Pentacoordinate silicon compounds based on 2,2'-dihydroxyazobenzene ligand

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Article info

Article history:
Received 3 September 2019
Received in revised form 18 October 2019
Accepted 19 October 2019
Available online 22 October 2019

Abstract

The preparation and structures of 6,6-diorganylbenzo[\textit{d},\textit{h}][1,3,6,7,2]dioxadiazasilonines containing the N\rightarrow Si intramolecular dative bond are described. The complexes were characterized by NMR (\textit{\textit{\textit{1}}H, \textit{\textit{13}}C, \textit{\textit{29}}Si), IR and UV spectra. The crystal structures of 6-methyl-6-phenyl- and 6-(chloromethyl)-6-methylbenzo[\textit{d},\textit{h}][1,3,6,7,2]dioxadiazasilonines were determined by X-ray diffraction.

1. Introduction

Hypervalent silicon compounds have attracted considerable attention due to their unique structures, physico-chemical properties and biological activity [see for example 1–5 and ref. therein]. In order to achieve hypercoordination at the silicon atom, the different types of chelating ligands are used. The silatranes XSi(OCH2CH2)3N resulting from the interaction between silanes XSi(OAlk)3 and the tetradentate triethanolamine ligand are one of the most extensively studied neutral pentacoordinate silicon compounds with intramolecular dative bond N\rightarrow Si. Unlike these, silicon complexes of O,N,O\textsuperscript{0} tridentate chelating ligand systems remain less studied, despite the fact that their first representatives were synthesized in the 70s of the last century [6] and ref. therein. In recent years, papers dealing with pentacoordinate silicon complexes stabilized by O,N,O\textsuperscript{0} tridentate Schiff base ligands have been published [7–16]. The prepared compounds were characterized by X-ray structure analysis, NMR and IR spectroscopy. The results of these investigations demonstrate the structural diversity and an interesting properties of pentacoordinate silicon compounds with O,N,O\textsuperscript{0} chelating ligands.

Azobenzene derivatives constitute a group of dyes which have photochromic properties and have been widely used in chemistry, medicine, biotechnology and industry [see for example rev. 17–23 and ref. therein]. 2,2'-Dihydroxyazobenzene and related compounds are excellent O,N,O\textsuperscript{0} tridentate ligands for the synthesis of different metal complexes (K, Na, Li, Ca, Mg, Zn, Co, Cr, Cu, Mo, Ni, Fe, Pd, Pt, V) [24–38]. Such complexes are promising precursors for luminescent materials, catalysts and molecular devices. There are only few complexes of group 14 elements (Si, Ge, Sn) with 2,2'-dihydroxyazobenzenes in the literature. 2,2-Dihydroxyazobenzenato-dimethyl-tin [Me\textsubscript{2}SnL] and 2,2- dihydroxyazobenzenato-dibutyltin [Bu\textsubscript{2}SnL] were obtained by the reaction of 2,2-dihydroxyazobenzene (H\textsubscript{2}L) with dialkyltin oxide [39]. The structure of these compounds was confirmed by spectral data and X-ray diffraction structural analysis. 6,6-Dimethylbenzo[\textit{d},\textit{h}][1,3,6,7,2]dioxadiazasilonine 1 is the first and so far the only example of the pentacoordinate silicon complex with 2,2'-dihydroxyazobenzene [40]. It is interesting to note that the silicon complexes of bidentate (O,N) chelating ligand 2-hydroxy-5-methylazobenzene exist as capped-tetrahedral coordination spheres under formation of five-membered pseudo-chelates and their diazo groups do not interact with silicon [41]. These results show that the use of 2,2'-dihydroxyazobenzenes as O,N,O\textsuperscript{0} tridentate ligands for synthesis of pentacoordinate silicon compounds is favoured. The study of structure and reactivity of similar compounds is of interest for development of chemistry including organic, physical, theoretical and analytical chemistry as well as materials science. Herein we report the investigation of pentacoordinate silicon compounds which were generated from O,N,O\textsuperscript{0}-chelating ligand 2,2'-...
dihydroxyazobenzene and diorganyldichlorosilanes (MePhSiCl2, CICH2MeSilCl2, Ph2SiCl2, (CH2=CH)MeSilCl2) or phenyltrichlorosilane (PhSilCl3).

