Synthesis and characterization of Ti(IV), Zr(IV) and Al(III) salen-based complexes

Joana Hipólito 1, Luis Alves 2,* and Ana Martins 1,*

1 Centro de Química Estrutural, Instituto Superior Técnico, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal  
joanahipolito@tecnico.ulisboa.pt ([J.H.], ana.martins@tecnico.ulisboa.pt (A.M.)

2 Centro de Química Estrutural, Associação do Instituto Superior Técnico para a Investigação e Desenvolvimento, Av. Rovisco Pais 1, 1049-003 Lisboa, Portugal  
luis.g.alves@tecnico.ulisboa.pt (L.A.)

* Corresponding author at: Centro de Química Estrutural, Instituto Superior Técnico, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal.  
e-mail: luis.g.alves@tecnico.ulisboa.pt (L. Alves) and ana.martins@tecnico.ulisboa.pt (A. Martins).

ABSTRACT

New Ti(IV), Zr(IV) and Al(III) salen-based complexes of formulae [(L)TiCl2], [(L)ZrCl2] and [(L)Al(CH2CH(CH3)2)]2 4, where L = meso-{RS}-diphenylethylene-salen, were synthesized in high yields. [(L)Al(CH2CH(CH3)2)]2 is a bimetallic complex that results from the reaction of H2L with either 1 or 2 equivalent of Al(CH2CH(CH3)2)3. The solid-state molecular structures of compounds 2 and 4-[C(H3)] were obtained by single-crystal X-ray diffraction. Crystal data for C62H72Cl2N2O2Ti (2a); monoclinic, space group C2/c (no. 15), a = 27.384(1) Å, b = 12.1436(8) Å, c = 28.773(2) Å, β = 112.644(2)°, V = 8830.6(9) Å3, Z = 8, μ(MoKα) = 0.350 mm –1, Dcalc = 1.146 g/cm3, 26674 reflections measured (5.204° ≤ 2θ ≤ 50.7°), 8072 unique (Rint = 0.0967, Rsgumo = 0.124) which were used in all calculations. The final R1 was 0.0640 (I > 2σ(I)) and wR2 was 0.1907 (all data). Crystal data for C62H72Cl2N2O2Ti (2b); monoclinic, space group P21/c (no. 14), a = 19.606(1) Å, b = 12.793(1) Å, c = 23.189(2) Å, β = 105.710(4°), V = 5599.0(7) Å3, Z = 4, μ(MoKα) = 0.291 mm –1, Dcalc = 1.182 g/cm3, 37593 reflections measured (3.65° ≤ 2θ ≤ 50.928°), 10304 unique (Rint = 0.0866, Rsgumo = 0.1032) which were used in all calculations. The final R1 was 0.0593 (I > 2σ(I)) and wR2 was 0.1501 (all data). Crystal data for C62H72AlN2O2 (4-[C(H3)]); triclinic space group P-1 (no. 2), a = 10.0619(9) Å, b = 16.612(2) Å, c = 21.308(2) Å, α = 77.576(5)°, β = 80.72(7)°, γ = 88.315(5)°, V = 37167.6(8) Å3, Z = 2, μ(MoKα) = 0.088 mm –1, Dcalc = 1.063 g/cm3, 42107 reflections measured (5.382° ≤ 2θ ≤ 51.624°), 12111 unique (Rint = 0.0624, Rsgumo = 0.0706) which were used in all calculations. The final R1 was 0.0568 (I > 2σ(I)) and wR2 was 0.1611 (all data). The solid-state molecular structure of [(L)Al(CH2CH(CH3)2)]2 reveals that both metal centres display a slightly distorted tetrahedral geometry bridged by the salen ligand. Both [(L)TiCl2] and [(L)ZrCl2] complexes display octahedral geometry with trans-chlorido ligands.

