Inorganica Chimica Acta 433 (2015) 78–91

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Amide-tethered organosilatranes: Syntheses, structural characterization and photophysical properties

Gurjaspreet Singh [a,*], Sunita Rani [a], Amandeep Saroa [a], Promila [a], Aanchal Arora [a], Duane Choquesillo-Lazarte [b]

[a] Department of Chemistry, Panjab University, Chandigarh 160014, India
[b] Laboratorio de Estudios Cristalográficos, IACT, CSIC-Universidad de Granada, Avda. de las Palmeras 4, 18100 Armilla, Granada, Spain

ARTICLE INFO

Article history:
Received 3 February 2015
Received in revised form 22 April 2015
Accepted 24 April 2015
Available online 9 May 2015

Keywords:
Organosilatrane
Amidopropylsilane
Acid chloride
Amide linkage
Metal ion complexation

ABSTRACT

A series of trimethoxysilanes and silatranes coupled with distinct aromatic moieties (biphenyl, thiophene, pyrazine and pyridine) through amide linkage are reported. The synthetic approach involved the amidation of 3-aminopropyltrimethoxysilane (APTMS) with various carboxylic acids *via* acid chlorides (**1a**–**1g**) to generate amidopropylsilanes (**2a**–**2g**). Transesterification of the resultant silanes with triethanolamine and tris(isopropanolamine) yielded unsubstituted (**3a**–**3g**) and 3,7,10-trimethylsubstitued organosilatranes (**4a**–**4g**), respectively. The compounds were successfully characterized by various spectroscopic techniques [IR, NMR (^{1}H, ^{13}C) and Mass] and elemental analysis. The complete structure elucidation for compounds **3a**, **3c**·H_2O and **3f** was carried out using single crystal X-ray diffraction analysis. The photophysical response was studied by UV–Vis absorption and fluorescence spectroscopy. These organosilatranes possess metal ion binding sites and can be put forth for advanced analytical applications.

1. Introduction

Silatranes, $XSi(OCH(Y)CH_2)_3N$ form a unique class of pentacoordinate silicon compounds having distorted trigonal bipyramidal geometry with the silicon atom residing in the bridgehead position [1–3]. These are relatively stable as compared to the open chain analogues (trialkoxysilanes) on account of their intact tricyclic caged structure and complementary transannular N → Si dative bond [4,5]. The integration of silatranyl cage with different functionalities leads to plethora of biological activities, adhesion properties and utility in various reactions, e.g. addition, nucleophilic substitution, exchange and photochemical reactions [6]. Organosilatranes are recently explored as new substrates for preparing advanced organic–inorganic hybrid materials by the surface functionalization of metal oxides *via* siloxyl bonds [7,8]. Earlier, organotriethoxysilanes (OTES) have been used to form siloxane monolayer on a metal oxide surface [9]. However, the oily nature of OTES and difficulties in handling, purification and storage remained the major drawbacks. The lesser reactivity, increased resistance against hydrolysis, capability of purification using column chromatography/crystallization and diminished polymerization chances of organosilatranes favour their selection as possible silicon source for the synthesis of superior hybrid materials [10]. Consequently, the thirst of developing modified organosilatranes is continuously growing.

Amide [–C(O)NH–] linkage is ubiquitous in nature and grabs an irreplaceable position in biological systems by forming the structural backbone of peptides and proteins [11]. The inclusion of amide linkage into organic molecules and following miscellaneous transformations is one of the most attractive areas of synthetic chemistry [12]. Amide group constructed on heterocyclic bases like pyridine, pyrazine, etc. constitutes the burgeoning class of ligand scaffold which binds metal ions very efficiently [13]. The utilization of amide functionality to generate novel amidopropylsilanes has gained importance owing to their applications in heterogeneous catalysis, dye sensitized solar cells, photoelectrochemical cells and as metal organic frameworks for the detection of heavy metals like Pd and Hg [14,15]. Recently, Xie et al. reported substituted benzoic acid derived amidopropylsilatranes which have shown better seed germination activity than their precursor aminopropylsilatrane [16].

The purpose of our investigation is threefold: firstly, to study the modification of silatranyl cage (Y = H or CH_3), secondly, to explore the effect of introducing amide linkage coupled with an

* Corresponding author. Tel.: +91 0172 2534428.
E-mail address: gjpsingh@pu.ac.in (G. Singh).

http://dx.doi.org/10.1016/j.ica.2015.04.034
0020-1693/

aromatic substituent on the overall geometry and photophysical properties of the organosilatranes and thirdly, to carry out the complexation of these silatranes with metal ions. With this aim, a series of fourteen new compounds (**3a**–**3g** and **4a**–**4g**) enclosing the framework of γ-amidopropylsilatrane are synthesized. Their photophysical properties and coordination with copper ions have been studied through UV–Vis, fluorescence and IR spectroscopic techniques.

