Supplementary Data

Ionic Character of Ge(II)-Centered Dications from Ge K-edge X-ray Absorption Near Edge Structures

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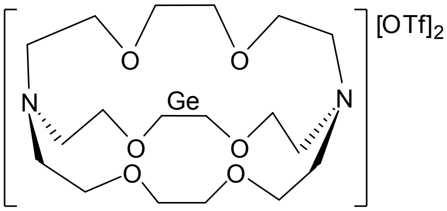
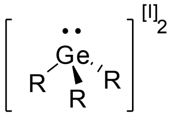
Synthesis of 1-3

The triflate salt of Ge(cryptand[2.2.2])$^{2+}$ (**1**),[1] $GeCl_2$·dioxane (**2**),[2] and the iodide salt of $[Ge(NHC)_3]^{2+}$ (**3**)[3] were synthesized according to literature procedures (Chart S1).

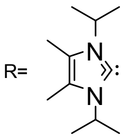
Chart S1. Compounds **1**, **2**, and **3**

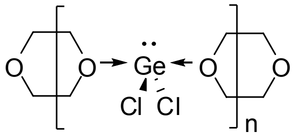


1[OTf]$_2$



2[I]$_2$





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XANES Experimental Details and Derivation of Table 1

X-ray absorption near edge spectroscopy (XANES) for samples **1**, **2**, **3**, and GeO_2 were collected on the PNC/XOR BM-20 beam line at the Advanced Photon Source (APS) at Argonne National Laboratories.[4] Briefly, powdered samples of **1-3** (to be referred to herein as "the samples") were synthesized under inert atmosphere in a glove box and each sample was then sealed in a vial to prevent atmospheric exposure during shipping to APS. The samples were then transferred to a nitrogen filled glove box where they were unpackaged from the shipping vials. Each powdered sample was then transferred to strips of Kapton tape with a spatula and rubbed into a uniform thickness layer with a clean gloved finger; the tape was then sealed to prevent the samples from being exposed to air during data collection. The tape was then folded several times to ensure that the powdered sample was uniform, pinhole free, and was thick enough to present sufficient absorption cross section. The samples were removed from the glove box, placed on a multi-sample holder, and then placed on the sample stage of the BM-20 beam line between two ionization detectors, I_o and I_T, respectively. For each sample the X-ray energy was then scanned from ~150 eV below the Ge *K*-edge (1*s* excitation threshold) of 11103 eV to ~900 eV above the edge. The X-ray flux was measured before passing through the sample (I_o) and after passing through the sample (I_T). The X-ray absorption coefficient (μ) for a sample of given thickness (t) is then calculated using Beer's law of absorption by taking the natural logarithm of the ratio of I_o to I_T (Equation 1).

Equation 1. $$\mu(E)t = \ln\left(\frac{I_o}{I_T}\right)$$

The spectra were then aligned using a germanium oxide standard for reference and normalized to unit edge jump using the Athena[5] software platform. The normalized absorption spectra for **1-3** and GeO_2 were then plotted as a function of photon energy and stacked for clarity.

To track the unoccupied electronic states where Ge 4*p* character is mostly localized in a Ge(II) ion with the highest ionic character, as in the case of **1,** and more diffused or delocalized character, when there is increasing interaction between the ion and the ligand as in the case of **2** (dative bonding) and **3** (highly polarized covalent bond), we take the first derivative of the XANES and estimate the height and the rising half width of the rising edge of the first resonance where Ge 4*p* character is located. The separation between the point of inflection and the whiteline (WL) maximum ($d\mu/dE = 0$ for single component and the bottom of the valley for overlapping peaks) is taken as the half width. Although this procedure will introduce larger uncertainty if the WL overlaps with intense multiple scattering peaks beyond the whiteline, as is the case for **2** and **3**, it can still provide a self-consistent and semi-quantitative measure of the extent of the broadening, and hence, delocalization due to bonding which together with the accompanying reduction in whiteline intensity, can indicate the extent of the interaction between the Ge(II) ion and the surrounding environment. Figure S1 shows the XANES spectra and the corresponding first derivative. The separation between the vertical lines shows the half width of the rising edge of the WL for **2**. A similar procedure was used to obtain parameters listed in Table 1.

