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Synthesis, structure, and reactivity of bis(*N*,*N*′-bis(2-hydroxybenzylidene)-2-hydroxyphenylmethanediaminato)zirconium(IV), a Schiff base complex with 6,4,6-membered chelate rings

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Abstract

The title complex $Zr(dshpm)_2$ has been successfully prepared by heating a 1:2 mole ratio of $Zr(OBu^n)_4$ and the free ligand in absolute ethanol. It is mononuclear and eight-coordinate in the solid state with a dodecahedral coordination sphere. The two O,N,N,O donor atom quadridentate Schiff base ligands each form 6,4,6-membered chelate rings. As expected, the change in a chelate ring sizes from 6,5,6- to 6,4,6- resulted in significantly more labile complex, as indicated by TLC and NMR of heated solutions and its subsequent chemical reactions. The 0.010 Å shorter average Zr–N bond distance was not anticipated, and appears to result from the zirconium atom's preference that the oxygen atoms occupy certain locations. Preparations of two heteroleptic complexes from the title complex were undertaken to evaluate potential of the title compound as a synthon. A new fluorine-substituted homoleptic Schiff base Zr complex was also prepared, for comparison purposes. Despite the reasonable stability of $Zr(dshpm)_2$ in air, the decomposition of labilized Hdshpm(2-) ligand on silica gel and in heated solution interfered with the purifications of the desired heteroleptic products. © 2002 Published by Elsevier Science Ltd.

Keywords: Eight-coordinate; Schiff base; Zirconium complexes; X-ray crystal structure; Synthon; Heteroleptic

1. Introduction

The recent publication of articles dealing with early transition metal eight-coordinate complexes reflects a continuing interest in this subject, especially with regard to their structural aspects [1–6] intramolecular dynamics [7–10] and ligand exchange properties [11–14]. Our current interest is in the development of a more facile route to heteroleptic (mixed ligand) bis(quadridentate) complexes for use as polymer pendent groups [15]. Commercially available entry points for the preparation of zirconium(IV) complexes include zirconium tetraalkoxides and zirconium tetrachloride, which are polymeric to some degree and/or susceptible to atmospheric hydrolysis, and tetrakis(acetylacetonato)zirconium(IV), which can exhibit varying degrees of ligand substitution.

Bis(quadridentate) Schiff base complexes of zirconium(IV), which have fused 6,5,6-membered chelate rings and two O,N,N,O donor atom sets, are sufficiently inert that chromatographic separation on silica gel can be accomplished [15]. However, we have observed that the temperatures needed to overcome this inertness cause decomposition of the freed ligands in dimethyl sulfoxide. By choosing a quadridentate Schiff base ligand capable of forming fused 6,4,6-membered chelate rings

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upon coordination, we hoped to isolate a mononuclear complex with a convenient balance of ligand lability and air stability to serve as a new reaction intermediate (synthon). The increased lability would be a consequence of the greater ring strain, i.e. poorer overlaps, in the 4-membered chelate ring portion of the complex. The quadridentate Schiff base that we chose to use is *N*,*N*′ - bis(2 - hydroxybenzylidene) - 2 - hydroxyphenylmethanediamine, also called *N*,*N*′-bis(salicylidene)-2-hydroxy-α,α benzyldiamine, or more commonly *N*,*N*′-di(salicylidene) - 2 - hydroxyphenylmethanediamine, H_3dshpm. It can be made by mixing reagents found in most synthetic chemistry labs, ammonium hydroxide and salicylaldehyde, at room temperature [16,17]. This reaction is an example of one of the earliest known 'spontaneous assembly' reactions [18]. This compound allows facile modification of its structure [19–23] and is known to form complexes with other transition metals [24].

The synthesis, structural characterization and further reactions of the title complex, $Zr(dshpm)_2$, are reported here (Fig. 1).

2. Experimental

Zirconium *n*-butoxide (80% in *n*-butanol), salicylaldehyde, 3-fluorosalicylaldehyde, deuterated methylene chloride and deuterated dimethyl sulfoxide were obtained from Aldrich and used as received. The ammonium hydroxide and all solvents used were of reagent grade. Silica Gel (Merck), grade 60, 230–400 mesh, 60 Å pore size was obtained from Aldrich, and silica TLC plates were obtained from Kodak.

Prior to all TLC separations, silica plates were activated by heating at 110 °C for approximately 10 min, cooled in a desiccator for at least 5 min, and then stored for approximately 1 h or less in a glove bag filled with dry dinitrogen. Ligands and complexes were spotted while in the glove bag, and the plates returned to the oven for at least 2 min to drive away the spotting solvent.

Infrared spectra were obtained on a Perkin–Elmer FT-IR X spectrophotometer as KBr pellets using polystyrene for external calibration. ^{1}H NMR spectra for preliminary identification purposes were obtained on either a Nicolet NT-200 or a Bruker WP200 SY NMR instrument using tetramethylsilane as internal standard. ^{1}H, ^{19}F (using α,α,α-trifluorotoluene or internal referencing based on sample solvent), and all 2-D NMR spectra for detailed analyses were obtained on a Bruker Avance 400 NMR instrument.

