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1,1'-Diphenyl-bis(silatrane) as the First Structurally Characterized bis(silatrane)

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Abstract—1,1'-Diphenyl-bis(silatrane) (**I**) was obtained by the reaction of tris(1,3-dihydroxypropan-2-yl)amine (L) with $PhSi(OEt)_3$ in toluene. The molecular structure of complex **I** was established by X-ray diffraction (CIF file CCDC no. 2078347). Study of the redox properties of new bis(silatrane) **I** demonstrated that its radical ions generated by cyclic voltammetry are stable since the radical center located on the nitrogen atom is sterically protected within the bis(atrane) cage.

Keywords: bis(silatranes), X-ray diffraction, redox properties, cyclic voltammetry

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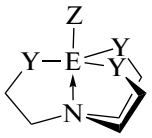
INTRODUCTION

Atranes represent a broad class of compounds containing the N–(C–C–Y)3 tricyclic moiety (Y = O, S, NR) (Scheme 1). Currently, atrane structures with group 1, 2, and 12–15 elements are known [1]. Historically, silatranes (E = Si, Y = O) were the first representatives of atranes. M.G. Voronkov and co-workers are rightly considered to be the founders of silatrane chemistry [2]; after their publication, the total number of studies on this subject has been permanently increasing (Fig. 1) [3].



Scheme 1.

The popularity of this research area is caused by several factors: (1) facile synthetic procedure comprising the reaction of triethanolamine with substituted trialkoxysilanes; (2) fundamental interest in studying the length of the transannular Si ← N bond (to get acquainted with the range of the lengths of this bond, see [4]); (3) applied interest related to the pharmacological properties [3] (antitumor, anticancer [5], antibacterial [6–9], anti-inflammatory, and fungicidal activities [10–12]; stimulating effect for animal husbandry [13], and seed germination effect [14, 15]), including biological activities [2, 16] inherent in silatranes. They are successfully used in sol–gel processes [17], to obtain new molecular sieves [18], and even for DNA-imaging in atomic force microscopy [19–26].

Currently, the interest in the atrane chemistry experiences a new rise. This is largely associated with the use of new ligand systems. The synthesis of tris(1,3-dihydroxypropan-2-yl)amine [27] brought about a surge in the research dealing with the synthesis and study of the properties of bis(metallatrane) derivatives based on this compound. Presumably, these bismetallatranes would exhibit all properties of complexes containing one atrane moiety, but would surpass them in the intensity of these properties. This may open up new promising applications, in particular, for the design of new semiconducting elements and compounds exhibiting the "molecular muscle" properties. A number of bis(germatranes) with thienyl [28] and phenyl substituents [29] have already been synthesized and studied for their redox properties. It is of interest that, in comparison with metallatranes with a single atrane moiety [30, 31], bis(metallatranes) show higher stability of the radical cations formed in the redox processes [29, 30].

The purpose of this study is to prepare new 1,1'-diphenyl-bis(silatrane) complex (**I**) based on tris(1,3-dihydroxypropan-2-yl)amine (L) and to study the structure of the complex by various methods, includ-

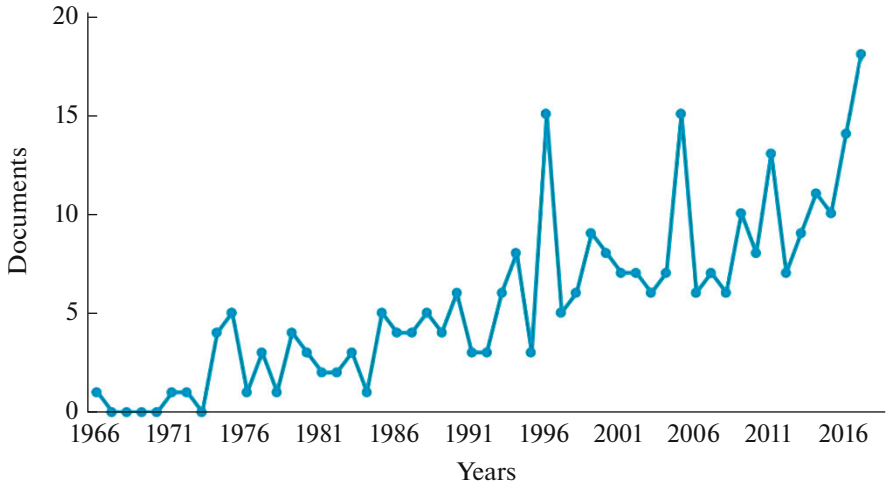


Fig. 1. Yearly distribution of publications on silatranes.

ing X-ray diffraction, and to study in detail the redox properties of the complex.

