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Sn^{IV} and Zr^{IV} Compounds of a C_3-Symmetric Ligand with Amine [ONN] and [ONNO] Coordination Sites

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Abstract

This contribution describes the synthesis and structural characterization of a triaminoguanidinium (*TAG*)-based ligand $[H_6(OMe)_3L_{imin}]BF_4$ (**1**) containing imine bonds (L_{imin}) and its reduction with a dimethylamino borane complex to the corresponding amine compound (L_{amin})$[H_9(OMe)_3L_{amin}]OTs$ (**2**). In solution, both ligands are C_3-symmetric but crystal structures show the great influence of the reduction on the molecular structure. We show that the planar imine ligand is converted to a highly flexible compound which has nine potential coordination sites, three phenoxy and six amine donors, for binding metal ions. First solid state structures of 1:1 (metal:ligand) coordination compounds with Sn^{IV} and Zr^{IV} are presented. Sn^{IV} exhibits an octahedral coordination sphere and is bound in a facial [ONN] coordination pocket. Zr^{IV} is pentagonal bipyramidal coordinated and the ligand stabilizes this with its' [ONNO] binding sites.

Keywords

Reduction, Triaminoguanidinium, [ONN]/[ONNO] Binding Pockets, Sn^{IV} Complex, Zr^{IV} Complex

1. Introduction

Triaminoguanidinium salts are easily prepared by a substitution reaction between guanidinium salts with hydrazine [1]. Their amine functionalities can be used to perform condensation reactions with aromatic and aliphatic aldehydes and ketones leading to imine compounds [2] [3] [4] [5]. The use of salicylalde-

hyde derivatives lead to trigonal building blocks that are known to form trinuclear complexes through coordination of metal ions in their three coplanar [ONN] coordination pockets [6]. They have been used for the construction of various supramolecular architectures [7] [8] [9] [10] [11]. Nonetheless, condensation reactions are reversible and during our work with these hydrazone derived ligands, we observed their decomposition especially under extreme conditions. To circumvent this problem, the imine double bond can be reduced. Maas *et al.* [12] reported a method to reduce TAG-based molecules with dimethylamino borane complex according to Ghelfi *et al.* [13]. This resulted in a loss of its threefold symmetry in solid state with an enhancement of structural flexibility. Applying this method to *tris* (salicylidene) triaminoguanidinium salts leads to a new ligand type with three phenoxy and six amine donor sites. The new compound type promises to form very stable complexes. Thus, we were interested in the coordination behavior of a ligand with nine potentially strongly coordinating binding sites. The preparation and structural characterization of the ligand before and after the reduction and two coordination compounds with Sn^{IV} and Zr^{IV} are reported herein.

2. Experimental

2.1. General Remarks

All chemicals were used without further purification. Borane dimethylamine complex and $Zr(acac)_4$(acac: acetylacetonate) were purchased from abcr, *p*-toluenesulfonic acid monohydrate, $AgBF_4$ and 2-hydroxy-3-methoxybenzaldehyde were purchased from Sigma-Aldrich, Inc., and $SnCl_4{\cdot}5H_2O$ from ACROS. *TAG*Cl was synthesized according to published procedures [1].

2.2. Measurements

NMR spectroscopic data were recorded with UltraShield TH 400 Plus or Avance II Bruker spectrometer at room temperature. ^1H and ^{13}C NMR spectroscopic data are referenced to residual non-deuterated solvent.

Elemental analyses were performed using Heraeus CHN-O-Rapid Vario EL.

Mass spectra were recorded on a ThermoFisher Scientific LTQ-Orbitrap XL.

X-Ray diffraction data of compounds **1**, **3** and **4** were obtained with a Bruker Apex-I CCD diffractometer with Mo radiation (λ = 0.71073 Å) und data of **2** were obtained with a Bruker Apex-II CCD diffractometer with Cu radiation (λ = 1.54178 Å). Structures were solved by direct methods using SHELXS-2014and refined with SHELXL-2014 [14].