X-ray crystallographic data for the title compound were obtained as follows: Large yellow block crystals were mounted on fine glass fibers and found to be monoclinic with systematic absences for *C* centering and a *c* glide along *b* indicating either *Cc* or *C*2/*c* as

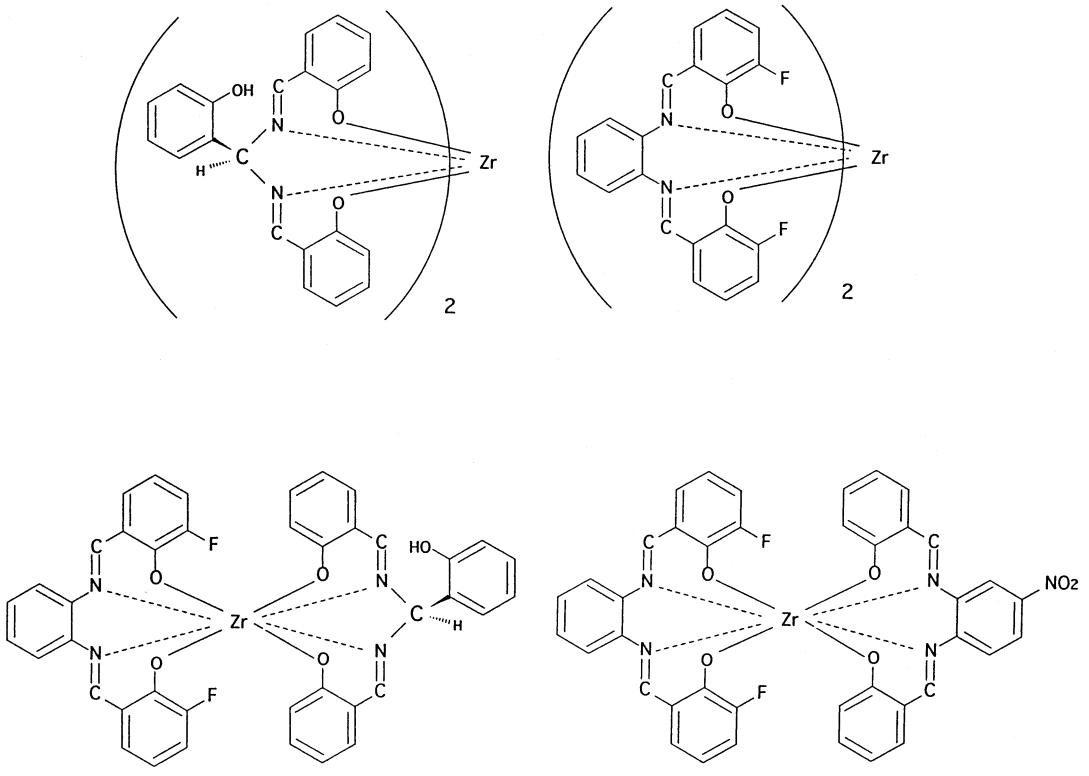

Fig. 1. Proposed structures for all new complexes in this report. Top left, $Zr(dshpm)_2$; top right, $Zr(3\text{-}Fdsp)_2$; bottom left, Zr(dshpm)(3-Fdsp); bottom right, Zr(ndsp)(3-Fdsp).

possible space groups. The latter was confirmed by the presence of a crystallographic twofold rotation axis in the Zr complex and the stability of the refinement in the centrosymmetric setting. The structure was solved by direct methods. All nonhydrogen atoms were refined anisotropically and hydrogen atoms were included as idealized isotropic contributions. All computations used the programs contained in the SHELXTL library (version 4, G. Sheldrick, Siemens XRD, Madison, WI).

2.1. *N,N′-di(salicylidene)-2-hydroxyphenylmethanediamine*, *H_3dshpm*

In a 125 ml Erlenmeyer flask was placed 20.5 g (0.168 mole) salicylaldehyde. Concentrated ammonium hydroxide was added almost to the top (ca. 115 ml), the flask stoppered and vigorously shaken. Bright yellow precipitate formed almost immediately. The flask was allowed to sit unopened for 3 days. At this point, the flask contained tamped-down, fused-looking yellow orange precipitate with a clear yellow supernate. The solution was gravity filtered, and the precipitate washed with ethyl ether. A powdery yellow solid containing some shiny orange spheres was obtained. Trituration of this product in 40 ml of absolute ethanol failed to completely remove the orange spheres. Yield, 13.0 g (66.9%).

