 (s, 2 H, H), 7.128 (s, 8 H, C_6H_4). ^1H NMR (300.15 MHz, C_6D_6, 295 K, TMS external): **2**, δ 1.905 (s, 12 H, CH_3), 5.074 (s, 2 H, H), 6.942 (s, 8 H, C_6H_4); **3**, δ 1.859 (s, 12 H, CH_3), 4.608 (s, 2 H, H), 6.873 (s, 8 H, C_6H_4); **4**, δ 1.749 (s, 12 H, CH_3), 4.480 (s, 2 H, H), 6.945 (s, 8 H, C_6H_4); **6**, δ 1.849 (s, 12 H, CH_3), 4.505 (s, 2 H, H), 6.794 (s, 8 H, C_6H_4); **7**, δ −0.197 (s, 3 H, In–CH_3), 1.925 (s, 12 H, CH_3), 4.572 (s, 2 H, H), 6.864 (s, 8 H, C_6H_4). IR: **2**, ν(CO) 2050 vs (A_1), 1967 s (E), 1951 vs (A_1) cm^{-1}; **4** ν(CO) 2045 vs (A_1), 1971 s (E), 1965 vs (A_1) cm^{-1}. MS (EI, 70 eV): **1**, *m/e* 412–419 (M^+); **2**, *m/e* 602–612 (M^+); **3**, *m/e* 454–467 (M^+); **4**, *m/e* 646–660 (M^+); **5**, *m/e* 446–451 (M^+); **6**, *m/e* 490–495 (M^+); **7**, *m/e* 470–475 (M^+). HRMS (EI): **2**, calcd for $C_{27}H_{22}N_4O_5Cr_1Ge_1$ (M^+) *m/e* 604.023 780, found *m/e* 604.021 771; **3**, calcd for $C_{22}H_{22}N_4Sn_1$ (M^+) *m/e* 458.086 190, found *m/e* 458.086 968; **4** calcd for $C_{27}H_{22}N_4O_5Cr_1Sn_1$ (M^+) *m/e* 650.001 237 3, found *m/e* 649.999 911; **6**, calcd for $C_{22}H_{22}N_4Cl_1In_1$ (M^+) *m/e* 492.057 175, found *m/e* 492.056 612; **7**, calcd for $C_{23}H_{25}N_4In_1$ (M^+) *m/e* 472.111 797, found *m/e* 472.112 069. Mp: **1**, 250–264 °C dec; **2**, 270–273 °C; **3**, 314–317 °C dec; **4**, 235–242 °C dec; **5**, >360 °C; **6**, 212–225 °C dec; **7**, 173–178 °C dec.

(6) Crystal data for the compounds are as follows **1** ($C_{22}H_{22}N_4Ge$): triclinic, $P1$, with $a = 8.366$ (1) Å, $b = 11.735$ (2) Å, $c = 12.240$ (3) Å, $\alpha = 75.26$ (2)°, $\beta = 77.29$ (1)°, $\gamma = 71.53$ (2)°, $V = 1088$ (1) Å^3, $Z = 2$, $d_{calcd} = 1.401$ g cm^{-3}, μ(Mo Kα) = 14.24 cm^{-1}. **3** ($C_{22}H_{22}N_4Sn$): monoclinic, $P2_1/n$, with $\alpha = 14.994$ (2) Å, $b = 8.205$ (1) Å, $c = 15.582$ (1) Å, $\beta = 98.60$ (1)°, $V = 1895$ (1) Å^3, $Z = 4$, $d_{calcd} = 1.62$ g cm^{-3}, μ(Mo Kα) = 12.6 cm^{-1}. **5** ($C_{22}H_{22}N_4GaCl$): monoclinic, $P2_1/c$, with $a = 9.055$ (2) Å, $b = 23.204$ (5) Å, $c = 13.194$ (4) Å, $\beta = 92.58$ (1)°, $V = 2769.3$ (3) Å^3, $Z = 4$, $d_{calcd} = 1.360$ g cm^{-3}, μ(Mo Kα) = 11.16 cm^{-1}. Totals of 3528 (**1**), 2013 (**2**), and 4391 (**5**) reflections were collected at 298 K on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å) and the $\theta/2\theta$ scan mode. The structures of **1** and **5** were solved using direct methods. The structure of **3** was solved by Patterson methods. The three structures were refined (full matrix, least squares) to final *R* values of 0.0456 (**1**), 0.066 (**3**), and 0.0579 (**5**).

(7) Kadish, K. M.; Swistak, C.; Boisselier-Cocolios, B.; Barbe, J. M.; Guilard, R. *Inorg. Chem.* **1986**, *25*, 4336.

