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Computational search for redox isomerism in Ge and Sn bis-chelates with α-diimine ligands

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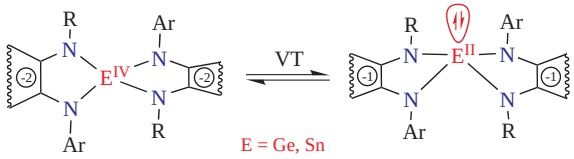
The first examples of germanium and tin complexes with α-diimine ligands undergoing reversible redox isomeric (valence tautomeric) rearrangements were demonstrated based on the computational modeling of their dynamic behavior using DFT at the B3LYP/Def2TZVP level.



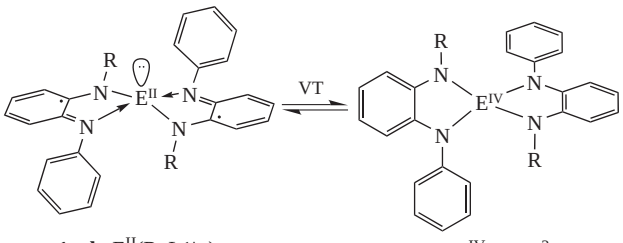
Keywords: group 14 elements, diimines, bis-chelates, valence tautomerism, DFT calculations.

The phenomenon of redox isomerism or valence tautomerism (VT) of transition metal complexes with redox-active ligands has been known for more than 40 years.[1,2] Rearrangements of electronic isomers (electromers)[3] of the complexes are driven by the intramolecular electron transfer between the metal ion and the redox-active ligand, which can be accompanied by the spin state change[4,5] ensuring promising applications of VT systems in information storage and processing devices.[6–9] The VT rearrangements of metal complexes do not lead to any substantial deformations of the coordination polyhedron and leave its principal stereochemistry intact.[4,5,8,10–12]

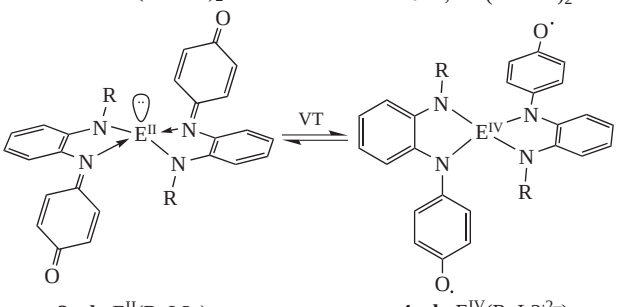
In the last decade, there has been a rapidly growing interest in main group element compounds containing redox-active ligands.[13–27] It has been revealed that under certain conditions, these compounds exhibit properties characteristic of transition metal complexes, such as catalytic activity in various transformations and participation in addition reactions of compounds with multiple bonds and reactions of oxidative addition and reductive elimination.[28–35] Recently, the possibility of participating bis-*o*-iminoquinonate complexes of Group 14 elements in the redox-isomeric interconversion accompanied by switching between different spin states was theoretically substantiated[36] and experimentally observed in the case of a bis-chelate tin complex.[37] It was shown that, in contrast to the VT rearrangements of transition metal complexes, proceeding as one-electron transfer reactions, redox-isomeric rearrangements of Group 14 element complexes require the concerted intramolecular transfer of two electrons between the main group element and the redox-active ligands and are accompanied by significant changes in the stereochemical configuration of the central atom.

In this work, we predicted novel types of main group element coordination compounds capable of switching their magnetic properties *via* VT rearrangements. For this purpose, the comprehensive quantum-chemical calculations of the structure and rearrangements of germanium and tin complexes with α-diimine ligands L1 and L2 (Scheme 1) were performed using the DFT method (B3LYP/Def2TZVP) from the Gaussian 16 program suit.[38] The choice of these group 14 element compounds was motivated by the data of an earlier investigation,[36] which reported the formation of isomers of germanium and tin complexes with various oxidation states of the complexing ion and redox ligands.