EXPERIMENTAL

All operations involved in the synthesis were carried out under argon using tris(1,3-dihydroxypropan-2-yl)amine, synthesized by the procedure described in [27], and $PhSi(OEt)_3$, obtained by the reaction of $Si(OEt)_4$ with PhCl in the presence of excess magnesium. The solvents were purified by standard methods [32].

Synthesis of complex I. A solution of $PhSi(OEt)_3$ (0.38 g, 1.6 mmol) in toluene was added to a solution of the ligand L (0.19 g, 0.8 mmol) in methanol. The reaction mixture was refluxed with stirring, while methanol was distilled off. Then toluene was evaporated on a rotor evaporator, and the residue was washed successively with petroleum ether and chloroform. Compound **I** was formed as a white crystalline powder in 71% yield.

^{1}H NMR (300 MHz; $CDCl_3$; δ, ppm): 7.7–7.68 (m, 4H, CH_{arom}), 7.44–7.33 (m, 6H, CH_{arom}), 3.82 (dd, J = 4.6 Hz, 11.5 Hz, 6H, CH_2), 3.77–3.70 (m, 6H, CH_2), 3.55–3.45 (m, 3H, CH). ^{13}C NMR (75 MHz; $CDCl_3$; δ, ppm): 134.20, 131.68, 130.37, 127.83, 61.00, 57.47.

HRMS: for ^{28}Si isotope, 461.155 $[M + NH_4]^+$ (calcd. 461.1559), 466.1101 $[M + Na]^+$ (calcd. 466.1113), 482.0837 $[M + K]^+$ (calcd. 482.0852).

Electrochemical measurements. The redox behaviors of complex **I** and ligand L were studied by cyclic voltammetry (CV). The preparation of solutions and all measurements were carried out in a dry glove box filled with argon, with oxygen and moisture contents not exceeding 1 ppm. Before measurements, acetonitrile (Acros, HPLC grade) with a water content not exceeding 100 ppm was additionally dried over molecular sieves (4 Å), which were preliminarily annealed in vacuum at 200–250°C for 4 h. The supporting electrolyte salt Bu_4NClO_4 (Sigma Aldrich) was also dried in vacuum at 70–80°C for 4 h. The content of water in the supporting electrolyte solution (0.1 M Bu_4NClO_4/MeCN) did not exceed 20 ppm, according to the Karl Fischer titration data (Mettler-Toledo C10SD Titrator). The analytes dissolved in the supporting electrolyte were subjected to electrochemical testing in a standard three-electrode glass cell at a potential sweep rate of 0.05–1 V s^{-1}. A glassy carbon disk electrode with a disk diameter of 1.7 mm served as the working electrode. Prior to use, the electrode surface was polished by sandpaper and then by the GOI polishing paste to attain mirror gloss. A platinum wire, preannealed in a gas burner flame to remove oxides and other possible pollutants from the surface, was used as the auxiliary electrode. The electrode potentials were measured relative to the reference electrode, which represented a silver chloride-coated silver wire, separated from the electrolyte bulk by an electrolyte bridge filled with a supporting electrolyte solution. The reference electrode was calibrated against the ferrocene/ferrocenium pair (E^0 = 0.400 V versus the standard hydrogen electrode).

Electronic spectra (UV and visible range) were measured on an Agilent 8453 spectrometer for a 5 × 10^{-4} M solution of **I** in acetonitrile using a 10-mm quartz cell with a Teflon lid. The solution was prepared in a dry glove box; before the cell was taken out, the contact between the lid and cell was sealed with the Parafilm band. Then the spectra were recorded within several minutes.

