Monatshefte für Chemie 111, 1391—1397 (1980) **Monatshefte für Chemie**

N-Substituted Salicylaldimines Derivatives of Germanium(IV)

R. V. Singh and **J. P. Tandon** *

Department of Chemistry, University of Rajasthan, Jaipur-302004, India

(Received 14 March 1978. Revised 2 August 1978. Accepted 25 September 1978)

Hexa-coordinated *Schiff* base complexes of germanium of the general type $Ge(OC_2H_5)_2(SB)_2$ (SB^- is the anion of the monofunctional bidentate *Schiff* base, *SBH*) have been synthesized by the reaction between ethyl-orthogermanate and the *Schiff* base in benzene medium. Always a 1:2 complex is obtained irrespective of the molar ratios in which the reactants are used. The resulting new complexes have been characterized by elemental analysis, molecular weight determinations, infrared and proton magnetic resonance spectra and found to be non-electrolytes in *DMF*.

(Keywords: Complexes, Ge(IV); Germanium(IV), complexes; Schiff bases, complexes)

N-Substituierte Salicylaldimin-Komplexe des Germanium(IV)

Es wurden hexa-koordinierte *Schiff*-Basen Komplexe des Germanium(IV), vom generellen Typ $Ge(OC_2H_5)_2(SB)_2$ (SB^- ist das Anion der monofunktionellen, zweizähnigen *Schiff*-Base *SBH*), über die Reaktion von Ethylorthogermanat mit der entsprechenden *Schiff*-Base hergestellt. Es wurden durchwegs 1:2-Komplexe erhalten. Elementaranalyse, Molgewichtsbestimmung und IR- und NMR-Spektroskopie wurden zur Charakterisierung der Komplexe herangezogen.

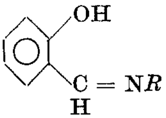
Introduction

1:2 Molar adducts of group IV tetrachlorides with *Schiff* bases have been reported in the literature[1–5]. Germanium(IV) chloride complexes with *o*-hydroxy anils of aromatic aldehydes have also been described[6]. In view of the success achieved earlier in synthesizing a wide variety of *Schiff* base derivatives by the reaction of metal alkoxides with the *Schiff* bases in anhydrous medium, it was considered worthwhile to study the reactions of $Ge(OC_2H_5)_4$ with the *Schiff* bases.

The present paper describes the synthesis and important properties of some of these derivatives. They have been prepared by the reaction of

0026-9247/80/0111/1391/$ 01.40

ethylorthogermanate with N-substituted monofunctional bidentate *Schiff* bases in 1:2 molar ratios. The *Schiff* bases used were of the type:



(where $R = C_2H_5$, n-C_3H_7, *iso*-C_3H_7, n-C_4H_9, *iso*-C_4H_9, *sec*-C_4H_9, *tert*-C_4H_9, C_6H_5, o-$C_6H_4CH_3$, m-$C_6H_4CH_3$, p-$C_6H_4CH_3$, o-$C_6H_4OCH_3$, m-$C_6H_4OCH_3$ and p-$C_6H_4OCH_3$).

Experimental

Materials and Methods

As ethylorthogermanate and the *Schiff* base complexes are moisture sensitive, reactions were carried out under strictly anhydrous conditions. The apparatus used for the preparative studies was equipped with Quickfit interchangeable joints. All distillations were carried out on a column packed with *Raschig* rings which was fitted with a ratio head. The condenser was protected with calcium chloride (anhydrous)guard tubes.

Benzene (B.D.H., A.R.) was dried by refluxing over sodium wire for several hours and was finally distilled azeotropically with ethanol. Absolute alcohol was dried by refluxing over calcium oxide, sodium and magnesium wires respectively for several hours and finally distilled azeotropically with benzene. Ethylorthogermanate was prepared by the ammonia method[7]. It was distilled at 80 °C/9.0 mm before use and then analyzed (Found: Ge, 28.69; OC_2H_5, 71.01. Calcd. for Ge $(OC_2H_5)_4$: Ge, 28.71; OC_2H_5, 71.29%).