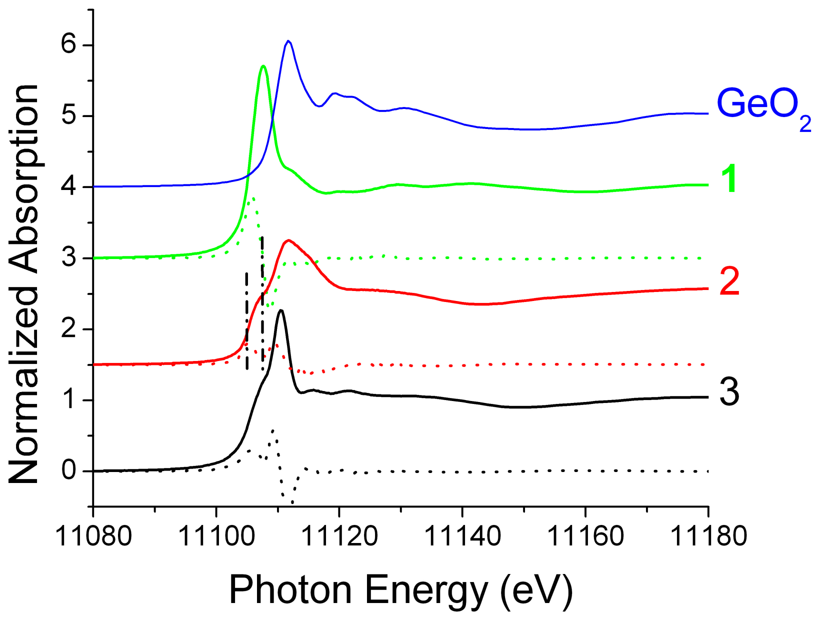


Fig. S1 Ge *K*-edge XANES (solid lines) and the corresponding first derivatives (dashed lines) in which the first peaks and valleys (dμ/dE = 0 for single component) correspond to the point of inflection of the rising edge and the WL peak maximum. Data are shifted vertically for clarity. The vertical lines show how the half width (separation between them) and the height of the white line were estimated for **2**. A similar procedure was applied to **1** and **3**. The GeO_2 XANES is also shown for reference.

Computational details of 1-3

The XANES calculation of the molecular germanium compounds **1**, **2**, and **3** are described as follows. The germanium *K*-edge was modeled for each compound using the *ab initio* self-consistent real-space-multiple-scattering (RSMS) code of FEFF8,[6] and includes all electrons of molecular clusters based on the molecular structures as experimentally determined by X-ray crystallography, which are then described by a real space relativistic Green's function formalism.[7] Molecular clusters of 769, 577, and 491 atoms for compounds **1**, **2** and **3** respectively, had been originally chosen for the RSMS computation. Slight overlapping of the atomic sites inside the compounds was allowed in the FEFF8 code for computation, however, in the case of all three molecular Ge compounds no overlapping was necessary since the distance of the first nearest neighbor to the central Ge atomic site is far from the normal bond length; as is the case in **1** where the nearest neighbor is an O atom at 2.4855 Å compared to a typical Ge-O bond length of 1.80 Å. The boundary conditions of these wave-functions dictate the matching conditions of the respective atomic Green's functions.[8] Compound **1** has a trigonal symmetry of P321 (D_3^2). Compounds **2** and **3** have group symmetries of cubic $P2_13$ (T^4), and monoclinic C2/c (C_{2h}^6), respectively. The multiple path of the incident spherical wave scattered by the scattering atomic centers inside the large molecular cage are restricted to 4 (Nleg =4) for the simplicity of computation. The Ge scattering center of **1** has 6 O atoms as the nearest neighbors at 2.4855Å and the second nearest neighbors of N at 2.524 Å. The Ge scattering center of **2** has 3 C at 2.0699 Å, 3 H at 2.604 Å, and 3I at 2.670 Å as the nearest sites, whereas that of **3** has 2 Cl at 2.813 Å and 2O at 2.392 Å.

Partial Density of States

The Ge partial density of states (DOS) of **1** (Figure S2), **2** (Figure S3), and **3** (Figure S4) were calculated once the self-consistent RSMS was minimized for the lowest energy states of the system. The K-shell for germanium in these compounds corresponds to the transition of the 1s core state to the 4p state of Ge. E_{Fermi} corresponds to the Fermi energy.

