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Theoretical Rationalization of Structure of Transannular Bonded Germanium Complexes Containing Amide Functionality

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Penta and tetra coordinated germanium complexes have been synthesized from *N,N'-bis*(2-pyridyl)pyridine-2,6-dicarboxamide (H_2L) and *N*-(pyridine-2-yl)picolinamide (HL^1) with dialkyl/aryl and trialkyl/aryl germanium halides in 1:1 molar ratios. The molecular structures and electronic properties of complexes were well analyzed by GAUSSIAN 03 suit of programs. The transannular bonding observed in penta coordinated complexes have been well established by natural bond orbital, Wiberg bond index and molecular electrostatic potential analysis.

Keywords: Germanium complexes, Amide ligand, NBO, MESP.

INTRODUCTION

Amide functional group, ubiquitous in biochemistry, is important ligand construction unit for coordination chemists. In recent years, chemists have been interested in developing ligand systems containing pyridine carboxamide functionality [1,2] due to their influence on novel geometric and electronic properties imparted onto various metal centers [3]. They have found use in catalysis [4,5], molecular receptors [6,7] and dendrimer synthesis [8]. Nowadays a significant amount of research has been devoted to the elucidation of transannular intramolecular bonding in hetero-substituted ring system [9]. There is a report on the sulfur to germanium transannular bonding in spirocyclic derivative [10]. Involved in organometallic chemistry, we are interested in the structural and pharmacological activity of metallic complexes of group 14. These elements have shown great chemical versatility, as a result of their ability to increase their coordination spheres. Germanium is a trace element found in several organic substances and its compounds are known to have a broad range of biological activities.

In the context mentioned above and in continuation to our work on metallic complexes of group 14 [11-14], U-shaped *N,N'-bis*(2-pyridyl)pyridine-2,6-dicarboxamide (H_2L) and *N*-(pyridine-2-yl)picolinamide (HL^1) are prepared as ligands. Structures of these ligands are promising one and H_2L is a multifunctional bridge with two picolinamide pendants. Germanium complexes of these ligands showed extensive transannular bonding due to the presence of pyridine moiety. In order to gain a better insight into the factors responsible for the existence of these forms of bonding, in this work we studied these systems using the Gaussian 03 [15] suit of programs. We calculated the energies of all molecular structures and well studied the electronic properties of these newly synthesized complexes by density functional theory (DFT) with mixed valence basis set.

EXPERIMENTAL

In this work, 2-aminopyridine, picolinic acid and 2,6-pyridine dicarbonyldichloride are purchased from Sigma-Aldrich and used as received. Other chemicals were commercially available and used without further purification. Some reagents in ligand preparation, such as thionyl chloride and all solvents were dried to remove water [16]. All the reactions were carried out in presence of nitrogen atmosphere. The melting points are recorded on a Perfit apparatus and are uncorrected. The IR spectra from 4000-400 cm^{-1} were recorded on Nicolet Shimadzu Spectrometer in KBr pellets and CCl_4 solution. The ^1H ($CDCl_3$, DMSO, 300 MHz) and ^{13}C ($CDCl_3$, DMSO, 75.5