Preparation of Schiff Bases

Schiff bases were prepared by the usual condensation method of salicylaldehyde with amines and then either distilled under reduced pressure or recrystallized from alcohol. Physical properties are recorded in Tab. 1. The analyses for C, H and N were corresponding with the expected structures.

Synthesis of Germanium(IV) Schiff Bases

Ethylorthogermanate was taken in a 100 ml round-bottomed flask containing 40 ml of dry benzene and the calculated amount of aldimine was added. The contents were refluxed using a fractionating column and the ethanol liberated in the reaction was removed azeotropically with benzene. The solvent was removed and the product dried under vacuum. The details of their synthesis, analysis and physical properties are recorded in Tab. 2.

Analytical Method

The accurate analysis of germanium presents some difficulties. However, the following two methods were used for its estimation:

(i) The sample (0.05-0.1 g) was placed in a weighed silica crucible and was hydrolysed with aqueous ammonia (3 ml) and alcohol (1 ml). The solution was carefully evaporated to dryness, ignited at 900 °C and then weighed as GeO_2[8].

Table 1. *Physical properties of the Schiff bases*

No.	*Schiff* base	State and m.p. (°C)	b.p./mm pressure (°C)
1.	*N*-Ethylsalicylideneamine ($C_9H_{11}NO$)	Yellow liquid	75/0.4
2.	*N*-*n*-Propylsalicylideneamine ($C_{10}H_{13}NO$)	Deep yellow liquid	90/1.0
3.	*N*-Isopropylsalicylideneamine ($C_{10}H_{13}NO$)*	Deep yellow liquid	55/1.0
4.	*N*-*n*-Butylsalicylideneamine ($C_{11}H_{15}NO$)	Yellow liquid	84/0.1
5.	*N*-Isobutylsalicylideneamine ($C_{11}H_{15}NO$)*	Yellow liquid	102 105/2.5
6.	*N*-*sec*-Butylsalicylideneamine ($C_{11}H_{15}NO$)*	Yellow liquid	75/0.05
7.	*N*-*tert*-Butylsalicylideneamine ($C_{11}H_{15}NO$)*	Yellow liquid	94 95/2.4
8.	*N*-Phenylsalicylideneamine ($C_{13}H_{11}NO$)	Yellow solid 50	148 150/1.8 2.0
9.	*N*-*o*-Tolylsalicylideneamine ($C_{14}H_{13}NO$)	Yellow solid 44	136 139/0.1
10.	N-m-Tolylsalicylideneamine ($C_{14}H_{13}NO$)*	Brownish yellow liquid	144/0.01
11.	*N*-*p*-Tolylsalicylideneamine ($C_{14}H_{13}NO$)*	Organic solid 94	—
12.	*N*-*o*-Anisylsalicylideneamine ($C_{14}H_{13}NO_2$)	Yellow solid 52	
13.	*N*-*m*-Anisylsalicylideneamine ($C_{14}H_{13}NO_2$)*	Yellow solid 57—58	142 143/0.1
14.	*N*-*p*-Anisylsalicylideneamine ($C_{14}H_{13}NO_2$)*	Grayish green solid 84	

---

* Has been used to distinguish between the compounds of same molecular formula.