1. Introduction

Salen- and salen-type compounds have been largely explored in coordination chemistry but the latter present various advantages [1]. Due to their rigid structure, salen-type ligands are ideal for equatorial coordination to transition metals, leaving two axial sites available for the coordination of ancillary ligands. Depending on the chemical nature of the N and O donor atoms, salen-type ligands may offer thermodynamic and kinetic stability to a large variety of metal centers [2-6]. The presence of bulky substituents in the phenolate rings may provide additional stereochemical protection [7-9]. Moreover, the incorporation of chiral centers within the salen backbone reveals an important role in enantioselective catalysis [9-12]. Most of the catalytic studies have been focused on middle and late d-block transition metal-salen complexes as catalysts for olefin epoxidation [13-14], cyclopropanation [15-17], azaamination [18-20], sulfoxidation [21-23], ring-opening polymerization of cyclic esters [24-29] and copolymerization of CO2 and epoxides [30-32]. Early transition metal complexes supported by salen ligands are relatively less reported [33-37]. Nevertheless, vanadium derivatives have been widely explored for diverse applications [38-41]. Despite a large variety of mononuclear aluminum complexes supported by salen-type ligands have been reported mainly as catalysts for the ring-opening polymerization of cyclic esters [26-28], bimetallic derivatives have not been well studied [42-44]. In this work, we present the synthesis and structural characterization of new Ti(IV), Zr(IV) and Al(III) complexes based on meso- {RS} -diphenylethylene-salen ligand.

2. Experimental

2.1. General considerations

meso-{RS}-diphenylethylene-salen (H2L, 1) was prepared according to a described procedure [45].
Commercial NaH (60% dispersion in mineral oil) was washed several times with n-hexane and dried under vacuum. All other reagents were commercial grade and used without further purification. All manipulations were performed under an atmosphere of dry oxygen-free nitrogen by means of standard Schlenk and glovebox techniques. Solvents were pre-dried using 4 Å molecular sieves and refluxed over sodium-

16 H at room temperature. The red/orange solution obtained was evaporated to dryness and the residue was extracted with toluene. Evaporation of the solvent to dryness afforded a yellow crystalline solid (Scheme 1). Color: Yellow. Yield: 88%. 1H NMR (300 MHz, C6D6, δ, ppm): 1.20 (s, 18H, C(CH3)2), 1.87 (s, 18H, C(CH3)2), 6.17 (s, 2H, C6(CH3)N), 7.25-6.72 (overlapping, 14H total, C6H5O and C6H5N), 8.02 (s, 2H, N=CH2). 13C{1H} NMR (75.5 MHz, C6D6, δ, ppm): 30.3 (C(CH3)2), 31.3 (C(CH3)2), 34.3 (C(CH3)2), 35.9 (C(CH3)2), 75.5 (C6(CH3)N), 123.4 (C6(CH3)N), 128.2 (C6H5NO), 128.8 (C6H5N), 129.2 (C6H5N), 130.7 (C6H5O), 132.2 (C6H5O), 135.4 (C6H5O), 135.5 (1BuC6O), 139.4 (1BuC6O), 158.7 (O6C6O), 169.2 (N=CH). Anal. calcd. for C44H54N2O2Ti: C, 69.36; H, 7.15; N, 3.68. Found: C, 69.36; H, 7.15; N, 3.68.