A portion of this product was dissolved in acetone, petroleum ether added, and the volume of solvents reduced using rotary evaporation to induce recrystallization. After filtering, and washing with pertroleum ether, the fluffy yellow solid obtained lacked any visible orange component, and was only slightly soluble in methylene chloride; m.p. 159–160 °C. *Anal.* Calc. for $C_{21}H_{18}N_2O_3$: C, 72.8; H, 5.20; N, 8.09. Found: C, 72.58; H, 5.31; N, 8.09%. ^{1}H NMR (acetone-d_6): δ 13.1 (br) [1], 8.7 [2], 7.5–6.8 [12], 6.35 [1]. IR (cm^{-1}): 1628s, 1276m.

2.2. *Bis(N,N′-di(salicylidene)-2-hydroxyphenylmethanediaminato)zirconium(IV)*, *$Zr(dshpm)_2$*

A 1.69 g (4.86 mmol) portion of the yellow and orange H_3dshpm product was covered with 80 ml absolute ethanol in a 500 ml round bottom flask. Under a dinitrogen tmosphere, 0.50 ml (1.2 mmol) of $Zr(OBu^n)_4$ was then precipitated to the flask, causing the immediate formation of a cloudy, white precipitate. The flask was heated at reflux for 24 h, and filtered, to give a fine yellow powder; m.p. ca. 250 °C (slow dec.). Yield, 0.62 g (67%).

The sample submitted for elemental analysis was dried in vacuo at 100 °C for 3 days. *Anal.* Calc. for $C_{42}H_{32}N_4O_6Zr$: C, 64.7; H, 4.11; N, 7.19. Found: C, 64.56; H, 4.14; N, 6.97%. ^{1}H NMR (CD_2Cl_2): δ 9.5 (br) [2], 8.2 [2], 8.0 [2], 7.6–6.5 [28]. IR (cm^{-1}): 1638s, 1604s, 1310m, 1288m.

2.3. *N,N′-Di(3-fluorosalicylidene)-1,2-phenylenediamine*, *$H_2$3-Fdsp*

A 1:2 mole ratio of 1,2-phenylenediamine and 3-fluorosalicylaldehyde, respectively, were heated at reflux in absolute ethanol for 6 h, concentrated, and chilled to give an orange precipitate; m.p. 148–150 °C.

Anal. Calc. for $C_{20}H_{14}F_2N_2O_2$: C, 68.2; H, 3.98; N, 7.95. Found: C, 67.95; H, 3.86; N, 7.87%. ^{1}H NMR (CD_2Cl_2): δ 13.2 (br) [2], 8.9 [2], 7.5–6.9 [10]. ^{19}F NMR (CD_2Cl_2): -140.6. IR (cm^{-1}): 1620s, 1275m, 1250s, 1230s.

2.4. *Bis(N,N′-di(3-fluorosalicylidene)-1,2-phenylenediaminato)zirconium(IV)*, *$Zr(3\ Fdsp)_2$*

Under a dinitrogen atmosphere, 0.49 ml (0.52 g, 1.1 mmole) $Zr(OBu^n)_4$ were added to 0.80 g (2.3 mmole) $H_2$3-Fdsp in 50 ml absolute ethanol and heated at reflux for 1 h, suction filtered, washed with absolute ethanol, and allowed to dry to give a bright yellow powder; m.p. approximately 416 °C (422 °C dec.). Yield, 0.73 g (81%).

The sample submitted for elemental analysis was dried in vacuo at 100 °C for 3 days. *Anal.* Calc. for $C_{40}H_{24}F_4N_4O_4Zr$: C, 60.7; H, 3.06; N, 7.08. Found: C, 60.86; H, 3.03; N, 7.00%. ^{1}H NMR (CD_2Cl_2): δ 8.7 [4], 7.5–6.4 [20]. ^{19}F NMR (CD_2Cl_2): -137.4. IR (cm^{-1}): 1615s, 1320m, 1255m, 1240m.

2.5. *(N,N′-di(salicylidene)-2-hydroxyphenylmethanediaminato)(N,N′-di(3-fluorosalicylidene)-1,2-phenylenediaminato)zirconium(IV)*, *Zr(dshpm)(3-Fdsp)*

2.5.1. *Method 1*

In 200 and 100 ml portions of methylene chloride, 1.97 g (2.5 mmole) $Zr(dshpm)_2$ and 0.30 g (0.85 mmole) $H_2$3-Fdsp, respectively, were separately dissolved. The former solution was heated to reflux, and the latter added in five increments with 2 h intervals between additions, and reflux maintained overnight. TLC separation of the resulting solution (using methylene chloride eluent on silica) indicated that some unreacted Schiff base remained, whereupon 100 ml absolute ethanol was added. Reflux was maintained, periodically monitoring the reaction with TLC. A pale spot having a value of R_F clearly lower than those for the reactants or $Zr(3\text{-}Fdsp)_2$ or H_3dshpm appeared. After 22.5 h at reflux, TLC of the reaction solution revealed a spot due to $Zr(3\text{-}Fdsp)_2$, at which time the reaction was stopped. The volume was reduced by rotary evaporation to one half of its original volume, 80 ml absolute ethanol added, and concentrated again to induce precipitation. The impure product was redissolved in minimal methylene chloride and subjected to column chromatography