Table 2. *Synthesis and properies of* Ge(IV) *Schiff base complexes*

No.	Ge(O*Et*)$_4$ (g)	*Schiff* base (g)	Molar ratio	Compound, yield(g), nature	Analyses (%) Ge Found (calcd)	Analyses (%) N Found (calcd)	C=N Complex (*Schiff* base)	Mol. Weight Found (calcd)
1.	0.86	$C_9H_{11}NO$ (1.02)	1:2	Ge(O*Et*)$_2$($C_9H_{10}NO$)$_2$, (1.35), Yellow solid, soluble in benzene.	15.79 (15.81)	6.15 (6.10)	1640 (1630)	462.7 (458.96)
2.	1.05	$C_{10}H_{13}NO$ (1.36)	1:2	Ge(O*Et*)$_2$($C_{10}H_{12}NO$)$_2$, (1.83), Yellow solid, soluble in benzene.	14.99 (14.90)	5.82 (5.75)	1638 (1630)	495.0 (487.14)
3.	0.95	$C_{10}H_{13}NO$	1:2	Ge(O*Et*)$_2$($C_{10}H_{12}NO$)$_2$, (1.64), Yellow solid, soluble in benzene.	15.01 (14.90)	5.79 (5.75)	1630 (1628)	490.2 (487.14)
4.	0.76	$C_{11}H_{15}NO$ (1.06)	1:2	Ge(O*Et*)$_2$($C_{11}H_{14}NO$)$_2$, (1.35), Brownish yellow, soluble in benzene.	13.80 (14.08)	5.28 (5.43)	1635 (1635)	529.3 (516.20)
5.	0.99	$C_{11}H_{15}NO$ (1.39)	1:2	Ge(O*Et*)$_2$($C_{11}H_{14}NO$)$_2$, (1.92), Yellow, soluble in benzene.	13.76 (14.08)	5.38 (5.43)	1630 (1627)	505.1 (516.20)
6.	1.35	$C_{11}H_{15}NO$	1:2	Ge(O*Et*)$_2$($C_{11}H_{14}NO$)$_2$, (2.51), Yellow solid, soluble in benzene.	14.20 (14.08)	5.55 (5.43)	1635 (1630)	522.9 (515.20)
7.	1.11	$C_{11}H_{15}NO$ (1.49)	1:2	Ge(O*Et*)$_2$($C_{11}H_{14}NO$)$_2$, (2.00), Yellow solid, soluble in benzene.	14.18 (14.08)	5.41 (5.43)	1624 (1615)	535.3 (515.20)
8.	0.74	$C_{13}H_{11}NO$ (1.16)	1:2	Ge(O*Et*)$_2$ ($C_{13}H_{10}NO$)$_2$, (1.45), Yellow solid, insoluble in benzene.	13.31 (13.07)	5.22 (5.04)	1630 (1615)	— (555.16)
9.	0.93	$C_{14}H_{13}NO$ (1.55)	1:2	Ge(O*Et*)$_2$($C_{14}H_{12}NO$)$_2$, (1.87), Yellow solid, insoluble in benzene.	12.59 (12.45)	5.01 (4.80)	1610 (1610)	— (583.24)
10.	1.45	$C_{14}H_{13}NO$ (2.42)	1:2	Ge(O*Et*)$_2$($C_{14}H_{12}NO$)$_2$, (3.24), Light yellow solid, insoluble in benzene.	12.51 (12.45)	4.99 (4.80)	1627 (1620)	— (583.24)
11.	1.21	$C_{14}H_{13}NO$ (2.02)	1:2	Ge(O*Et*)$_2$($C_{14}H_{12}NO$)$_2$, (2.53), Reddish yellow solid, insoluble in benzene.	12.42 (12.45)	4.78 (4.80)	1625 (1625)	(583.24)
12.	1.00	$C_{14}H_{13}NO_2$ (1.80)	1:2	Ge(O*Et*)$_2$($C_{14}H_{12}NO_2$)$_2$, (2.03), Brownish yellow solid, insoluble in benzene.	11.68 (11.81)	4.47 (4.55)	1631 (1626)	— (615.22)
13.	0.97	$C_{14}H_{13}NO_2$ (1.75)	1:2	Ge(O*Et*)$_2$ ($C_{14}H_{12}NO$)$_2$, (2.01), Yellow solid, insoluble in benzene.	12.05 (11.80)	4.67 (4.55)	1629 (1620)	— (615.22)
14.	0.88	$C_{14}H_{13}NO_2$ (1.58)	1:2	Ge(O*Et*)$_2$($C_{14}H_{12}NO_2$)$_2$, (1.99), Greenish yellow solid, insoluble in benzene.	11.83 (11.80)	4.50 (4.55)	1633 (1625)	— (615.22)

(ii) Germanium was estimated as GeO_2 by the direct ignition of the complex after treating with two drops each of sulphuric (A.R.) and nitric acids (A.R.).

