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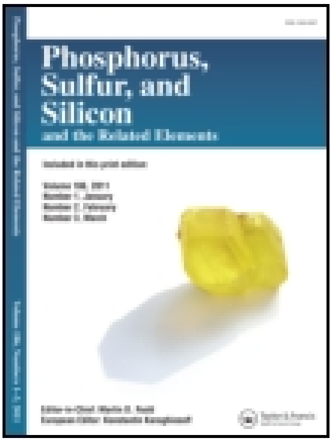

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Synthesis, Spectroscopic, and Structural Properties of Organogermanyl(IV) Complexes of Pyridine Oximes

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SYNTHESIS, SPECTROSCOPIC, AND STRUCTURAL PROPERTIES OF ORGANOGERMANYL(IV) COMPLEXES OF PYRIDINE OXIMES

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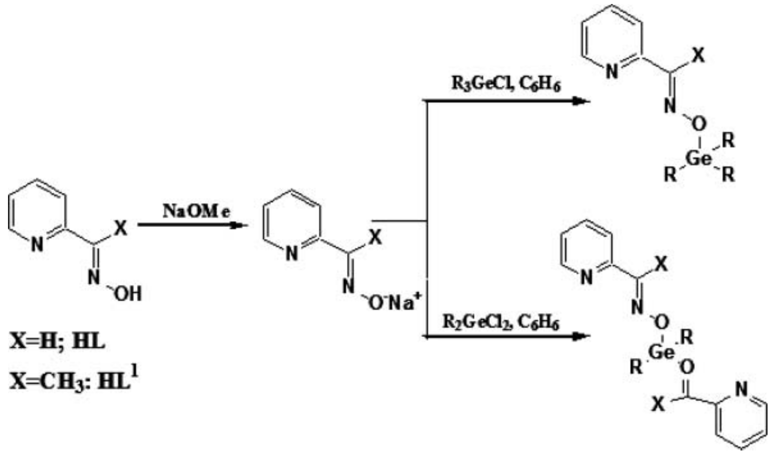
GRAPHICAL ABSTRACT



Abstract *Reactions of triorganogermanyl(IV) chlorides and diorganogermanyl(IV) dichlorides with sodium salts of pyridine-2-carbaldehyde oxime and 2-acetylpyridine oxime, respectively, in 1:1 and 1:2 molar ratio produced organogermanyl(IV) oximates. All the derivatives have been characterized by spectroscopic techniques and tetrahedral structures have been proposed on the basis of spectroscopic data and molecular orbital calculations.*

Keywords Pyridine-2-carbaldehyde oxime; 2-acetylpyridine oxime; organogermanium complexes; DFT study

INTRODUCTION

Organometallic compounds of group 14 elements (Ge, Sn, and Pb) are of great interest owing to a wide variety of structural features ranging from monomers[1] to clusters[2–4] as well

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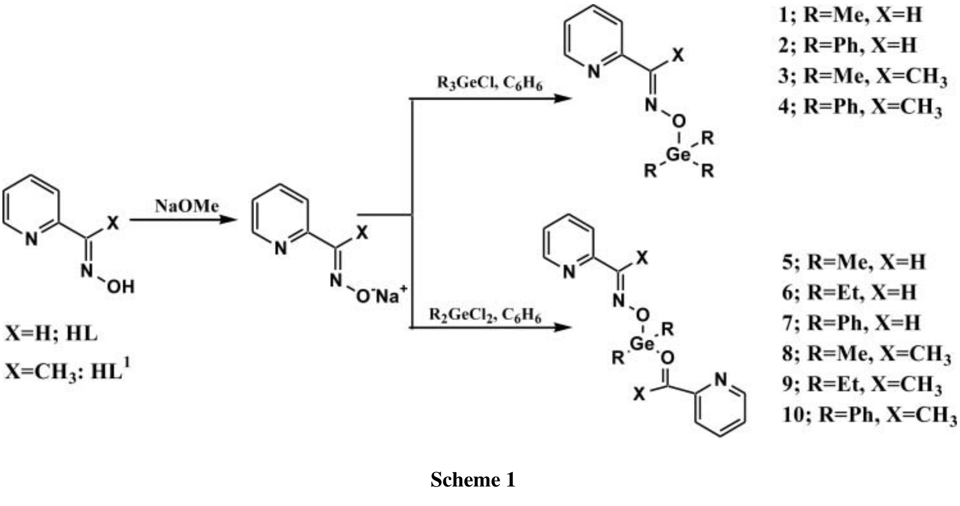
as pharmacological importance and industrial applications.[5] Oximes are also well known synthons due to their biological activities and ability to form complexes through oximate oxygen and amido nitrogen.[6] Pyridine-2-carbaldehyde oxime, one of the ligands used in the present study, is commonly used in human and veterinary practices as acetyl cholinesterase reactivators. Their metal complexes can act as drugs since complexation protects the active site against enzymatic degradations and its activity can be reinforced at a specific organ.[7]

