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RESEARCH ARTICLE

Silicon (IV) complexes containing bidentate ligands; Syntheses, Characterization and Catechol oxidase activity

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Abstract

Two silicon complexes, $[Si^{IV}(Quin)(Sal)]Cl_2$ (**1**) and $[Si^{IV}(Quin)(Naf)]Cl_2$ (**2**), containing bidentate ligands have been synthesized and characterized by elemental analysis, IR and UV–vis spectral measurements. In both complexes, silicon is four-coordinated with oxidation state 4. Catecholase activity was measured against 3,5-di-tert-butylcatechol (3,5-DTBC) in methanol saturated with oxygen. By comparison with the enzyme itself (K_{cat}= 2.29 sec^{-1}), complexes **1** and **2** show moderate catecholase activity (K_{cat}= 1.15 and 1.354 sec^{-1}), respectively with the activated 3,5-DTBC. The K_M (19 and 17 mM for complexes **1** and **2**, respectively), is rather large. Large K_M values seem typical of the faster model complexes, and indeed the enzyme itself. The reaction rate for both complexes is linearly dependent on the concentration of the complex, indicating a first-order dependence on catalyst concentration.

Introduction

Catechol oxidase, also known as o-diphenol oxidase or polyphenol oxidase (EC 1.10.3.1), forms the third member of type-3 copper proteins (1-3). This enzyme catalyzes a two-electron transfer reaction during the oxidation of a broad range of o-diphenols (like caffeic acid) to the corresponding o-quinones by molecular oxygen. The resulting highly reactive quinones auto-polymerize to form brown polyphenolic catechol melanins, a process thought to protect the damaged plant from pathogens or insects (4). In 1998, Krebs and co-authors have reported the crystal structures of catechol oxidase from Ipomoea batatas(sweet potato) which reveals a nitrogen-rich coordination environment, with three histidine donors to each copper [5]. Design and study of model complexes for catechol oxidase and other type 3 copper centers has been an area of much interest [6–13]. Most of the reported models use transition metals, especially copper centers [6, 14-19], but none of these models use non-transition metals. One of the non-transition metals is silicon which is the second most abundant element in the Earth's crust after oxygen. It is an essential element for mammals, where it is thought to be important for the development of bone and connective tissue. Although silicon was first reported to be an essential nutrient some 35 years ago, it is only in the last few years that one has begun to understand just why it is important for mammals. Silicon can account for up to 10% of the dry weight of shoots. Roots take up silicon in the form of silicic acid, and recently both influx and efflux transporters for silicic acid of the MIP family have been identified in grasses, including rice, barley, and maize.[20] Since d-orbitals of silicon tend to be rather diffused and of higher energy than its s- and p-orbitals, thus its complexes with donor ligands having silicon with coordination number higher than four seems to be somewhat rare [21]. Recently, it has been shown that silicon can form complexes with penta-, hexa- and even heptacoordination numbers [22]. The interest in organosilicon (IV) compounds is due to their versatile applicability in the

pharmaceutical industries. Generally, organosilicon compounds seem to own their antitumour properties to the immune defensive system of the organism [23-26]. The ability of silicon centers to have more than one oxidation state prompted us to investigate the catechole oxidase activity of some silicon (IV) complexes.

To obtain functional oxidase models it is necessary to have free or exchangeable cis-coordination sites on the metal ion for the intermediate adduct formation during the catalytic oxidation cycle. Therefore, metal chelates that incorporate good leaving groups, e.g. H_2O, Cl etc., and ligands with a low number of donor atoms seem to be of great promise. Furthermore, it is known that coordination number asymmetry in metalloenzymes presents the possibility of "open" coordination sites for direct interaction of the metal centre with substrate. Herein, we reported the synthesis of silicon (IV) complexes as functional model of catechol oxidase using ligand which should be provide one or more open coordination sites. However, oxidation with dioxygen under the mild conditions, catalyzed by the reported complexes is important with respect to both the modeling of oxidase enzymes and synthetic applications. 3,5-di-tertbutylcatechol (3,5-DTBC) has been widely employed as a substrate in catecholase model complex studies. Owing to its low redox potential, the substrate is readily oxidized and the bulky substituents prevent further reactions such as ring opening.