2. Experimental section

2.1. General

The 1H, 13C and 29Si NMR spectra of solutions of compounds in CDCl3 were registered on a Bruker DPX 400 spectrometer (400.1, 100.6 and 79.5 MHz respectively) with HMDS or cyclohexane as internal standard. The FTIR spectra were recorded in KBr tablets or films at room temperature on a FTIR spectrometer Varian 3100. The UV–visible spectra were recorded in acetonitrile at room temperature on a JASCO spectrometer V-570.

All reactions were performed in the flame dried glassware under an atmosphere of dry argon. The used solvents were purified according to standard procedures [42]. As a further precaution, diethyl ether was dried by filtration through column packed with neutral alumina under a positive pressure of argon. The solvents were stored under argon over molecular sieves 4A.

2.2. Synthesis

2.2.1. 6-Methyl-6-phenyl-benzo[d,h][1,3,6,7,2]dioxadiazasilonine

2.2.2. 6-(Chloromethyl)-6-methyldibenzo[d,h][1,3,6,7,2]dioxadiazasilonine

A solution of 2,2'-dihydroxyazobenzene (1.71 g, 8.00 mmol) and triethylamine (1.62 g, 16.00 mmol) in benzene (30 mL) was stirred at ambient temperature, and a solution of MePhSilCl2 (1.53 g, 7.40 mmol) in 20 mL benzene. Reaction time 80 h. Compound 3 was isolated by the recrystallization from Et2O-PhSilCl3 (0.70 g, 3.30 mmol) and triethylamine (1.00 g, 10.00 mmol, excess) in 30 mL benzene, 2,2'-dihydroxyazobenzene (0.71 g, 3.30 mmol) in 20 mL benzene. Reaction time 50 h. Compound 3 as dark orange solid was isolated by the recrystallization from toluene. Yield 0.51 g (1.45 mmol, 44%). M. p. 198 ⁰C with the decomposition.

2.2.3. 6,6-diphenyldibenzo[d,h][1,3,6,7,2]dioxadiazasilonine

The same procedure as for 2 applies. Starting materials used: PhSiCl3 (1.11 g, 4.40 mmol) and triethylamine (0.90 g, 8.80 mmol) in 30 mL benzene, 2,2'-dihydroxyazobenzene (0.94 g, 4.40 mmol) in 20 mL benzene. Reaction time 90 h. Compound 4 as red solid was isolated by the recrystallization from benzene-hexane (3 : 1). Yield 1.32 g (3.35 mmol, 76%). M. p. 204–206 ⁰C 1H NMR (CDCl3, δ ppm): 7.06–7.78 (m, Ph, 2C6H4), 13C NMR (CDCl3, δ ppm): 119.9, 122.0, 127.6, 128.8, 134.1, 134.7, 135.2, 137.9, 139.4, 153.1 (Ph, 2C6H4), 29Si NMR (CDCl3, δ ppm): -83.7. Anal. Calcd. For C24H18N2O2Si: C, 73.07; H, 4.60; N, 7.10. Found: C, 72.95, H, 4.54; N, 7.19.

2.2.4. 6-Methyl-6-vinylidobenzod[h][1,3,6,7,2]dioxadiazasilonine 5

The same procedure as for 2 applies. Starting materials used: (CH2=CH)MeSilCl2 (1.04 g, 7.40 mmol) and triethylamine (1.50 g, 14.80 mmol) in 30 mL benzene, 2,2'-dihydroxyazobenzene (1.59 g, 7.40 mmol) in 20 mL benzene. Reaction time 90 h. Compound 5 as dark red solid was isolated by the recrystallization from Et2O-pentane (10 : 1). Yield 1.19 g (4.21 mmol, 57%). M. p. 124–126 ⁰C. 1H NMR (CDCl3, δ ppm): 0.16 (s, 3H, Me), 5.83–6.07 (3H, CH2=CH), 7.06–7.78 (m, 8H, 2C6H4), 13C NMR (CDCl3, δ ppm): 0.2 (Me), 120.2, 121.6, 123.4, 131.5, 134.8, 137.9, 139.6, 152.6, (CH2=CH, 2C6H4), 29Si NMR (CDCl3, δ ppm): -68.1. Anal. Calcd. For C18H13ClN2O2Si: C, 63.80; H, 5.00; N, 9.92. Found: C, 63.97; H, 5.14; N, 9.78.