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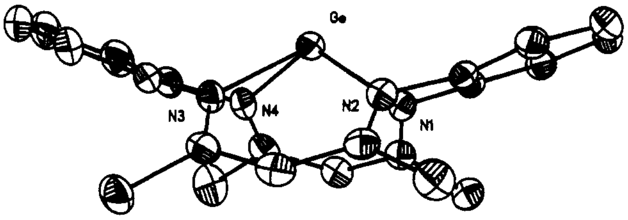

Figure 1. View of the crystal structure (ORTEP) of **1**. Important bond distances (Å) and angles (deg): Ge–N(1) = 2.097 (4) (Sn–N(1) = 2.28 (1)), Ge–N(2) = 2.110 (4) (Sn–N(2) = 2.26 (1)), Ge–N(3) = 2.104 (4) (Sn–N(3) = 2.26 (2)), Ge–N(4) = 2.117 (4) (Sn–N(4) = 2.27 (1)); N(1)–Ge–N(2) = 75.2 (1) (N(1)–Sn–N(2) = 80.1 (5)), N(2)–Ge–N(3) = 82.9 (2) (N(2)–Sn–N(3) = 70.5 (5)), N(3)–Ge–N(4) = 74.9 (2) (N(3)–Sn–N(4) = 79.6 (5)), N(4)–Ge–N(1) = 83.95 (14) (N(4)–Sn–N(1) = 70.2 (5)). The values in parentheses are the metric parameters for the analogous tin compound, **3**.

However, for both **1** and the analogous tin compound **3** (see below), the M–N bond distances may be lengthened by repulsions involving the M(II) lone pair and the electron-rich nature of the tmtaa ligand.

The availability of **1** provided an opportunity to examine the reactivity of a Ge(II) center in an unusual environment. Specifically, facile reaction of **1** with electrophiles was anticipated on the basis of (a) accessibility of the Ge lone pair and (b) N$\rightarrow$Ge dative bonding. Compound **1** undergoes a virtually instantaneous reaction with (THF)Cr(CO)$_5$ at 25 °C to afford (tmtaa)GeCr(CO)$_5$ (**2**).[5] It has not proved possible to isolate crystals of **2** suitable for X-ray analysis; however, the similarity of the NMR spectra of **1** and **2** suggests that the square pyramidal geometry at Ge is retained. Moreover, the pattern of IR-active CO stretching frequencies is consonant with C_{4v} local symmetry at Cr.

The Sn(II) complex Sn(tmtaa) (**3**) has been prepared in 56% yield via a metathetical procedure similar to that employed for the synthesis of **1**. An X-ray analysis[6] reveals that, as anticipated on the basis of NMR data,[5] **3** possesses a similar structure to that of **1**. The most remarkable aspect of the structure is the displacement of the Sn atom from the N$_4$ plane (1.15 (1) Å). Compound **3** is also very reactive toward electrophiles; e.g., treatment with (THF)Cr(CO)$_5$ readily affords the intermetallic derivative (tmtaa)SnCr(CO)$_5$ (**4**).[5]

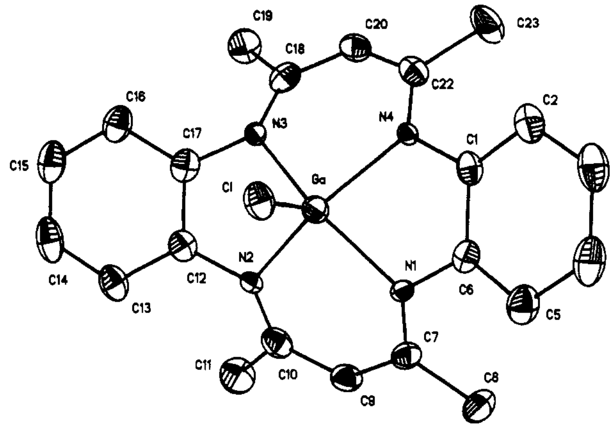

Figure 2. View of the crystal structure (ORTEP) of **5**. Important bond distances (Å) and angles (deg): Ga–Cl = 2.222 (2), Ga–N(1) = 1.980 (4), Ga–N(2) = 1.992 (4), Ga–N(3) = 1.987 (4), Ga–N(4) = 1.991 (4); N(1)–Ga–N(2) = 92.4 (2), N(2)–Ga–N(3) = 80.7 (2), N(3)–Ga–N(4) = 92.2 (2), N(4)–Ga–N(1) = 81.3 (2).

In marked contrast to the group 14 chemistry described above, ligation of group 13 moieties by tmtaa results in significantly dimished reactivity. The reaction of MCl$_3$ (M = Ga, In) with Li$_2$(tmtaa) in THF solution at −78 °C, followed by recrystallization from benzene or toluene, afforded orange crystals of Ga(tmtaa)Cl (**5**) and In(tmtaa)Cl (**6**) in yields of 54 and 58%, respectively. An X-ray crystal structure of **5** (Figure 2) revealed that the Ga atom possesses an unusual[8] five-coordinate square pyramidal geometry. The N$_4$–metal distance in **5** (0.480 (4) Å) is considerably shorter than those in **1** and **2**. Normally, Ga–Cl and In–Cl bonds are very susceptible to nucleophilic attack. However, **5** fails to react with LiH, Li[BEt$_4$H], MeLi, or Na[Co(CO)$_4$]. Likewise, **5** does not undergo reductive coupling with Na/K or Na[naphthalenide]. However, **6** will undergo a slow reaction with MeLi to afford In(tmtaa)Me (**7**).[5]

Acknowledgment. We thank the National Science Foundation and the Robert A. Welch Foundation for generous financial support.

Supplementary Material Available: Tables of bond distances, bond angles, atomic coordinates, and thermal parameters and ORTEP structures for **1**, **3**, and **5** (21 pages). Ordering information is given on any current masthead page.

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(8) Atwood, J. L.; Bott, S. G.; Jones, C.; Raston, C. L. *Inorg. Chem.* **1991**, *30*, 4868.