Coordination Germanium(IV) Compounds with Nitrosubstituted Benzoylhydrazones of Salicylaldehyde

I. I. Seifullina, N. V. Shmatkova, and A. V. Mazepa

Mechnikov University, ul. Petra Velikogo 2, Odessa, 270100 Ukraine Bogatskii Physicochemical Institute, National Academy of Sciences of Ukraine, Chernomorskaya doroga 86, Odessa, 270080 Ukraine Received December 13, 2000

Abstract—New germanium(IV) complexes with *N*-[X-benzoyl]hydrazones of salicylaldehyde (X-H₂L, where X = 2-, 3-, and 4-NO₂; H₂L = C₆H₄–CO–NH–NCH–C₆H₄OH) with the compositions [Ge(2-NO₂–L)₂], [Ge(3-NO₂–L)₂], and [Ge(4-NO₂–L)₂] were synthesized. The data of IR, UV, and ¹H, ¹³C NMR spectroscopy showed that the complexes had an octahedral structure and ligand coordination through the nitrogen atom of the azomethine group and two oxygen atoms of the doubly deprotonated form of the ligand. The thermal stability of the complexes was studied. The specific features of the mass spectrometric behavior of the substances in the gas phase under electron impact were considered.

INTRODUCTION

In order to establish the regularities that govern the correlation between the physicochemical properties and structure, researchers usually study coordination compounds of a complex-forming agent with certain organic molecules which have different substituents or arrangements of these substituents. This is of particular urgence in biologically active substances because it is important to extend this series of compounds and establish the correlation between the properties and biological activity.

In this work, we chose germanium tetrachloride (GeCl₄) and three benzoylhydrazones of salicylaldehyde (H₂L = C₆H₄-CO-NH-NCH-C₆H₄OH) with the nitro group in different (2-, 3-, 4-) positions of the benzene ring (X-H₂L, where X = 2-, 3-, 4-NO₂) as the objects of study for the following reason. Researchers' interest in the diverse biological activity exhibited by both germanium-containing compounds [1] and benzoylhydrazones and their complexes with various metals [2, 3] has increased in recent years.

The task of the present study was to develop procedures for the synthesis of new coordination compounds of germanium(IV), to perform a comprehensive study of them using mass spectrometry and UV, IR, and ¹H, ¹³C spectroscopy, and to establish the influence of the nitro group position on the ligand coordination and some physicochemical properties of the complexes formed.

EXPERIMENTAL

GeCl₄ (special purity grade), hydrazides of 2-, 3-, and 4-nitrosubstituted benzoic acid prepared according to the general procedure through hydrazinolysis of the

corresponding nitrobenzoic chlorides [4], and salicylaldehyde (high-purity grade) were used. Organic solvents (methanol, diethyl ether, DMF, and acetone) were dehydrated in accordance with known procedures [5].

Hydrazones were prepared through condensation of salicylaldehyde with the above-mentioned hydrazides in methanol using the general procedure from [6] in 60–80% yields. Salicylalhydrazones were identified using elemental analysis data, the presence of a peak in the mass spectra with m/z = 285 [M]⁺, and the melting points of 190, 200, and 260°C for 2-, 3-, and 4-NO₂–H₂L, respectively.

For $C_{14}H_{11}N_3O_4$ anal. calcd. (%):	C 58.95	H 3.86	N 14.74
Found (%):			
$2-NO_2-H_2L$	C 58.80	H 3.84	N 14.68
3-NO ₂ -H ₂ L	C 58.87	H 3.89	N 14.81
$4-NO_2-H_2L$	C 59.10	H 3.87	N 14.79

The complexes $[Ge(2-NO_2-L)_2]$ (I), $[Ge(3-NO_2-L)_2]$ (II), and $[Ge(4-NO_2-L)_2]$ (III) were synthesized according to the following procedure. $GeCl_4$ (0.0025 mol) was added with continuous stirring to a hot saturated solution of $2-NO_2-H_2L$ ($3-NO_2-H_2L$)(0.005 mol) or a suspension of $4-NO_2-H_2L$ (0.005 mol) in methanol (200 ml). The resulting solutions of I and II were boiled with a reflux condenser for 1 and 0.5 h, respectively, until crystallization began followed by distillation of methanol to V = 30 ml. Then, II was left to stand for a day for further crystallization. The mixture obtained from the synthesis of III was stirred at $T = 50-60^{\circ}C$ until the white color of the precipitate changed to yellow (0.5 h). All products of the synthesis were separated on a Schott filter. Compounds I and II were

