Synthesis, Crystal Structure and Electrochemical Studies of a Hydrazone Schiff Base Complex of Titanium(IV)

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Z. Naturforsch. **2009**, *64b,* 409 – 414; received December 25, 2009

The *in situ* formed hydrazone Schiff base ligand (*E*)-*N′*-(2-hydroxy-3-methoxybenzylidene)-benzohydrazide (L^{2-}) reacts with bis(acetylacetonato)titanium(IV) oxide in methanol to a mononuclear [Ti(L)(OCH_3)(acac)] complex which crystallizes in the monoclinic space group $P2_1/c$, a = 18.2786(13), b = 8.2609(5), c = 13.9008(10) Å, β = 96.809(3)° with Z = 4. Cyclic voltammetric experiments of the species in acetonitrile solution reveals a reversible peak at $E^{o'} = -0.768$ V (*vs.* Ag/AgCl) relating to the Ti^{IV}/Ti^{III} redox process.

Key words: Titanium(IV), Hydrazone, Schiff Base, Molecular Structure, Cyclic Voltammetry

Introduction

The Schiff bases are widely employed as ligands in coordination chemistry [1, 2]. These ligands are readily available, versatile and, depending on the nature of the starting materials (primary amines and carbonyl precursors), they exhibit various denticities and functionalities. Moreover, the number, the nature, and the relative position of the donor atoms of a Schiff base ligand allow a good control over the stereochemistry at the metallic centers, as well as over the number of the metal ions within homo- and heteropolynuclear complexes [3]. All these advantages make Schiff bases very good candidates in the effort to synthesize metal complexes of interest in bioinorganic chemistry, catalysis, encapsulation, transport and separation processes, and magnetochemistry.

Titanium Schiff base complexes are used in catalytic asymmetric pinacol coupling of aromatic aldehydes [4], polymerization of ethene and propene [5], as precatalysts for aldehyde allylation [6], for asymmetric additions to aldehydes and the ring opening of cyclohexene oxide [7], for titanium-catalyzed enantioselective cyanation of aldehydes [8], and asymmetric oxidation of sulfides with H_2O_2 [9]. Titanium complexes also catalyze the 3-component coupling of an isonitrile, a 1,1-disubstituted hydrazine, and an alkyne [10]. The alkyne is formally iminohydrazinated during this process.

The hydrazone functional group $>N{-}N{=}C<$ belongs to a large group of azomethines which are distinguished from other members of this class (*e. g.* imines, oximes) by the presence of two adjacent N atoms. The hydrazones are known to have a variety of applications as catalysts [11] and hole-transporting agents [12 – 14], as organic layer photoconductors, in pharmaceutical industry [15 – 18] as drugs for treatment of cancer, schizophrenia, leprosy, *etc.*, besides their uses in synthetic and industrial chemistry [19]. In recent years, the hydrazones have been drawing much attention from coordination chemists, because of the strong tendency of aroyl hydrazones to chelate transition metals [20 – 25], lanthanides [26, 27], and main group metals [28, 29]. It has also been suggested that nucleophilic substitution [30] of hydrazone ligands may be an important route to assemble nanoscale molecular clusters. Qi and Wang [31] have reported the preparation of novel dendritic mixed-valence ruthenium complexes, which can act as variable attenuators for the control of optical signals.

To the best of our knowledge, there is no report on a hydrazone Schiff base complex of titanium(IV) [32]. Herein, we report the first crystal structure and spectral

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and electrochemical properties of a hydrazone Schiff base complex of titanium(IV).

Experimental Section

Benzhydrazide, 2-hydroxy-3-methoxybenzaldehyde, titanyl acetylacetonate ($TiO(acac)_2$) and solvents with high purity were purchased from Merck and Fluka and used as received. IR spectra were recorded in KBr disks with a Matson 1000 FT-IR spectrophotometer in the range of 4000 – 450 cm^{-1}. UV/VIS spectra of solutions were recorded on a Shimadzu 160 spectrometer. Microanalytical (CHN) data were obtained with a Carlo ERBA Model EA-1108 analyzer. ^1H and ^{13}C NMR spectra were obtained on a Bruker spectrometer at 250 MHz in $[D_6]$DMSO.