Fig. S2 Ge partial DOS of the triflate salt of **1** ($Ge[2.2.2]^{2+}$)

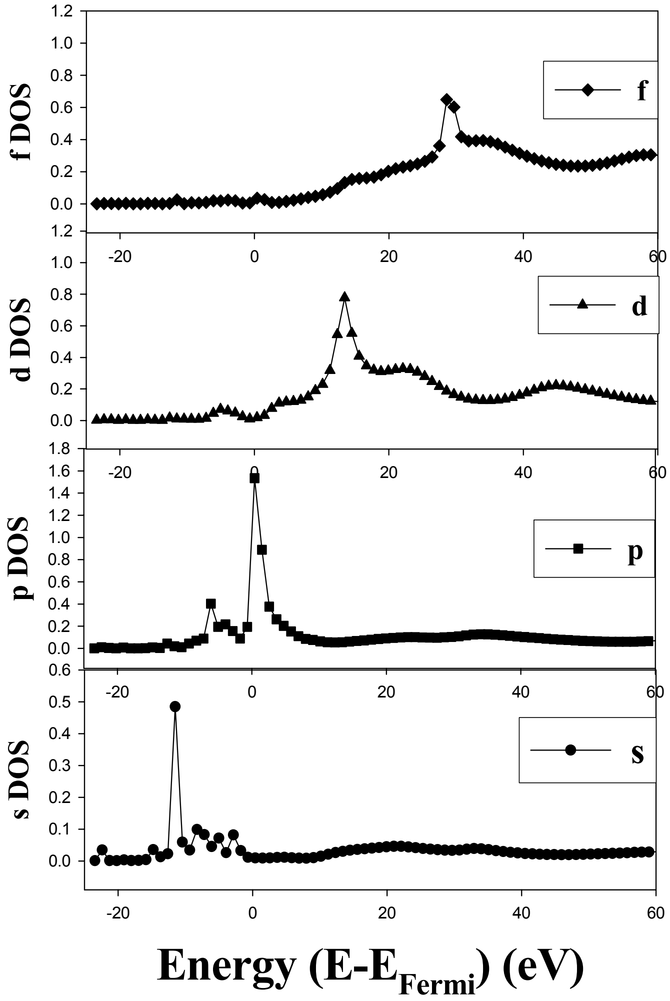


Fig. S3 Ge *p*DOS of the iodide salt of **2** (Ge[NHC]$_3^{2+}$).