I II		III			
m/z	<i>I</i> , %	m/z	<i>I</i> , %	m/z	<i>I</i> , %
76	17.1	76	17.9	76	28.6
77	26.4	77	19.8	77	18.0
104	22.0	104	30.0	104	69.7
150	17.4	150	58.5	150	96.1
179	11.4	179	10.0	179	10.2
191	20.6	191	13.5	191	19.3
193	20.6	193	17.2	193	31.7
195	37.2	195	21.2	195	36.6
636	60.8	636	52.8	636	50.8
637	18.6	637	22.3	637	22.0
638	72.1	638	73.7	638	81.7
639	50.2	639	51.8	639	55.8
640	100.0	640	100.0	640	100.0
641	27.4	641	33.8	641	33.6
642	32.3	642	23.4	642	25.9

Data from the mass spectrometric study of complexes I-III

washed with ether, **III** was washed with hot acetone, and all products were dried above CaCl₂. The yields were 85, 80, and 70%, for **I**, **II**, and **III**, respectively.

Elemental analysis of the products obtained was performed on a semiautomatic CHN-analyzer. Chlorine was determined mercurometrically [7], and germanium was determined through potentiometric titration of tripyrocatechol-germanic acid on an Ionomer EV-74 instrument [8].

For $C_{26}H_{18}N_6O_8Ge$	C 52.62	H 2.82	N 13.15 Ge 11.37
Found (%):			
I	C 52.60	H 2.81	N 13.17 Ge 11.10
II	C 52.00	H 2.82	N 13.14 Ge 11.30
III	C 52.40	H 2.82	N 13.13 Ge 11.34

IR absorption spectra (400–4000 cm⁻¹) were recorded on a Specord 75 IR spectrophotometer according to the procedure of molding samples with KBr.

UV spectra of solutions of the complexes in DMF were recorded on a Specord UV-VIS spectrophotometer.

The molar electroconductivity of 10^{-3} M solutions of the complexes in DMF was measured using a C.L.R.E. 7-8 conductometer.

Thermogravimetric studies were performed on a Q derivatograph (Paulik-Paulik-Erdey system). The samples were heated in air from 20 to 1000°C at a rate of 10 K/min.

Mass spectra were obtained on an MX-1320 instrument by directly injecting a sample into the ionization region at an ionizing voltage of 70 eV.

Diffraction patterns of the compounds were obtained on a DRON-3 diffractometer with CoK_{α} radiation and an Fe filter.

NMR spectra of solutions of the complexes in DMSO- d_6 were recorded on a VXR-300 spectrometer (Varian) with frequencies of 300 and 75.4 MHz for ¹H and ¹³C, respectively. Chemical shifts of signals were recalculated relative to TMS.

RESULTS AND DISCUSSION

The molar ratio Ge : L = 1 : 2 corresponds to the found empirical formula of complexes I–III. Taking into account the data on electroconductivity (λ , Ohm⁻¹ cm² mol⁻¹: I, 8.3; II, 12.9; and III, 9.5) and mass spectrometry (*m*/*z* 640[Ge(X–L)₂]), these compounds are nonelectrolytes with the composition [Ge(X–L)₂].

X-ray powder diffraction analysis confirmed that compounds **I–III** were individual and pure. Their X-ray diffraction diagrams are characterized by an intrinsic set of interplanar distances, which excludes admixtures of the initial ligands.

Complexes **I–III** are crystalline yellow substances soluble in DMF and nitrobenzene and insoluble in other organic solvents.

Comparing the thermogravimetric patterns of hydrazones and the complexes, we found that the thermolysis of the latter was not accompanied by ligand elimination. This was indicated by the absence of ligand melting effects in the thermogravimetric patterns of complexes I–III. Complexes I–III are characterized by a high thermal stability: at first, melting takes place at 300, 310, and 420°C, respectively, and then the exothermic process of thermodecomposition occurs to form GeO₂.