*Synthesis of $[Ti^{IV}(L)(OCH_3)(acac)]$, **1**, and preparation of its single crystals*

Crystals of $[Ti^{IV}(L)(OCH_3)(acac)]$, **1**, were grown through diffusion of the reactants in a thermal gradient, namely by the ‘branched tube’ method [33]. To isolate single crystals of **1**, (H_2L = (1*Z*,*N*′*E*)-*N*′-(2-hydroxy-3-methoxybenzylidene)benzohydrazonic acid; Hacac = acetylacetone) benzhydrazide (0.20 g, 1.47 mmol), 2-hydroxy-3-methoxybenzaldehyde (0.25 g, 1.47 mmol) and titanyl acetylacetonate (0.38 g, 1.47 mmol) were placed in the main arm of the branched tube. Methanol was carefully added to fill the arms, the tube was sealed and the arm containing the reagents immersed in an oil bath at 60 °C while the other arm was kept at ambient temperature. After 3 weeks, red-orange crystals were deposited in the cooler arm, which were filtered off, washed with methanol and air-dried (0.42 g yield, 65 %). In another experiment, noncrystalline **1** was obtained by heating the starting reagents for 3 h under reflux conditions. Analysis for $C_{21}H_{22}N_2O_6Ti$: calcd. C 56.52, H 4.97, N 6.28; found C 56.5, H 5.1, N 6.9. – IR (KBr): ν = 3077 (w), 3015 (w), 2931 (w), 1592 (s) (C=O), 1562 (s) (C=N), 1523 (s), 1454 (s), 1354 (s), 1269 (s), 1108 (s), 1031 (m), 877 (m), 708 (m), 600 (s), 469 (m) cm^{-1}. – ^1H NMR ($[D_6]$DMSO): δ = 8.46 (1H, s, -C*H*=N-), 8.03 – 6.49 (8H, m, arom), 5.79 (1H, s, H of acac ligand), 4.35 (3H, s, (aryl)-OCH_3), 3.80 (3H, s, Ti–OCH_3), 3.46 (3H, s, CH_3 of acac ligand) and 1.93 (3H, s, CH_3 of acac ligand). – $^{13}C\{^1H\}$ NMR ($[D_6]$DMSO): δ = 189.55, 170.01, 154.40, 151.82, 147.18, 130.98, 128.39, 128.08, 124.64, 122.03, 119.62, 116.90, 105.45, 66.89, 56.42, 30.92, 26.35, 24.85.

X-Ray structure determination

A red-orange crystal of **1** (0.174 × 0.065 × 0.03 mm^3) was investigated at 200(2) K on a Nonius Kappa CCD diffractometer with monochromatized MoK_α radiation (λ = 0.71073 Å) obtained from graded multilayer X-ray optics. The structure was solved by Direct Methods with SIR97 [34], and refined with full-matrix least-squares techniques on F^2 with SHELXL-97 [35]. The crystal data and refinement parameters are presented in Table 1. The hydrogen atoms were calculated in idealized geometry riding on their parent atoms. The molecular structure plot was prepared using ORTEP-III [36].

Table 1. Crystallographic data for **1**.

Formula	$C_{21}H_{22}N_2O_6Ti$
M_r/g mol^{-1}	446.276
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	18.2786(13)
b, Å	8.2609(5)
c, Å	13.9008(10)
β, deg	96.809(3)
V, Å^3	2084.2(2)
Z	4
Calc. density, g cm^{-3}	1.42226(14)
μ(MoK_α), mm^{-1}	0.451
θ range, deg	3.15 – 24.15
Refls. measured/unique/R_{int}	11814/3317/0.0512
Mean $\sigma(I)/I$	0.0531
Observed refls.	2380
Refined parameters	275
$R1$ (F_{obs})[a]	0.0490
$wR2$ (F^2)[b]	0.1302
A, B (weighting scheme)[b]	0.0551, 1.5006
GoF[c]	1.024
shift/error$_{max}$	0.001
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.443/−0.370

[a] $R1 = \|F_o| - |F_c\|/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [c] $\mathrm{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

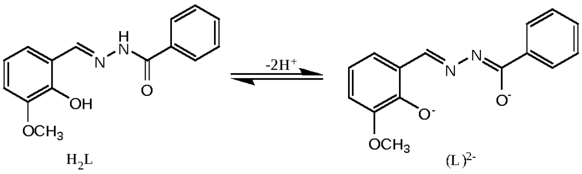
CCDC 693974 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Electrochemistry