using methylene chloride eluent on silica gel. Fractions containing only the trailing spot (as shown by TLC) were combined, and the solvent evaporated to give a yellow product. Subsequent recrystallizations and column separations failed to produce a product having experimental elemental analyses within established limits from their theoretical values. ^{1}H NMR (CD_2Cl_2): δ 9.0 br [less than 1], 8.5 [1], 8.4 [1], 8.0 [2], 7.5–5.8 [ca. 29] ^{19}F NMR (CD_2Cl_2): -138.5, -133.5. IR (cm^{-1}): 1641s, 1616s, 1317m, 1300m, 1238m.

2.5.1.1. Derivative preparation. An impure sample of Zr(dshpm)(3-Fdsp) was mixed with *N*,*N*′-di(salicylidene)-4-nitro-1,2-phenylenediamine, H_2ndsp, in 30:70 methylene chloride and absolute ethanol, respectively, and heated at reflux. The reaction was monitored by TLC using the TLC system noted above. When the spots attributed to the starting materials were no longer apparent, the reaction solution was concentrated by rotary evaporation to give a red solid. A 0.1 g portion of this product was separated on a silica gel column using methylene chloride as eluent. Fractions having single spot TLCs which appeared to correspond with the desired product were consolidated and evaporated to give a red product. The sample submitted for elemental analysis was dried in vacuo at 100 °C for 3 days. *Anal.* Calc. for $C_{40}H_{25}F_2N_5O_6Zr$ [Zr(ndsp)(3-Fdsp)]: C, 60.0; H, 3.15; N, 8.74. Found: C, 61.24; H, 3.50; N, 8.60%. ^{1}H NMR (CD_2Cl_2): δ 8.6–8.2 [6], 7.5–5.9 [19]. These NMR signals matched those for a sample of Zr(ndsp)(3-Fdsp) prepared directly from $Zr(OBu^n)_4$ and the corresponding free Schiff base ligands, to be reported elsewhere (Found: C, 60.66; H, 3.44; N, 8.52%).

2.5.2. Attempted method 2

Under a dinitrogen atmosphere, 1:1:1 mole ratio amounts of H_3dshpm, $H_2$3-Fdsp, and $Zr(OBu^n)_4$ were heated at reflux in absolute ethanol for 7 h, until the TLC spot from H_3dshpm was no longer apparent (using a 16:1 petroleum ether to ethanol eluent). After being allowed to cool, the mixture was filtered to give a bright yellow powder.

2.5.3. Attempted method 3

Under a dinitrogen atmosphere, 1:1 mole ratio amounts of $Zr(dshpm)_2$ and $Zr(3\text{-}Fdsp)_2$ were separately dissolved in d^6-DMSO. The solutions were mixed, and heated for 20 h intervals at 40, 43, and 50 °C. Changes in the reaction solution were monitored by TLC (using a 16:1 petroleum ether–ethanol eluent), and compared with those for the separate complexes.

3. Results and discussion

The physical and spectroscopic data collected in this study are consistent with the following reaction schemes:

Reaction Scheme I.

$$3NH_3\ (aq) + 2\ \text{salicylaldehyde}\ (aq) \xrightarrow{(-3\ H_2O)} H_3\text{dshpm}\ (s)$$

$$2\ H_3\text{dshpm} + Zr(OBu^n)_4 \xrightarrow{(-4\ HOBu)} Zr(\text{dshpm})_2 \xrightarrow{(H_2\text{3-Fdsp})} Zr(\text{dshpm})(\text{3-Fdsp}) \xrightarrow{(H_2\ \text{ndsp})} Zr(\text{ndsp})(\text{3-Fdsp})$$

Reaction Scheme II.

$$\text{1,2-phenylenediamine} + 2\ \text{3-fluorosalicylaldehyde} \xrightarrow{(-2\ H_2O)} H_2\text{3-Fdsp}\ (s)$$

$$2\ H_2\text{3-Fdsp} + Zr(OBu^n)_4 \xrightarrow{(-4\ HOBu)} Zr(\text{3-Fdsp})_2$$

The 1628 and 1276 cm^{-1} infrared bands for H_3dshpm are comparable to those observed for the dsp-type ligands used in our previous studies [25,26] and are assigned to imine stretching and ring-to-oxygen stretching, respectively. The broad ^{1}H NMR signal at 13.1 ppm is assigned to exchangeable salicylidene O–H, the 8.7 ppm singlet to the two imine protons, 7.5–6.8 ppm multiplets to the 12 aromatic protons, and a singlet at 6.35 to a methine proton. The appearance of an orange component in the initial product, the variety of melting points reported [16,17,27] and the differences between the NMR spectra in deuterated acetone versus methylene chloride (of poor quality due to low solubility) indicate the presence of tautomeric forms of this material. Very similar observations were made for the ethyl ester substituted H_2dsp ligand, for which either tautomer gave the same product upon complexation [28].