Results and Discussion

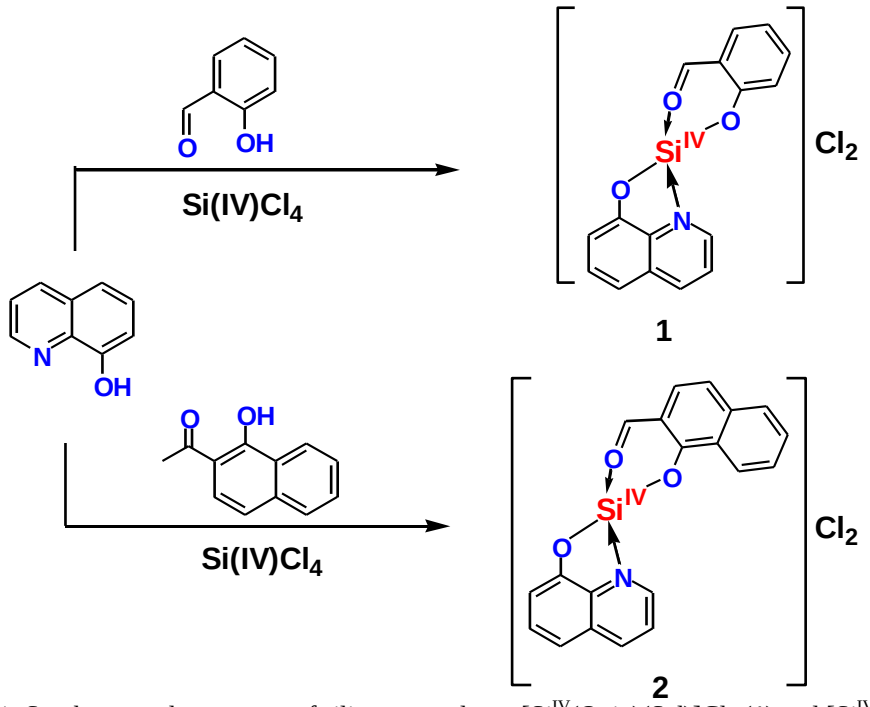
Synthesis and structure of $[Si^{IV}(Quin)(Sal)]Cl_2$ (1) and $[Si^{IV}(Quin)(Naph)]Cl_2$ (2)

Complexes **1** and **2** have been synthesized in high yield from the condensation of equimolar amounts of $Si^{IV}Cl_4$, and 8-hydroxy quinoline with either equimolar amounts of salicylaldehyde or 2-hydroxy-1-naphthaldehyde, respectively.Both complexes did not present any purification difficulties and have been identified and characterized, principally, based on the elemental analysis. Physical and analytical data, are in close agreement with the calculated values for the molecular formulae assigned to these metal chelates $[Si^{IV}(Quin)(Sal)]Cl_2$ and $[Si^{IV}(Quin)(Naph)]Cl_2$ for complexes **1** and **2**, respectively. The analytical data of these complexes showed that the solids are stable and can be stored for months without any significant change in their formulae. These new silicon (IV) complexes are crystals or crystalline powder, and their color being light orange. They are insoluble in water, slightly soluble in EtOH, and freely soluble in DMF and DMSO.

The IR spectra of the reported compounds were measured as KBr disk and reveal the absorptions expected for the proposed structures in scheme 1. It was noted that a strong band is present in the spectra of the free salicylaldehydeand 2-hydroxy-1-naphthaldehyde near 1660 cm^{-1} corresponding to ν(C=O) groups which are absent in the spectra of synthesized silicon (IV) complexes. The disappearance of this band and the appearance of a new strong absorption band within 1600 – 1620 cm^{-1} rang confirms the formation of the Schiff-base linkage as this band may be assigned to ν(C=N) stretching vibrations [78]. The frequency values of the ν(C=N) are lower than that usually found for the azomethine linkage [79]. These lower values of ν(C=N) stretching energy may be explained on the basis of a drift of the lone pair density of the azomethine nitrogen towards the silicon (IV) central atom [79,80], indicating that the coordination takes place through the nitrogen atom of the ν(C=N) group.