Voltammetric experiments were performed using a Metrohm computrace voltammetric analyzer model 757 VA. A conventional three-electrode system was used with a polished glassy carbon electrode (area 3.14 mm^2) as working electrode and a platinum wire counter electrode. The reference was an aqueous Ag/AgCl saturated electrode, separated from the bulk of the solution by a bridge with solvent and supporting electrolyte. The solutions in the bridge were changed periodically to avoid aqueous contamination from entering the cell *via* the Ag/AgCl electrode. Before each experiment the working electrode was cleaned by polishing with alumina 0.05 mm and rinsed thoroughly with distilled water and acetone. The electrolytic medium consisted of 0.1 mol L^{-1} tetrabutylammonium perchlorate (TBAP) as

Table 2. UV/Vis data for H_2L and $[Ti^{IV}(L)(OCH_3)(acac)]$ in acetonitrile.

Compound	λ_{max} (nm)/ε (M^{-1} cm^{-1})	Assignment
H_2L	224/10730	$n \rightarrow \pi^*$
	297/12590	$\pi \rightarrow \pi^*$
$[Ti^{IV}(L)(OCH_3)(acac)]$	229/8900	$n \rightarrow \pi^*$
	275/7040	$\pi \rightarrow \pi^*$



(*E*)-*N*′-(2-hydroxy-3-methoxybenzylidene)benzohydrazide

Fig. 1. *In situ* generation of H_2L and its deprotonation in the formation the complex **1**: $Ti^{IV}O(acac)_2 + H_2L + CH_3OH \rightarrow [Ti^{IV}(L)(OCH_3)(acac)] + H_2O + Hacac$.

supporting electrolyte in acetonitrile, and all experiments were carried out at r. t. The solutions were freshly prepared before use, and were purged with N_2 saturated with solvent for *ca.* 15 min prior to taking measurements in order to remove dissolved O_2. Voltammograms were recorded in the range from 1.0 to −1.0 V *vs.* Ag/AgCl.

Results and Discussion

Synthesis of [Ti^IV (L)(OCH₃)(acac)] (1)

The hydrazone Schiff base dianion $(L^1)^{2-}$ is formed *in situ* when equimolar quantities of 2-hydroxy-3-methoxybenzaldehyde and benzohydrazide are reacted with titanyl acetylacetonate in methanol [37]. The complex $[Ti^{IV}(L)(OCH_3)(acac)]$ (**1**) is soluble in common organic solvents. The hydrazone Schiff base ligand (H_2L) exhibits three bands in the range 3215–3569 cm^{-1} due to phenolic and NH vibrations. Absence of these bands in the spectrum of the complex, and a 46 cm^{-1} red shift of the azomethine (-C=N-) band of the hydrazone Schiff base, indicate coordination of H_2L through the phenolic oxygen atom after deprotonation, the azomethine nitrogen atom and benzocarboxide groups (Fig. 1).

Table 2 provides electronic spectral data of the ligand H_2L and the complex along with their assignments. The electronic spectrum of the complex in CH_3CN exhibits two bands at 229 and 275 nm. These bands appear at 229 and 284 nm in the polar solvent CH_3OH, so they are due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ ligand transitions, respectively. The electronic spectra of H_2L and **1** are reproduced in Fig. 2.

Table 3. Selected bond lengths (Å) and angles (deg) for **1**.

Ti–O1	1.956(2)	O1–Ti–O2	154.17(10)
Ti–O2	1.866(2)	O1–Ti–O4	83.36(9)
Ti–O4	2.086(2)	O1–Ti–O5	94.05(10)
Ti–O5	1.946(2)	O1–Ti–O6	96.04(11)
Ti–O6	1.758(2)	O1–Ti–N2	73.78(10)
Ti–N2	2.146(3)	O2–Ti–O4	84.35(10)
N1–N2	1.411(4)	O2–Ti–O5	106.92(10)
N1–C1	1.308(4)	O2–Ti–O6	97.13(11)
N2–C8	1.292(4)	O2–Ti–N2	82.74(10)
O4–C17	1.260(4)	O4–Ti–O5	83.14(9)
O5–C19	1.302(5)	O4–Ti–O6	177.51(10)
C18–C19	1.373(5)	O4–Ti–N2	85.82(9)
C17–C18	1.400(6)	O5–Ti–O6	94.51(10)
O6–Ti–N2	96.34(10)	O5–Ti–N2	164.45(10)

