

Schiff base complexes of zirconium(IV) derived from Zr(acac)₄

Prashanta K. Mishra, Vivekananda Chakravorty and Kailash C. Dash*

Department of Chemistry, Utkal University, Vani Vihar, Bhubaneswar-751004, India

Summary

Zr(acac)₄ undergoes ligand exchanges with various tri- and tetradentate Schiff base ligands, forming compounds of the Zr(L)₂ type (H₂L = tetradentate H₂Sal₂en, H₂Sal₂pn, H₂Sal₂*o*-phen and the tridentate H₂SAP) and Zr(acac)₂L' (H₂L' = H₂SAN, H₂SAE). Upon reaction with a combination of tri- and tetradentate ligands, Zr(acac)₄ yields Zr(L)(L') complexes (H₂L = H₂Sal₂en or H₂Sal₂*o*-phen; H₂L' = H₂SAN, H₂SAE, or H₂SAP), which have been characterised by analytical data, m.p.s, electrical conductivities, i.r. and n.m.r. (¹H and ¹³C) spectra, they have a coordination number of 6, 7 or 8.

Introduction

The chemistry of zirconium is largely dominated by compounds in oxidation state IV. The relatively large size and high charge of the zirconium(IV) ion give it a marked preference for higher coordination numbers^(1,2). The ligand-field stabilisation of bonding orbitals and hence the stereochemical preferences due to partly filled d-shell are absent in zirconium(IV) with its d⁰ configuration, resulting in a variety of coordination geometries. Among the common starting materials for zirconium(IV) complexes are ZrCl₄, ZrOCl₂·8H₂O and Zr(acac)₄. Of these, ZrCl₄ is prone to easy hydrolysis and ZrOCl₂·8H₂O has a tetrameric structure⁽³⁾, that forms tetrameric complexes⁽⁴⁾ with double hydroxobridges. However, Zr(acac)₄ is stable and is rather labile⁽⁵⁾, making it a convenient source of stable zirconium(IV) complexes, by partial or total exchange of acac ligands with other suitable ligands. Thus, Zr(acac)₄ with an eight-coordinate square-antiprismatic structure⁽⁶⁾ reacts with other less volatile β-diketonates⁽⁷⁾, salicylaldehyde, 3-methoxysalicylaldehyde and ethyl acetoacetate^(8,9), and with carboxylic acids⁽¹⁰⁾ to form the corresponding tetrakis complexes.

This report describes new, stable, zirconium(IV) complexes obtained by the ligand exchanges of Schiff base ligands with Zr(acac)₄ in a non-aqueous medium. The tetradentate ligands form eight-coordinate Zr(L)₂ complexes (H₂L = H₂Sal₂en, H₂Sal₂pn and H₂Sal₂*o*-phen). The tridentate ligand H₂SAP the six-coordinate Zr(SAP)₂ complex and the tridentate ligands H₂SAN and H₂SAE from the seven-coordinate Zr(acac)₂(L') complexes. A stoichiometric ratio (1:1) of the tri- and tetradentate ligands yields the seven-coordinate Zr(L)(L') complexes (H₂L = H₂Sal₂en or H₂Sal₂*o*-phen and H₂L' = H₂SAN, H₂SAE and H₂SAP).

Experimental

Zr(acac)₄ (Fluka), *o*-aminophenol (BDH), anthranilic acid (BDH), ethanolamine and propylenediamine (Sisco-

Chem, India) were used as such. *o*-Phenylenediamine (Koch-Light) was recrystallised from hot H₂O and salicylaldehyde and ethylenediamine (S. Merck, India) were freshly distilled before use. The tetradentate ligands were synthesised⁽¹¹⁾ by condensing salicylaldehyde with ethylenediamine (H₂Sal₂en), propylenediamine (H₂Sal₂pn) and *o*-phenylenediamine (H₂Sal₂*o*-phen) and the solid tridentate ligands were obtained⁽¹²⁾ by condensing salicylaldehyde with anthranilic acid (H₂SAN) and *o*-aminophenol (H₂SAP). The H₂SAE ligand was prepared by the reaction of salicylaldehyde with ethanolamine *in situ*. The ligands were characterised by i.r. and n.m.r. spectral data. Zr was estimated⁽⁴⁾ by slow decomposition of the complexes with conc. HNO₃ (AR) and then weighing as ZrO₂ after igniting to 1000°C. N was determined by a micro-Kjeldahl's apparatus and C, H microanalyses were from CDRI, Lucknow.

The i.r. spectra were recorded as KBr discs in the 4000–400 cm⁻¹ region using a Nicolet 20 FTIR spectrometer; ¹H and ¹³C n.m.r. measurements were made in a Jeol 90 MHz FTNMR spectrometer using 5 mm probe tubes. The electrical conductances in DMSO solution (10⁻³ M) were measured in a Systronics-304 conductivity meter. All compounds were observed to be non-electrolytic.