The important feature common to both complexes is the occurrence of a strong absorption bandsof quinolineν(C=N) at 1594 and 1596 cm^{-1}, in **1** and **2,** respectively and was greatly reduced in intensity. The observed shift of this bands from the spectra of the uncoordinated quinolinemoiety ν(C=N) at 1558 to higher wave numbers in the spectra of both complexes suggests coordination through the nitrogen atom of (C=N) to the silicon (IV) centre. A characteristic IR (KBr) feature of the complexes is the disappearance of the O–H stretching frequency at 3450 cm^{-1} as a result of the deprotonation of via coordination with silicon ions. New bands observed at 755 and 600 cm^{-1} assigned to $\gamma_{si\text{-}O}$ and at 576 and 500 cm^{-1} assigned to $\gamma_{Si\leftarrow N}$ for complexes **1** and **2**, respectively [27,28]. This further supports the coordination of the ligands under investigation to the silicon ions.

The molar conductance values of **1** and **2**, measured on 0.001 M solution in DMF at room temperature are 147 and 181.5 Ω^{-1} cm^2 mol^{-1}, respectively. These values are in the range expected for 1:2 electrolytes [29] suggesting the presence of two counter anion in the coordination sphere of the central silicon(IV) ion as they do in the solid state. These results reveal that neither solvolysis nor variation in the nature of the coordination sphere around the silicon (IV) center takes place in solution. The magnetic moment measurements show that both complexes are diamagnetic which is typical for the silicon complexes with silicon ions with oxidation 4.



Scheme 1. Syntheses and structures of silicon complexes $[Si^{IV}(Quin)(Sal)]Cl_2$ (**1**) and $[Si^{IV}(Quin)(Naph)]Cl_2$ (**2**).

Electronic spectroscopy of of$[Si^{IV}(Quin)(Sal)]Cl_2$ (1) and $[Si^{IV}(Quin)(Naph)]Cl_2$ (2)

Figure 1 shows the electronic spectra of solutions of **1** and **2** in methanol at 298 K. The spectrum of the ligand shows bands at 372 nm which can be assigned to the n–π^* transitions. This band shows a blue shift upon coordination to silicon and appears at 311 and 319 nm for complexes **1** and **2** respectively. This shift is due to the polarization within the –OH caused by the metal-ligand electron interaction during the chelation [30]. The bands at 294 and 307 nm of quinoline, assigned to $\pi - \pi^*$ transition within the benzene ring and –C=N, are shifted to lower wavelength at 247 and 250 nm via coordination to silicone center in **1** and **2**, respectively.

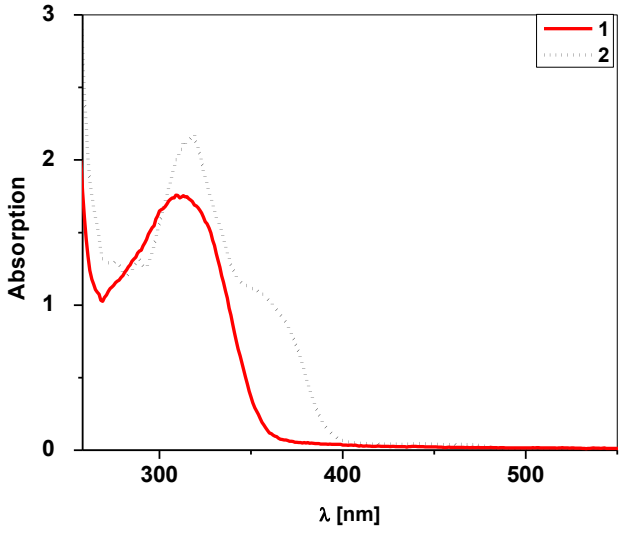


Figure 1. Electronic spectra of solutions of **1** (solid line, c = 10^{-4} M) and **2** (dashed line, c = 10^{-4} M) in methanol at 293 K.

Thermogravimetric analysis (TGA and DTG)

The aim of the thermal analysis study is to obtain information concerned the thermal stability of the investigated metal chelates, for example, to decide whether water or solvent molecules are inside or outside the coordination sphere and to suggest a general Scheme for the thermal decomposition of these silicon (II) chelates. In the present study TGA & DTG method is utilized. The TG and DTG thermograms of representative complexes were recorded under a dynamic N_2 atmosphere and some important characteristics are listed in table 1. The TG curve was redrawn as mg mass loss versus temperature. The decomposition stages, temperature ranges and the percentage losses in masses are given in figure 2. List of the activation parameters for the decomposition of both complexes are shown in table 1**.** The thermogravimetric curves of two complexes show three stages of decomposition within the temperature range of ambient temperature to 800^0 C. The first stage at in the region of 50 – 100 ^{0}C shows the dehydration process associated with the loss of one and two molecules of water for complexes **1** and **2**, respectively. The second stage in the range of 100 – 220 ^{0}C corresponding to the loss of chloride and portion of the organic ligands. The final stage corresponds to the complete removal of the organic portion in successive decomposition steps within the temperature range 220 – 800 ^{o}C leaving silicon oxide. The observed overall weight loss amounts are in a good agreement with the calculated values based on the suggested formulae of these complexes (table 1).