2.2.5. 6-Choro-6-phenyldibenzod[h][1,3,6,7,2]dioxadiazasilonine 6

The same procedure as for 2 applies. Starting materials used: PhSiCl3 (0.70 g, 3.30 mmol) and triethylamine (1.00 g, 10.00 mmol, excess) in 30 mL benzene, 2,2'-dihydroxyazobenzene (0.71 g, 3.30 mmol) in 20 mL benzene. Reaction time 50 h. Compound 6 as dark orange solid was isolated by the recrystallization from toluene. Yield 0.51 g (1.45 mmol, 44%). M. p. 198 ⁰C with the decomposition.

2.3. X-ray study and refinement

The molecular structures of compounds 2 and 3 were determined by single-crystal X-ray analysis. Suitable single crystals were obtained by crystallization from Et2O. Slow cooling of the saturated solution of these compounds promotes formation of pure crystals. Crystal data were collected on a Bruker D8 Venture diffractometer with MoKα radiation (λ = 0.71073) using the θ and 2θ scans. The structures were solved and refined by direct methods using the SHELX programs set [43]. Data were corrected for absorption effects using the multi-scan method (SADABS). Nonhydrogen atoms were refined anisotropically using SHELX programs set [43]. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 1916627 (2) and 1916628 (3). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystal data, data collection and structure refinement details are summarized in Table 1.

2.4. Quantum chemical calculations

All calculations, including NBO analysis [44,45], were performed by the DFT B3LYP/6-311 + G(d,p) methods with full geometry optimization using the Gaussian 09 suite of programs [46]. All calculated structures are minima on the potential energy surfaces as proved by positive eigenvalues of the corresponding Hessian matrices.

3. Results and discussion

3.1. Synthesis

Reaction of 2,2'-dihydroxyazobenzene with the diorganyldichlorosilanes RR'SiCl2 in a 1:1 M ratio (in the presence of triethylamine as base) delivered 6,6-diorganyldibenzod[h][1,3,6,7,2]dioxadiazasilonines 2–6 (Scheme 1). Dry benzene was used as...
3.2. NMR studies

The values of the $^{29}$Si NMR chemical shifts for compounds 2–6 fall in the range from −67.9 ppm to −96.6 ppm (Table 2). Notice that the value of the $^{29}$Si NMR chemical shift for the pentacoordinate silicon compounds 1 and 7–16 (Scheme 2) featuring the ONO$^-$ tridentate ligands lie between −43.9 ppm and −104.3 ppm [8–12,40,47]. The degree of interaction D → Si (D = O, N) of pentacoordinate silicon compounds (the contribution of the coordination constituent of the hypervalent fragment to the shielding of the silicon atom) is determined by the difference between the values of chemical shifts for pentacoordinate silicon compounds $\Delta S = \delta_{SV} - \delta_{SVV}$ [48]. The authors of this work noted that the correct estimation of the degree of the coordination interaction depends heavily on the correctly choose of the model tetracoordinate silicon compound with the similar chemical environment of the silicon atom. Therefore diphenoxysilanes RR'Si(OPh)$_2$ are the suitable model compounds for diorganylbenzo[d,h][1,3,6,7,2]dioxadiazasilinones 1–6. The values of $^{29}$Si NMR chemical shifts of these

Table 2

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<th>$\Delta \delta^b$</th>
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<td>−43.9</td>
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$^a \Delta S = \delta_{SV} - \delta_{SVV}$

$^b \Delta \delta = \delta_{SV} - \delta_{SVV}$
silanes (4) fall range from −6.1 ppm to −37.4 ppm [49–52] (Supp. Inf. Table 1S) and value of coordination shift (Δδ) for compounds 1–5 lies in the range from 44.1 ppm to −47.3 ppm. Unfortunately we have failed with synthesis of pure ClPhSi(OPh)2 as model silane for compound 6. The choose of model tetracoordinate silanes for compounds 7–14 is more difficult due to the feature of structure of such O,N,O tridentate ligands. The silanes RR’Si(OAlk)2 may be used as model compounds, but in this case, the value of the coordination shift Δδ2 is slightly higher for compounds 1–16 (Table 2).