3.1. Zr(dshpm)$_2$

The shift in salicylidene ring-to-oxygen vibration frequency from 1276 to 1310 cm^{-1} upon Zr complexation is analogous to those seen for all H_2dsp-type ligands studied previously by us [25,26]. The essentially non-shifted band at 1288 cm^{-1} is assigned to the phenyoxy ring-to-oxygen vibration since coordination does not take place at this site (vide infra). Either of the bands at 1638 or 1604 cm^{-1} could be assigned to an imine vibration. However, the former is more the likely, given the increase in frequency upon complexation noted above. The absence of a peak near 13.1 ppm in the ^{1}H NMR spectrum of $Zr(dshpm)_2$ is expected, as the Zr displaces the salicylidene O–H protons of each ligand.

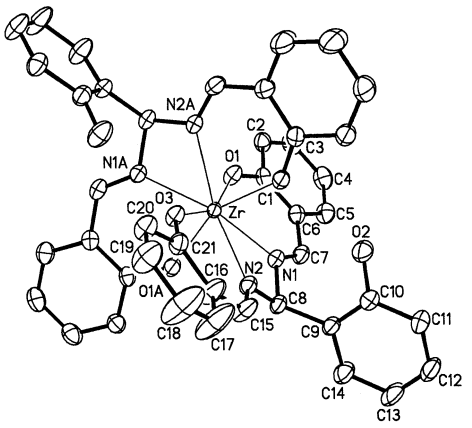

Fig. 2. Labeled thermal ellipsoid drawing for $Zr(dshpm)_2$.

The broad signal at 9.5 ppm, which integrates for a little less than two protons, is assigned to an exchangeable phenoxy proton on each ligand. The imine protons become nonequivalent upon complexation, giving singlets at 8.2 and 8.0 which each integrate for 2. The methine proton signal from each ligand occurs among the aromatic proton multiplets which extend from 7.6 to 6.5 ppm, the region integrating for 28 protons. The upfield shift upon Zr complexation, especially for the salicylidene protons *meta* to the oxygen, is comparable to those observed for all H_2dsp-type ligands studied by us [25,26]. The doublets at 7.0 and 6.8 ppm which have no apparent fine structure and integrate for one proton each, are most likely from the methine protons. If these assignments are accurate, as indicated by the 2-D COSY spectrum, then the salicylidene and/or phenyoxy rings must have different average positions in solution, e.g. an equilibrium could exist between coordinated phenoxy and salicylidene moieties, or, less likely, the short bite N–C–N moieties could span different edges in the coordination sphere in solution to create different methine proton environments.

Table 1
Selected bond lengths, bond angles, and coordination sphere parameters for $Zr(dshpm)_2$; see Fig. 2

Bond lengths (Å)					
Zr–O(1)	2.090(2)	O(1)–C(1)	1.323(5)	N(1)–C(7), imine	1.270(5)
Zr–O(3)	2.151(3)	O(3)–C(21)	1.324(4)	N(2)–C(15), imine	1.263(5)
Zr–N(1)	2.318(3)			N(1)–C(8), methine	1.468(4)
Zr–N(2)	2.334(3)	O(2)–C(10)	1.364(4)	N(2)–C(8), methine	1.476(5)
Bond angles (°)					
O(1)–Zr–O(3)	154.0(1)	Zr–O(1)–C(1)	142.1(2)	Zr–N(1)–C(7)	135.5(2)
O(1)–Zr–N(1)	74.2(1)	Zr–O(3)–C(21)	139.4(3)	Zr–N(1)–C(8)	102.0(2)
O(1)–Zr–N(2)	131.2(1)			Zr–N(2)–C(15)	135.6(3)
O(3)–Zr–N(2)	74.4(1)			Zr–N(2)–C(8)	101.0(2)
O(3)–Zr–N(1)	131.3(1)	C(7)–N(1)–C(8)	122.4(3)		
N(1)–Zr–N(2)	57.0(1)	C(15)–N(2)–C(8)	123.4(3)	N(1)–C(8)–N(2)	97.9(3)
Deviations from planarity (Å)					
O(1)–N(1)–N(2)–O(3)	0.0047(5)				
Zr–N(1)–N(2)–C(8)	0.2360(3) [a]	O(1)–N(1)–N(2)–O(3)–Zr	0.0211(3)		
'*a*' *Edges* [b] (Å)					
N(1)–N(2)	2.220(4)				
'*b*' *Edges* [b] (Å)					
O(1)–O(1a)	3.126(5)				
O(1)–O(3a)	3.096(5)				
'*m*' *Edges* [b] (Å)					
O(1)–N(1)	2.666(4)				
O(3)–N(2)	2.714(5)				
O(1a)–N(1a)	2.803(5)				
O(3a)–N(2a)	2.714(5)				
'*g*' *Edges* [b] (Å)					
O(1)–N(1a)	2.803(5)				
O(1)–N(2a)	2.757(5)				
O(3)–N(1a)	2.917(5)				
O(3)–N(2a)	2.835(5)				
Mean edge length ratios					
b/*a*	1.38				
b/*m*	1.14				
b/*g*	1.085				

[a] The deviation of C(8) from the N(1)–Zr–N(2) plane is away from the phenoxy group.
[b] Standard Hoard and Silverton symbolism [29]. The remaining dodecahedral edge lengths for $Zr(dshpm)_2$ are dictated by symmetry.