Complexes of germanium have received less attention as compared to the other elements of this group. Germanium complexes usually prefer tetracoordinated structures though pentacoordinated and hexacoordinated derivatives have also been reported.[8] Germanium derivatives are important constituents in optical devices like optical wave guides[9,10] and in the field of medicine.[11,12] Hence in continuation to our interest in complexes of group 14 elements,[13–15] we are reporting herein syntheses of various diorganogermanyl(IV) and triorganogermanyl(IV) pyridine oximates. Newly synthesized complexes are characterized by different methods like IR, ^{1}H, and ^{13}C NMR spectroscopy and elemental analysis. Theoretical calculations have been performed at the DFT-B3LYP level on GAUSSIAN 03 program to understand the mode of chelation in the complexes.

RESULTS AND DISCUSSION

The ligands pyridine-2-carbaldehyde oxime and 2-acetylpyridine oxime have been synthesized and converted into respective sodium salts by refluxing with sodium methoxide in methanol. The triorganogermanyl(IV) oximates and diorganogermanyl(IV) oximates were prepared with above 75% yield by reaction of R_3GeCl and R_2GeCl_2 with sodium salts of ligands in 1:1 and 1:2 molar ratios, respectively, as depicted in Scheme 1. All the complexes are moisture sensitive and have been handled in dry conditions or inert atmosphere with utmost care. They are readily soluble in organic solvents like methanol, ethanol, benzene, chloroform, etc. and have been characterized by physical analysis as well as various spectroscopic techniques (Tables 1 and 2).



Scheme 1

Table 1 Physical and analytical data of oximes and their organogermanyl(IV) complexes

				Elemental analysis % found (calculated)			
Compound	Appearance	Yield (%)	mp (^{o}C)	C	H	N	Ge
HL	Off-white solid	75	111	58.34 (59.01)	4.43 (4.95)	23.26 (22.94)	—
HL^1	Light violet powder	83	122	58.34 (59.01)	4.43 (4.95)	23.26 (22.94)	—
1	Violet solid	75	135	44.35 (45.26)	6.04 (5.91)	11.42 (11.73)	31.21 (30.40)
2	Light brown solid	82	142	67.41 (67.82)	4.55 (4.74)	6.98 (6.59)	16.88 (17.08)
3	Reddish brown solid	79	96	47.67 (47.50)	6.66 (6.38)	11.54 (11.08)	28.24 (28.72)
4	Light violet powder	83	146	68.87 (68.39)	4.86 (5.05)	6.42 (6.38)	16.85 (16.54)
5	Light yellow powder	83	85	48.84 (48.25)	4.76 (4.68)	16.64 (16.24)	19.94 (21.05)
6	Dark red powder	87	132	51.86 (51.53)	53.73 (5.41)	14.86 (15.02)	19.67 (19.47)
7	Dark brown solid	84	170	61.58 (61.46)	4.62 (4.30)	12.05 (11.94)	15.72 (15.45)
8	Brown solid	78	88	51.88 (51.53)	5.47 (5.41)	15.11 (15.02)	19.79 (19.47)
9	Black solid	77	91	53.74 (53.91)	6.27 (6.03)	14.21 (13.97)	18.36 (18.11)
10	Dark brown	82	128	62.97 (62.82)	4.72 (4.87)	11.54 (11.27)	14.84 (14.61)