Ethanol was determined by oxidation[9] with normal potassium dichromate solution in 12.5% sulphuric acid and nitrogen by *Kjeldahl*'s method.

Physical Measurements

The molecular weight of the resulting derivatives (soluble in benzene) were obtained ebullioscopically. The infrared spectra were recorded as Nujol mulls in the range 4,000–400 cm^{-1} with a Perkin-Elmer 337 Grating IR spectrophotometer.

The ^1H NMR spectra were recorded in CCl_4 solution (*TMS* internal standard) by a Perkin-Elmer RB-12 spectrometer.

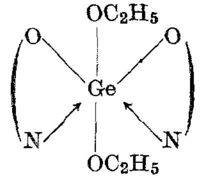
The conductivity was determined by a conductivity bridge (type 235 ANUVIDYUT, ROORKEE).

Results and Discussion

The reaction of ethylorthogermanate with monofunctional bidentate *Schiff* bases (*SBH*) in 1:2 molar ratio can be represented as follows:

$$Ge(OC_2H_5)_4 + 2SBH \rightarrow Ge(OC_2H_5)_2(SB)_2 + 2C_2H_5OH.$$

The resulting diethoxy bis *Schiff* base germanium complexes have been obtained either as coloured solids or semi-solids. The word semisolid is used for a viscous compound which tends to solidify on keeping. The ebullioscopic determinations of the molecular weights in boiling benzene show them to be monomers indicating thereby stable hexacoordinated environment for the central germanium atom as shown below:



In the resulting derivatives, the two remaining ethoxy groups have been found to be labile and to undergo exchange reactions with 2-methyl-2,4-pentanediol. The resulting derivatives are more stable in comparison to the original products.

Conductance

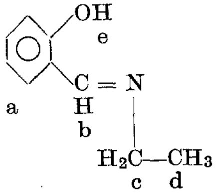
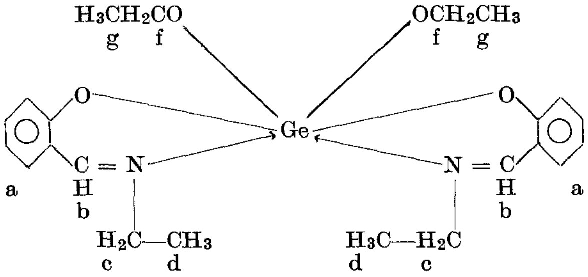
Conductance measurements have shown the nonelectrolyte nature of the germanium *Schiff* base derivatives in *DMF*.

Infrared Spectra

A comparsion of the characteristic i. r. absorption bands of the *Schiff* bases with those of the corresponding germanium complexes reveals the following important features:

(i) In the case of monobasic bidentate *Schiff* bases, no OH stretching frequency is observed possible due to both types of hydrogen bonding, intermolecular (O—H . . . O) as well as intramolecular (O—H . . . N). The frequency of hydrogen-bonded OH is lowered considerably and it overlaps with ν C—H vibrations.

Table 3. *PMR spectral data of Schiff base and a corresponding complex,* δ (ppm)

	Compound	a	b	c	d	e	f	g
(i)		6.53–7.3	8.2	3.5	1.2	12.95	—	—
(ii)		6.6–7.6	8.55	3.5	1.05	—	3.98	1.55

(ii) The absorption frequency of the —CH=N-group in the region 1,635-1,610 cm^{-1} is shifted to higher values in the complexes (Tab. 2). This probably indicates that the coordination due to the π electrons might have led to a decrease in the wave number of the —CH=N stretching vibrations[10, 11].