3.3. X-ray single crystal structure analysis

The single crystals of compounds 2 and 3 were obtained by recrystallization from diethyl ether. In order to investigate their molecular structure and intermolecular interactions in the solid state, X-ray structure analysis was carried out. The molecular structures are depicted in Fig. 1. The values of the selected bond lengths and angles given in Table 3. Principal bond distances, bond angles and torsion angles are presented in Table 2S (Supporting Information).

Compound 2 crystallizes in the monoclinic space group P21/c with one independent molecule in the asymmetric unit, and

![Molecular structures of 2 and 3](ORTEP, 30% thermal ellipsoid plots).

Table 3

<table>
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<tr>
<th>Compound</th>
<th>Si–Si, Å</th>
<th>Si–O1, Å</th>
<th>Si–O2, Å</th>
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compound 3 – in triclinic space group P-1 also with one independent molecule in the asymmetric unit. The silicon atoms in the molecules of compounds 2 and 3 have a distorted trigonal-bipyramidal configuration, which is usually typical for the similar pentacoordinate silicon compounds with O,N,O' tridentate ligands [8–12,40,53,54]. In compound 2 the two oxygen atoms of the bicycle (Si1–O1 and Si1–O2) and phenyl group (Si1–C3) build the equatorial plane, while the axial positions are occupied by the nitrogen atom (Si1–N1) of the bicycle and the methyl group (Si1–C17). Silicon atom of compound 3 has methyl group (Si1–C10) and two oxygen atoms of the bicycle (Si1–O1 and Si1–O2) in the equatorial positions and the nitrogen atom of the bicycle (Si1–N1) and the carbon atom of the chloromethyl group (Si1–C11) take up the axial positions.

The sum of the bond angles constitute the equatorial plane around the Si atom is 354.95(2)° for compound 2 and 356.40(2)° for compound 3. The deviation of Si atom from equatorial plane in direction to carbon atom of methyl group is 0.222 Å in compound 2 and 0.165 Å in direction to carbon atom of CH2Cl group in compound 3. The C–Si–N angles equal 162.5° and 163.9° in compounds 2 and 3 respectively that almost on 20° off linearity. The lengths of dative bonds Si–N consist 2.171 Å and 2.079 Å in compounds 2 and 3 respectively that on 0.02–0.22 Å less than in compound 1 (2.193 Å) [40].

This value of lengths of dative bonds Si–N in related compounds with O,N,O’ tridentate ligands varies in the range from 1.834 Å to 2.680 Å [8–12,53,54]. The shortening of Si–N bond length in compound 3 in comparison with compounds 1 and 2 is due to electronegativity inductive effect of chloromethyl group CH2Cl. The pentacoordination character TBP is 84.0% and 88.6% for compounds 2 and 3 according to the Tamao equation [55].

Some azobenzenes show orientational disorder in the crystals as a result of a flipping of the orientation of the C–N=N–C unit [56–58]. It is worth noting that the conformational interconversion through pedal motion takes place [57,58]. The same behavior in the crystal of 6,6-dimethylbenzo[ghi,j]1,3,6,7,2’dioxadiazasilinone 1 has been demonstrated previously by Böhme [40]. The authors of this work showed that the population of the two conformers in the single crystal depends on the temperature and cooling rate. Experimental data show that the N and O atoms in the crystal of compound 2 are disordered. The occupancy of the minor conformation is 11.3% that is approx 6% less than in compound 1 at room temperature.

3.4. DFT calculations, FTIR and UV–Vis study

IR spectra of compounds 2–6 were recorded (Supp. Inf. Figs. 25–65). The experimental and theoretical FT-IR spectra of the molecules 2 and 3 are displayed in Fig. 2. The DFT calculated wave numbers are typically higher than that of their experimental values, and thus a proper scaling factor [59,60] (0.970) is employed to have a better agreement with the experimental wave numbers. The experimental and computed vibrational wave numbers with assignment for 2 and 3 are given in Table 4. Comparison of calculated (scaled) and experimental data shows good agreement.