In **2**, one toluene molecule was found to be disordered over an inversion center. Due to the low data to parameter ratio, it was eliminated by the *SQUEEZE* procedure [15]. In **3**, the disorder of one phenyl group could not be modelled properly. Thus, EADP and SIMU restraints are applied to the corresponding hydroxyl and methoxy oxygen atoms and the carbon atoms.

Crystal data can be taken from **Table 1**.

Table 1. Crystal data.

	1	2	3	4
Empirical formula	$C_{27}H_{30}BF_4N_7O_6$	$C_{32}H_40N_6O_9S$	$C_{25}H_{31}Cl_3N_6O_6Sn$	$C_{64}H_{78}N_{14}O_{16}Zr_2$
Formula mass	635.39	684.76	736.60	1481.84
λ [Å]	0.71073	1.54178	0.71073	0.71073
T [K]	100 (2)	100 (2)	10 (2)	100 (2)
Crystal system	monoclinic	triclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	P-1	$P2_1/n$	$Pbca$
a [Å]	19.771 (2)	8.7537 (12)	15.378 (3)	15.746 (2)
b [Å]	22.536 (2)	14.076 (3)	11.639 (2)	19.289 (3)
c [Å]	13.450 (1)	15.822 (3)	16.859 (3)	22.002 (3)
α [˚]		71.271 (14)		
β [˚]	98.834 (2)	75.117 (11)	102.85 (3)	
γ [˚]		76.870 (11)		
V [Å^3]	5921.9 (9)	1761.8 (5)	2941.8 (11)	6683 (2)
Z	8	2	4	4
D_c [g cm^{-3}]	1.425	1.291	1.663	1.473
μ [mm^{-1}]	0.118	1.322	1.192	0.390
F(000)	2640	724	1488	3072
Crystal size [mm]	0.24 × 0.30 × 0.42	0.05 × 0.2 × 0.4	0.07 × 0.18 × 0.28	0.13 × 0.36 × 0.42
θ range [˚]	2.270 - 24.842	3.01 - 65.94	2.39 - 23.61	2.22 - 27.68
Reflections collected	62300	20908	23263	68722
independent reflections [R(int)]	10175 [0.0936]	6109 [0.0767]	5213 [0.0878]	5885 [0.2807]
Reflections [I > 2σ(I)]	7569	4040	4052	3842
Data/restraints/ parameters	10175/0/825	6109/4/457	5214/75/363	5885/3/448
Goodness-of-fit on F^2	1.038	1.043	1.048	0.925
Final R_1, wR_2 [I > 2σ(I)]	0.0796, 0.2153	0.0531, 0.1309	0.0607, 0.1627	0.0603, 0.1413
Final R_1, wR_2 (all data)	0.1015, 0.2365	0.0869, 0.1491	0.0775, 0.1757	0.0946, 0.1543
Max/min difference [e·A^{-3}]	1.31/−0.56	0.26/-0.40	0.97/−0.91	1.24/−1.47

2.3. Synthesis

***TAG*BF$_4$** To a solution of *TAG*Cl (1.00 g, 7.11 mmol, 1 eq.) in 10 mL water was added a solution of $AgBF_4$ (1.39 g, 7.11 mmol, 1 eq.) in 5 mL water under exclusion from light. The mixture was stirred overnight. The precipitate was removed

by filtration and the solvent was removed under reduced pressure. A colorless powder could be isolated Yield: 1.32 g, (6.89 mmol, 97%). $CH_9N_6BF_4$ (191.93): calcd. C 6.26, H 4.73, N 39.59; found C 6.18, H 5.19, N 39.65. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): 8.59 (s, 3H, NH), 4.48 (s, 6H, NH_2) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ = 159.0 ppm.