Table 2 Spectroscopic data of ligands and their organogermanyl(IV) complexes

Comp	IR (cm^{-1})				NMR (δ value)	
	ν_{OH}	$\nu_{C=N}$	ν_{Ge-O}	ν_{Ge-C}	^{1}H	^{13}C
HL	3222–3014	1515	–	–	11.74 (s, 1H, NOH), 8.84–7.18 (m, 4H, ArH + s, 1H)	152.16, 148.94 (ArC=N), 149.10 (C=NOH), 136.80–120.14 (Ar–C)
HL^1	3258–3103	1490	–	–	11.37 (s, 1H NOH), 8.23–7.11 (m, 4H, ArH), 2.24(s, 3H, CH_3)	154.00, 153.77 (ArC=N), 148.20 (C=NOH), 137.20–120.35 (Ar–C), 10.51(CH_3)
1	–	1506	832	670	8.55–7.18 (m, 4H, ArH + s, 1H), 1.66 (s, 9H, Ge–Me)	151.83, 149.64 (ArC=N), 149.02 (C=NOH), 136.97–120.97 (Ar–C), 23.92 (Ge-Me)
2	–	1490	855	623	8.62–7.19 (m, 20H, ArH + PhH + 1H)	151.22, 148.02 (ArC=N), 148.01 (C=NOH), 135.91–118.82 (Ar–C + Ph-C)
3	–	1485	836	680	8.58–7.18 (m, 4H, ArH + s, 1H), 2.40 (s, 3H,CH_3), 1.64 (s, 9H, Ge–Me)	156.45, 154.31 (ArC=N), 148.80 (C=NOH), 136.53–120.63 (Ar–C), 23.45 (Ge-Me), 10.85 (CH_3)
4	–	1480	860	672	8.64–7.18 (m, 19H, ArH + PhH), 2.40 (s, 3H, CH_3)	156.76, 154.29 (Ar–C =NOH), 148.87 (C=N), 137.44–120.55 (Ar–C + Ph–C), 10.73 (CH_3)
5	–	1510	820	660	8.55–7.19 (m, 5H, ArH + 1H), 0.70 (s, 9H, Ge-Me)	151.93, 149.67 (Ar–C=N), 149.03 (C=N), 136.91–120.86 (Ar–C), 4.52 (Ge-Me)
6	–	1512	845	685	8.56–7.20 (m, 5H, ArH + 1H), 1.51 (q, 2H, CH_2CH_3), 1.02 (t, 3H, CH_2CH_3)	150.99, 149.64 (Ar–C=N), 147.59 (C=N), 136.27–119.53 (Ar–C), 14.36 (CH_2CH_3), 6.31 (CH_2CH_3)
7	–	1495	840	620	7.68–7.10 (m, 20H, ArH + PhH + 1H)	149.04 145.09 (Ar–C=N), 144.92 (C=N), 138.76–120.29 (Ar–C + Ph–C)
8	–	1485	842	652	8.57–7.17 (m, 4H, ArH), 2.16 (s, 3H, CH_3), 0.69 (s, 9H, Ge–Me)	156.12, 154.22(Ar–C=N), 146.37(C=N), 137.91–120.66 (Ar–C), 4.33 (Ge–Me), 10.79 (CH_3)
9	–	1486	833	655	8.57–7.18 (m, 4H, ArH), 2.29 (s, 3H, CH_3), 1.25 (q, 2H, CH_2CH_3), 1.01 (t, 3H, CH_2CH_3)	155.94, 154.15 (Ar–C=N), 148.52 (C=N), 136.83–120.70 (Ar–C), 15.43 (CH_2CH_3), 7.10 (CH_2CH_3), 10.75(CH_3)
10	–	1483	862	640	7.72–7.18 (m, 19H, ArH + PhH), 2.31 (s, 3H, CH_3)	150.16, 149.52 (Ar–C=N), 148.66 (C=N), 136.68–120.66 (Ar–C + Ph–C), 10.58(CH_3)