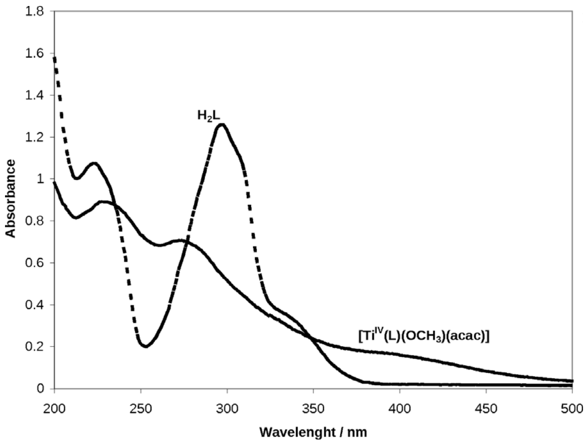


Fig. 2. Electronic spectra of H_2L (----) and $[Ti^{IV}(L)(OCH_3)(acac)]$ (——) in CH_3CN.

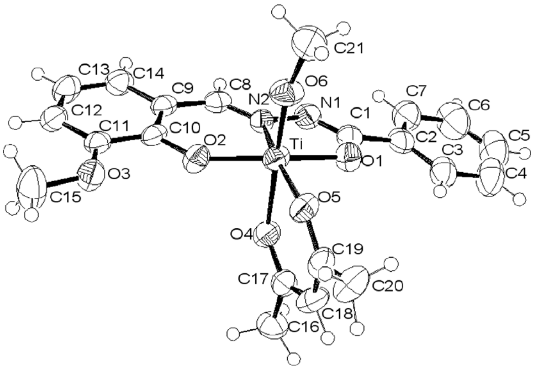


Fig. 3. Molecular structure of **1** with crystallographic numbering scheme adopted (displacement ellipsoids are drawn at the 50 % probability level).

Solid-state molecular structure of [Ti^IV (L)(OCH₃)(acac)] (1)

The molecular structure of **1** and the atomic numbering adopted are depicted in Fig. 3. Some relevant

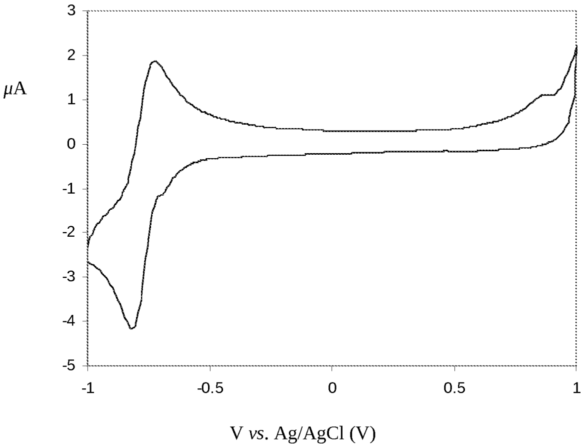


Fig. 4. Cyclic voltammogram of 10^{-3} mol L^{-1}[Ti^{IV}(L)-(OCH_3)(acac)] in acetonitrile and TBAP (0.1 mol/L); scan rate 100 mV s^{-1} in the potential range -1.0 to 1.0 V.

bond lengths and bond angles are collected in Table 3. The two oxygen atoms of L are *trans* to each other, as expected from the planar structure of this ligand. Indeed, all atoms on the L ligand are essentially coplanar except for the phenyl group which deviates with a mean value of 0.523 Å. The titanium atom is meridionally coordinated by the O,N,O donor set of the ligand. The hydrazone Schiff base acts as a doubly deprotonated dianion ligand (L^{2-}). The bidentate acetylacetonate ligand and the methanolate group complete the distorted pseudooctahedral metal coordination sphere. No π-π stacking interactions with centroid-centroid contacts less than 6.0 Å and parallel π planes could be detected [38].