***Tris*(2-hydroxy-3-methoxybenzylidene) triaminoguanidiniumtetrafluoroborate ($[H_6(OMe)_3L]BF_4$ (1))** *TAG*BF_4 (161.5 mg, 0.84 mmol, 1 eq.) and 2-hydroxy-3-methoxybenzaldehyde (383.6 mg, 2.52 mmol, 3 eq.) were dissolved in 5 mL EtOH/H_2O (1:3) at 50˚C. Both solutions were combined and stirred over night at room temperature. The solvent was removed under reduced pressure to obtain a yellowish solid. Yield: 482.5 mg (0.81 mmol, 97%). $C_{25}H_{27}N_6O_6BF_4$ (594.32): calcd. C 50.52, H 4.58, N 14.14; found C 50.49, H 4.83, N 14.10. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ = 11.88 (s, 3H, NH), 9.58 (s, 3H, OH), 9.08 (s, 3H, CH = N), 7.76 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.5 Hz, 3H, CH_{arom}), 7.08 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.5 Hz, 3H, CH_{arom}), 6.89 (t, $^3J_{HH}$ = 7.9 Hz, 3H, CH_{arom}), 3.86 (s, 9H, OCH_3) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ = 148.7, 148.0, 147.4, 146.8, 119.9, 119.1, 118.4, 113.9, 55.9 ppm. MS-ESI: m/z 507.20 [M^+]. Crystals suitable for single crystal analysis were obtained by slow evaporation of an acetonitrile/toluene mixture (1:1) at room temperature.

***Tris*(2-hydroxy-3-methoxybenzyl) triaminoguanidiniumtosylate** ($[H_9(OMe)_3L_{amin}]$OTs (**2**)) To a stirred solution of *tris*(2-hydroxy-3-methoxybenzylidene) triaminoguanidinium tetrafluoroborate (**1**) (1.36 g, 2.29 mmol, 1 eq.) and dimethylamino borane complex (862.2 mg, 14.6 mmol, 5 eq.) in 30 mL acetonitrile was added a solution of *p*-toluenesulfonic acid monohydrate (13.42 g, 78.58 mmol, 24 eq.) in 9 mL of methanol/acetonitrile (1:2) dropwise. The solution was stirred for 12 hours, diluted with 30 mL dichloromethane and 15 mL of a saturated solution of Na_2CO_3 was added. The phases were separated and the aqueous phase was extracted two times with dichloromethane. The organic phases were combined and the solvent was removed under reduced pressure to obtain a brown solid. Yield: 1.81 g (91%). $C_{32}H_{40}N_6O_9S$ (684.76): calcd. (**2**·3H_2O) C 52.02 H 6.28 N 11.38; found C 52.61 H 5.90 N 11.46. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): 8.73 (s, 3H, NH), 8.57 (s, 3H, OH), 7.47 (m, 2H, CH_{arom}(OTs)), 7.11 (m, 2H, CH_{arom}(OTs)), 6.89 (dd, 3H, $^3J_{HH}$ = 8,0 Hz, $^4J_{HH}$ = 1.6 Hz, CH_{arom}), 6.80 (dd, 3H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.6 Hz, CH_{arom}), 6.73 (t, 3H, $^3J_{HH}$ = 7.8 Hz, CH_{arom}), 5.18 (t, 3H, $^3J_{HH}$ = 5.9 Hz, NH), 3.78 (s, 9H, OCH_3), 3.76 (d, 6H, $^3J_{HH}$ = 5.7 Hz, CH_2), 2.29 (s, 3H, CH_3(OTs)) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ = 157.2, 147.5, 145.9, 144.6, 137.7, 128.1, 125.6, 123.6, 122.2, 118.7, 111.2, 55.9, 49.6, 20.9 ppm. MS-ESI: m/z 513.24 [M^+]. Crystals suitable for single crystal analysis were obtained by slow evaporation of a chloroform/toluene mixture (1:1) at room temperature.