Spectroscopic Studies

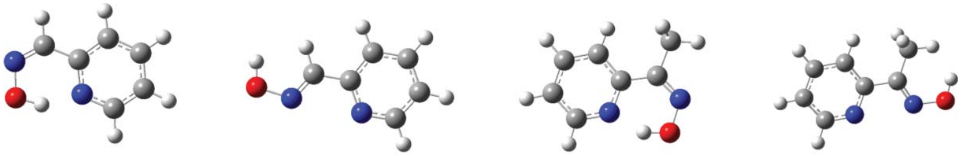
The IR spectra of the complexes were interpreted by comparison with the spectra of free oximes. The $\nu_{C=N}$ absorption band for oximes HL and HL^1 appeared at 1515 and 1480 cm^{-1}, respectively. The hydroxyl absorption peak of the oxime ligands in the region 3258–3014 cm^{-1} was absent in the IR spectra of all the derivatives indicating metal-ligand bond formation through the oxygen atom. The $\nu_{C=N}$ and $\nu_{N–O}$ absorption bands for oximes are shifted to lower wave number on complexation. The formation of complexes is further confirmed by the appearance of two new bands in the region 860–820 cm^{-1} and 680–620 cm^{-1}, which can be assigned to $\nu_{Ge–O}$[16] and $\nu_{Ge–C}$[17], respectively.

The ^{1}H and ^{13}C NMR spectra of all compounds exhibited characteristic signals and multiplicities for R–Ge and ligand protons. The hydroxyl proton of free ligands at δ 11.74 and δ 11.37 was absent in all these complexes suggesting the deprotonation of the NOH group[18] and complexation with metal through the Ge–O bond. There is no appreciable shift for ligand ring protons indicating the absence of coordination through heteroatom present in the aromatic ring in these complexes. In the ^{1}H NMR, trimethyl derivatives showed a singlet at δ 1.66 and δ 1.64 of methyl protons in compounds **1** and **3**, respectively, while dimethyl derivatives **5** and **8** showed singlets at δ 0.70 and δ 0.69, respectively. For diethyl derivatives **6** and **9,** multiplets were observed in the range δ 1.01–δ 1.51.

In the ^{13}C NMR spectra of ligands **HL** and **HL^1**, carbon resonance due to >C=NOH carbon appeared at δ 149.10 and δ 148.20, whereas in complexes, only a slight deviation in ligand ring carbon signals was observed, thus confirming that the nitrogen atom in the pyridine ring is not involved in coordinate bond formation with the central metal atom. For trimethylgermanyl(IV) oximates **1** and **3**, methyl carbon signal was observed at δ 23.92 and δ 23.45, the dimethyl derivatives **5** and **8** showed corresponding methyl resonance at δ 4.52 and δ 4.33.

Theoretical Studies

In order to confirm the structure of the synthesized complexes, molecular orbital calculations have been carried out using GAUSSIAN 03 suit of program at DFT/B3LYP level with 3-21G as basis set.[19] These types of calculations are very useful in detecting the mode of chelation in the molecules. In ligands HL and HL^1, s*yn* isomer is more stable than the *anti* isomer with a difference of 17.41 and 14.58 kcal/mol, respectively. It may be attributed to the formation of a hydrogen bond with the pyridine nitrogen ligand. The optimized geometries of ligands are shown in Figure 1.



syn HL (-260169.83kcal/mol)

anti HL (-260155.25kcal/mol)

***syn* HL^1** (-284709.88kcal/mol)

***anti* HL^1** (-284692.47kcal/mol)

Figure 1 Optimized geometries of ligands (Color figure available online).