Detailed analysis of the mass spectra of **I**–**III** (table) showed the presence of a group of peaks of molecular ions, whose mass corresponded to the complex species GeL_2 mainly containing the most abundant germanium isotope ⁷⁴Ge. The main course of fragmentation under electron impact results in the formation of fission germanium-containing ions, which is characteristic of stable complexes of the chelate type:

$$M^+ \longrightarrow [GeO_2C_7H_6]^+, m/z \ 195.$$

The intensity of this process is determined by the ligand structure and increases with an increase in the distance between the nitro group and germanium ion. The intensity of the peak of ions m/z 195 for compounds **I–III** is equal to 19.4, 21.2, and 36.6%, respectively. This correlates with an increase in the thermal stability of complexes **I–III** and values of the energy of formation calculated for them using the HyperChem 5.02 program according to the AM-1 molecular

mechanics method (*E*, kcal/mol): -6979.2 (**I**), -7156.8 (**II**), and -7257.2 (**III**).

The comparison of the UV spectra of solutions of the ligands and complexes in DMF shows that the bands in the spectra of the ligands (v, cm⁻¹ (ln ϵ): 2-NO₂, 30569 (9.45); 3-NO₂, 30000 (9.66); and 4-NO₂, 29330 (9.76)) corresponding to the transitions of the $\pi \longrightarrow \pi^*$ azomethine bond [9] in the spectra of complexes I and III undergo a hypsochromic shift; in the spectrum of II, the shift is bathochromic (v, cm⁻¹ (ln ϵ): I, 31000 (10.47); II, 29800 (10.69); III, 29625 (10.57). This indicates that the electron density redistribution in molecules of I–III is caused by N-coordination at the azomethine group.

This is reflected in the IR spectra of **I–III** as the lowfrequency shift of the v(C=N) band by 10–15 cm⁻¹ compared to the spectra of the ligands and as the appearance of a new band in the region of 610–620 cm⁻¹ due to vibrations of the Ge \leftarrow N bond [10, 11].

Compared to the spectra of the corresponding ligands, the IR spectra of all complexes lack the bands v(OH) and v(NH) in the region of 3220 to 3350 cm⁻¹ and v(C=O) at 1660 to 1680 cm⁻¹. The bands due to the v(N-N) and v(Ph-O) vibrations are shifted to the high-frequency region by 20–30 cm⁻¹ compared to similar bands in the IR spectra of the ligands (970–980 and 1260–1270 cm⁻¹, respectively) [12]. This indicates that the ligands are present in the complexes in doubly deprotonated form with formation of Ge–O bonds with oxygen atoms of the oxyazine and deprotonated hydroxo groups. The intense band at 670 cm⁻¹ assigned to stretching vibrations of the Ge–O bond appears simultaneously in the IR spectra of the complexes [11].

We used the ¹H and ¹³C NMR spectra of the complexes and ligands to confirm the data obtained from IR and UV spectroscopy. The ¹H NMR spectrum of 2-NO₂-H₂L contains, along with a multiplet in an interval of 6.900–8.181 ppm with an intensity of 8H (aromatic protons of both cycles), singlet signals at 8.5 (H–C=N), 12.247 (HN–C=O), and 10.954 ppm (Ar–OH) [13]. It is noteworthy that in the spectrum of complex I, the last signal disappears and the singlet of the azomethine proton is shifted to the low field to 9.365 ppm. The ¹³C NMR spectrum of complex I exhibits downfield shifts of the following singlet signals of carbon atoms of 2-NO₂-H₂L (δ , ppm): 148.326 (H–C=N), 161.160 (N–C=O), and 156.505 (C_{Ar}–OH) to 161.755, 163.969, and 161.160 ppm, respectively.

The possible involvement of the nitro group of $2\text{-NO}_2\text{-H}_2\text{L}$ into coordination was ruled out because the signal of carbon of the $C_{Ar}\text{-NO}_2$ group at 147.20 ppm remains virtually unchanged during complexation and appears in the ¹³C NMR spectrum of complex I at 148.84 ppm. The coordination of the NO₂ group in complexes II and III is still more improbable because, in these cases, the formation of six- and seven-membered metallocycles is energetically hindered com-

pared to the formation of the five-membered cycle in complex I.

CONCLUSIONS

Thus, our studies suggest that, in complexes **I–III**, the ligands manifest themselves as tridentate, their coordination gives five- and six-membered conjugated metallocycles, and a coordination number of 6 is realized, which is characteristic of Ge(IV) [14].



Therefore, regardless of the position of the nitro group in the molecules of the ligands, complexes with the same structure are formed. The thermal stability and intensity of the peak of germanium-containing ions in the mass spectra of the complexes increase in the series **I–II–III**.

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