ChemComm

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2014, **50**, 7979

Received 11th February 2014,
Accepted 4th June 2014

DOI: 10.1039/c4cc01109k

www.rsc.org/chemcomm

Exploring structural trends for complexes of $Me_2E(OSO_2CF_3)_2$ (E = Si, Ge, Sn) with pyridine derivatives†

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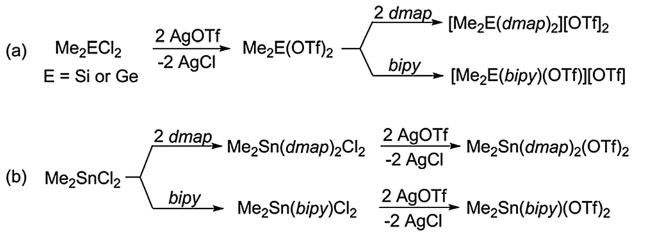
The coordination of $Me_2E(OTf)_2$ (E = Si, Ge, Sn) acceptors by dmap or 2,2′-bipy furnishes two series of complexes which exhibit distinct structural trends that correlate with the covalent radii of the tetrael elements, and which contrast complexes of these ligands with EX_4 (X = Cl or Br).

The formation of donor–acceptor complexes has been applied extensively to describe the chemistry of the transition metals and the group 13 elements.[1] Heavier p-block elements also engage an array of ligand types, but coordination chemistry of the lighter p-block elements is apparently limited by atomic size and acceptor orbital availability. Consequently, there are significant differences in the classification of the structure and bonding for the group 14 elements. For example, a vast array of coordination complexes has been established for compounds of tin,[2] while compounds involving silicon or carbon as acceptors are rare. Nevertheless, silicon, germanium and tin-tetrahalides (EX_4; E = Si, Ge, Sn; X = Cl or Br) are all sufficiently Lewis acidic to form isolable octahedral complexes of the general formula *trans*-EX_4L_2 (E = Si, Ge, Sn; L = PMe_3 or pyridine)[3–8] with monodentate donors, while chelating ligands give *cis* configurations.[9–11] Interestingly, despite previous reports of complexes of the related acceptor Me_2SnCl_2,[12,13] analogous compounds have not been observed for Me_2SiCl_2 or Me_2GeCl_2. Recognizing that exchange of halide substituents at a potential tetrael acceptor centre for weakly-coordinating anions can facilitate coordination of neutral ligands,[3,14–18] we have studied complexes of $Me_2E(OTf)_2$ (E = Si, Ge, Sn; OTf = OSO_2CF_3, trifluoromethanesulfonyl) with pyridine derivative ligands. Herein we describe structural trends which evolve the coordination chemistry of the tetrael elements, and have implications for the p-block elements in general.



Scheme 1 Synthesis of dmap and bipy complexes of $Me_2E(OTf)_2$ (E = Si, Ge or Sn).

Two series of complexes with generic formulae $Me_2E(dmap)_2(OTf)_2$ and $Me_2E(bipy)(OTf)_2$ [E = Si, Ge, Sn;[19] dmap = 4-(dimethylamino)pyridine, bipy = 2,2′-bipyridine], were prepared by a combination of halide abstraction and donor coordination steps. For E = Si or Ge, the complexes were prepared in high yield through treatment of Me_2ECl_2 with AgOTf, to generate $Me_2E(OTf)_2$ *in situ*, and subsequently with dmap or 2,2′-bipy at −30 °C (Scheme 1a). In contrast, Me_2SnCl_2 was found to be unreactive towards AgOTf at ambient temperature, thus the tin complexes were accessed *via* halide abstraction from the *in situ* generated adducts $Me_2Sn(dmap)_2Cl_2$ and $Me_2Sn(bipy)Cl_2$[11] in MeCN (Scheme 1b).