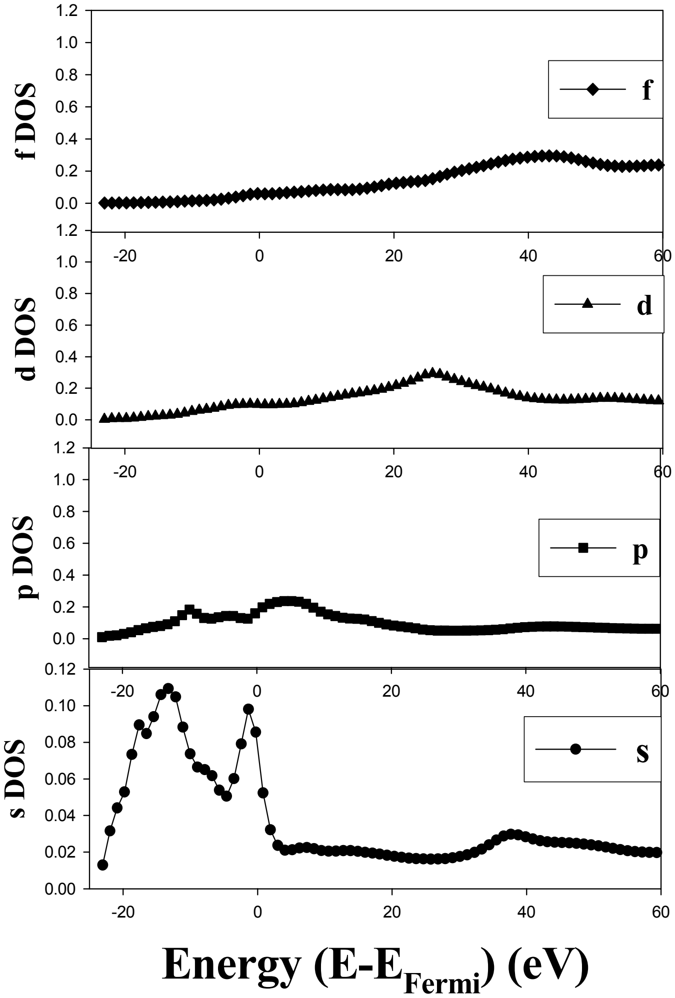
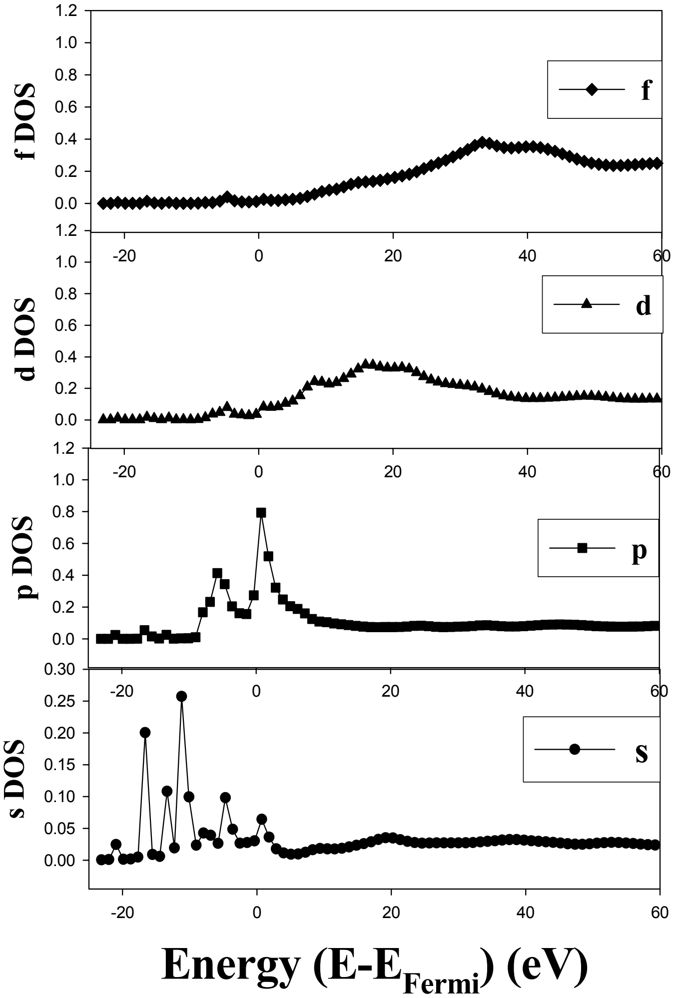


Fig. S4 Ge partial DOS of **3** ($GeCl_2$·dioxane)



References

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[1] P. A. Rupar, V. N. Staroverov, K. M. Baines, *Science*, 2008, **322**, 1360.

[2] W. J. Leigh, C. R. Harrington, I. Vargas-Baca, *J. Am. Chem. Soc.*, 2004, **126**, 16105.

[3] P. A. Rupar, V. N. Staroverov, P. J. Ragogna, K. M. Baines, *J. Am. Chem. Soc.*, 2007, **129**, 15138.

[4] S. M. Heald, D. L. Brewe, E. A. Stearn, K. H. Kim, F. C. Brown, D. T. Jiang, E. D. Crozier, R. A. Gordon, *J. Synchrotron Rad.*, 1999, **6**, 347.

[5] B. Ravel, M. Newville, *J. Syncrtron Rad.*, 2005, **12**, 537.

[6] A. L. Ankudinov, B. Ravel, J. J. Rehr, S. D. Conradson, *Phys. Rev. B*, 1998, **58**, 7565.

[7] A. L. Ankudinow, S. D. Conradson, J. M. deLeon, J.J. Rehr, *Phys. Rev. B*, 1998, **57**, 7518.

[8] T. L. Loucks, *Augmented Plane Wave Method*, Benjamin, New York, 1967.