Results of X-ray crystallography on $Zr(dshpm)_2$ establish its solid state structure as eight-coordinate with a dodecahedral coordination sphere, point group $2/m$, and space group $C2/c$. A labeled thermal ellipsoid drawing is shown in Fig. 2. Important bond lengths, bond angles, and coordination sphere parameters are summarized in the Table 1. Comparisons with bis(*N*,*N*′-disalicylidene-1,2-phenylenediaminato)zirconium(IV), $Zr(dsp)_2$ [26] and bis(*N*,*N*′-disalicylidene-1,2-*trans*-diaminocyclohexanato)zirconium(IV), $Zr(trans\text{-}dsd)_2$ [25] which have fused 6,5,6-membered Schiff base ligands, reveal the following: While the mean Zr–O distances are approximately equal for each complex, the mean Zr–N distance for $Zr(dshpm)_2$ is approximately 0.010 Å shorter. Considering the ring strain normally associated with four-membered rings, poor bonding overlaps would justify longer bonds. In this case, the shorter bonds probably arise due to zirconium's preference for the oxygen atoms to be located in certain positions, the 'B' positions of a dodecahedron [29], which is consistent with theory for d^0 dodecahedral systems [30]. The imine bond is highly localized in $Zr(dshpm)_2$, as for the other complexes, and the methine-to-nitrogen bond lengths are ordinary. The O–Zr–O bond angles are larger for $Zr(dshpm)_2$ than for the other complexes, which indicates that the 6,4,6 ligands do not engulf the Zr as extensively. The N–Zr–N bond angle is the smallest for $Zr(dshpm)_2$, due to the limited reach of the methine diamine moiety versus those of the phenylenediamine and diaminocyclohexane moieties [25,26]. The above mentioned bond length and angle constraints produce a dodecahedron having the shortest N–N distance ('a edges'), and a Zr–N (ave.) to Zr–O (ave.) bond length ratio of 1.09. The latter is closer to the Hard Sphere Model (1.00) and Most Favorable Model (1.03) [29] than the other members of this series. The angle made between the trapezoidal O,N,N,O donor atom planes is 89.0° for $Zr(dshpm)_2$, which is comparable to those for $Zr(dsp)_2$ and $Zr(trans\text{-}dsd)_2$ [25,26]. The angle made between the phenoxy ring and the donor atom plane of the same ligand is 85.2°. The corresponding value for the other ligand is equivalent by symmetry.

In vitro tests conducted by the National Cancer Institute, Developmental Therapeutics Program (Sample and Test Identification NSC: 657558-U/0-1/38), indicated that this compound was inactive against nine cancers and HIV.

3.2. $Zr(3\text{-}Fdsp)_2$

The preparation of $Zr(3\text{-}Fdsp)_2$ was undertaken so that its spectral data could be compared with those of Zr(dshpm)(3-Fdsp) and Zr(ndsp)(3-Fdsp), see Reaction Scheme II and the final two legs of Reaction Scheme I (see Section 3). The method employed is well established [15,25,28]. The IR bands at 1615 and 1320 cm^{-1} are assigned to the imine and coordinated-oxygen-to-ring stretching vibrations, respectively [25,26], while the band at 1255 or 1240 cm^{-1} arises from a fluorine-to-ring stretching vibration. The absence of the proton NMR signal at 13.2 ppm, observed for the free ligand, is consistent with ligand coordination. The imine proton signals are virtually equivalent, and shifted upfield by approximately 0.15 ppm from that of the free ligand. Similar upfield shifts are observed in the $Zr(dsp)_2$ and $Zr(trans\text{-}dsd)_2$ systems [25,26]. Symmetrical multiplets at 7.5–7.4 ppm arise from the 1,2-phenylenediamine protons, as observed for $Zr(dsp)_2$ [26]. Nearly identical doublets at 7.1–7.0 arise from the salicylidene ring protons *para* to F and *meta* to O; less similar doublets at 6.9–6.7 arise from the salicylidene ring protons *ortho* to F and *meta* to O; and two distinct triplets at 6.5–6.4 arise from the salicylidene ring protons *meta* to F and *para* to O. Off diagonal features in the ROESY (with 400 ms mixing) and DQF COSY NMR experiments confirm these assignments and indicate interactions between the imine protons and aromatic protons of the phenylenediamine (α and β) and salicylidene (*para* to F) moieties.