2.2.2. [(meso-(R,S)-Diphenylethylene-salen)ZrCl2], 4

To a toluene solution of compound 1 (0.31 g, 0.48 mmol) cooled at -80 °C was slowly added 1.0 mL of a triisobutyl aluminum solution (1.1 M in toluene). The mixture was allowed to come to room temperature, and it was left stirring overnight. After filtration, the solvent was evaporated to dryness affording a white solid that was washed with EtO (Scheme 1). Color: White. Yield: 81%. 1H NMR (300 MHz, C6D6, δ, ppm): 1.11-1.25 (overlapping, 32H total, 8H, C(CH3)2), 1.25 (s, 18H, C(CH3)2), 1.54 (s, 18H, C(CH3)2), 2.00 (m, 4H, CH2C6H4), 2.21 (s, 2H, C6(CH3)N), 6.67 (d, 3JH-H = 2Hz, 2H, C6H5N), 6.88 (d, 3JH-H = 8Hz, 2H, C6H5N), 6.98 (t, 3JH-H = 8Hz, 4H, C6H5N), 7.31 (d, 3JH-H = 8Hz, 4H, C6H5N), 7.63 (d, 3JH-H = 2Hz, 2H, C6H5N), 7.68 (C6(CH3)2) NMR (75.5 MHz, C6D6, δ, ppm): 30.0 (C(CH3)2), 30.9 (C(CH3)2), 33.9 (C(CH3)2), 35.6 (C(CH3)2), 76.7 (C6(CH3)N), 125.7 (NCH3CN), 128.1 (C6H5N), 128.2 (ν-C6H5NO), 129.7 (p-C6H5NO), 130.7 (m-C6H5O), 131.6 (C6H5O), 136.9 (C6H5O), 137.1 (1BuC6O), 143.7 (1BuC6O), 160.9 (O6C6O), 166.8 (N=CH) Anal. calcd. for C60H90Al2N2O2·(Et2O)3: C, 75.35; H, 10.54; N, 2.47%. Found: C, 75.22; H, 9.63; N, 2.47%.

2.3. General procedure for X-ray crystallography

Suitable crystals of compounds 2 (2a and 2b) and 4 (C4H4) were coated and selected in Femblin® oil under an inert atmosphere of nitrogen. Crystals were then mounted on a loop external to the glovebox environment and data collected using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Bruker AXS-KAPPA APEX II diffractometer equipped with an Oxford Cryosystem open-flow nitrogen cryostat. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all observed reflections [46]. Absorption corrections were applied using SADABS [47]. The structures were solved by direct methods using SIR97 [48] and SIR2004 [49]. Structure refinement was done using SHELXL [50]. These programs are part of the WinGX software package version 1.80.05 [51]. The hydrogen atoms were inserted in fixed positions and allowed to refine riding on the parent carbon atom. Compound 2a also crystalized with half-molecules of toluene in the asymmetric unit. As all attempts to model the disordered solvent molecule did not lead to acceptable solutions, the SQUEEZE/PLATON [52] sequence was applied.

Scheme 1. Synthesis of the salen-based complexes 2, 3, and 4.
Crystalllographic and experimental details of data collection and crystal structure determinations are available in Table 1. Illustrations of the molecular structures were made with ORTEP-3 [53] for Windows.

3. Results and discussion

Treatment of TiCl4 or ZrCl4 with the sodium salt of meso-(R,S)-diphenylethylene-salen (Na2L), prepared by reaction of 2 equiv. of triisobutylaluminum led to the formation of the bimetallic complex 

\[
[(L)Al(TiCl2)]
\]

in 81% yield. The reaction of compound 1 with 2 equiv. of NaH with H2L, respectively, in high yields. The reaction of compound 1 with 2 equiv. of triisobutylaluminum led to the formation of the salen-based complexes 2. 3 and 4 are shown in Scheme 1.

The structures of salen derivatives of Al(III) described in the literature reveal that these ligands may coordinate in a \(\text{N}=\text{O}\) fashion, leading to mononuclear square pyramidal geometry complexes or bridge two metal centers, leading to tetrahedral coordinated Al. The mononuclear compounds are the kinetic products and are preferentially formed when the reactions are carried out at room temperature in a 1:3 stoichiometry. When the reactions are carried out above room temperature, typically in the range 70-110 °C, the products obtained are predominantly bimetallic species that correspond to the thermodynamic products [26,44]. The dimerization reactions also take place upon addition of 1 equiv. of AlR3 to a solution of [(L)Al(R)] (R = alkyl), which suggests the formation of a phenolate bridged intermediate between [(L)Al(R)] and AlR3, tentatively shown in Scheme 2. This type of bridge has been structurally characterized for diamino-bis(phenolate) Sc(III) complexes when the ortho-substituents of the phenolate rings are not bulky enough to prevent dimerization [54]. The strong ionic nature of the interaction between the N,O moiety of the salen ligand and Al(III), the high oxophilicity of Al(III) and the high acidity of AlR3 are, altogether, the driving force for the extra stability of bimetallic mononuclear complexes.