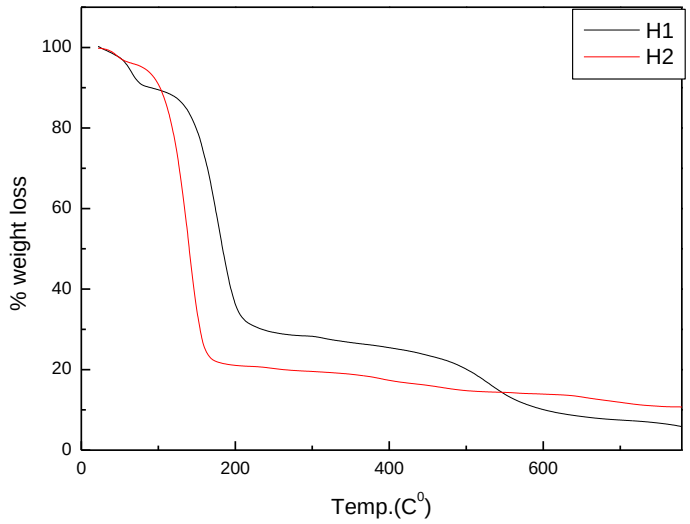


Figure 2. TGA diagrams of complexes **1** (solid line) and **2** (dashed line).

The stability of the obtained silicon (IV) complexes was investigated kinetically by using Coats-Redfern [31]. The data in Table 1 show that the values of the activation energies of the investigated complexes reflect the thermal stability of these complexes. On the other hand in most cases the activation energy values of the first stage of the decomposition of complex **1** are lower than that of complex **2**. This may attributed to the less steric strain in **1** (contain phenyl) compared to that of **2** (containing naphthyl moiety). It is clear from the data of the kinetic and thermodynamic parameters that, in most cases the removal of the counter anion and water content of the complex molecule have lower E^* and ΔH^* values than the removal of the organic moiety of the coordinated ligand to yield the SiO_2 as a final product.

The values of $\Delta G^{\#}$ increase for the subsequently decomposition stages due to increasing the values of $T\Delta S^{\#}$ from one step to another which override the value of $\Delta H^{\#}$. This increase reflects that the rate of the subsequent removal of the organic ligand portion will be lower than that of the precedent ligand. This may be ascribed to the structural rigidity of the remaining complex after the explosion of one and more coordinated ligand species, as compared with precedent complex, which require more energy for its rearrangement before undergoing any compositional change. The positive values of $\Delta H^{\#}$ means that the thermal decomposition processes are endothermic. For both complexes, the $\Delta S^{\#}$ values are negative but almost close to zero which is indication for I_a interchange mechanism for all stages with a more ordered activated complex than the reactant and/or the reactions are slow.

Table 1. List of the activation parameters for the decomposition of complexes **1** and **2**.

Complex	Step	T (K)	A	r	$\Delta E^{\#}$	$\Delta H^{\#}$	$\Delta S^{\#}$	$\Delta G^{\#}$
1	1st	323	8.36	0.905	34.5	31.58	-0.236	107.8
	2nd	378	5.44	0.925	40.88	37.96	-0.241	129
	3rd	798	5.55	0.982	13.28	10.36	-0.247	207.6
2	1st	308	20.52	0.913	66.68	63.76	-0.228	134
	2nd	398	6.31	0.964	41.62	38.7	-0.24	134.22
	3rd	808	4.72	0.911	14.13	11.21	-0.248	211