All three dmap complexes were isolated as colourless crystalline solids, and characterised by multinuclear NMR spectroscopy, elemental microanalysis and X-ray crystallography. In the solid-state, $Me_2Si(dmap)_2(OTf)_2$ contains a distinct $[Me_2Si(dmap)_2]^{2+}$ moiety in the asymmetric unit, along with two triflate anions and two molecules of CH_2Cl_2 (Fig. 1a). The silicon centre adopts a distorted tetrahedral geometry [105.3 (N–Si–N); 115.7° (C–Si–C); Average: 109.4°] with the two N–Si bonds averaging 1.80 Å [Σ_{CR} = 1.87 Å].[20] The interion Si–O distances are greater than the sum of the covalent radii for Si and O [Si–O = 3.476(3) and 3.819(3) Å; Σ_{CR} = 1.79 Å], and we interpret the compound as a salt containing an Me_2Si^{2+} moiety stabilised by two dmap ligands. In contrast, the solid-state structure of $Me_2Sn(dmap)_2(OTf)_2$ evidences a hexacoordinate Sn centre with two *cis*-configured dmap ligands (N–Sn–N = 87.9°), two *cis*-configured triflate substituents (O–Sn–O = 100.5°) and two *trans*-configured methyl substituents (C–Sn–C = 158.6°) (Fig. 1c).

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† Electronic supplementary information (ESI) available: Details of the synthesis and characterisation of all six described complexes, and further crystallographic parameters. CCDC 977497–977502. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc01109k

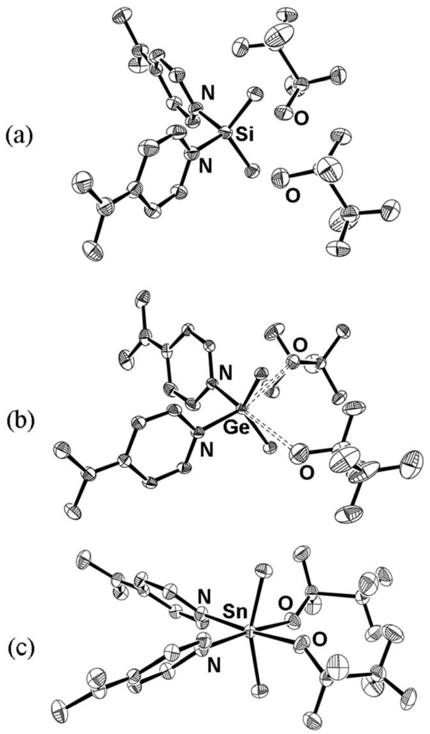

Fig. 1 Solid-state structures of (a) $[Me_2Si(dmap)_2][OTf]_2$, (b) $[Me_2Ge(dmap)_2][OTf]_2$ and (c) $Me_2Sn(dmap)_2(OTf)_2$. All hydrogen atoms and solvent molecules are omitted for clarity.

Both triflate anions strongly coordinate to the Sn centre, which exhibits a distorted octahedral geometry with relatively long Sn–OTf bonds [2.420(1) Å; Σ_{CR} = 2.03 Å]. The degree of anion coordination in the solid-state observed for $[Me_2Ge(dmap)_2][OTf]_2$ is intermediate in character to those of the four-coordinate cation observed in $[Me_2Si(dmap)_2][OTf]_2$ and the six-coordinate neutral complex $Me_2Sn(dmap)_2(OTf)_2$. The geometry at the germanium centre is best approximated as tetrahedral, but long interactions with two triflate anions [Ge–O = 2.824(2) and 3.297(2) Å; Σ_{CR} = 1.84 Å] impart distortion towards an octahedral geometry [N–Ge–N = 93.7°; C–Ge–C = 126.0°] (Fig. 1b). As such, the three structures demonstrate differing degrees of triflate displacement from the $Me_2E(OTf)_2$ acceptors, and *conceptually* can be considered as snapshots of the reaction profile for two in-tandem S_N2-type processes: $[R_2EX_2 + 2L \rightarrow R_2E(L)_2][X]_2$.