3.3. Zr(dshpm)(3-Fdsp)

Method 2, the reaction of Zr butoxide and the free ligands in 1:1:1 mole ratio, has successfully been used to prepare heteroleptic complexes [15]. However, the yellow product obtained in this research was determined to be mostly $Zr(3\text{-}Fdsp)_2$, based on TLC and proton NMR analyses. Since the solubilities of $Zr(3\text{-}Fdsp)_2$ and the desired Zr(dshpm)(3-Fdsp) are very similar, recrystallization was precluded as an effective method of purification. Furthermore, since $Zr(dshpm)_2$ decomposes rapidly on a silica gel column (on the elution time scale) and is the fastest moving of the three Zr products, the Zr(dshpm)(3-Fdsp) band becomes contaminated. This precludes chromatography as a convenient method of purification. With purification proving to be difficult, Method 2 was deemed ineffective in this case.

While $Zr(3\text{-}Fdsp)_2$ withstood heating in d^6-DMSO up to 148 °C with no change in its TLC or proton NMR, $Zr(dshpm)_2$ was shown to undergo chemical change upon heating to only 40 °C. Heating a 1:1 mole ratio mixture of the two complexes, as per Method 3, resulted in labilization and decomposition of the H_3dshpm ligand at low temperature without any evidence of mixed ligand complex formation.

The relative success of Method 1 is, based upon stopping the addition of $H_2$3-Fdsp to $Zr(dshpm)_2$ as soon as $Zr(3\text{-}Fdsp)_2$ appears in the reaction solution's TLC. The approximately equal mixture of unreacted $Zr(dshpm)_2$ and Zr(dshpm)(3-Fdsp) which resulted

could be substantially purified due to the limited solubility of the former in absolute ethanol. However, despite repeated recrystallizations followed by a column separation, contamination of the desired product persisted, as reflected by the elemental analyses. The impurities, which are likely to arise from on-going labilization of Hdshpm(2-), probably contributed to our inability to grow a crystal suitable for X-ray crystallography. Fortunately, the composition of the new material could be established using IR and NMR spectroscopies, and by preparing chemical derivatives.

For the substantially purified product, infrared bands at 1641 and 1616 cm^{-1} are assigned as imine stretching vibrations arising from the Hdshpm(2-) and 3-Fdsp(2-) ligands, respectively, by analogy to the corresponding homoleptic complexes. The band at 1317 cm^{-1} and its shoulder are assigned as 'coordinated O-to-salicylidene ring' stretching vibrations for the two ligands. The band at 1238 cm^{-1} and/or its higher frequency shoulder are assigned as an aromatic ring-to-F vibration, analogous to that for $Zr(3\text{-}Fdsp)_2$. Thus, all IR assignments are consistent with the Zr(dshpm)(3-Fdsp) formulation.

While strong parallels between Zr(dshpm)(3-Fdsp) and the corresponding homoleptic complexes are readily apparent from the IR spectra of solid state samples, fewer parallels are evident from their solution ^1H NMR spectra. The absence of a signal around 13.2 ppm is consistent with the presence of coordinated ligands. Small singlets at 11.0 and 9.9 ppm match signals observed for salicylaldehyde, which is a likely decomposition by-product from the Hdshpm(2-) ligand. The broad signal at 9.0 ppm, which integrates for less than one proton, is assigned to an exchangeable phenoxy O–H and is consistent with the presence of one Hdshpm(2-) ligand. This chemical shift is 0.5 ppm upfield from the analogous signal for $Zr(dshpm)_2$, which, from examination of molecular models, could result from a nearby fluorine on the opposing 3-Fdsp(2-) ligand. The singlets at 8.5 and 8.4 ppm, which integrate for one proton each, are assigned to the imine protons of the 3-Fdsp(2-) ligand, protons which had been equivalent for $Zr(3\text{-}Fdsp)_2$ at 8.7 ppm. The singlet at 8.0 ppm, which integrates for two protons, is assigned to the imine protons of the Hdshpm(2-) ligand, protons which had been inequivalent for $Zr(dshpm)_2$ at 8.2 and 8.0 ppm. Signals in the 7.5–5.8 ppm range are assigned to the aromatic protons of the ligands. The upfield end of this range appears higher than observed for either of the homoleptic complexes, 6.4 ppm in both cases. The integration over this range, corresponding to approximately 29 protons, is higher than expected for 22 aromatic protons and one methine proton, and is consistent with the presence of some impurity, e.g. salicylaldehyde. We also note that the aromatic signals for Zr(dshpm)(3-Fdsp) appear poorly resolved in CD_2Cl_2, a poor H-bonding solvent, and appear strikingly different in d^6-DMSO, a good H-bonding solvent, while the imine proton signal at 8.0 ppm appears the same in each solvent. Furthermore, in the d^6-DMSO spectrum, the phenoxy O–H signal is a sharp singlet which integrates for one proton; the aromatic range extends down to 8.1 ppm; and, the integration of the aromatic region corresponds to 22.8 protons, which is much closer to the expected number of 23.