The \(\text{H}\) NMR spectra of compounds 2-4 are compatible with C symmetric species showing two singlets for the tert-butyl groups, one singlet for the two protons of the C2 bridge between the nitrogen atoms, one singlet assigned to the N=C protons, and several resonances for the aromatic phenolate and phenyl moieties. The protons of the isobutyl groups in compound 4 appear as a multiplet at 2.00 ppm and between 1.24 and 1.13 ppm. The \(1^\text{H}\) NMR spectra display two sets of signals assigned to the \(\text{Bu}\) groups, while the imine carbons and the carbons of the C2 bridge give rise to one signal each. The other carbon atoms of the phenolate and phenyl moieties show up in the aromatic region and the carbons of the isobutyl groups attached to the aluminum appear in the high field region of the spectrum. The NMR spectra of complexes 2-4 are presented as Supplementary Information.

Single crystals of compound 2 suitable for X-ray diffraction were obtained from a concentrated toluene solution, 2a, and from a concentrated deuterated benzene solution in the NMR tube, 2b. In the first case, the complex crystallized in the monoclinic system, space group C2/c, while in the NMR tube it crystallized in the monoclinic system, space group P2_1/c with three molecules of benzene in the asymmetric unit.
Table 2. Selected bond lengths (Å) and angles (°) of 2a, 2b, and 4-(C7H8).

| Bond | 2a         | 2b         | 4-(C7H8) |
|------|------------|------------|----------|
| Distances (Å) |           |            |          |
| M-O(1) | 1.831(2) | 1.807(2) | 1.767(2) |
| M-O(2) | 1.826(3) | 1.812(2) | 1.768(2) |
| M-N(1) | 2.137(3) | 2.133(2) | 1.985(2) |
| M-N(2) | 2.127(3) | 2.175(2) | 1.966(2) |
| M-Cl(1) | 2.342(1) | 2.330(1) | -        |
| M-Cl(2) | 2.362(1) | 2.378(1) | -        |
| Al(1)-C(45) | -        | -        | 1.960(2) |
| Al(1)-C(49) | -        | -        | 1.975(2) |
| Al(2)-C(53) | -        | -        | 1.979(2) |
| Al(2)-C(57) | -        | -        | 1.969(3) |

| Angles (°) |          |            |          |
| O(1)-M-O(2) | 110.1(1) | 110.52(9) | -        |
| O(1)-M-N(1) | 86.3(1)  | 86.09(9)  | -        |
| N(1)-M-N(2) | 76.3(1)  | 76.72(9)  | -        |
| N(2)-M-O(2) | 87.3(1)  | 86.55(9)  | -        |
| X(1)-M-X(2) | 169.95(5)| 172.57(4) | -        |
| N(1)-Al(1)-C(45) | -        | -        | 108.51(9) |
| N(1)-Al(1)-C(49) | -        | -        | 112.76(8) |
| O(1)-Al(1)-C(45) | -        | -        | 113.27(9) |
| O(1)-Al(1)-C(49) | -        | -        | 107.61(9) |
| C(45)-Al(1)-C(49) | -        | -        | 93.87(7)  |
| N(2)-Al(2)-C(53) | -        | -        | 118.2(1)  |
| N(2)-Al(2)-C(57) | -        | -        | 102.44(8) |
| O(2)-Al(2)-C(53) | -        | -        | 110.37(9) |
| O(2)-Al(2)-C(57) | -        | -        | 109.53(9) |
| O(2)-Al(2)-N(2) | -        | -        | 107.0(1)  |
| C(53)-Al(2)-C(57) | -        | -        | 94.63(7)  |
| C(53)-Al(2)-N(2) | -        | -        | 127.9(1)  |

Figure 1. ORTEP diagram of 2a (a) and 2b (b) showing thermal ellipsoids at 40% probability level. Co-crystallized molecules of benzene and hydrogen atoms are omitted for clarity.