$[SnCl_3(H_7(OMe)_3L_{amin})]$ (3) $[H_9(OMe)_3L_{amin}]$OTs (**2**) (11.7 mg, 0.02 mmol, 1 eq.) and $SnCl_4$·5H_2O (7.0 mg, 0.02 mmol, 1 eq.) were dissolved in 1 mL methanol. Slow evaporation of the solvent at room temperature led to colorless crystals

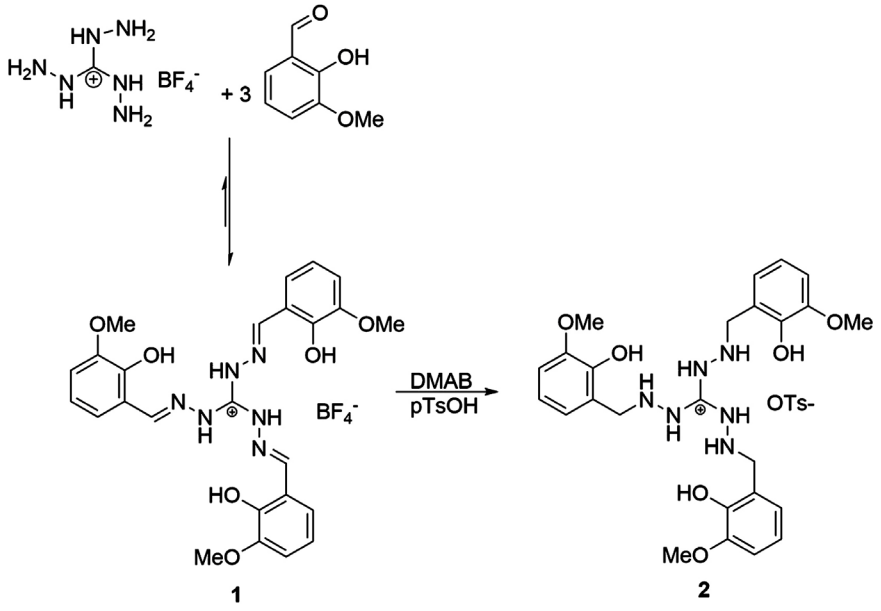
of compound **3**. Yield: 8.4 mg (57%) $C_{25}H_{31}Cl_3N_6O_6Sn$ (736.60).

[Zr(acac)($H_5(OMe)_3L_{amin}$)]$_2$ (4) $[H_9(OMe)_3L_{amin}]$OTs (**2**) (10.2 mg, 0.02 mmol, 1 eq.) and $Zr(acac)_4$ (9.8 mg, 0.02 mmol, 1 eq.) were dissolved in 1 mL acetonitrile and triethylamine (109.5 µL, 0.79 mmol, 90 eq.) was added. Slow evaporation of the solvent at room temperature led to colorless crystals of compound **4**. Yield: 12.7 mg (43%) $C_{60}H_{72}N_{12}O_{16}Zr_2{\cdot}2CH_3CN$ (1481.84). MS-ESI: m/z 1405.35 $[M\text{-}Li]^+$.

3. Results and Discussion

3.1. Structural Characterization of Ligands 1 and 2

Following a literature procedure, the imine type ligand is readily prepared via a single step condensation reaction between 2-hydroxy-3-methoxybenzaldehyde with triaminoguanidinium tetrafluoroborate (Scheme 1). [4] The reduction is carried out with dimethylamino borane complex (DMAB) as reducing agent in presence of *p*-toluenesulfonic acid (*p*TsOH). ^{1}H and ^{13}C NMR spectra clearly reveal signals of the successfully reduced species and the corresponding TsO^- counterion. In solution, both ligands exhibit a C_3-symmetric conformation on the NMR time scale. Due to their high exchange rates in solution, acidic protons (OH and NH) usually do not show a coupling to protons of neighboring carbon atoms. In the ^{1}H nmr spectrum of compound **2** it is striking that the signal of the outer NH protons splits to a triplet indicating a low exchange rate meaning a low acidity in comparison to the neighbored amine hydrogen atoms which show singlet signals. Both compounds have been subjected to single crystal X-ray analysis. The molecular structure of **1** is shown in Figure 1.