X-ray diffraction. The single crystal X-ray diffraction data of compound **I** were obtained at 100(2) K on a Bruker Quest D8 diffractometer equipped with a Photon-III detector (graphite monochromator, φ-

Table 1. Crystallographic data and X-ray experiment and structure refinement details for **I**

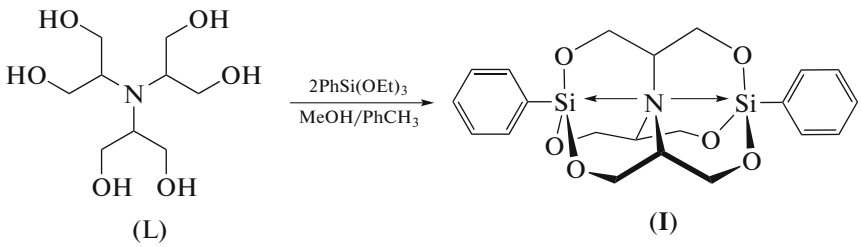
Parameter	Value
M	443.60
System	Monoclinic
Space group	$P2_1/c$
a, Å	10.4100(2)
b, Å	11.4017(2)
c, Å	17.4199(3)
β, deg	101.5437(7)
V, Å^3	2025.77(6)
Z	4
ρ(calcd.), g/cm^3	1.454
μ, mm^{-1}	0.216
F(000)	936
Crystal size, mm	0.15 × 0.08 × 0.05
Scanning range of θ, deg	1.997–34.350
Ranges of *hkl* indices	$-16 \le h \le 16$, $-18 \le k \le 18$, $-27 \le l \le 27$
Number of measured/unique reflections (R_{int})	76446/8490 (0.0531)
Number of reflections with $I > 2\sigma(I)$	6292
GOOF	1.026
R-factors ($I > 2\sigma(I)$)	$R_1 = 0.0444$, $wR_2 = 0.1068$
R-factors (for all reflections)	$R_1 = 0.0681$, $wR_2 = 0.1211$
Residual electron density (max/min), e/Å^3	0.585/–0.490

and ω-scan modes) using MoK_α radiation (λ = 0.71073 Å). The reflection intensities were integrated by the SAINT program [33] and corrected on the basis of equivalent reflections using the SADABS program [34] to apply corrections for absorption and crystal degradation. The structure was solved by direct methods by means of the SHELXT program package [35] and refined by the least squares method in the anisotropic (or isotropic for hydrogen atoms) full-matrix approximation on F^2 using the SHELXL software [36]. The hydrogen atom positions were calculated geometrically and refined in the rigid body approximation. The key crystallographic data and X-ray experiment details are summarized in Table 1.

Full tables of interatomic distances, bond angles, and atom coordinates and displacement parameters were deposited with the Cambridge Crystallographic Data Centre (CCDC no. 2078347; https://www.ccdc.cam.ac.uk/structures/).

RESULTS AND DISCUSSION

The reaction of tris(1,3-dihydroxypropan-2-yl)amine (L) with $PhSi(OEt)_3$ in toluene afforded 1,1'-diphenyl-bis(silatrane) (**I**) (Scheme 2).



(L) (**I**)

Scheme 2.

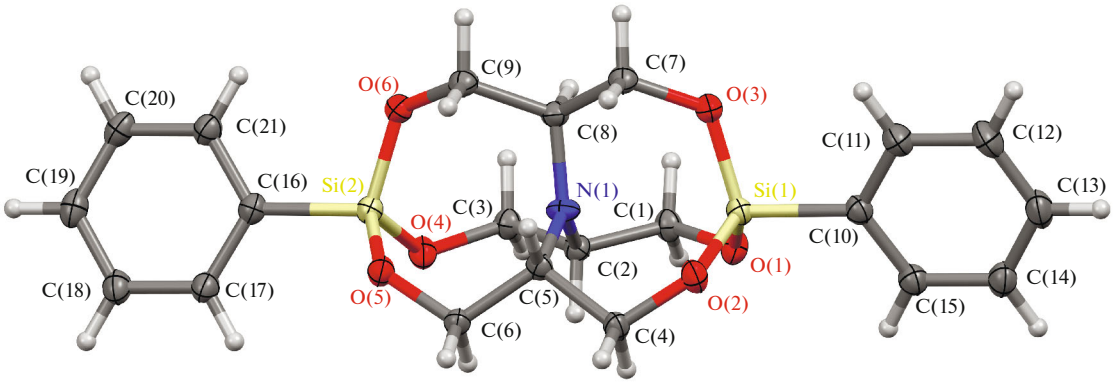


Fig. 2. Molecular structure of complex **I** (p = 50%). The disorder of the –O–CH_2–CH–CH_2–O– moieties is not shown.