Catecholase activity

In most of the catecholase like activity studies of synthetic model complexes, 3,5-di-tert-butylcatechol (3,5-DTBC) has been employed as substrate. The product 3,5-di-tert-butyl-o-quinone (3,5-DTBQ), is considerably stable and has a strong absorption at λ_{max}= 400 nm. Therefore, activities and reaction rates can be determined using electronic spectroscopy by following the appearance of the absorption maximum of the quinone. The reactivity studies were performed in methanol solutions because of the good solubility of the complexes, the substrate (3,5-DTBC) and its product (3,5-DTBQ) in these solvents. Prior to a detailed kinetic study, it was first necessary to estimate approximately the ability of the complexes to oxidize 3,5-DTBC. For this purpose, 0.1 mM solutions of complexes **1** and **2** in methanol were treated with 100 mM of 3,5-DTBC in the presence of air. The course of the reaction was followed by UV/VIS spectroscopy over the first 200 min. The first results indicated that both complexes catalyze the aerobic oxidation of 3,5-DTBC to 3,5-DTBQ in methanol. The reactivity of complex **2** is slightly higher than that of **1**, and can be expressed in turnover numbers of 11 min^{-1} for **2** versus 9 min^{-1} for **1**. The rate of oxidation is depending on the donating properties of the imine ligands attached to the metal ion. There are a number of factors that could help to elucidate the difference in the catalytic activates of the reported catechol oxidase functional models. These include (a) the redox potential of the couple Si(II)/Si(IV) in the investigated complexes during the catalytic cycle, (b) the Lewis acidity of the silicon (IV) center created by the donating properties of the imine ligands, and (c) the steric features of the parent ligands.**2**, containing naphthyl derivative is assumed to have higher Lewis acidity than **1**, containing phenyl derivative and the catalytic reactivity of these complexes follows the same order of the Lewis acidity.

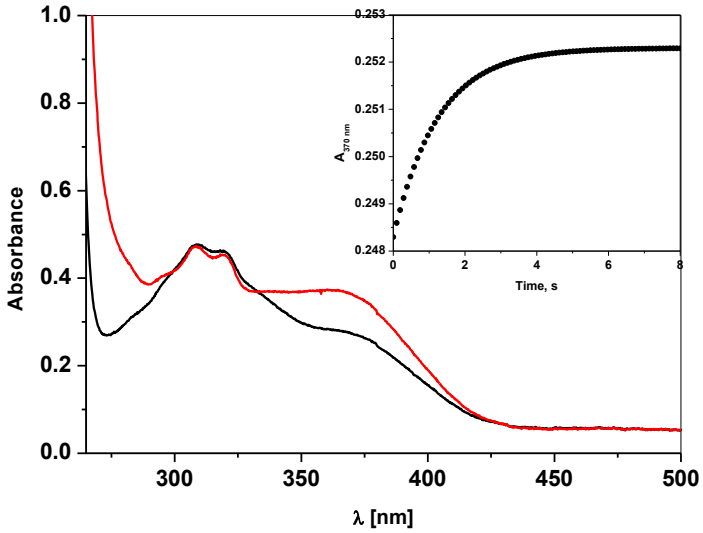


Figure 3. UV/Vis spectral changes recorded for the first reaction step of the complex **1** (0.1mM) with 3,5-DTBC (100 mM) in MeOH at 296 K. Inset: representative kinetic trace obtained by stopped-flow spectrophotometry monitored at 380 nm.

It is clear from the results in Figure 3 that the addition of 100 mM of 3,5-DTBC to the complex has an immediate influence on the UV/Vis spectrum. The bands in the charge-transfer region change with respect to position and intensity. Therefore, binding of 3,5-DTBC to the silicon (IV) center should definitely be considered as the first rapid step. Due to the developing product bands in the UV/Vis spectrum of the complex, it is difficult to make a clear statement about the nature of the coordination of catechol to the metal center by using UV spectrometer. We have therefore used stopped-flow techniques to study the rapid reaction with 3,5-DTBC in more detail. The kinetics of the subsequent reaction was studied by the initial rate method by monitoring the absorbance change at 380 nm (see inset in Figure 3).