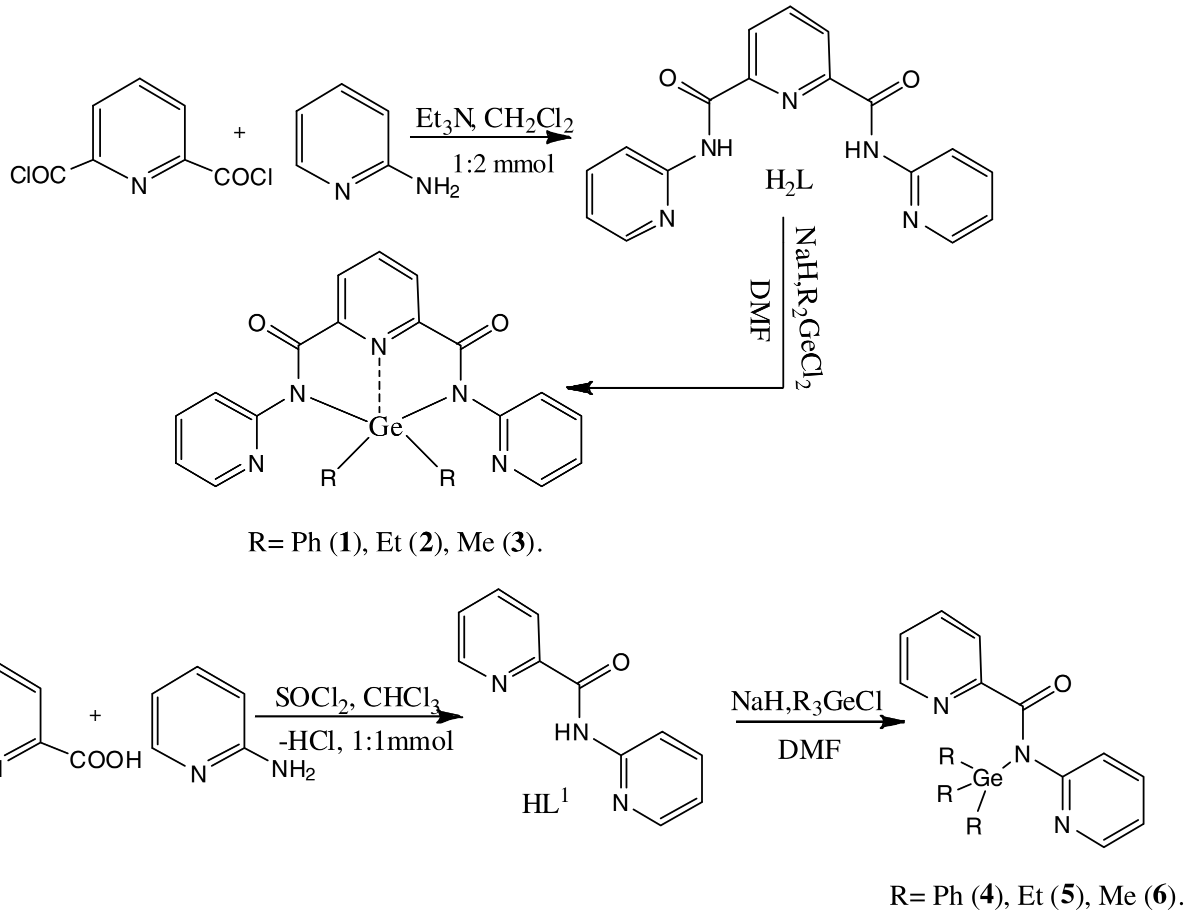
MHz) NMR spectra of complexes have been recorded at room temperature on a JEOL 300AL FTNMR spectrometer using TMS as internal standard. Germanium was estimated as germanium oxide using platinum crucible and nitrogen was estimated as reported in the literature method [17].

Computational details: Molecular geometries of all the Ge(IV) complexes under study have been carried out using Gaussian 03 suit of programs. Optimizations were done by the DFT method. The density functional B3LYP can produce accurately and economically the heats of formation for compounds containing transition metal [18,19]. This method is combined with a mixed valence basis set of 631-g(d) for non-metallic atoms and LanL2DZ for metallic atoms. For essentially all levels, the minimum character of all optimized structures was verified by evaluation of the harmonic vibrational frequencies. The nature of bonding and hyperconjugative interactions were well evaluated by NBO 3.0 version incorporated in Gaussian 03 software. Atomic charges in all the structures were obtained using the natural population analysis (NPA) method within the natural bond orbital approach. The relative bond strengths have been estimated using the Wiberg bond index analysis. At the optimized geometries, MESP topological analyses are carried out employing the DFT/6-31G(d) wave functions and using the UNIPROP package.

***N,N'-Bis*(2-pyridyl)pyridine-2,6-dicarboxamide (H_2L):** To a solution of 2,6-pyridine dicarbonyldichloride (0.408 g, 2 mmol) in dichloromethane (10 mL) at 0 °C, a solution of 2-aminopyridine (0.430 g, 4.53 mmol) in the same solvent was added. The colour of the solution changed from light green to yellow. After 15 min stirring, triethylamine is added dropwise to the stirring mixture. Then white precipitate is formed to begin and mixture was stirred for 6 h to ensure completion of reaction. Filtered, dried and the precipitate was washed with saturated solution of sodium bicarbonate, water and acetone. Dried under vacuum and ligand obtained as white powder (60 %).