In turn, silicon bis-chelates with similar redox-active ligands are stabilized in the tetravalent state, while lead compounds, on the contrary, have a square pyramidal structure and the +2 oxidation state of the central ion. The complexes with diimine ligands L1 containing a divalent complexing ion are paramagnetic (S = 1), while the pseudo-tetrahedral structures are diamagnetic (S = 0). The presence of *p*-iminoquinoid moiety in the compounds with L2 ligands results in the opposite: the low-valent pyramidal structure is diamagnetic, and the isomer with the central ion in the +4 oxidation state contains one unpaired electron for each ligand (see Scheme 1). It was expected that a systematic variation of the substituents R (H, Me, Ph and Bu^t) at the nitrogen atom of diimine ligands could lead to finding new systems with kinetic and thermodynamic parameters characteristic of the thermally initiated VT behavior. The stationary points on the potential



1a–h, $E^{II}(R–L1^{\cdot -})_2$ **2a–h**, $E^{IV}(R–L1^{2-})_2$



3a–h, $E^{II}(R–L2^{-})_2$ **4a–h**, $E^{IV}(R–L2^{\cdot 2-})_2$

a E = Ge, R = H
b E = Ge, R = Me
c E = Ge, R = Ph
d E = Ge, R = Bu^t
e E = Sn, R = H
f E = Sn, R = Me
g E = Sn, R = Ph
h E = Sn, R = Bu^t

Scheme 1

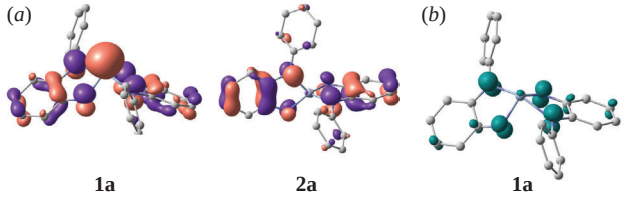


Figure 1 (*a*) The shapes of HOMO in electromers $Ge^{II}(H–L1)_2$ **1a** and $Ge^{IV}(H–L1)_2$ **2a** of complex $Ge(H–L1)_2$ and (*b*) the spin density distribution in electromer **1a**. Here and in Figure 2, hydrogen atoms are not shown.

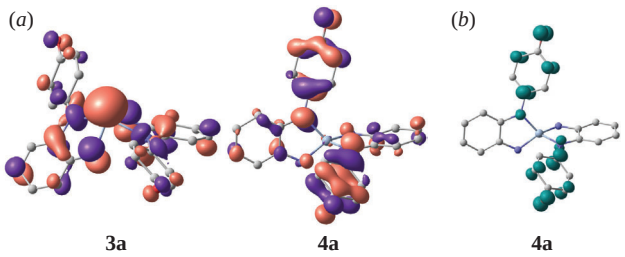


Figure 2 (*a*) The shapes of HOMO in electromers $Ge^{II}(H–L2)_2$ **3a** and $Ge^{IV}(H–L2)_2$ **4a** of complex $Ge(H–L2)_2$ and (*b*) the spin density distribution in electromer **4a**.

energy surfaces (PESs) were localized by a full geometry optimization with the calculation of force constant matrices and checking for the stabilities of the DFT wave function. In compounds with a small energy difference between the electromers, the energy barriers of spin-forbidden reactions were evaluated by the implementation of the program code developed by Harvey *et al.*[39]

As follows from the calculation results, the $Ge^{II}(R–L1)_2$ electromers **1a**–**d** found on the triplet PES are characterized by the square pyramidal geometry with a lone electron pair on the germanium ion, as shown in Figure 1. Analysis of the spin density distribution in electromer $Ge^{II}(H–L1)_2$ **1a** indicates the localization of unpaired electrons predominantly on the nitrogen atoms of the radical anion ligands. Diamagnetic isomers **2a**–**d** (Table S1 and Figure S1, Online Supplementary Materials) with the electronic structure of $Ge^{IV}(R–L1)_2$, characterized by a pseudo-tetrahedral coordination geometry, correspond to the ground states of complexes $Ge(R–L1)_2$ (R = H, Me, Ph and Bu^t).