2. Experimental

2.1. Materials

All the solvents were purchased commercially and dried according to standard procedures [17]. Biphenyl-4-carboxylic acid (SDFCL), thiophene-2-carboxylic acid (Aldrich), pyrazine-2-carboxylic acid (Merck), picolinic acid (Aldrich), nicotinic acid (Aldrich), isonicotinic acid (Aldrich), 2,6-pyridinedicarboxylic acid (Spectrochem), APTMS (Aldrich) and triethanolamine (Merck) were used directly as received. Thionyl chloride (SDFCL), triethylamine (Merck) and tris(isopropanol)amine (Merck) were distilled prior to use. It is worth noting that the tris(isopropanol)amine used in this manuscript consist of a diastereomeric mixture.

2.2. Physical measurements

The infrared spectra were recorded as neat spectra on a Thermo Scientific NICOLET IS50 spectrophotometer. Elemental analyses were obtained on a FLASH-2000 organic elemental analyzer. Mass spectral measurements (ESI source with capillary voltage, 3000 V) were carried out with a WATERS, Q-TOF micro MASS spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL (AL 300 MHz) spectrometer using $CDCl_3$ as an internal reference and chemical shifts were reported relative to tetramethylsilane. Melting points were measured in a Mel Temp II device using sealed capillaries. Electronic spectral measurements were carried out using JASCO V-530 double beam spectrophotometer. Fluorescence spectroscopy was performed on a Perkin Elmer LS 55 Fluorescence Spectrometer.

2.3. X-ray structure determination

Measured crystals were prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation and then they were mounted on a MiTeGen Micromounts™ and this sample was used for data collection. Data were collected with a Bruker D8 Venture diffractometer. Data were processed with APEX2 and corrected for absorption using SADABS [18,19]. The structures were solved by direct methods which revealed the position of all non-hydrogen atoms [20]. These atoms were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and included as fixed contributions riding on attached atoms with isotropic thermal displacement parameters 1.2 times those of the respective atom. Drawings were produced with Olex^2 [21].

2.4. General procedure for the synthesis of acyl chlorides

Acid chlorides were prepared by following the literature method [22]. Typical procedure involved is as follows: carboxylic acid (1.00 g) and catalytic amount of N,N dimethylformamide (3 drops) were taken in a round-bottomed flask maintained at 0 °C, this was followed by the slow addition of excess thionyl chloride (10.00 equivalents w.r.t. acid, Table T1, supporting information). The mixture was then heated at 80 °C for 3 h. The residual thionyl chloride was evaporated in *vacuo* followed by washing with petroleum ether (10 ml) which yielded corresponding acyl chloride.

2.5. General procedure for the synthesis of amidopropylsilanes

To a suspension of acid chloride (1.00 equiv.) in 30 ml THF at 0 °C, triethylamine (3.00 equiv.) was added drop-wise and the reaction mixture was stirred for 15 min. APTMS (1.00 equiv.) was then added slowly at 0 °C under nitrogen atmosphere. The resulting solution was heated to reflux for 24 h at 55–60 °C, cooled to room temperature and then filtered to remove the precipitated salt. The filtrate was concentrated in *vacuo* after which the final product was obtained as highly viscous oil.

2.5.1. N-(3-(trimethoxysilyl)propyl)biphenyl-4-carboxamide (**2a**)

The reactants used were as follows: (**1a**) (1.00 g, 4.62 mmol), APTMS (0.83 ml, 4.62 mmol), Et_3N (1.93 ml, 13.85 mmol). Yield: 1.40 ml, 3.90 mmol, 84%. IR (Neat, cm^{-1}): 3288 (υ N–H), 1639 (υ C=O), 1076 (υ Si–O). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.63 (m, 2H, $SiCH_2$), 1.67 (m, 2H, CCH_2C), 3.38 (m, 2H, CH_2NH), 3.49 (s, 9H, OCH_3), 6.67 (s, 1H, NH), 7.31 (m, 3H, $H^{9,10,11}$), 7.51 (m, 4H, $H^{3,5,8,12}$), 7.77 (d, 2H, $H^{2,6}$, J = 8.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 6.55 ($SiCH_2$), 22.69 ($C\mathbf{C}H_2C$), 42.18 (CH_2NH), 50.40 (OCH_3), 126.95 (C^{10}), 127.10 ($C^{8,12}$), 127.57 ($C^{3,5}$), 127.78 ($C^{2,6}$), 128.79 ($C^{9,11}$), 133.59 (C^{1}), 140.16 (C^{7}), 143.92 (C^{4}), 167.00 (C=O).