***N*-(Pyridine-2-yl)picolinamide (HL^1):** Pyridine carbonyl chloride prepared from picolinic acid (0.492, 4 mmol) dissolved in chloroform (15 mL) and cooled to 0 °C. To this 2-aminopyridine (0.364 g, 4 mmol) is added and stirred. The colour of solution changes from green to blue. After 0.5 h stirring, solution refluxed for 5 h. Colour changes to dark blue. Following a brief period of cooling filtered and the filterate washed thrice with water. Chloroform layer evaporated under vacuum and the product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (8/1 v/v) as eluent to afford the ligand as white crystals (75 %).

Reaction of H_2L with diphenyl germanium dichloride (1): Sodium hydride (0.025 g, 1.168 mmol) was washed with hexane under dinitrogen and then added to a solution of H_2L (0.186 g, 0.584 mmol) in DMF. Stirred and after colour changes diphenyl germanium dichloride (0.1738 g, 0.584 mmol) in DMF was added to the above solution. A precipitate of NaCl is formed, stirred and dried under vacuum following washing the product with hexane gives a light yellow product (**Scheme-I**). All other germanium complexes are produced in the same



R= Ph (**1**), Et (**2**), Me (**3**).

R= Ph (**4**), Et (**5**), Me (**6**).

Scheme-I: Preparation of germanium complexes manner in 1:1 molar ratio with H_2L and HL^1 reacting with different R_2GeCl_2 and R_3GeCl, respectively. All complexes are soluble in organic solvents like benzene, hexane, chloroform, *etc*.

Spectral data

***N,N'-Bis*(2-pyridyl)pyridine-2,6-dicarboxamide (H_2L):** White solid, yield ~ 60 %, m.p.: 215 °C, IR (KBr, ν_{max}, cm^{-1}): 1691 (C=O), 3354 (N-H). ^1H NMR ($CDCl_3$, 300 MHz): δ 10.55 (s, NH), 8.63-7.31 (m, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.68 (2, C=O), 150.88 (3, C=N), 149.08-123.54 (6, C=C). Anal. calcd. (found) (%) for $C_{17}H_{13}N_5O_2$: C, 63.94 (63.11); H, 4.10 (4.03); N, 21.93 (21.98).

***N*-(Pyridine-2-yl)picolinamide (HL^1):** White crystal, yield ~ 75 %, m.p.: 102 °C, IR (KBr, ν_{max}, cm^{-1}): 1698 (C=O), 3350 (N-H). ^1H NMR ($CDCl_3$, 300 MHz): δ 10.59 (s, NH), 8.57-7.36 (m, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.11 (1, C=O), 150.24 (2, C=N), 149.83-123.94 (4, C=C). Anal. calcd. (found) (%) for $C_{11}H_9N_3O$: C, 66.32 (66.21); H, 4.55 (4.73); N, 21.09 (20.98).

Compound 1: Yellow solid, yield ~ 42 %, m.p.: 232 °C, IR (KBr, ν_{max}, cm^{-1}): 1688 (C=O), 524 (Ge-C). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.61-7.32 (m, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.45 (2, C=O), 149.99 (3, C=N), 149.77-122.14 (12, C=C). Anal. calcd. (found) (%) for $C_{29}H_{21}N_5O_2Ge$: C, 64.01 (64.22); H, 3.89 (3.73); N, 12.87 (12.58); Ge, 13.34 (13.11).

Compound 2: Cream solid, yield ~ 68 %, m.p.: 225 °C, IR (KBr, ν_{max}, cm^{-1}): 1690 (C=O), 529 (Ge-C). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.56-7.12 (m, ArH), 0.61 (t, Ge-$CH_2\mathbf{CH_3}$), 0.93 (q, Ge-$C\mathbf{H_2}CH_3$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.35 (2, C=O), 151.99 (3, C=N), 149.26-122.62 (6, C=C), 7.99 (2, Ge-$CH_2\mathbf{CH_3}$), 12.73 (2, Ge-$\mathbf{C}H_2CH_3$). Anal. calcd. (found) (%) for $C_{21}H_{21}N_5O_2Ge$: C, 56.30 (56.12); H, 4.72 (4.23); N, 15.63 (16.58); Ge, 16.21 (16.99).