To determine the dependence of the observed reactions on the substrate concentration, solutions of complex **1**and **2** were treated with different concentrations of 3,5-DTBC in methanol. A first-order dependence on the substrate concentration was observed at low concentrations of 3,5-DTBC. At higher substrate concentrations, saturation kinetics was observed (see Figure 4 and 5). The irreversible conversion into the quinone product is considered to be the rate-determining step, i.e. $k_2 << k_{-1}$ and $K_1 = k_1/k_{-1}$. Although a much more complicated mechanism may be involved, the results show that this simple model is sufficient for a kinetic description. The rate law for the reaction sequence in (3) is given by (4):

$$Si^{IV}\text{complex} + 3,5\text{–DTBC} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Si^{IV}\text{–DTBC adduct} \xrightarrow[k_2]{O_2} Si^{IV}\text{complex} + \text{DTBQ} \quad (3)$$

$$V = \frac{d[\text{DTBQ}]}{dt} = k_2[Si^{IV}\text{complex} - \text{adduct}] = \frac{k_2 K_1\,[Si^{IV}\text{complex}][3,5-\text{DTBC}]}{1 + K_1[3,5-\text{DTBC}]}$$

where V is the rate of product formation, which can be rewritten as

$$\frac{V}{[Si^{IV}\text{complex}]} = \frac{k_2 K_1\,[3,5-\text{DTBC}]}{1 + K_1[3,5-\text{DTBC}]} \qquad (4)$$

The maximum rate constant, k_2, is reached when the catalyst is completely saturated with 3,5-DTBC, i.e. at high [3,5-DTBC].Complexes **1** and **2** show moderate catecholase activity (K_{cat}= 1.15 and 1.35 sec^{-1}), respectively compared to the enzyme itself (K_{cat}= 2.29 sec^{-1}). At a V/[Si^{IV}complex] value of $k_2/2$, the [3,5-DTBC] = $1/K_1$, which according to Figure 4 and 5 results in K_1, coordination affinity of 3,5-DTBC,≈ 19 mM^{-1} for **1** and 17 mM^{-1} for **2**. K_1 is rather large for both complexes and this seems typical for faster models, and indeed the enzyme itself ($25mM^{-1}$)[32].The reaction rate is linearly dependent on the concentration for both complexes, indicating a first-order dependence on catalyst concentration (Figure 4 and 5).

Table 2. Comparison of catalytic parameters of selected catechol oxidase model systems and catechol oxidase from Ipomoea batatas.

Complex	$K_{cat}(s^{-1})$	$K_M(M)$
[Si(IV)(Quin)(Sal)]Cl_2 (**1**)	1.15	19 x 10^{-3}
[Si(IV)(Quin)(Naf)]Cl_2 (**2**)	1.34	17 x 10^{-3}
Catechol oxidase from I. batatas [32]	2.29	2.5 x 10^{-3}

