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Derivatization of 3-aminopropylsilatrane to introduce azomethine linkage in the axial chain: Synthesis, characterization and structural studies

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ABSTRACT

Some new silatranes containing an azomethine group as coordinating system in the axial chain are reported. This system is introduced into the chain by the treatment of 3-aminopropylsilatrane with different carbonyl compounds like acetylacetone (**1**), 2-acetylphenol (**2**), paeonol (**3**) and salicylaldehyde (**4**) in the presence of anhydrous sodium sulphate. All the compounds were characterized by elemental analysis, spectroscopic techniques and X-ray diffraction analysis. The thermal stability of all silatranes was studied by TGA/DTG/DSC techniques, which is in agreement with the Mass spectrometry and X-ray diffraction studies.

1. Introduction

Silatranes have captured much attention due to higher stability than their ethoxy silane analogues as well as a wide diversity of their axial substituent [1–3]. In our recent studies on silatranes, we worked on the modification of the axial substituent to form isothiocyanate, azide and various urea derivatives [4–6]. The observed reactivity of the functional group attached to the axial chain, without affecting silatranyl moiety, is in agreement with the stability achieved due to the presence of the robust silatrane cage which accommodates the Si–N transannular bond. To further explore the area of silatranes which bear functionalized long chains in the axial position, we worked on the synthesis of silatranes containing Schiff base moieties in this arm due to their wide application potential in the field of biological systems and industries, especially in catalysis, dyes and pharmaceutics, which arises from the additional ligand moiety [7].

Schiff base (or azomethine), named after its discovery by Hugo Schiff in 1864 [8], is a functional group that contains a carbon-nitrogen double bond with general formula $R^1R^2C{=}NR^3$, where R^2 is an OH-functionalized aryl or alkyl group that stabilizes the imine moiety by an intramolecular O–H···N hydrogen bridge. The probably most important applications of Schiff base metal complexes are found in the field of catalysis, where they act as homogeneous as well as heterogeneous catalysts in a wide range of oxidation reactions [9]. It was found that heterogeneous catalysts are more suitable than homogeneous catalysts because of easy separation of product and recovery of catalyst. Hence, a number of reports are available in the literature, where Schiff base complexes with metal ions have been converted to heterogeneous catalysts by grafting on an organic or inorganic support [10]. Most important among these are mesoporous silica supported Schiff base complexes, which can be prepared by sol–gel processes, i.e. hydrolysis of various alkoxysilanes containing the Schiff base moiety. In sol gel processes, selection of suitable precursor(s) is a very important step and alkoxysilanes are found to be highly susceptible towards hydrolysis. Therefore, some suitable precursors are required for the modification of silica so that morphology of surfaces can be tuned according to the requirement of the catalytic reaction [2].

Silatranes bearing a Schiff base moiety can be used as precursors to achieve the desired characteristics of heterogeneous catalysts because they are more stable toward hydrolysis than their ethoxysilane analogues. Besides this, silatranes can be obtained in solid form and can thus also be purified by recrystallization,

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whereas it is difficult in case of the more flexible alkoxysilanes due to their oily nature. In the present work, four silatranes **1**–**4** with azomethine functional group were derived from widely used 3-aminopropylsilatrane and corresponding carbonyl compounds (acetylacetone, 2-acetylphenol, paeonol, and salicylaldehyde). Recently, compound **4** was published by Cazacu et al. [11], while our work on those silatranes was underway. Despite this earlier report, we include our results of a crystallographic analysis of compound **4**, which originate from a data set collected at lower temperature (150 K), thus providing significantly better bond length and angle precision than the initial report. All the compounds **1**, **2**, **3** and **4** were characterized by spectroscopic techniques and X-ray diffraction analysis.

2. Materials and methods

2.1. General details

2.1.1. Synthesis and characterization

Synthesis of all the compounds was performed under a dry nitrogen atmosphere using Schlenk technique. Benzene and toluene were refluxed over sodium benzophenone and distilled prior to use. 3-Aminopropyl(triethoxy)silane (Aldrich), triethanolamine (Merck), acetylacetone (Qualigens), salicylaldehyde (Qualigens), 2-acetylphenol (Acros organics), paeonol (Acros organics) and sodium sulphate (Merck) were used as such without any purification. 3-aminopropylsilatrane was prepared by the method reported earlier [4–6].

Infrared spectra were routinely obtained as thin films or Nujol mulls and KBr pellet on a Perkin–Elmer RX-I FT IR Spectrophotometer. Mass spectral measurements (ESI source with capillary voltage, 2500 V) were carried out on a VG Analytical (70-S) spectrometer. C, H and N analyses were obtained on a FLASH-2000 organic elemental analyzer. The solution NMR spectra were recorded at 25 °C on Bruker Avance II FT NMR (AL 400 MHz) spectrometers (^{1}H, ^{13}C) and a Bruker DPX 400 spectrometer (^{29}Si) using $CDCl_3$ as the solvent. Chemical shifts in ppm are reported relative to tetramethylsilane (TMS).