Compound 3: White solid, yield ~ 53 %, m.p.: 195 °C, IR (KBr, ν_{max}, cm^{-1}): 1692 (C=O), 521 (Ge-C). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.55-7.22 (m, ArH), 0.13 (s, Ge-Me). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.31 (2, C=O), 149.98 (3, C=N), 149.44-123.62 (6, C=C), 4.32 (2, Ge-Me). Anal. calcd. (found) (%) for $C_{19}H_{17}N_5O_2Ge$: C, 54.34 (54.22); H, 4.08 (4.12); N, 16.68 (16.34); Ge, 17.29 (17.99).

Compound 4: Off white solid, yield ~ 54 %, m.p.: 132 °C, IR (KBr, ν_{max}, cm^{-1}): 1697 (C=O), 528 (Ge-C). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.65-7.26 (m, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.45 (1, C=O), 150.93 (2, C=N), 148.44-128.32 (13, C=C). Anal. calcd. (found) (%) for $C_{29}H_{23}N_3OGe$: C, 69.37 (69.72); H, 4.62 (4.33); N, 8.37 (8.39); Ge, 14.23 (Ge, 14.46).

Compound 5: Cream solid, yield ~ 45 %, m.p.: 171 °C, IR (KBr, ν_{max}, cm^{-1}): 1697 (C=O), 523 (Ge-C). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.60-7.01 (m, ArH), 0.67 (t, $GeCH_2\mathbf{CH_3}$), 0.99 (q, Ge-$C\mathbf{H_2}CH_3$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.50 (1, C=O), 151.09 (2, C=N), 149.24-122.32 (4, C=C), 7.81 (3, Ge-$CH_2\mathbf{CH_3}$), 12.16 (3, Ge-$\mathbf{C}H_2CH_3$). Anal. calcd. (found) (%) for $C_{17}H_{23}N_3OGe$: C, 57.03 (59.02); H, 6.48 (6.33); N, 11.74 (11.39); Ge, 20.28 (20.13).

Compound 6: Brown solid, yield ~ 55 %, m.p.: 154 °C, IR (KBr, ν_{max}, cm^{-1}): 1695 (C=O), 528 (Ge-C). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.58-7.20 (m, ArH), 0.31 (s, Ge-Me). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.50 (1, C=O), 151.07 (2, C=N), 149.23-122.02 (4, C=C), 4.85 (3, Ge-Me). Anal. calcd. (found) (%) for $C_{14}H_{17}N_3OGe$: C, 53.23 (53.08); H, 5.42 (5.83); N, 13.30 (13.33); Ge, 22.98 (22.13).

RESULTS AND DISCUSSION

In the IR spectra of the ligands there is a peak in the range 3354-3350 cm^{-1}which is assigned to ν(N-H) of amide ligand which disappears on complex formation. Peak corresponding to ν(C=O) remains almost unchanged in all the complexes which means there is no coordination from it. The ^1H and ^{13}C NMR spectra of all the germanium complexes exhibited characteristic signals and multiplicities for R-Ge and ligand protons. In ^1H NMR spectrum of ligand, deuterium exchangeable amide protons resonated in the region 10.58-10.59 ppm which disappears on complex formation suggesting deprotonation of amide protons and subsequent Ge-N formation. ^{13}C NMR spectrum gives characteristic signals for R-Ge resonances.

Computational calculations

Structural studies: The structures of ligands and complexes were well studied by different computational methods using Gaussian 03 suite of programs. All the structures are optimized by DFT-B3LYP method using mixed valence basis set (6-31g(d) + LanL2DZ). The optimized parameters of the complexes are listed in Table-1.

In the ligand (H_2L), there is a parallel displaced π-π stacking interaction between two pyridyl rings with a distance of 4.02 Å between the centeres and an angle of 22.5°. In Fig. 1, H_2L shows the attractive electrostatic interaction between the σ framework and the π electron density in the ligand. This is mainly due to the presence of nitrogen in the ring which has an electron withdrawing effect that reduces the π electron density and thus increases π–π interactions. In HL, *anti-anti* conformation is the most stable one because in *cis* form there is lone pair repulsion between N and O. In anti form there is an intramolecular hydrogen bonding and this conformation remains unchanged in complexes also.