Scheme 1. Formation of $[H_6(OMe)_3L_{imin}]BF_4$ (1) inEtOH/H_2O (1:3) at 50˚C and reduction with dimethylamino borane complex (DMAB) in presence of *p*-toluenesulfonic acidin acetonitrile at room temperature to $[H_9(OMe)_3L_{amin}]$OTs (2).

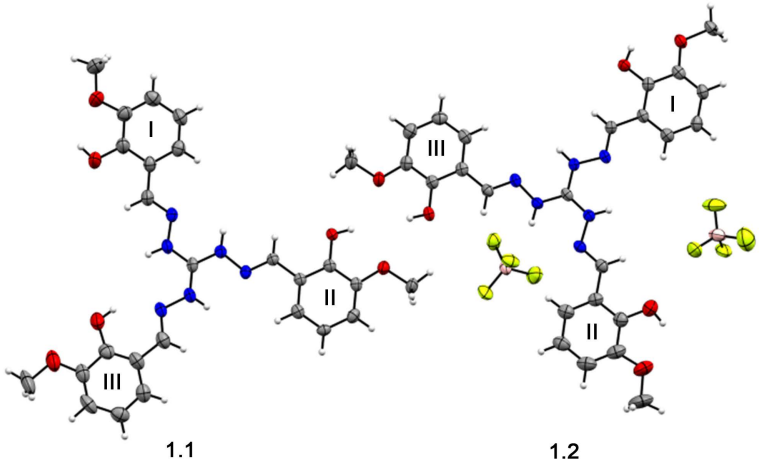


Figure 1. ORTEP drawing of $[H_6(OMe)_3L_{imin}]BF_4$ (1) with thermal ellipsoids at 50% probability level with numbered aromatic rings. Cocrystallized solvent molecules are omitted for clarity.

The molecules in the asymmetric unit display different conformations of the hydroxyphenyl group to the imine nitrogen (denoted by **1.1** and **1.2** with aromatic rings numbered with Roman numerals). In **1.1**, the *anti*-conformation of the OH groups can be observed in ring I and II and the OH group of ring III exhibits a *syn*-conformation. This is stabilized by intramolecular hydrogen bonding between OH and N_{imine} (Table 2). Intramolecular hydrogen bonding between OH and methoxy oxygen stabilizes *anti*. Molecule **1.2** adopts the *all-anti*-conformation promoted by hydrogen bonds to either counterion (ring I) or methoxy O (ring II and III).

Regarding the molecular structure of **2** (Figure 2), the most striking difference to ligand **1** is its spatial arrangement. Figure 3 illustrates the loss of planarity caused by the reduction.

This is in accordance with observations of Maas *et al.* and following his nomenclature, the ligand exhibits an *endo, exo, exo*-conformation of the benzyl rings with respect to their position to the central CN_3 unit. The increased flexibility of the reduced ligand results in completely new possibilities to stabilize coordination environments of metal ions. In the following part, two coordination compounds, especially regarding the coordination spheres around the metal centers, are presented.

3.2. Structural Characterization of Ligand Complexes

The reaction of $[H_9(OMe)_3L_{amin}]OTs$ (**2**) with $SnCl_4{\cdot}5H_2O$ in methanol results in a coordination compound with the molecular formula $[SnCl_3(H_7(OMe)_3L_{amin})]$ (**3**) (Scheme 2).

The X-ray structure is illustrated in Figure 4.

The Sn^{IV} ion is coordinated in an [ONN] binding pocket. To complete the octahedral coordination sphere, three chloride ions are bound. The ligand occupies facial positions and forms a nearly planar five membered ring and a folded six

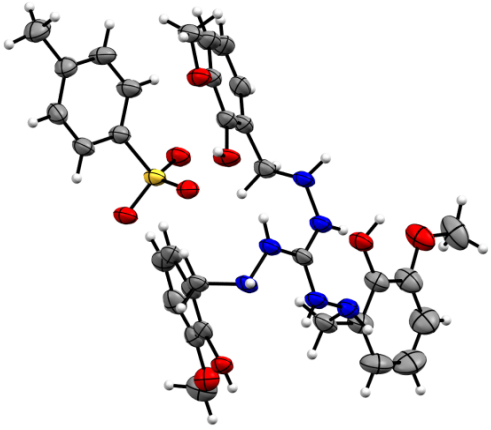


Figure 2. ORTEP drawing of $[H_9(OMe)_3\text{Lamin}]OTs$ (2) with thermal ellipsoids at 50% probability level.