2.5.2. N-(3-(trimethoxysilyl)propyl)thiophene-2-carboxamide (**2b**)

The reactants used were as follows: (**1b**) (0.70 ml, 6.54 mmol), APTMS (1.17 ml, 6.54 mmol), Et_3N (2.73 ml, 19.62 mmol). Yield: 1.51 ml, 5.22 mmol, 80%. IR (Neat, cm^{-1}): 3311 (υ N–H), 1635 (υ C=O), 1076 (υ Si–O). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.60 (m, 2H, $SiCH_2$), 1.65 (m, 2H, $C\mathbf{C}H_2C$), 3.32 (m, 2H, CH_2NH), 3.47 (s, 9H, OCH_3), 6.96 (t, 1H, H^3, J = 4.5), 7.35 (d, 1H, H^2, J = 4.9), 7.49 (d, 1H, H^4, J = 3.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 6.40 ($SiCH_2$), 22.63 ($C\mathbf{C}H_2C$), 42.06 (CH_2NH), 50.32 (OCH_3), 127.39 (C^3), 127.74 (C^4), 129.04 (C^2), 129.43 (C^1), 161.83 (C=O).

2.5.3. N-(3-(trimethoxysilyl)propyl)pyrazine-2-carboxamide (**2c**)

The reactants used were as follows: **1c** (1.00 g, 7.01 mmol), APTMS (1.25 ml, 7.01 mmol) and Et_3N (2.93 ml, 21.03 mmol). Yield: 1.59 ml, 5.58 mmol, 80%. IR (Neat, cm^{-1}): 3312 (υ N–H), 1665 (υ C=O), 1077 (υ Si–O). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.63 (m, 2H, $SiCH_2$), 1.68 (m, 2H, CCH_2C), 3.40 (m, 2H, CH_2NH), 3.48 (s, 9H, OCH_3), 7.96 (s, 1H, NH), 8.42 (m, 1H, H^4), 8.67 (d, 1H, H^3, J = 3.5 Hz), 9.30 (d, 1H, H^2, J = 1.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 6.50 ($SiCH_2$), 22.45 ($C\mathbf{C}H_2C$), 43.41 (CH_2NH), 51.38 (OCH_3), 141.86 (C^4), 144.82 (C^2), 146.95 (C^1), 148.43 (C^3), 162.88 (C=O).

2.5.4. N-(3-(trimethoxysilyl)propyl)picolinamide (**2d**)

The reactants used were as follows: **1d** (1.00 g, 5.61 mmol), APTMS (1.00 ml, 5.59 mmol) and Et_3N (2.35 ml, 16.86 mmol). Yield: 1.23 ml, 4.35 mmol, 78%. IR (Neat, cm^{-1}): 3273 (υ N–H), 1645 (υ C=O), 1063 (υ Si–O). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.56 (m, 2H, $SiCH_2$), 1.62 (m, 2H, CCH_2C), 3.30 (m, 2H, CH_2NH), 3.43 (s, 9H, OCH_3), 7.24 (m, 1H, H^4), 8.07 (m, 1H, H^3), 8.52 (d, 1H, H^2, J = 4.7 Hz), 8.92 (s, 1H, H^5). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 6.26 ($SiCH_2$), 22.32 ($C\mathbf{C}H_2C$), 42.11 (CH_2NH), 49.96 (OCH_3), 123.91 (C^2), 130.39 (C^4), 135.07 (C^3), 148.05 (C^5), 151.29 (C^1), 165.49 (C=O).

2.5.5. N-(3-(trimethoxysilyl)propyl)nicotinamide (**2e**)

The reactants used were as follows: **1e** (1.00 g, 5.61 mmol), APTMS (1.00 ml, 5.61 mmol) and Et_3N (2.35 ml, 16.86 mmol). Yield: 1.31 ml, 4.63 mmol, 83%. IR (Neat, cm^{-1}): 3303 (υ N–H), 1648 (υ C=O), 1063 (υ Si–O). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C):