The Ti–O1 and Ti–O2 bond lengths are found to be 1.956(2) and 1.866(2) Å, respectively, the Ti–O4 and Ti–O5 distances 2.086(2) and 1.946(2) Å, respectively. The environment of the titanium atom is completed by Ti–N2 and Ti–$O6_{\mathrm{methoxide}}$ with distances at 2.146(3) and 1.758(2) Å, respectively. Oxygen atom O4 is *trans* to the oxygen atom $O6_{\mathrm{methoxide}}$, and the corresponding Ti–O4 bond length of 2.086(2) Å is longer than Ti–O5 of 1.945(2) Å, presumably partially due to the *trans* influence of the methoxide. The bond lengths are within the expected range for titanium(IV) complexes with Schiff base ligands [39–41]. The bond angles within the coordination sphere range from 73.78(10) to 106.92(10)°, which indicates a significant distortion. The O1–Ti–O2 angle of 154.17(10)° is far from the ideal 180° owing to ring constraints. The *trans* oxygen atoms O4 and O6 form an angle O4–Ti–O6 of 177.51(10)° which is closer to 180 than O1–Ti–O2 because the methoxide ligand can adjust its position without constraint.

The Ti–O distances are shorter (0.06–0.388 Å) than the Ti–N distance. This is due a partial double bond character by the donation of oxygen lone-pair electrons into the empty π orbitals on Ti(IV). Ti1–O6 is particularly short because the methoxide can be positioned to maximize the formation of a partial double bond.

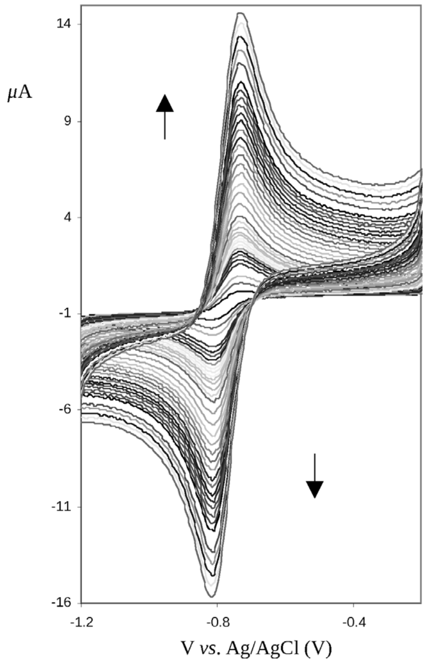


Fig. 5. Cyclic voltammogram of 10^{-3} mol L^{-1} [Ti^{IV}(L)(OCH_3)(acac)] in acetonitrile and TBAP (0.1 mol L^{-1}); scan rate 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 160, 180, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, 900, 950, 1000, 1100, 1200, 1300, 1400 and 1500 mV s^{-1}.

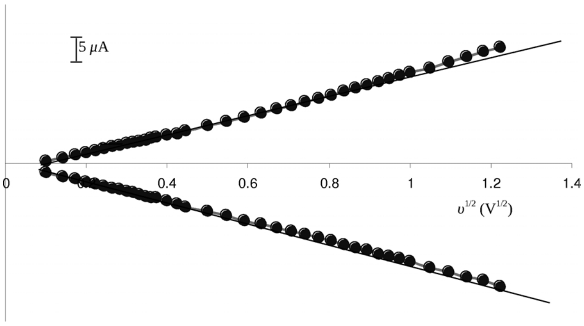


Fig. 6. Plot of cathodic and anodic currents *versus* the square root of sweep rate ($\upsilon^{1/2}$) for the complex **1**.

Electrochemical studies

Electrochemical cyclic voltammetry measurements were carried out to probe the redox stability of complex **1** in solution [25]. The cyclic voltammogram in acetonitrile displays a reversible peak at E^o = −0.768 V (*vs.* Ag/AgCl) (Fig. 4). It can be assigned to the Ti^{IV}/Ti^{III} redox process. The $\Delta Ep = (Epa-Epc)$ value was 77 mV and ipa/ipc = 0.72. This finding shows a near reversibility of this redox process. Fig. 5 illustrates the cyclic voltamograms of complex **1** at different scan rates from 10 to 1500 $mV\,s^{-1}$. There is a linear relationship between the cathodic and anodic peak currents and the square root of the scan rate ($\upsilon^{1/2}$) in the 10 to 800 $mV\,s^{-1}$ range (Fig. 6). This behavior is diagnostic of an electron transfer process controlled by diffusion.

Acknowledgement

We thank the Zanjan University, the Faculty of Chemistry and Biochemistry of the Ludwig-Maximilians-Universität München and the School of Chemistry, Galway, for financial support of this study.

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