An increase in the bulkiness of the substituents R in the order of H < Me < Ph < Bu^t enhances the distortion of the chelate rings of the $Ge^{II}(L1)_2$ isomers (see Figure S1) consisting in the exit of the germanium center from the chelate plane (by 0.37–0.85 Å). These structural changes entail additional destabilization of the high-spin isomers: the predicted ΔE values grow from 29.6 kcal mol^{-1} for complex $Ge(H–L1)_2$ to 55.8 kcal mol^{-1} for compound $Ge(Bu^t–L1)_2$ (see Table S1). Thus, the computational data lead to the conclusion that only diamagnetic isomers $Ge^{IV}(L1)_2$ **2a**–**d** with a pseudo-tetrahedral coordination geometry will be observed for complexes $Ge(R–L1)_2$ (R = H, Me, Ph and Bu^t).

Germanium complex $Ge(H–L2)_2$ with ligand L2 (R = H) is characterized by an energy difference of 9.6 kcal mol^{-1} between isomers $Ge^{II}(H–L2)_2$ **3a** and $Ge^{IV}(H–L2)_2$ **4a** in favor of the latter (see Table S1). The calculated spin density distribution in high-spin isomer $Ge^{IV}(H–L2)_2$ **4a** (Figure 2) differs from that found for compound $Ge(H–L1)_2$: it is almost completely localized on the phenoxyl group. In order to elucidate the ability of this complex to exhibit a thermally initiated VT rearrangement, we undertook a search for the minimum-energy crossing point (MECP), the point with the minimum energy on the seam of two intersecting PESs of different multiplicity. As follows from the results presented in Figure S2 and Table S1, the structure of $MECP_{3a–4a}$ is 20.1 kcal mol^{-1} higher in energy compared to the energy-preferred isomer $Ge^{IV}(H–L2)_2$ **4a**. This value, which determines the highest theoretically estimated limit for the barrier of the considered spin-forbidden reaction, points to an incomplete redox isomeric transition between isomer $Ge^{IV}(H–L2)_2$ **4a** in the triplet state and diamagnetic isomer $Ge^{II}(H–L2)_2$ **3a**.

The symmetrical low-spin form of the $Ge(Me–L2)_2$ complex with a square pyramidal coordination geometry corresponds to the transition state structure, the gradient descent from which leads to a minimum for $Ge^{II}(Me–L2)_2$ **3b**, characterized by nonequivalent Ge–N(phenoxyl) bonds with lengths equal to 2.178 and 2.733 Å (see Figure S2). The latter value is close to the sum of the van der Waals radii of germanium and nitrogen atoms, pointing to a weak interaction between these atoms. The impossibility of forming a tetracoordinated square pyramidal isomer is due to steric hindrances created by the ligand structure. The energy difference between the ground state $Ge^{IV}(Me–L2)_2$ **4b** of this complex and isomer $Ge^{II}(Me–L2)_2$ **3b** exceeds 19 kcal mol^{-1} (see Table S1). This value indicates a very low probability of the VT rearrangement. For the $Ge(Ph–L2)_2$ compound, two structures were found, $Ge^{II}(Ph–L2)_2$ **3c** and $Ge^{IV}(Ph–L2)_2$ **4c**, with the C_2 symmetry group. However, according to the calculated relative energies, the low-spin isomer $Ge^{II}(Ph–L2)_2$ **3c** is thermally unattainable. An unexpected result was obtained when searching for a structure related to the square pyramidal isomeric form of the $Ge(Bu^t–L2)_2$ complex. For this structure, no stable wave function was found on the singlet PES. A stable solution is represented by a pseudo-tetrahedral structure corresponding to the broken-symmetry state of isomer $Ge^{IV}(Bu^t–L2)_2$ **4d**. The estimated[40] spin coupling parameter (–1 cm^{-1}) means a negligible effect of exchange interactions on the magnetic properties (S = 1) of the $Ge(Bu^t–L2)_2$ complex.

Thus, the ground states of all considered germanium compounds, $Ge(R–L)_2$ (R = H, Me, Ph and Bu^t; L = L1 and L2), are represented by the pseudo-tetrahedral isomers **2a**–**d** and **4a**–**d** containing the complexing ion in the +4 oxidation state. An incomplete thermally initiated intramolecular VT interconversion is possible for the $Ge(H–L2)_2$ compound.