After complexation, a new H-bond interaction is observed in complexes **1-3** between carbonyl oxygen and hydrogens from two pyridyl rings. The pyridine-2,6-dicarboxamido unit

TABLE-1
OPTIMIZED PARAMETERS OF COMPLEXES **1-6**

Compound	r (C=O)	R (Ge-N^1)	R (Ge-N^2)	R (Ge-N^3)	θ (N^1,Ge,N^2)	θ (N^2,Ge,N^3)	θ (N^1,Ge,N^3)	E (Kcal/mol)
1	1.227	2.070	2.010	2.070	77.18	77.18	146.90	-3617.353
2	1.235	2.141	2.046	2.140	75.58	75.59	151.06	-3312.540
3	1.224	2.044	2.046	2.044	76.50	76.51	153.58	-3233.883
4	1.229	3.760	1.930	4.040	69.44	46.69	102.38	-2993.274
5	1.231	3.290	1.960	3.860	65.25	52.81	103.53	-2976.537
6	1.231	3.580	1.960	4.010	63.93	53.80	102.84	-2858.597

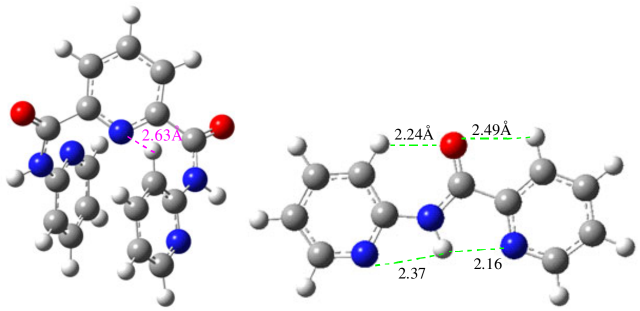


Fig. 1. Optimized structure of ligands H_2L and HL^1

is a strong chelator. This is reflected in the short Ge-N_{py} and Ge-N_{amido} bond distances 2.04-2.01 Å and 2.14-2.04 Å, respectively and this remains almost same in all the germanium complexes. In these complexes, the two carboxamido nitrogens are *trans* to each other with equal Ge-N bond lengths and have a mirror plane along. Due to the close bite of the pyridine-2-carboxamido units, both five membered rings force the N_{amido}-Ge-N_{py} angles very close to 76° (Table-1). Thus there forms transannular interaction from the pyridyl nitrogens with a bond distances 2.04-2.14 in these complexes. The intramolecular hydrogen bonding observed in HL^1 as shown in Fig. 1 have no significant differences after complexes formation (**4-6**). The optimized structures of complexes are shown in Fig. 2.

In the MESP plot of ligand, the electron density is concentrated on the oxygen atom, whereas in complexes this is spread around O-C-N region due to hyperconjugation. By this delocalization, the electron density on nitrogen increases and the positive charge on carbon decrease on complex formation. The MESP plot and NPA charges of respective atoms are shown in Fig. 3.

In addition there is an increase in the carbonyl carbon to oxygen bonds of ~ 0.002 Å and a decrease in the carbonyl carbon to nitrogen bond length of ~ 0.023 Å indicate binding of amide functionality to metal ions through nitrogen atom [20]. In complexes **1-3**, Ge-N_{Py} (central) and Ge-N_{Py} (sides) bond distances are in the order 2.01-2.04 Å and ~ 4.01 Å, respectively. In complexes **4-6,** two Ge-N_{Py} distances are in the order 3.29-4.04 Å. This indicates, in the case of complexes **1-3**, the coordination is from the central NPy out of three pyridine rings and from the amide nitrogens, whereas in the case of **4-6**, only amide nitrogen is involved in bonding to germanium.

The participation and non-participation of lone pair of nitrogen from pyridine ring in complexes **1-3** and **4-6**, respectively have been confirmed from Wiberg bond index analysis and the important bond indexes for complexes **3** and **6** are shown in Fig. 4. The C=O bond index in H_2L is 1.6861 which is slightly lowered after complexation and C-N bond index is 1.1253 which is slightly increased in complex. From the figure it is clear that in diamide complex, the coordination is only from central pyridine ring and in the case of monoamide complex, there is no coordination from pyridine ring nitrogens.