Preparation of complexes

Zr(Sal₂en)₂

H₂Sal₂en (0.27g, 1 mmol) was dissolved in warm MeOH (10 cm³) and the solution was brought to room temperature. To this solution was added, with constant stirring Zr(acac)₄ (0.5 mmol, 0.24 g) in MeOH (5 cm³). A yellow microcrystalline compound separated gradually. Stirring was continued for further 3 h in order to ensure complete reaction. The product was collected on a glass frit, washed with MeOH and dried *in vacuo*. Yield, 93%. Zr(Sal₂pn)₂ and Zr(Sal₂*o*-phen)₂ were prepared in a similar way.

Zr(acac)₂(L') (H₂L' = H₂SAN, H₂SAE)

These complexes were prepared as above using the ligand (1 mmol) and Zr(acac)₄ (0.5 mmol) in MeOH or Me₂CO. Refluxing the reactant mixture was necessary. In these preparations only two acac groups were replaced, even when an excess of ligand was used. Yield, 80%.

Zr(L)(L') (H₂L = H₂Sal₂en, H₂Sal₂*o*-phen; H₂L' = H₂SAN, H₂SAE, H₂SAP)

These complexes were made using the tetradentate ligand H₂Sal₂en or H₂Sal₂*o*-phen, the tridentate ligand H₂SAN, H₂SAE or H₂SAP and Zr(acac)₄ in equimolar proportions in a mixture of 1:1 MeOH—Me₂CO. The light yellow compounds were formed in good yield (80–90%) in all cases.

* Author to whom all correspondence should be directed.

*Zr(SAP)*₂

This complex was prepared by reacting Zr(acac)₄ (0.5 mmol) and H₂SAP (1 mmol) in refluxing MeOH. Yield, 80%.

All the complexes neither melt nor decompose below 250° C, except Zr(acac)₂(SAN) and Zr(acac)₂(SAE) which decompose at 250° C and 230° C, respectively.

Results and discussion

The complexes prepared are reported in Table 1 together with characteristic data. The complexes are sparingly soluble in most common organic solvents thus precluding molecular weight determination by the cryoscopic method⁽¹³⁾. Determination of relative molecular masses of the complexes was attempted by the Rast method, but their high m.ps and inhomogeneity with known solid solvents of high cryoscopic constants produced no success. All compounds were non-electrolytic and diamagnetic.

The displacement of either two or four acetylacetonato groups from Zr(acac)₄ to form compounds of the type Zr(L)₂ (H₂L = tetradentate H₂Sal₂en, H₂Sal₂pn, H₂Sal₂-*o*-phen); the type Zr(acac)₂(L') (H₂L' = tridentate H₂SAN, H₂SAE); Zr(Sal₂en)(L'); Zr(Sal₂-*o*-phen)₂(L') and Zr(SAP)₂ was confirmed by the quantitative isolation of Cu(acac)₂ from the filtrate after reaction of Zr(acac)₄ with the ligands. Further confirmation for this fact is obtained from i.r. and n.m.r. (¹H and ¹³C) spectra as discussed below. As already discussed, evidence for such exchanges of Zr(acac)₄ with other ligands have been reported in literature^(7–10). Surprisingly, several bidentate Schiff bases did not react with Zr(acac)₄ even though the tri- and tetradentate Schiff bases did so. Of these complexes, only one, *i.e.* Zr(Sal₂-*o*-phen)₂, was reported previously⁽⁹⁾. However, this complex was obtained by a different procedure where tetrakis (salicylaldehydato)

zirconium(IV), Zr(Sal)₄, was reacted with *o*-phenylenediamine in CH₂Cl₂ under nitrogen to produce a yellow compound. The present synthetic procedure is a simpler and more direct method involving ligand exchange between Zr(acac)₄ and the solid di(salicylidene) *o*-phenylenediamine yield of the same compound.

Strong i.r. bands in the 1600–1640 cm⁻¹ region are due to the coupled ν(C=N) of the Schiff bases derived from salicylaldehyde⁽¹⁴⁾. These bands shift somewhat to higher frequencies upon ligand coordination. A rather sharp band at 1260–1300 cm⁻¹ is assigned to the phenolic C—O strength of the coordinated ligands. The complexes containing acac groups have additional i.r. bands at 1580 and 1400 cm⁻¹ due to ν_s(C≡O) and ν_{as}(C≡O) of the acac groups⁽²⁾. The medium sharp bands seen at 450–460 cm⁻¹ and 430–450 cm⁻¹ may be due to the symmetric and asymmetric Zr—O and/or Zr—N stretching frequencies of the coordinated Schiff bases and/or acac groups.