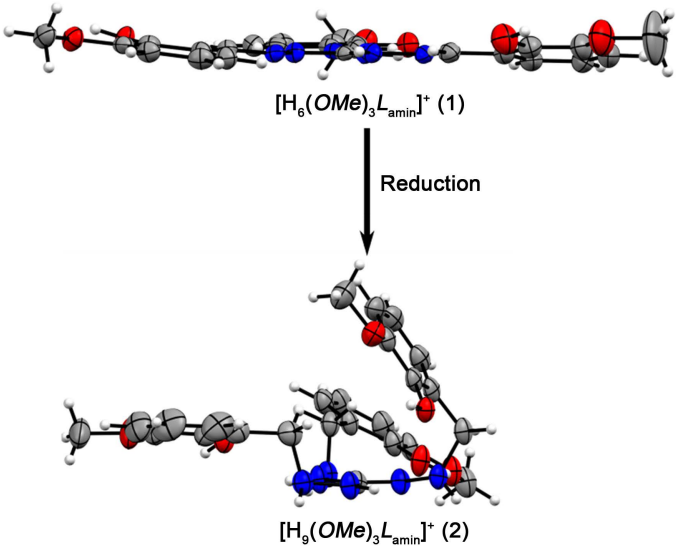


Figure 3. ORTEP-drawings at 50% probability level of molecular structures of the ligand before (1) and after (2) the reduction. Counterions are omitted for clarity.

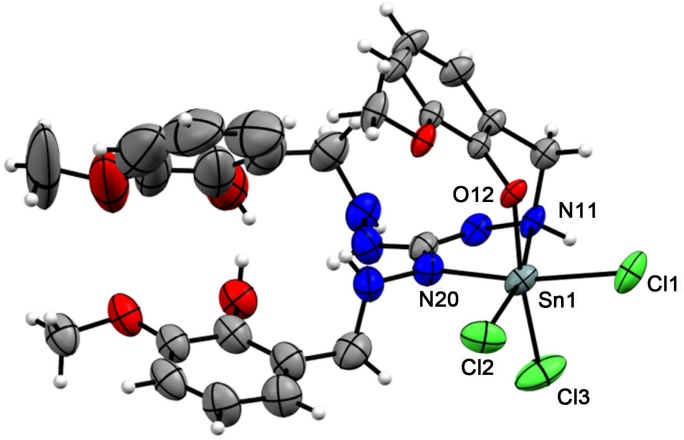
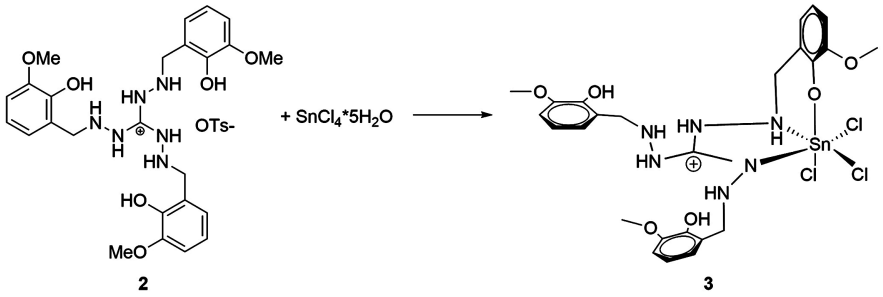


Figure 4. ORTEP drawing of $[SnCl_3(H_7(OMe)_3L_{amin})]$ (3) with thermal ellipsoids at 50% probability level with numbered coordinating atoms.