From NBO analysis it is observed that the significant donor acceptor interactions are occurred between germanium and two amide nitrogens (103.07-92.50 kcal/mol) and germanium

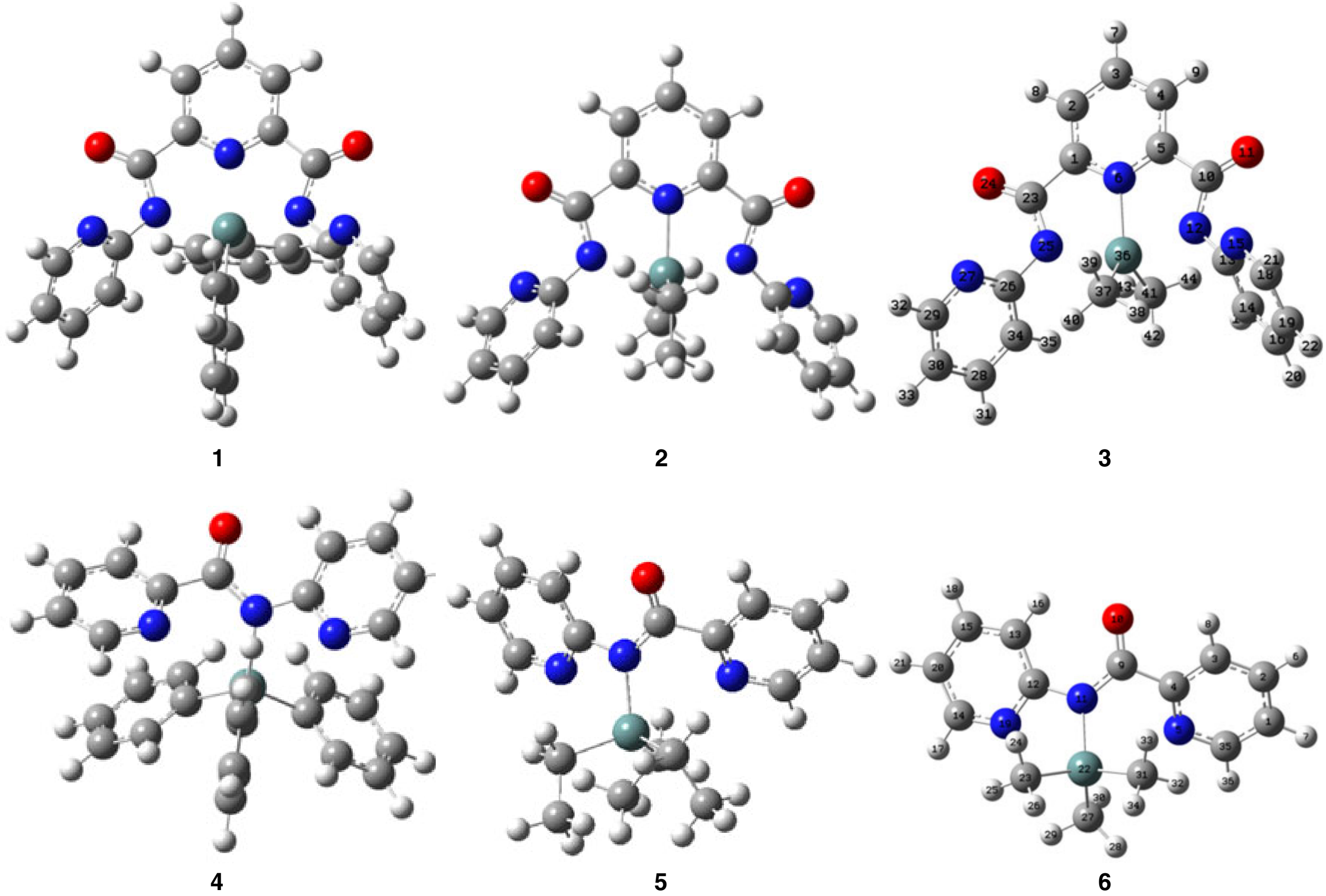
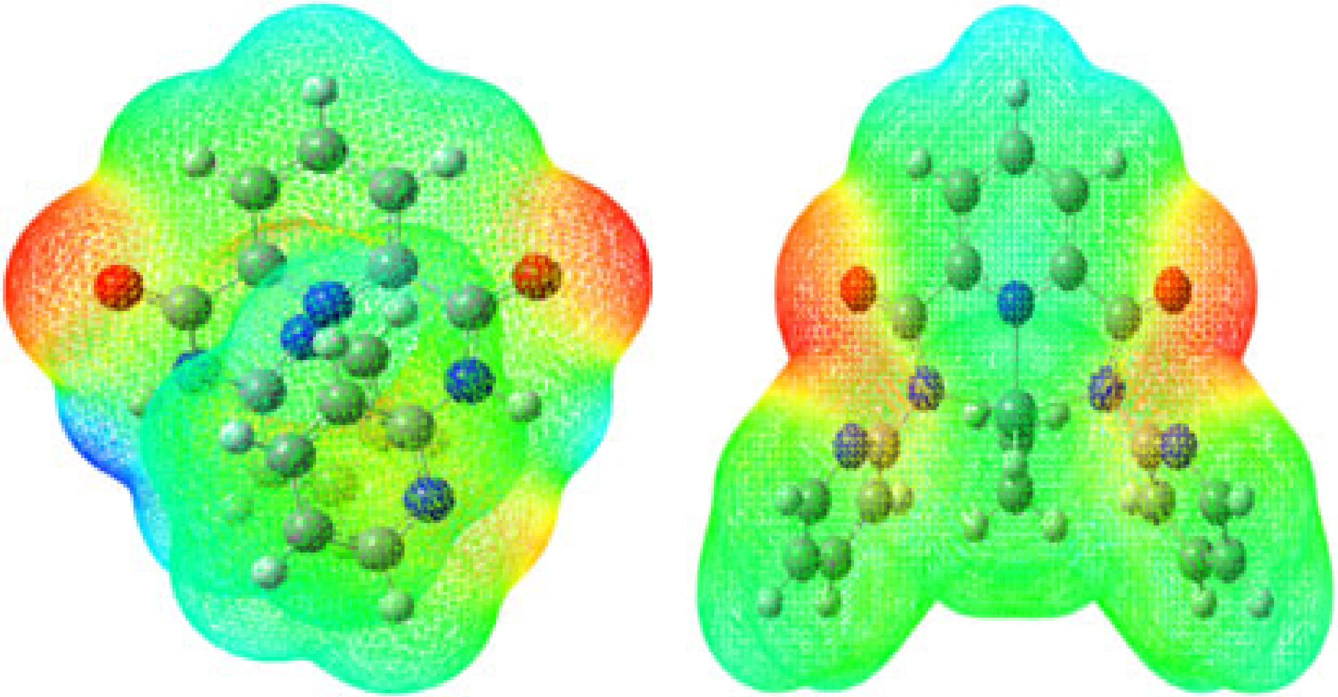