In addition to TLC evidence, rapid disproportionation of Zr(dshpm)(3-Fdsp) in solution to form a 1:1 mole ratio of homoleptic complexes was ruled out by observing the CD_2Cl_2 ^1H NMR spectrum of a mixture of separately prepared $Zr(3\text{-}Fdsp)_2$ and $Zr(dshpm)_2$. The spectrum showed all of the signals apparent in the spectra of the separate complexes with no perceptible shifts, i.e. with no sign of interaction.

The $^{19}F\{^1H\}$ NMR of the proposed Zr(dshpm)(3-Fdsp) product shows two proton decoupled signals, neither of which matches the ^{19}F signal from $Zr(3\text{-}Fdsp)_2$. The ^{19}F signal from a mixture of $Zr(3\text{-}Fdsp)_2$ and $Zr(dshpm)_2$ was identical with the latter. The coordinated Hdshpm(2-) ligand evidently imposes a different chemical environment on the two fluorines of the opposing 3-Fdsp(2-) ligand. $^1H\{^{19}F\}$ NMR (i.e. proton observe with decoupled ^{19}F using the above ^{19}F NMR frequencies) of the proposed Zr(dshpm)(3-Fdsp) product in CD_2Cl_2 solution indicates that each F atom couples with the nearest imine proton and nearest salicylidene protons (*ortho* and *meta*).

A plausible explanation for some of the observed NMR differences between Zr(dshpm)(3-Fdsp) and the corresponding homoleptic complexes is the presence of H bonding between the phenoxy O–H of Hdshpm(2-) and a fluorine atom on the opposing 3-Fdsp(2-). Such an interaction would render the ^{19}F NMR chemical shifts of the 3 Fdsp(2-) inequivalent. Since the above decoupling experiment established that each fluorine is coupled to the nearest imine proton, the different Zr(dshpm)(3-Fdsp) fluorine environments could explain the separate imine proton signals at 8.5 and 8.4 ppm. The imine protons for $Zr(3\text{-}Fdsp)_2$, where analogous H-bonding is not possible, gave a singlet at 8.5 ppm. However, alternate explanations for these observations, such as coordination sphere structure in solution and ligand puckering, cannot be ruled out.

3.4. Zr(ndsp)(3-Fdsp)

In light of the less-than-convincing elemental analysis for Zr(dshpm)(3-Fdsp), the inability to obtain a suitable single crystal, and the complexity of its NMR results, corroboration of its composition was sought using chemical means. In this case, the 6,4,6-chelating Hdshpm(2-) was replaced by the 6,5,6-chelating ndsp(2-). As expected, the proposed Zr(ndsp)(3-Fdsp) derivative

was demonstrated by NMR to be identical to the heteroleptic product from the 1:1:1 mole ratio reaction of H_2ndsp, $H_2$3-Fdsp, and $Zr(OBu^n)_4$. The latter had a satisfactory elemental analysis. Its NMR spectrum shows four proton signals in the imine proton region (8.6–8.3), attributed to the two imine protons and the two protons adjacent to the nitro group; the multiplet at 7.5–7.4 which integrates for five protons is attributed to the remaining phenylenediamine protons [four from 3-Fdsp(2-) and one from ndsp(2-), *meta* to the nitro group]; and the series of triplets and doublets over the 7.3–5.9 range, which each integrate for two protons each, are assigned to salicylidene ring protons, and correspond to the signals observed for the homoleptic complexes [31].

4. Conclusions

The title complex $Zr(dshpm)_2$ has been successfully prepared. Based on X-ray crystallographic results, it is mononuclear, and eight-coordinate in the solid state with a dodecahedral coordination sphere, as observed for other similar Schiff base Zr complexes [15,25,26]. The two quadridentate ligands employ O,N,N,O donor atoms to form 6,4,6-membered chelate rings, while the phenyoxy moieties are not coordinated. Although the coordination sphere dimensions of $Zr(dshpm)_2$ are closer to the Hard Sphere Model and the Most Favored Model [29] than previously studied 6,5,6- Schiff base Zr complexes [15,25,26], the change in chelate ring sizes resulted in a significantly more labile complex, as indicated by TLC, NMR of heated solutions, and chemical reactivity. The 0.010 Å shorter average Zr–N bond distance was not anticipated, and appears to result from the zirconium atom's preference that the oxygen atoms occupy certain locations.

Despite the respectable stability of the title complex in air, the decomposition of labilized ligands on silica gel and in heated solutions seriously detracts from its utility as a synthon. Complete purification of the two heteroleptic complexes prepared from it were not achieved. Zr complexes having more resilient 6,4,6-chelating ligands are expected to give more promising results.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center, reference number CCDC 150144. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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