2.1.2. X-ray crystallography

Single-crystal X-ray structure analyses were carried out on a Bruker X8 APEX II CCD diffractometer (**1** and **4**) and a Stoe IPDS-2T diffractometer (**2** and **3**) using Mo Kα-radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97) and refined with full-matrix least-squares method (refinement of F^2 against all reflections with SHELXL-97) [12]. All non-hydrogen atoms were anisotropically refined. The Schiff base hydrogen atoms in compounds **1** and **4** were located as residual electron density peaks and refined isotropically without restraints (Table 1).

2.2. Synthesis of silatranes

2.2.1. 4-[3-(2,8,9-Trioxa-5-aza-1-sila-bicyclo[3.3.3]undeca-1-yl)-propylimino]-pent-2-ene-2-ol (*1*)

3-Aminopropylsilatrane (2.00 g, 4.31 mmol) was dissolved in dry benzene (10 mL) and anhydrous sodium sulphate (1.00 g) was added. Acetylacetone (0.44 g, 4.31 mmol) was added to the reaction mixture drop wise with the help of a syringe. The mixture was stirred for about 2 h at room temperature. After stirring, the contents were filtered and the filtrate was refluxed for 3 h. Benzene was evaporated and a light brown coloured solid appeared which was dried under reduced pressure. Crystals suitable for X-ray diffraction were obtained from chloroform/hexane. Yield: (2.25 g, 7.16 mmol, 83%). M.p.: 155–160 °C. Anal. Calcd for $C_{14}H_{25}N_2O_4Si$: C, 53.47; H, 8.33; N, 8.91. Found: C, 52.0; H, 8.21; N, 8.63. IR (KBr pellet, cm^{-1}): 579.1 m ν (Si ← N), 715.2 s, 757.7 s (ν_s Si–O), 877.3 w (ν C–N),

Table 1
X-ray crystal data and structure refinement of **1**–**4**.

	Compound **1**	Compound **2**	Compound **3**	Compound **4**
Empirical formula	$C_{14}H_{26}N_2O_4Si$	$C_{17}H_{26.20}N_2O_{4.10}Si$	$C_{18}H_{28}N_2O_5Si$	$C_{16}H_{24}N_2O_4Si$
Formula weight	314.46	352.29	380.51	336.46
T (K)	150(2)	220(2)	200(2)	150(2)
λ(Å)	0.71073	0.71073	0.71073	0.71073
Crystal system, space group	Monoclinic, *C2/c*	Triclinic, *P-1*	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
Unit cell dimensions				
a (Å)	14.1562(7)	6.9393(4)	12.4512(6)	12.2126(3)
b (Å)	11.4860(5)	12.7615(8)	11.3866(4)	14.2643(3)
c (Å)	19.9796(10)	20.7076(11)	13.4313(6)	19.3672(5)
α (°)	90	81.189(5)	90	90
β (°)	96.984(2)	80.328(5)	94.885(4)	92.532(1)
γ (°)	90	88.635(5)	90	90
V (Å^3)	3224.5(5)	1786.38(18)	1897.33(14)	3370.55(14)
Z	8	4	4	8
ρ_{calc}(Mg/m^3)	1.295	1.310	1.332	1.326
$\mu_{MoK\alpha}$(mm^{-1})	0.163	0.155	0.155	0.161
F(000)	1360	756	816	1440
Crystal size (mm)	0.55 × 0.50 × 0.05	0.40 × 0.25 × 0.20	0.22 × 0.18 × 0.15	0.60 × 0.45 × 0.20
Limiting indices	$-18 \le h \le 18$, $-14 \le k \le 14$, $-26 \le l \le 26$	$-8 \le h \le 8$, $-15 \le k \le 15$, $-24 \le l \le 24$	$-15 \le h \le 15$, $-14 \le k \le 14$, $-16 \le l \le 17$	$-17 \le h \le 16$, $-19 \le k \le 19$, $-27 \le l \le 27$
Reflections collected	20,851	21,443	20,345	30,538
Unique	3843 [R(int) = 0.0345]	6273 [R(int) = 0.0278]	4143 [R(int) = 0.0389]	9725 [R(int) = 0.0270]
θmax (°)/completeness (%)	28.0/98.8	25.0/99.6	26.99/99.9	30.00/98.9
Absorption correction	Semi-empirical	Integration	Integration	Semi-empirical
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3843/0/196	6273/107/526	4143/0/241	9725/0/476
GoF on F^2	1.056	1.051	1.042	1.095
R [$I > 2\sigma(I)$]	$R_1 = 0.0398$, $wR_2 = 0.0984$	$R_1 = 0.0370$, $wR_2 = 0.0934$	$R_1 = 0.0408$, $wR_2 = 0.1076$	$R_1 = 0.0407$, $wR_2 = 0.1074$
R (all data)	$R_1 = 0.0695$, $wR_2 = 0.1085$	$R_1 = 0.0587$, $wR_2 = 0.1032$	$R_1 = 0.0523$, $wR_2 = 0.1143$	$R_1 = 0.0634$, $wR_2 = 0.1153$
Largest diff. peak and hole (eÅ^{-3})	0.314 and −0.245	0.262 and −0.206	0.237 and −0.290	0.415 and −0.250