The ¹H and ¹³C n.m.r. spectra of complexes in dms_o-d₆ clearly reveal the coordination of the ligands to zirconium(IV). All ligands derived from salicylaldehyde and their complexes exhibit signals⁽¹⁵⁾ at δ 7.1, 6.5 and 6.0 ppm corresponding to the aromatic protons, and at 8.5 ppm due to the aldiminic proton. They also exhibit signals⁽¹⁶⁾ at δ 165, 140 and 122 ppm in the ¹³C n.m.r. spectra corresponding to the aromatic carbons, and at 190 ppm due to the aldiminic carbon. The H₂Sal₂-*o*-phen ligand and its complexes show an additional multiplet at *ca.* 7.2 ppm due to the protons of aromatic diamine whereas the ¹³C n.m.r. spectra exhibit additional signals at 190 and 145 ppm due to the corresponding carbons. Furthermore, the complexes containing acac groups, *viz.* Zr(acac)₂(L') (H₂L = H₂SAN, H₂SAE) give additional proton signals at 5.4 and 2.0 ppm for the C—H and CH₃ protons, and at 190, 98 and 26 ppm for the C—O, C—H

Table 1. Analytical data of Schiff base complexes of Zr(acac)₄.

Compound	Mol. formula Mol. wt.	Colour	Found (Calcd.)%			
			Zr	C	H	N
Zr(Sal ₂ en) ₂	ZrC ₃₂ H ₂₈ N ₄ O ₄ (623)	light yellow	(14.6)	(61.6)	(4.5)	(9.0)
Zr(Sal ₂ pn) ₂	ZrC ₃₄ H ₃₂ N ₄ O ₄ (651)	yellow white	14.2 (14.0)	62.4 (62.7)	4.9 (4.9)	8.5 (8.6)
Zr(Sal ₂ - <i>o</i> -phen) ₂	ZrC ₄₀ H ₂₈ N ₄ O ₄ (719)	yellow	12.5 (12.7)	66.8 (66.8)	4.0 (3.9)	7.6 (7.8)
Zr(SAP) ₂	ZrC ₂₆ H ₁₈ N ₂ O ₄ (513)	yellow	17.7 (17.7)	60.5 (60.8)	3.5 (3.5)	5.4 (5.5)
Zr(acac) ₂ (SAN)	ZrC ₂₄ H ₂₃ NO ₇ (528)	yellow white	17.3 (17.2)	54.2 (54.5)	4.4 (4.4)	2.8 (2.7)
Zr(acac) ₂ (SAE)	ZrC ₁₉ H ₂₃ NO ₆ (452)	yellow white	20.0 (20.1)	50.4 (50.4)	5.2 (5.1)	3.1 (3.1)
Zr(Sal ₂ en)(SAP)	ZrC ₂₉ H ₂₃ N ₃ O ₄ (568)	yellow	16.3 (16.0)	61.0 (61.3)	4.0 (4.0)	7.3 (7.4)
Zr(Sal ₂ en)(SAN)	ZrC ₃₀ H ₂₃ N ₃ O ₅ (596)	light yellow	15.1 (15.3)	60.2 (60.4)	3.8 (3.9)	7.0 (7.0)
Zr(Sal ₂ en)(SAE)	ZrC ₂₅ H ₂₃ N ₃ O ₄ (520)	light yellow	17.6 (17.5)	57.8 (57.7)	4.4 (4.4)	8.1 (8.1)
Zr(Sal ₂ - <i>o</i> -phen)(SAP)	ZrC ₃₃ H ₂₃ N ₃ O ₄ (616)	yellow	14.6 (14.8)	64.3 (64.3)	3.6 (3.7)	6.7 (6.8)
Zr(Sal ₂ - <i>o</i> -phen)(SAN)	ZrC ₃₄ H ₂₃ N ₃ O ₅ (644)	yellow	14.0 (14.1)	63.6 (63.4)	3.6 (3.6)	6.6 (6.5)
Zr(Sal ₂ - <i>o</i> -phen)(SAE)	ZrC ₂₉ H ₂₃ N ₃ O ₄ (568)	yellow	16.2 (16.0)	61.2 (61.3)	3.9 (4.0)	7.3 (7.4)

and CH₃ carbons, confirming the presence of acac groups in these complexes. On prolonged heating at 120°C (24–30 h), the Zr(acac)₂(L') complexes gradually lose weight corresponding to the total loss of volatile acac ligands.

The results thus indicate the formation of six-coordinate Zr(SAP)₂, seven-coordinate Zr(acac)₂(L') (H₂L' = dibasic tridentate Schiff base) and eight-coordinate Zr(L)₂ (H₂L = dibasic tetradentate Schiff base) complexes. The partial replacement of acac groups from parent Zr(acac)₄ is not unusual and other metal acetylacetonates are known to form such compounds for MoO₂⁺ core^(17–19), VO²⁺ core⁽²⁰⁾ and also Co(acac)-(Sal₂en)⁽²¹⁾.

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