The DFT calculations of complexes $Sn(R–L1)_2$ (R = H, Me, Ph and Bu^t) reveal the relationship between the type of substituents at the nitrogen atoms of ligand L1 and the electronic structure of the ground state. The most stable isomers of compounds $Sn(H–L1)_2$ and $Sn(Me–L1)_2$ are represented by pyramidal high-spin electromers $Sn^{II}(H–L1)_2$ **1e** and $Sn^{II}(Me–L1)_2$ **1f**, whose energy preferences relative to pseudo-tetrahedral isomers $Sn^{IV}(H–L1)_2$ **2e** and $Sn^{IV}(Me–L1)_2$ **2f** are 3.9 and 0.7 kcal mol^{-1}, respectively (Table S2 and Figure S3). In the $Sn(Ph–L1)_2$ complex, electromers $Sn^{II}(Ph–L1)_2$ **1g** and $Sn^{IV}(Ph–L1)_2$ **2g** are virtually isoenergetic, while in the $Sn(Bu^t–L1)_2$ species, the energy difference reaches 8.8 kcal mol^{-1} in favor of the diamagnetic isomer $Sn^{IV}(Bu^t–L1)_2$ **2h**. The computational data point to the possibility of low-barrier transitions between the electromers of the considered tin complexes. This conclusion is confirmed by the calculated MECPs ($MECP_{1e–2e}$, $MECP_{1f–2f}$ and $MECP_{1g–2g}$) for these VT rearrangements, which are destabilized with respect to the corresponding ground states by only 3.9–5.4 kcal mol^{-1}. These values undoubtedly indicate possible fast interconversions of the isomers and their coexistence in equilibrium at room temperature. The relative energy of $MECP_{1h–2h}$ is 12.3 kcal mol^{-1}, which gives reason to expect the fixation of two electromers in the $Sn(Bu^t–L1)_2$ compound.

The ground states of complexes $Sn(R–L2)_2$ (R = H, Me and Ph) are represented by diamagnetic electromers $Sn^{II}(R–L2)_2$ **3e**–**g** with a square pyramidal coordination geometry (see Table S2 and Figure S4). With an increase in the bulkiness of substituents R in the series from hydrogen to methyl and phenyl, the energy gaps ΔE narrow from 26.7 to 19.9 and 17.3 kcal mol^{-1}, respectively, but do not reach the values characteristic of typical VT transitions. The presence of tert-butyl groups in the $Sn(Bu^t–L2)_2$ complex

stabilizes isomer $Sn^{II}(Bu^t–L2)_2$ **3h** with a three-coordinated tin atom. The high-spin electromer $Sn^{IV}(Bu^t–L2)_2$ **4h** is destabilized by 2.2 kcal mol^{-1} compared to the ground state. Calculation of the MECP between the singlet and triplet PESs and the subsequent gradient descent from the corresponding $MECP_{4h–3'h}$ structure showed the presence of a local minimum, $Sn^{II}(Bu^t–L2)_2$ **3′h**, with a square pyramidal geometry (see Figure S4). The calculated energy level of $MECP_{4h–3'h}$ (11.1 kcal mol^{-1}) points to the capability of the $Sn(Bu^t–L2)_2$ complex to exhibit VT rearrangement, accompanied by switching of magnetic properties.

In summary, a systematic study by the DFT method showed the possibility of rearrangements with the switching of spin states caused by the VT transitions in the Ge and Sn bis-chelates with α-diimine ligands. Varying the substituents at the nitrogen atom of the redox ligand controls the relative stability of the electromers. The germanium complex $Ge(Bu^t–L2)_2$, capable of participating in an incomplete thermally initiated VT process, has been identified. The bis-chelate tin complexes $Sn(Bu^t–L1)_2$ and $Sn(Bu^t–L2)_2$ are predicted to have optimal energy parameters for the occurrence of redox processes and the fixation of both electronic states. The synthetic availability of the considered structural motifs and the diversity of diimine ligands[41–43] open up broad prospects for synthesizing new compounds with promising properties.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.01.015.

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