Scheme 2. Formation of $[SnCl_3(H_7(OMe)_3L_{amin})]$ (3).

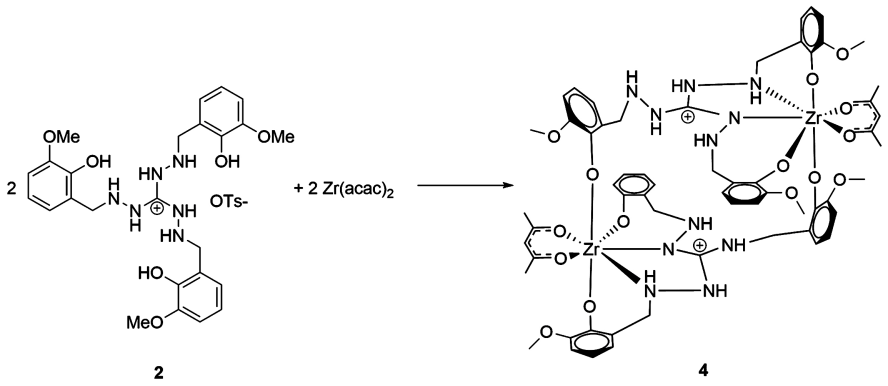
Table 2. Hydrogen bonds between hydroxyphenyl group and the corresponding acceptor of $[H_6(OMe)_3L]BF_4$ (2) (* = intramolecular).

	Ring	Acceptor (A)	OH···A [Å]	O···A [Å]	OH···A [°]
1.1	I	$O_{Methoxy}$	2.15*	2.623 (5)*	115*
	II	$O_{Methoxy}$	2.19*	2.655 (4)*	115*
	III	N_{imine}	2.05*	2.771 (5)*	143*
1.2	I	$F\left(BF_4^-\right)$	2.01	2.779 (3)	151
	II	$O_{Methoxy}$	2.13*	2.601 (5)*	116*
	III	$O_{Methoxy}$	2.18*	2.637 (4)*	114*

membered ring with Sn^{IV}. Therefore, the coordination sphere is slightly distorted (N(11)-Sn(1)-N(20) 73.6(2)˚, Cl(1)-Sn(1)-Cl(2) 100.14(7)˚, O(12)-Sn(1)-Cl(3) 171.8(1)˚). Nitrogen N(11) stays protonated verifying the low acidity indicated by ^{1}H NMR spectroscopy. Thus, the Sn(1)-N(11) bond (2.294(5) Å) is significantly longer than the Sn(1)-N(20) bond (2.126(5) Å). Additionally, a hydrogen bond between N(11) and a methoxy oxygen of another molecule can be observed (N(11)H···O 2.15 Å, N(11)···O 3.064(6) Å, N-H···O 152˚). The aromatic rings are arranged in an *endo,exo,exo* conformation. It is conceivable to bind further metal ions in remaining free coordination sites. The ligand's general ability of binding adjacent metal ions is confirmed by compound **4**.

By reacting $[H_9(OMe)_3L_{amin}]OTs$ (**2**) with $Zr(acac)_4$ in acetonitrile in the presence of NEt_3 compound **4** with the molecular formula $[Zr(acac)(H_5(OMe)_3L_{amin})]_2$ is formed (Scheme 3). The composition could be verified by mass spectrometry and the molecular structure by single crystal X-ray analysis (Figure 5).

The centrosymmetric compound consists of two ligand molecules which are connected by two Zr^{IV}ions binding one acaccoligand each. The Zr^{IV} ions are seven coordinated in a pentagonal bipyramid coordination geometry (Figure 6). The ligand coordinates one Zr^{IV} ion in an [ONNO] binding pocket formed by O(22), N(21), N(10), and O(12).The outer nitrogen N(21) is not deprotonated despite the presence of a base in the reaction mixture. The presence and the position of the hydrogen atom is confirmed by an intramolecular hydrogen bond between N(21) and a methoxy oxygen of a symmetry generated molecule (N(21)H···O 2.08(3)˚, N(21)···O 2.936(4)˚, N-H···O 157(4)˚). The N(10)-Zr(1)



Scheme 3. Formation of $[Zr(acac)(H_5(OMe)_3L_{amin})]_2$ (4).