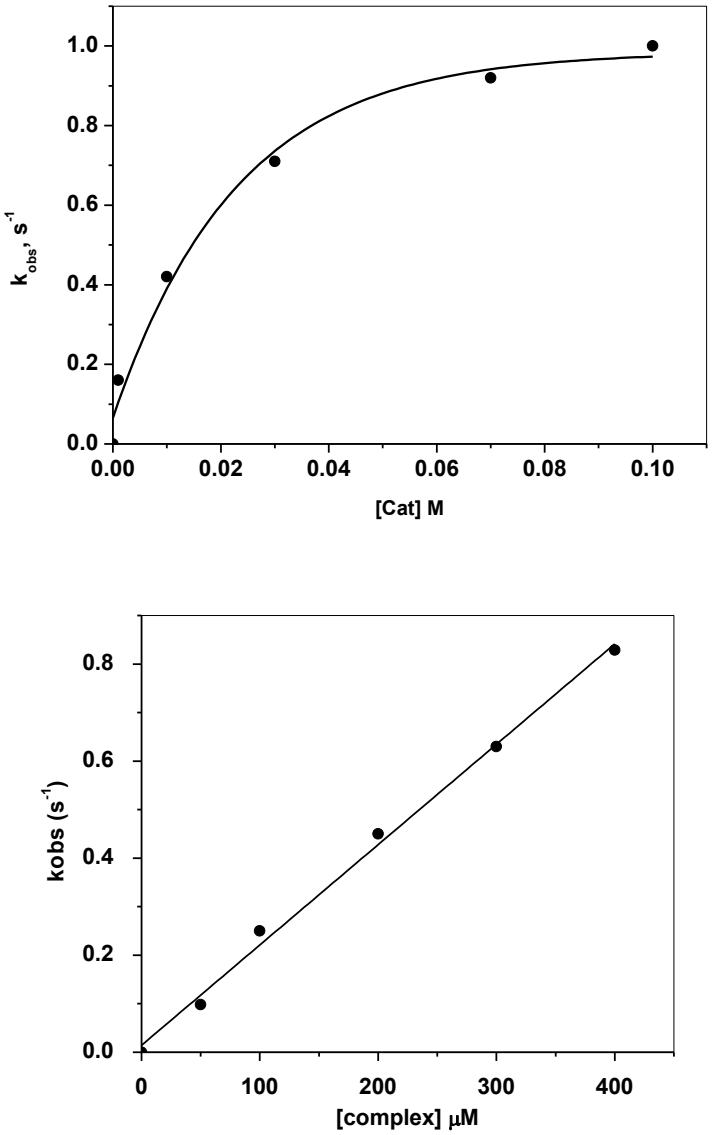


Figure 3. Substrate (3,5-DTBC) a and complex b dependence of oxidation of catechol by complex **1**.

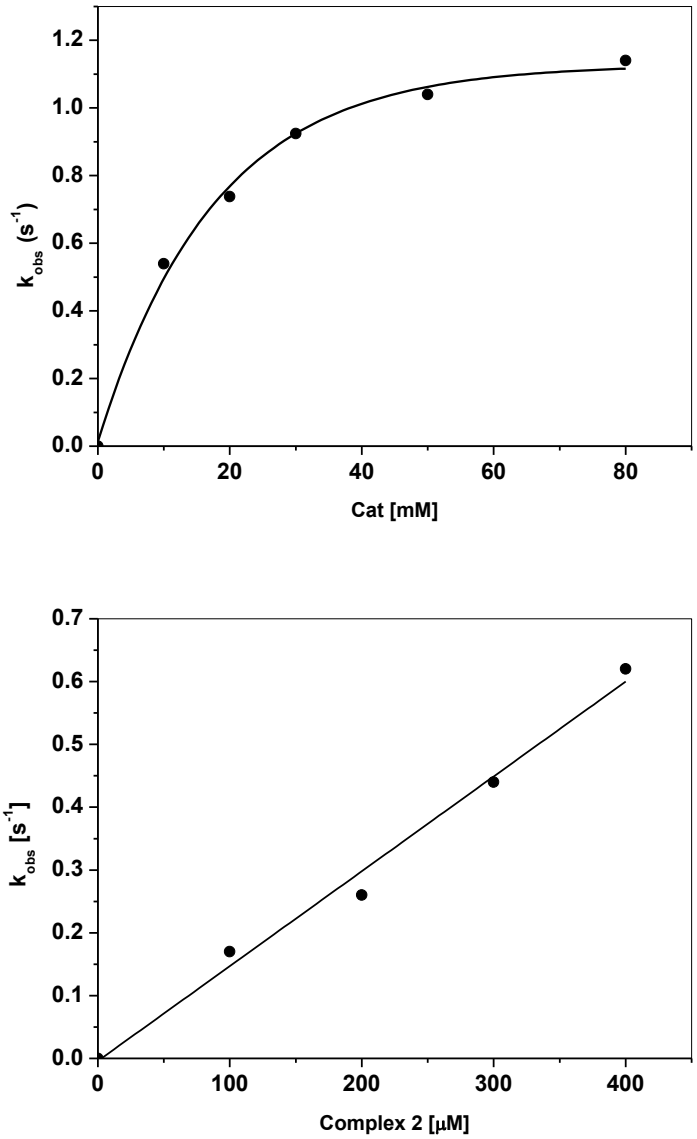


Figure 4. Substrate (3,5-DTBC) a and complex b dependence of oxidation of catechol by complex **2**.

Conclusion

As a conclusion, new silicon complexes, $[Si^{IV}(Quin)(Sal)]Cl_2$ (**1**) and $[Si^{IV}(Quin)(Naf)]Cl_2$ (**2**), containing bidentate ligands have been synthesized and completely characterized and silicon center was found to be four-coordinated with oxidation state of 4. Catecholase activity against 3,5-di-tert-butylcatechol was measured in methanol saturated with oxygen. Complexes **1** and **2** show moderate catecholase activity (K_{cat} = 1.15 and 1.354 sec^{-1}), respectively compared to the enzyme itself (K_{cat} = 2.29 sec^{-1}). Complexes **1** and **2** are relatively faster model complexes as they show large values of K_M (1.9 x 10^{-2} and 1.7 x 10^{-2}, respectively). These large K_M values seem typical of faster model complexes and shows that both complexes can act as model for catalyst. The reaction rate for both complexes is linearly dependent on the concentration of the complex, indicating a first-order dependence on catalyst concentration.