The molecular structure of compound **I** was confirmed by X-ray diffraction data (Fig. 2), which showed the disorder of atoms in the –O–CH_2–CH–CH_2–O– moiety over two positions in the 0.8491(8) : 0.1509(8) ratio.

This compound is the first example of bis(silatrane) to be characterized by X-ray diffraction; therefore, the bond length and bond angle characteristics will be compared with those of compounds containing one atrane moiety.

Since the first synthesis of silatranes, quite a few such compounds with various substituents both at the metal atom and in the atrane moiety were obtained and fully characterized [4, 37]. A considerable body of data on the structures of these derivatives, in particular, the length of the transannular N → Si bond in the 3c–4e (three-center four-electron) C–Si ← N moiety was accumulated [38]. This length can vary over a broad range from 2.004 Å [39] to 3.19 Å [40]. The bond length is well correlated with the inductive effect of the Si-substituent: more electronegative substituents shift the electron density not only from the silicon atom, but also from the adjacent nitrogen atom, thus shortening the N–Si(X) dative bond. The transannular bonds in halogenated silatranes are among the shortest ones (X = F: 2.042 Å [41], 2.050 Å (210 K) [42], 2.056 (100 K) [8], 2.034 [43]; X = Cl: 2.022 [44], 2.023 [45]), while in the case of phenylsilatrane, which is the closest analogue of new bis(silatrane) **I**, this value is estimated as 2.193 Å [46].

The Si(1)–N(1) and Si(2)–N(1) bond lengths in **I** (2.7579(12) and 3.0293(12) Å, respectively) differ significantly from those obtained for phenylsilatrane. Nevertheless, these values are still markedly shorter than the sum of the van der Waals radii of silicon and nitrogen atoms (3.65 Å [47]), which unambiguously attests to a weak donor–acceptor bond between them in compound **I**. Thus, the C(16)–Si(2)–N(1)–Si(1)–C(10) system can be considered to be a common 5c–6e (five-center six-electron) bond; furthermore, the central 5c–6e axis is virtually linear: the C(16)Si(2)N(1), Si(2)N(1)Si(1), and N(1)Si(1)C(10) angles are close to 180° (178.71(5)°, 179.75(4)°, and 178.32(5)°, respectively).

Attention is also attracted by the fact that the Si(1)–N(1) and Si(2)–N(1) distances in **I** are considerably different (Δ = 0.271 Å). In our opinion, this difference can be a result of the energy compromise between the nitrogen intramolecular donor interaction and sterically forced five-coordination.

The central nitrogen atom is sp^2-hybridized, with the C(8)N(1)C(5), C(8)N(1)C(2), and C(2)N(1)C(5) angles being close to 120° (119.92(11)°, 118.84(11)°, and 120.00(11)°, respectively). The nitrogen atom slightly (by only 0.095(14) Å) deviates from the plane formed by the C(2), C(5), and C(8) atoms. Each silicon atom in the structure has a tetragonal environment (the average CSiO and OSiO angles in **I** are 106.2° and 112.5°, respectively). In this regard, compound **I** drastically differs from phenylsilatrane, in which the average CSiO angles are 97.1°, corresponding with the geometric parameters of a distorted trigonal bipyramid.

The redox properties of bis(silatrane) **I** were studied by CV on a glassy carbon disk electrode in a 0.1 M Bu_4NClO_4/MeCN solution. The current–voltage curves measured at potential sweep rates from 0.05 to 1 V s^{-1} (Fig. 3) correspond to an electrochemically quasi-reversible (approaching reversible) single-electron oxidation giving a radical cation. A comparison of the electrochemical behavior of this system with the behavior of ferrocene under the same conditions revealed slightly decreased currents of the forward and reverse peaks for bis(silatrane) **I**, with their ratio being 1 : 1. By extrapolation of the oxidation and reduction peak potentials to zero current, the gap between the peaks ΔE_p = 0.075 V was determined. This value slightly exceeds the theoretical value for electrochemically reversible reactions (0.059 V [48]), which is attributable to slower electron transfer [49]. The half-wave potential of bis(silatrane) is $E_{1/2}$ = 1.549 V.