Table 3 Minimum energy of complexes for different structures

Compound	Energy in kcal/mol Tetrahedral	Trigonal bipyramidal	Octahedral
1	−1631656.1517	−1631649.2933	–
2	−1990639.9829	−1990629.8135	–
3	−1656195.9793	−1656194.5825	–
4	−2015181.0703	−2015174.3223	–
5	−1849628.8641	–	−1848903.3371
6	−1915728.0262	–	−1915643.2759
7	−2105888.2558	–	−2105882.3309
8	−1915656.2806	–	−1915635.8928
9	−1964728.2006	–	−1964707.5516
10	−2154973.3563	–	−2154959.4618

The nitrogen atom of pyridine in ligands can coordinate with the central germanium atom to give trigonal bipyramidal and octahedral structures for triorganogermanyl(IV) oximates and diorganogermanyl(IV) oximates, respectively. The minimum energy values of optimized geometries are tabulated in Table 3. From the data mentioned in Table 3, it is evident that tetrahedral geometries are more stable than trigonal bipyramidal and octahedral geometries. During complex formation the more stable *syn* form of ligands tends to change into *anti* form. The central germanium metal prefers to stay in tetracoordinated nature rather than pentacoordinated and hexacoordinated, like tin and lead.

From the data mentioned in Table 3, it is evident that the minimum energy is high for ethyl complexes (**6** and **9**) as compared to methyl derivatives (**5** and **8**). This accounts for the high moisture sensitiveness of methyl derivatives as compared to ethyl and phenyl germanium complexes. The Ge–C and Ge–O bond lengths and C–Ge–O bond angle, obtained from the optimized geometries of tetrahedral structures, are tabulated in Table 4 and are in good agreement with the literature value.[20,21]

Table 4 Selected bond lengths and bond angles of organogermanium oximates

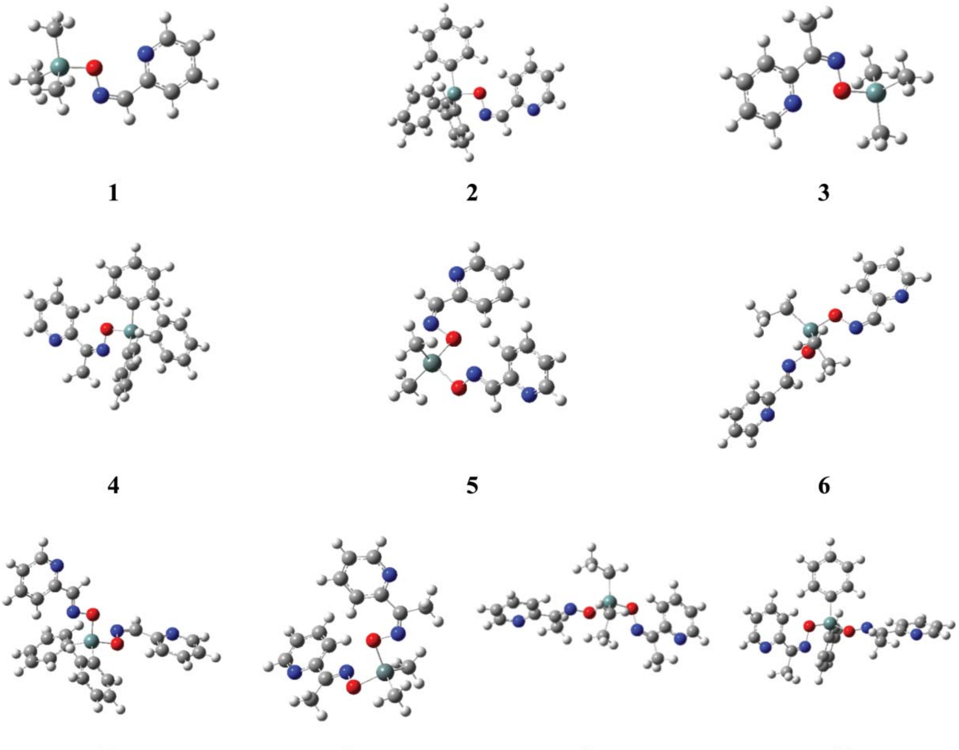
Compound	Bond length in Å Ge–O	Ge–C	Bond angle in ° O–Ge–C
1	1.8136	1.9553	109.1817
2	1.8196	1.9322	110.2251
3	1.8128	1.9558	109.2689
4	1.8174	1.9329	110.3522
5	1.8051	1.9421	110.1912
6	1.7953	1.9457	111.4307
7	1.8050	1.9219	111.9112
8	1.7924	1.9428	111.2554
9	1.7947	1.9473	111.6499
10	1.8042	1.9229	111.7471