(iii) A strong band at ~ 1,040 cm^{-1} may be assigned to the Ge—O—C absorption[12].

(iv) The maximum intensity band in the *Schiff* base complexes in the 900-800 cm^{-1} region may be attributed to the ν Ge—O band[12].

Proton Magnetic Resonance Spectra

The proton magnetic resonance spectra of N-ethylsalicylidineamine and the corresponding 1:2 derivatives have been recorded in CCl_4 and the chemical shift values (δ) of the different protons are recorded in Tab. 3. A comparison of the two spectra leads to the following conclusion and this is in conformity with the proposed structure of the germanium complexes:

(i) In the case of monofunctional bidentate *Schiff* base (i, Tab. 3), the signal observed at δ 12.95 ppm may be assigned to the phenolic OH. It has been observed that this signal disappears in the spectra of the corresponding germanium complex (ii, Tab. 2) providing a strong evidence for the desired complexation through the phenolic OH group.

(ii) The proton signal for methylene proton at 8.2 in N-ethylsalicylideneamine (Tab. 3) shifts downfield in the spectra of the germanium complex showing its deshielding. This possibly is due to the donation of a lone pair of electrons by the nitrogen to the central germanium atom to give the coordinate linkage.

(iii) A considerable shift in the position of the aromatic protons as well as the alkyl protons attached to nitrogen further substantiates the chelation of germanium to the nitrogen of the azomethine group.

(iv) Two proton signals at 3.98 and 1.55 (ii, Tab. 3) may be attributed to methine and methyl protons of the two ethoxy groups respectively, which are not observed in the spectra of N-ethylsalicylideneamine (i, same Tab.).

The authors thank the C.S.I.R., New Delhi, for financial assistance.

References

[1] *V. A. Kogan, O. A. Osipov, V. I. Minkin*, and *V. P. Sokolov*, Zhur. Neorg. Khim. **10**, 83 (1965) [Russ. J. Inorg. Chem., No. 1 (1965)].

[2] *V. A. Kogan, V. P. Sokolov*, and *O. A. Osipov*, Zhur. Neorg. Khim. **13**, 2314 (1968) [Russ. J. Inorg. Chem., No. 8 (1968)].

[3] *V. P. Sokolov, V. A. Kogan, O. A. Osipov*, and *L. T. Kolomin*, Zhur. Neorg. Khim. **14**, 2401 (1969) [Russ. J. Inorg. Chem., No. 9 (1969)].

[4] *L. A. Kaztsyna, A. A. Nilson, N. B. Kupletskaya*, and *O. A. Reutov*, Vestnik Moskov. Gos. Univ., Ser. Khim., No. 2, 95 (1966).

[5] *N. S. Birader* and *V. H. Kulkarni*, J. Inorg. Nucl. Chem. **33**, 3848 (1971).

[6] *V. L. Shelepina, O. A. Osipov, O. E. Shelepin, A. O. Garnovskii*, and *L. V. Orlova*, Zhur. Neorg. Khim. **14**, 3276 (1969) [Russ. J. Inorg. Chem., No. 12 (1969)].

[7] *D. C. Bradley, R. C. Mehrotra*, and *W. Wardlaw*, J. Chem. Soc. London **1952**, 2027.

[8] *D. C. Bradley, L. J. Kay*, and *W. Wardlaw*, J. Chem. Soc. **1956**, 4916.

[9] *D. C. Bradley, F. M. A. Halim*, and *W. Wardlaw*, J. Chem. Soc. **1950**, 3450.

[10] *N. I. Pirtakhalava* and *K. P. Giorgadze*, Russ. J. Inorg. Chem. **20**, 12 (1975).

[11] *V. A. Kogan, A. S. Egorov*, and *O. A. Osipov*, Zh. Neorg. Khim. **18**, 2091 (1973).

[12] *O. Johnson* and *H. Fritz*, J. Amer. Chem. Soc. **75**, 718 (1953).