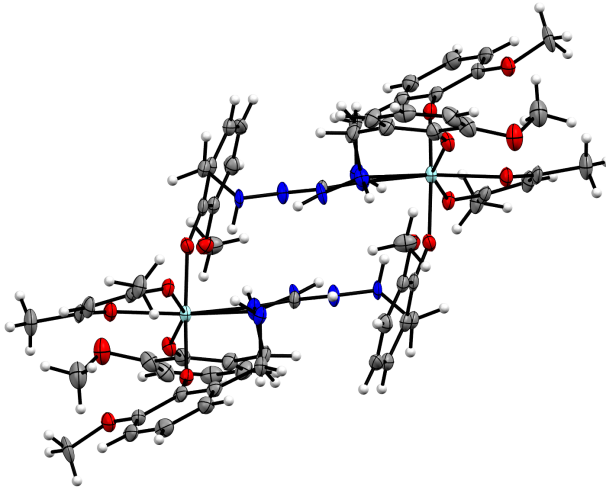


Figure 5. ORTEP drawing of $[Zr(acac)(H_5(OMe)_3L_{amin})]_2$ (4) with thermal ellipsoids at 50% probability level.

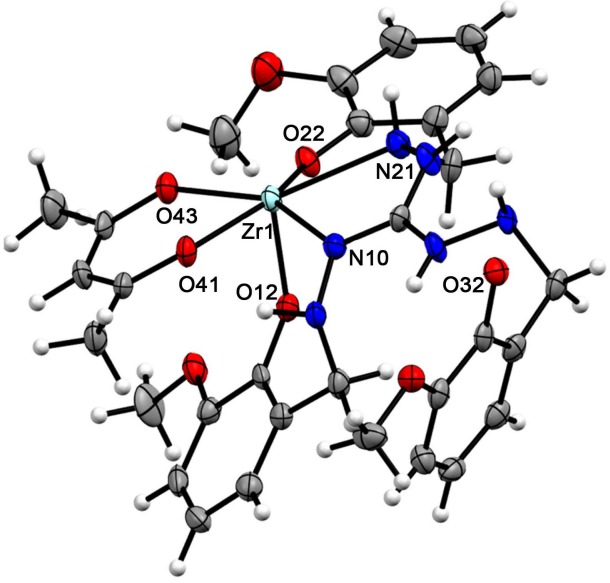


Figure 6. ORTEP drawing of the asymmetric unit of $[Zr(acac)(H_5(OMe)_3L_{amin})]_2$ (4) with thermal ellipsoids at a probability level of 50% with numbered coordinating atoms.

bond (2.277(4) Å) is much shorter than the N(21)-Zr(1) bond (2.466(4) Å). The phenolate oxygen O32 coordinates the second Zr^{IV} ion (Zr(1)'). The ligand forms three chelate rings. N(10) to O(12) is a facial, folded seven membered ring. N(10) to N(21) is a nearly planar, five membered ring and N(21) to O(22) is a meridional, folded six membered ring. The acaccoligand coordinates equatorial. The O(12)-Zr(1)-O(32)' angle is about 168.6(1)˚ and thus distorted away from linearity. The ligand is exhibits an *exo,exo,exo* conformation.

4. Conclusion

As this work demonstrates, the reduction of the three imine bonds of a C3-symmetric, planar molecule leads to a new class of compounds with a flexible, three-dimensional structure. It exhibits six amine and three phenoxy coordination sites in which metal ions can be bound strongly. The applied reduction method has been optimized to quantitative yields. The presented amine ligand is able to stabilize even unusual coordination environments due to its variable structure. Metal complexes of the Lewis acidic metal ions Sn^{IV} and Zr^{IV} could be successfully characterized what opens up a potential use as catalyst, being part of our present research.

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