Fig. 2. Optimized structure of germanium complexes **1-6**



O: -0.594; C: 0.688; N: -0.642   O: -0.600; C: 0.654; N: -0.759

Fig. 3. MESP plot and NPA charges of respective atoms for H_2L and complex **3**

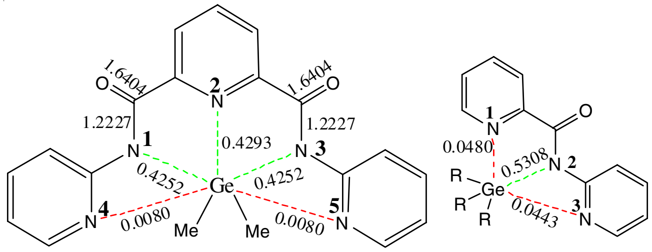


Fig. 4. Wiberg bond index analysis

and pyridine nitrogen from central ring (173.91-152.98 kcal/mol) in diamide derivatives. There is no delocalization from N_4 and N_5 to germanium in complexes **1-3**. In the case of mono-amide derivatives these interactions are significant only from amide nitrogen (116.43-98.27). Perturbation analysis of the methyl derivatives which has highest energy values is shown in Table-2 and the atom labeling patterns are corresponding to Fig. 4. Thus all these facts leads to the conclusion that complexes **1-3** contain penta coordinated germanium atom due to transannular bonding and **4-6** contains tetracoordinated germanium atom.