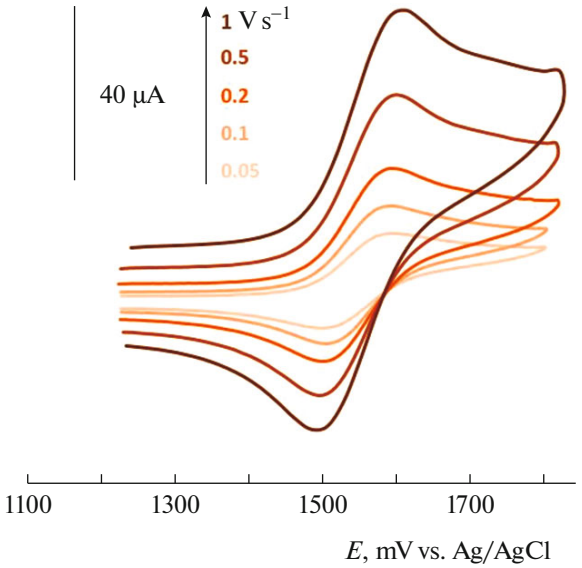


Fig. 3. CV curves recorded for a 3×10^{-3} M solution of **I** in 0.1 M Bu_4NClO_4/MeCN on a glassy carbon disk electrode at potential sweep rates of 0.05, 0.1, 0.2, 0.5, and 1 V s^{-1}.

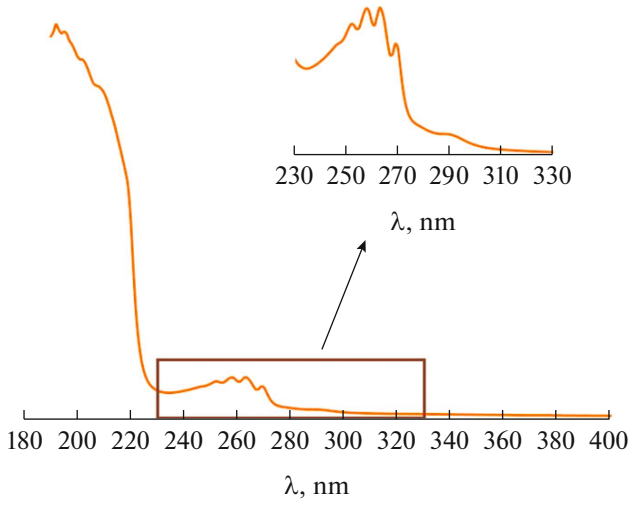


Fig. 4. UV absorption spectrum of a 5×10^{-4} M solution of **I** in acetonitrile.

Note that unlike 1,1'-diphenyl-bis(silatrane) **I**, phenylsilatrane shows chemically irreversible behavior up to potential sweep rates of ≥1 V [30]. This attests to higher stability of the bis(silatrane) radical cation caused by the fact that the radical center located on the nitrogen atom is sterically protected within the bisatrane cage. The oxidation peak potential E_p^{ox} is higher by 0.63 V for phenylsilatrane than for the starting triethanolamine because of the involvement of the nitrogen lone pair of silatrane into the N → Si dative interaction, which makes nitrogen less accessible for oxidation [30]. A similar shift in the oxidation peak potential is also observed in the case of **I** and L, but the magnitude of the shift is greater, 0.79 V (for L, E_p^{ox} = 0.801 V, which is consistent with the data of [27]). This attests to participation of the bis(silatrane) nitrogen atom in the double dative interaction Si ← N → Si, which further decreases the reactivity of this site towards oxidation.

Unlike 1,1'-diphenyl-bis(germatrane), the reduction curve of which does not show Faraday processes up to the discharge of the supporting electrolyte [29], bis-silatrane **I** is reduced at $E_p^{red} = -2.685$ V.

In the UV spectrum of **I**, the longest-wavelength (broad and weak) absorption band has a maximum at 289 nm (Fig. 4, inset), which is located to the right of the fine structure at 245–275 nm, characteristic of benzene [50]. The energy of this absorption (4.29 eV) is in good agreement with the potential difference between the oxidation and reduction peaks (4.27 V).

Thus, 1,1'-diphenyl-bis(silatrane) **I** was obtained for the first time and characterized by various physicochemical methods (including X-ray diffraction); and redox properties of compound **I** were studied.

FUNDING

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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