Key solid-state metrical parameters for the three derivatives of $Me_2E(dmap)_2(OTf)_2$ are compared in Table 1, and highlight distinct trends that correlate with the relative covalent radii of the tetrael elements. The C–E–C and N–E–N angles illustrate geometries at E ranging from tetrahedral to octahedral, with increasingly short E–OTf interactions apparent as the covalent radii of the tetrael increases, in line with the stronger coordination of the anions. The distinct structural differences for the series of $Me_2E(dmap)_2(OTf)_2$ derivatives is in marked contrast to the essentially invariant distorted octahedral structures of the series *trans*-ECl_4L_2, for E = Si, Ge or Sn, L = pyridine or PMe_3.[3–8] Furthermore, the observed *cis*-configuration of the ligands in all three complexes (Fig. 2a) contrasts the *trans*-configuration reported for derivatives of EX_4L_2 in the solid-state (Fig. 2b), and is consistent with that proposed for the solid-state structure of $Me_2SnCl_2(pyridine)_2$ based on IR spectroscopy.[12,13] The apparent preference for *cis*-configuration of the ligands at these acceptors may reflect the minimization of steric effects within the complexes, but the *trans* relationship between the ligands and the triflate anions also implicates a possible S_N2 anion displacement.

Table 1 Selected solid-state parameters for $Me_2E(dmap)_2(OTf)_2$

E	Covalent radius (Å)	Mean E–N bond length (Å)	N–E–N angle (°)	C–E–C angle (°)	Shortest E–OTf (Å)
Si	1.16	1.800(3)	105.3(1)	115.7(1)	3.476(3)
Ge	1.21	1.933(2)	93.66(8)	126.02(9)	2.824(2)
Sn	1.40	2.210(1)	87.93(4)	158.57(6)	2.420(1)

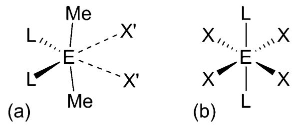

Fig. 2 Observed solid-state configurations for derivatives of (a) $Me_2EL_2X'_2$ and (b) EX_4L_2.

The corresponding bipy complexes of generic formula $Me_2E(bipy)(OTf)_2$ (E = Si, Ge, Sn) were obtained by analogous procedures to derivatives of $Me_2E(dmap)_2(OTf)_2$ (Scheme 1), and were characterised by multinuclear NMR spectroscopy, elemental microanalysis and X-ray crystallography. In the solid-state, the silicon centre of $[Me_2Si(bipy)(OTf)][OTf]$ adopts a distorted trigonal bipyramidal geometry, with the two nitrogen atoms of the bipy ligand in an equatorial and an axial site, respectively (Fig. 3a). An oxygen centre of a triflate substituent occupies the second axial position and the two methyl groups occupy the other equatorial sites. The Si–O bond [1.924(2) Å] is significantly shorter than the interaction with the second triflate anion [4.051(2) Å; Σ_{CR} = 1.79 Å], and contrasts the dicationic formulation of $[Me_2Si(dmap)_2][OTf]_2$, presumably reflecting the lesser steric demands of the essentially planar bipy ligand. The structure of $[Me_2Ge(bipy)(OTf)][OTf]$ (Fig. 3b) is very similar to that of the silicon derivative, with the germanium centre again trigonal bipyramidal, although the Ge–OTf bond is longer at 2.495(1) Å, a difference that cannot be explained solely on the basis of the greater covalent radius of Ge. The interaction with the second triflate anion [Ge–O = 3.594(1) Å] is slightly less than that in the silicon derivative, also evidenced by the greater C–Ge–C angle [133.34(7)°], which may partially explain the relatively long interaction with the first anion. The structure of $Me_2Sn(bipy)(OTf)_2$ (Fig. 3c) is analogous to that of $Me_2Sn(dmap)_2(OTf)_2$, with an octahedral geometry at tin distorted by the constrained chelate ligand, resulting in a narrower N–Sn–N angle [73.18(4)°], and larger O–Sn–O angle [115.85(4)°]. The structure of $Me_2Sn(bipy)(OTf)_2$ is also consistent with the reported solid-state structures of $R_2Sn(bipy)Cl_2$ (R = Me, iPr, *n*Bu, Bn, Ph).[21]

Relevant metrical parameters for the derivatives of $Me_2E(bipy)(OTf)_2$ are presented in Table 2. The difference in covalent radii of silicon and tin imparts a significant variation in the C–E–C angle consistent with the trigonal bipyramidal and octahedral geometries, respectively. The variation in the N–E–N angles (bite angle) is relatively small due to the constraints imposed by the chelating bipy ligand. The tabulated parameters also illustrate the deviation of the germanium complex from the trends defined by covalent radii relative to the silicon and tin analogues, and those illustrated for the dmap adducts. Notably, the structural