The electronic spectra of compounds 2 and 3 were measured in acetonitrile at room temperature. The excitation energies and oscillator strengths for the optimized geometries of compounds 2 and 3 were obtained in the framework of TD-DFT calculations with the CAM-B3LYP method. TD-DFT methods are computationally more expensive in comparison with semi-empirical methods, but allow easily studies of dye molecules [61,62]. According to literature data 6-311 + G(d,p) basis set was compatible with experimental results [63–65]. For systems with proton transfer or superconjugation CAM-B3LYP method was recommended [66].

The theoretical and experimental electronic spectra of compounds 2 and 3 are displayed in Fig. 3. The maximum absorption wavelengths, HOMO, LUMO energies and HOMO−LUMO energy gaps for compounds 2 and 3 are compared in Table 5. Experimentally determined maximum absorption values for compounds 2 and 3 coincide and consist 323 and 395 nm (in CH3CN), these maxima are close. These spectral features are explained by the existence of the Si–N intramolecular coordination interaction in compounds 2 and 3. It should be noted that the position of the absorption bands in the...
UV spectra of the studied compounds in the less polar hexane (compared with acetonitrile) does not significantly change (Table 5). However, the intensity of the shoulder at 434 nm is almost equal to the intensity of the peak at 400 nm. Probably, the presence of two peaks indicates the presence in the solution of two conformers of compounds 2 and 3.

Calculated values of \( \lambda_{\text{max}} \) are 395 nm and 393 nm for compounds 2 and 3 respectively. As in the experimental spectrum, the short-wavelength band at 297 nm (298 nm for compound 3) was observed in the calculated spectrum. Thus, for \( \pi - \pi^* \) transitions we can observe good agreement between experimental and theoretical data without using any scaling factors or special formulae to calculation of the values of \( \lambda_{\text{max}} \).

The HOMO and LUMO of compounds 2 and 3 are presented in Fig. 4. The estimated energy gaps \( (\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}) \) for both compounds are very close and consist approximately 3.28 eV (Table 5). The HOMO is localized on whole molecule except of methyl group for compound 2 and CH\( _2 \)Cl-group for compound 3 and LUMO is contributed mainly by the whole of the molecule without SiMePh (2) and SiMeCH\( _2 \)Cl fragments (3).

### 4. Conclusion

The interaction between the tridentate ligand 2,2'-dihydroxoyazobenzene and diorganylsilanes MePhSiCl\(_2\), ClCH\(_2\)MeSiCl\(_2\), Ph\(_2\)SiCl\(_2\), (CH\(_2\)═CH)MeSiCl\(_2\) and PhSiCl\(_3\) lead to formation of 6,6-diorganylbenzo[d,h][1,3,6,7,2]dioxadiazasilonines 2–6. The \(^{29}\)Si chemical shifts for compounds 2–6 lie in the range from \(-67.9\) ppm to \(-96.6\) ppm that is typical for pentacoordinate silicon compounds. The structure of compounds was proved by NMR spectroscopy. The structure of compound 2 and 3 was proved by X-ray diffraction. The values of length of N\( \rightarrow \)Si dative bond are 2.171 Å and 2.079 Å for compounds 2 and 3, respectively. The shortening of Si\( \rightarrow \)N bond in compound 3 in comparison with compound 2 is due to electronegativity inductive effect of chloromethyl group CH\(_2\)Cl. The degree of trigonal bipyramidality (TBP, %) estimated by Tamao formulae consist 84.0 and 88.6% for compounds 2 and 3 respectively. The comparative analysis of values of \(^{29}\)Si NMR chemical shifts and coordination shifts for compounds 1–6 and 7–14 shows that the compounds with the identical substitutes at silicon atom and much like structure of O,N,O\( ^0\) tridentatne ligand have the similar degree of N\( \rightarrow \)Si coordination interaction in solution.

### Table 4

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### Table 5

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<td>Energy gap, eV</td>
<td>3.275</td>
<td>3.283</td>
</tr>
</tbody>
</table>
Further investigation of physico-chemical properties of the synthesized compounds is now in progress.

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (Grant No 19-03-00143) using the analytical equipment of the Baikal Centre for Collective Use of the SB RAS.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.120997.

Fig. 4. HOMO (top) and LUMO (bottom) 3D shapes for compounds 2 (left) and 3 (right).

References


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