TABLE-2
SECOND ORDER PERTURBATION ANALYSIS

Donor (i)	Acceptor (j)	E (2) (kcal/mol)
	Complex **3**	
LP N_2	LP* Ge	173.91
LP N_1	LP* Ge	103.07
LP N_3	LP* Ge	103.07
	Complex **6**	
LP N_2	LP* Ge	116.43
LP N_2	LP* Ge	82.67
LP N_1	LP* Ge	3.98
LP N_3	LP* Ge	1.58

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. Z. He, C. He, Z.M. Wang, E.Q. Gao, Y. Liu and C.H. Yan, *Dalton Trans.*, 502 (2004); https://doi.org/10.1039/b315281b
2. D.S. Marlin, M.M. Olmstead and P.K. Mascharak, *Eur. J. Inorg. Chem.*, **2002**, 859 (2002); https://doi.org/10.1002/1099-0682(200203)2002:4<859::AID-EJIC859>3.0.CO;2-Z
3. D.S. Marlin and P.K. Mascharak, *Chem. Soc. Rev.*, **29**, 69 (2000); https://doi.org/10.1039/a905282h
4. D.A. Conlon and N. Yasuda, *Adv. Synth. Catal.*, **343**, 137 (2001); https://doi.org/10.1002/1615-4169(20010129)343:1<137::AID-ADSC137>3.0.CO;2-V
5. B.M. Trost and I. Hachiya, *J. Am. Chem. Soc.*, **120**, 1104 (1998); https://doi.org/10.1021/ja973298a
6. S.R. Collinson, J.H.R. Tucker, T. Gelbrich and M.B. Hursthouse, *Chem. Commun.*, 555 (2001); https://doi.org/10.1039/b009820p
7. I. Huc, M.J. Krische, D.P. Funeriu and J.M. Lehn, *Eur. J. Inorg. Chem.*, **1999**, 1415 (1999); https://doi.org/10.1002/(SICI)1099-0682(199909)1999:9<1415::AID-EJIC1415>3.0.CO;2-Y
8. J.D. Epperson, L.J. Ming, G.R. Baker and G.R. Newkome, *J. Am. Chem. Soc.*, **123**, 8583 (2001); https://doi.org/10.1021/ja015856y
9. T. Thompson, S.D. Pastor and G. Rihs, *Inorg. Chem.*, **38**, 4163 (1999); https://doi.org/10.1021/ic990460x
10. S.D. Pastor, A.R. Smith and G. Rims, *Phosphorus Sulfur Silicon Rel. Elem.*, **115**, 169 (1996); https://doi.org/10.1080/10426509608037964
11. R. Thomas, N. Joseph P, P. Pardasani and T. Mukherjee, *Heteroatom Chem.*, **23**, 545 (2012); https://doi.org/10.1002/hc.21048
12. P. Pardasani and D. Kumar, *Main Group Met. Chem.*, **27**, 233 (2004); https://doi.org/10.1515/MGMC.2004.27.4.233

13. M. Sharma and P. Pardasani, *Main Group Met. Chem.*, **31**, 227 (2008); https://doi.org/10.1515/MGMC.2008.31.5.227
14. M. Sharma, S. Jangir, C.K. Ojha and P. Pardasani, *Main Group Met. Chem.*, **28**, 193 (2005); https://doi.org/10.1515/MGMC.2005.28.4.193
15. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski and D.J. Fox, Gaussian Inc., Wallingford CT, Gaussian 09, Revision D.01 (2009).
16. W.L.F. Armarego and D.D. Perrin, Purification of Laboratory Chemicals, Butterworth: Oxford, edn 4 (1997).
17. A.I. Vogel, Textbook of Quantitative Chemical Analysis, Longman: London, edn 4 (1989).
18. Z.X. Chen, J.M. Xiao, H.M. Xiao and Y.N. Chiu, *J. Phys. Chem. A*, **103**, 8062 (1999); https://doi.org/10.1021/jp9903209
19. N.J. Mayhall, K. Raghavachari, P.C. Redfern and L.A. Curtiss, *J. Phys. Chem. A*, **113**, 5170 (2009); https://doi.org/10.1021/jp809179q
20. B.M. Rode, eds.: B. Pullman and N. Goldblum, The Investigation of Metal-Amide Interactions with the Aid of Quantum Chemical Model Calculations and Corresponding Model Experiments; In: Metal-Ligand Interactions in Organic Chemistry and Biochemistry, The Jerusalem Symposia on Quantum Chemistry and Biochemistry, vol 9-1. Springer: Dordrecht (1977).