CONCLUSION

On the basis of spectroscopic observations and molecular orbital calculations, tetrahedral structures have been proposed for diorganogermanyl(IV) and triorganogermanyl(IV) pyridine oximates. The optimized geometries of complexes (1–10) are shown in Figure 2.

EXPERIMENTAL

All chemicals have been purchased from Merck and Aldrich and used without further purification. All reactions were carried out under nitrogen atmosphere and moisture was rigorously excluded throughout the experimental manipulations. Solvents were dried by standard methods.[22] The IR spectra were recorded in KBr pellets on a Nicolet DX FTIR spectrometer in the range 4000–400 cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 solvent with TMS as internal standard on a JEOL 300AL FTNMR spectrometer operating at 300 and 75.47 MHz, respectively. The mps were recorded on a Perfit mp apparatus and are uncorrected. Germanium was estimated as germanium oxide.[23] Theoretical calculations have been performed at DFT-B3LYP level on GAUSSIAN 03 program with 3-21G as the basis set.



1 2 3

4 5 6

7 8 9 10

Figure 2 Optimized geometries of tri/diorganogermanyl(IV) oximates (Color figure available online).

Synthesis of Ligands

Pyridine-2-carbaldehyde oxime (HL): The ligand HL was prepared according to the literature method.[24]

2-Acetylpyridine oxime (HL^1): HL^1 was prepared by refluxing 2-acetylpyridine with hydroxylamine hydrochloride in the presence of a base.[25]

Synthesis of Complexes

Trimethylgermanyl(lV) pyridine-2-carbaldehyde oximate: To a methanolic solution (10 mL) of the sodium salt of the ligand (prepared by the reaction of Na [0.092 g, 4.0 mmol] with pyridine-2-carbaldehyde oxime [0.488 g, 4 mmol] in refluxing methanol), a benzene solution (10 mL) of trimethylgermanyl chloride (0.6433 g, 4.2 mmol) was added dropwise and refluxed for 4 h. NaCl formed during the reaction was filtered off and the filtrate was dried in vacuo and was recrystallized from dichloromethane:hexane (1:1) to obtain a violet colored crystalline solid (0.72 g, yield 75%).

All other triorganogermanyl(IV) oximates of pyridine-2-carbaldehyde oxime and 2-acetylpyridine oxime were prepared analogously.

Dimethylgermanyl(lV) 2-pyridinecarboxaldehyde oximate: To a methanolic solution (10 mL) of the sodium salt of ligand (prepared by the reaction of Na [0.092 g, 4.0 mmol] with pyridine-2-carbaldehyde oxime [0.488 g, 4 mmol] in refluxing methanol), a benzene solution (10 mL) of dimethylgermanyl dichloride (0.3645 g, 2.1 mmol) was added dropwise and refluxed for 6 h. NaCl formed during the reaction was filtered off and the filtrate was dried in vacuo to obtain a yellow solid, which was recrystallized from dichloromethane:hexane (1;1) to afford a light yellow powder (0.60 g, yield 83%).

All other diorganogermanyl(IV) oximates of pyridine-2-carbaldehyde oxime and 2-acetyl pyridine oxime have similarly been synthesized.

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