Experimental Section

Materials and general methods:

IR spectra were recorded using KBr disks in the 4000-200 cm^{-1} range on a Unicam SP200 spectrophotometer. UV–visible absorption spectra were measured on a Shimadzu 52 UV-2450 spectrophotometer. Magnetic moments were measured by Gouy's method at room temperature. The specific conductance of the complexes was measured using freshly prepared 10^{-3} M solutions in electrochemically pure DMF at room temperature, using an YSI Model 32 conductance meter. The thermogravimetric measurements were performed using a Shimadzu TG 50-Thermogravimetric analyzer in the 25-800 °C range and under an N_2 atmosphere. Elemental analyses were carried out at the Micro analytical Unit of Cairo University.

Kinetic investigations of the catecholase activity of complexes was performed on KinetAsyst SF-61DX2 and Applied Photophysics SX 18MV stopped-flow instruments coupled to an online data acquisition system (also thermostatted at 23.0±0.1 °C) with an optical pathlength of 1 cm at 400 nm. The temperature of the instruments was controlled with an accuracy of ± 0.1 °C. The catalytic activity was studied under pseudo-first-order conditions by using at least a ten-fold excess of catechol or complexes. All listed rate constants represent an average value of at least three kinetic runs under each experimental condition.

All chemicals used were of analytical reagent grade and of the highest purity commercially available. $Si(IV)Cl_4$ (Aldrich), 8-hydroxy quinoline (Across), salicylaldehyde (Across) and 2-hydroxy-1-naphthaldehyde (Across) were used without further purification.

Synthesis of $[Si(IV)(Quin)(Sal)]Cl_2$ (**1**)

$SiCl_4$ (0.02 mol, 3.40 g) in THF was added to a solution of 8-hydroxy quinoline (0.02 mol, 2.90 g) and salicylaldehyde (0.02 mol, 2.44 g). The mixture was heated at reflux for 3 h and the reaction mixture was allowed to stand overnight at room temperature. The resulting solid was filtered off, washed with little amounts of THF and ether and finally dried over CaO to give yellow solid material. IR (KBr): ν = 3372 (w, O–H), 1594 (s, C=N), 755 (w, Si–O), 576 (w, Si–N). Elemental analysis for $C_{16}H_{11}Cl_2NO_3Si$ (364.25): calcd. C 49.4, H 3.8, N 4.9: found C 50.3, H 4.4, N 5.9 %; Λ = 147 ($\Omega^{-1}cm^2\ mol^{-1}$).

Synthesis of $[Si(IV)(Quin)(Naph)]Cl_2$ (**2**)

$SiCl_4$ (0.02 mol, 3.40 g) in THF was added to a solution of 8-hydroxy quinoline (0.02 mol, 2.9 g) and 2-hydroxy-1-naphthaldehyde (0.02 mol, 3.44 g). The reaction mixture was heated at reflux for 4 h. The resulting reaction mixture was allowed to stand overnight at room temperature. The resulting solid was filtered off, washed with THF and ether and finally dried over CaO to give buff solid material. IR (KBr): ν = 3350 (w, O–H), 1596 (s, C=N), 600 (w, Si–O), 500 (w, Si–N), Elemental analysis for $C_{20}H_{13}Cl_2NO_3Si$ (414.31): C 55.7, H 3.8, N 3.2: found C 56.5, H 4.2, N 3.3%; Λ = 182 ($\Omega^{-1}cm^2\ mol^{-1}$).

Catecholase assays

Catecholase activity was measured against 3,5-di-tert-butylcatechol (3,5-DTBC). Kinetic assays were conducted in methanol (saturated with 1 atm O_2) at 298 K and formation of product was monitored at 390 nm. Under these conditions no formation of quinone was observed in the absence of the silicon complex. In substrate-dependent measurements, the concentration of both complexes was held constant at 0.5 x 10^{-4} M, and the concentration of 3,5-DTBC was varied between 10 and 80 mM. For measurement of complex dependence, the concentration of 3,5-DTBC was held constant at 25 mM, and the concentration of complexes was varied between 100 and 400 μM.

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