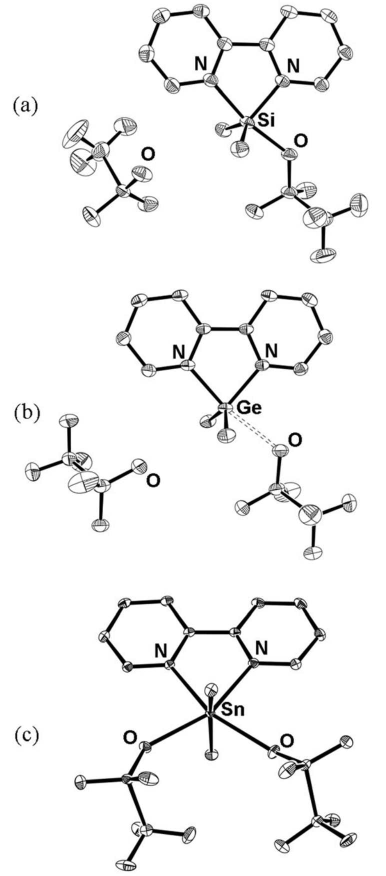

Fig. 3 Solid-state structures of (a) $[Me_2Si(bipy)(OTf)][OTf]$, (b) $[Me_2Ge(bipy)(OTf)][OTf]$ and (c) $Me_2Sn(bipy)(OTf)_2$. All hydrogen atoms are omitted for clarity.

Table 2 Selected solid-state parameters for $Me_2E(bipy)(OTf)_2$

E	Covalent radius (Å)	Mean E–N bond length (Å)	N–E–N angle (°)	C–E–C angle (°)	Shortest E–OTf (Å)
Si	1.16	1.918(2)	81.8(1)	128.5(1)	1.924(2)
Ge	1.21	1.968(1)	81.81(5)	133.34(7)	2.495(1)
Sn	1.40	2.255(1)	73.18(4)	159.42(6)	2.336(1)

differences observed between derivatives of $Me_2E(bipy)(OTf)_2$ again contrast the uniform geometries reported for the corresponding adducts of EX_4 (X = Cl or Br), for which *cis*-octahedral complexes, $EX_4(L–L)$, are exclusively formed.

Attempts to prepare the corresponding carbon derivatives $[Me_2C(dmap)_2][OTf]_2$ and $[Me_2C(bipy)][OTf]_2$ were unsuccessful (see ESI†). Nevertheless, compounds of the form $[H_2C(Donor)_2][X]_2$[4,22–24] can be formed *via* the activation of haloalkanes, including $[H_2C(dmap)_2][X]_2$ (X = Cl or I), and exhibit a tetrahedral geometry at carbon, in-line with our experimentally observed trends for Si, Ge and Sn. Remarkably, $[H_2C(dmap)_2][Cl]_2$ has been reported to form spontaneously under ambient conditions upon dissolution of dmap in CH_2Cl_2.[22] In contrast, no such reaction is observed upon the heating of a solution of dmap in Me_2CCl_2 over 100 h at 75 °C, nor upon thermolysis of a toluene solution of Me_2CX_2 (X = Cl or Br) and dmap at over 42 h 100 °C. Attempts to facilitate the interaction by halide abstraction from Me_2CX_2 were also unsuccessful. We postulate that the inductive effect of the methyl substituents that is expected to stabilise any developing positive charge is countered by their steric bulk, impeding nucleophilic attack.

In summary, we have prepared two series of compounds based on $Me_2E(OTf)_2$ (E = Si, Ge or Sn) acceptors ligated by dmap or bipy donors. The solid-state structures implicate cationic complexes for silicon in which one or both of the triflate anions can be regarded as non-coordinating, and neutral six-coordinate complexes for tin, in which both triflate anions coordinate to the Sn centre. The germanium complexes exhibit intermediate structural features. The distinct structural trends contrast previous observations for the corresponding complexes of EX_4 (X = Cl or Br), which have been characterised as octahedral molecular compounds. Ongoing work in our laboratories targets complexes of tetrael acceptors bearing higher numbers of weakly coordinating anions, which we perceive will lead to significant structural diversity, and novel bonding.

We thank the Natural Sciences and Engineering Council of Canada (NSERC) for funding.

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