ORTEP views of the molecular structures of compound 2 are depicted in Figure 1. In both, the titanium atoms are hexacoordinated in distorted octahedral environments, with the donor atoms of the salen ligand in the equatorial plane (O1, O2, N1 and N2) and the two chlorido ligands, Cl1 and Cl2, occupying the axial sites. The metric parameters that characterize the two molecules are very similar, with exception of the dihedral angles between the phenyl rings bonded to the carbons of the C2 bridge that link the imine nitrogens that are 47.04 and 79.96°, respectively, for 2a and 2b and the dihedral angles between the mean equatorial planes and the phenolate ring planes (5.18 and 6.72° for 2a and 5.88° and 8.43° for 2b). A slight deviation of 0.503(2) Å of the C8 atom to the mean equatorial plane is also observed in 2b as shown in Figure 2. The overall bond distances and angles are within the ranges reported for other dichloro titanium (IV) complexes supported by salen-type ligands [34, 55].

Crystals of compound 4 suitable for single crystal X-ray diffraction were obtained from a concentrated toluene solution at -20 °C.
The compound crystallized in the triclinic $P\bar{1}$ space group with one molecule of toluene in the asymmetric unit. The ORTEP view of the molecular structure of compound 4 depicted in Figure 3 shows a bimetallic complex with the Al centers displaying slightly distorted tetrahedral geometries. Each aluminum atom is coordinated to one oxygen and one nitrogen atom of the salen ligand and to two isobutyl groups. The two metal centers are almost coplanar with the planes of the phenolate groups directly attached to them with deviations of 0.322 and 0.338 Å from those planes that define a dihedral angle of 56.15°. The overall bond distances and angles are within the ranges reported for other tetrahedral Al(III) complexes supported by salen-type ligands (Table 2) [26,42-44].

The comparison of the M-O-C$_\text{Ph}$ (M = Ti, Al) with the H-O-C$_\text{Ph}$ angles suggests that the $sp^2$ character of the oxygen is higher in the complexes (139.6(2)-140.5(2)° in Ti and 130.9(1)-132.2(1)° in Al vs 101.7(16)° in H$_2$L) [45]. These differences may be the result of an extended conjugation in metal complexes in view to the neutral salen precursor. The slightly wider angle in the Ti complexes may reflect a higher covalent nature of the Ti-O bonds, as expected for a transition metal versus a main block metal.

4. Conclusion

New Ti(IV), Zr(IV) and Al(III) salen-based complexes of formulae [(L)TiCl$_2$], [(L)ZrCl$_2$] and [(L)Al(CH$_2$CH(CH$_3$)$_2$)$_2$] (L = meso-(R,S)-diphenylethylene-salen) were synthesized and fully characterized. The solid-state molecular structure of [(L)Al(CH$_2$CH(CH$_3$)$_2$)$_2$] reveals that both metal centers display a slightly distorted tetrahedral geometry. Both [(L)TiCl$_2$] and [(L)ZrCl$_2$] complexes display octahedral geometries around the metal centers.

Acknowledgements

The authors are grateful to Fundação para a Ciência e a Tecnologia, Portugal, for funding (UID/QUI/00100/2019 and CATSUS P/D/B/114399/2016).

Supporting information

CCDC 2058281-2058283 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.

Author contributions: L.G.A. and J.H. performed the synthesis and characterization of the compounds; L.G.A. and A.M.M. supervised the experiment and wrote the manuscript.

Ethical approval: All ethical guidelines have been adhered.

Sample availability: Samples of the compounds are available from the author.

Funding

Fundação para a Ciência e a Tecnologia, Portugal https://dx.doi.org/10.13039/501100001871
